Diffusion in Titanium

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Recent studies on self-diffusion and impurity diffusion in α - and β -titanium are reviewed. The transition metal elements and phosphorus exhibit fast diffusion in α -Ti, which are three to five orders of magnitude faster than the self-diffusion. The mechanism of the fast diffusion is discussed on the basis of the several features: the effect of $\alpha \rightarrow \beta$ phase transformation, the diffusion anisotropy, the atomic size effect and the correlation between solubility and diffusivity. In β -Ti self- and impurity diffusion exhibit marked upward curvatures in the Arrhenius plots, which are known as anomalous diffusion. Various models proposed to explain the anomalous behaviour are briefly reviewed.

KEY WORDS: diffusion; fast diffusion; interstitial mechanism; titanium; isotope effect.

1. Introduction

Titanium is an attractive material with excellent corrosion resistance and high strength-to-weight ratio. Industrial applications of titanium materials have recently expanded widely in many areas such as the aerospace, marine, chemical plants and even automobiles. The knowledge of diffusion is essential for the understanding of various processes in the relevant materials, *e.g.* the phase transformation, precipitation and creep *etc.*

This paper reviews diffusion studies in titanium and its alloys. The first part summarizes available data on self-diffusion, metallic and semi-metallic impurity diffusion and light interstitial diffusion, while the second part presents the understanding of the mechanism of self- and impurity diffusion: fast diffusion and anomalous diffusion.

2. Diffusion Data in Titanium

2.1. Self-diffusion, Metallic and Semi-metallic Impurity Diffusion in α -Ti

The diffusion coefficient is tensorial quantities. In cubic crystals, all the principal values are equal so that the diffusion is isotropic, while in non-cubic crystals such as hcp crystal, the diffusion is anisotropic. Earlier diffusion measurements on titanium were made by using polycrystalline materials; impurity diffusion coefficients of Ni,¹⁾ Co²⁾ and Mn,²⁾ and the self-diffusion coefficients³⁾ have been reported. Although these data are useful for practical purposes, the determination of the diffusion coefficients, using single crystals, along the principal crystallographic directions is essential for the basic understanding of the diffusion process. In 1983, the present authors have reported the diffusion coefficients

of Co in single crystal α -Ti.⁴⁾ Subsequently systematic measurements have been made for the diffusion of Fe,⁵⁾ Ni,⁶⁾ Mn,⁷⁾ Cr⁸⁾ and P.⁹⁾ On the other hand, Räsänen and Keinonen measured diffusivities of Al¹⁰⁾ and Si¹¹⁾ in polycrystalline Ti by a nuclear-reaction method. These data are compiled in Fig. 1. We note two remarkable

Fig. 1. Temperature dependence of self- and impurity diffusion coefficients in α -titanium: Co, Fe, Ni, Mn, Cr and P in single crystals, and Si, Al and Ti in polycrystals.

features;

(1) The transition metal elements and phosphorus exhibit fast diffusion, which are three to five orders of magnitude faster than the self-diffusion.

(2) The diffusion parallel to the c -axis is faster than that perpendicular to the axis except for P.

It is generally believed that the vacancy mechanism is operative for self-diffusion and also for substitutional impurity-diffusion; most of metallic impurity atoms dissolve as substitutional atoms. For such cases, the diffusion coefficients of impurity atoms, D_i , are expected to be of similar magnitudes to that of solvent self-diffusion, D_s . **Figure 2** shows the ratio of D_i/D_s for various elements in four matrix metals, copper, iron, lead and α -Ti. In copper, Sb is the fastest diffuser among various metallic solute elements, while Nb is the slowest; the ratio, D_i/D_s , ranges from 1/30 to 20. In iron, the ratio for all the metallic solute diffusion ranges from 10^{-1} to 10. In the same matrix carbon and nitrogen diffusivities are very high since these elements occupy the interstitial positions and diffuse by the interstitial mechanism.

Fast diffusion of metallic solute elements in metal crystals was first recognized for Au diffusion in lead in 1896.¹²⁾ In 1960 or thereabout, a number of systems were found to exhibit fast diffusion: monovalent metals (K, Na), the polyvalent metals (Pb, Sn, Tl, In), the lanthanide metals, actinide metals and semiconductors (Si, Ge).¹³⁾ Transition metal elements such as Fe, Co and Ni are very fast diffusers in Ti, Zr and Hf. Although the details of the mechanism of such fast diffusion are still controversial, some type of interstitial mechanism is believed to be operative on the basis of the following considerations.

Fig. 2. The ratio of impurity diffusivity to solvent self-diffusivity of various elements in four matrix metals, copper, iron, lead and α -titanium. (The diffusivity in Cu, Fe and Pb is taken at $0.8T_m$, and in α -Ti at 1073 K)

(1) Effect of Allotropic Transformation on Diffusion

On transformation from the α (hcp) to the β (bcc) phase, the diffusivity shows some changes. The ratios, D_β/D_α , at the transformation temperature, 1155 K, are:

Ti	Cr	Mn	Fe	Co	Ni	P
310	1.7	1.0	0.4	0.2	0.8	1.2,

where D_α is the value averaged over all the crystallographic directions:

$$D_\alpha = (2D_\perp + D_\parallel)/3.$$

While the self-diffusion coefficient of Ti exhibits a large increase on transformation, the other elements show relatively small changes. Anthony *et al.*¹⁴⁾ have observed a similar trend for thallium with Au and Ag as diffusers; while the self-diffusivity increases by about 30 times on transformation, the Au and Ag diffusivities are almost continuous or rather slightly decrease across the transformation temperature of 505 K. They regarded this as an indication of an interstitial type diffusion of Au and Ag; if these impurities diffuse by the vacancy mechanism as in the case of self-diffusion, one should observe the increase in the diffusivity of the same order of magnitude as that for self-diffusion. The same reasoning also applies to the diffusion in Ti.

(2) Diffusion Anisotropy

The ratios of the diffusivities, $D_\parallel/D_\perp$, at 1073 K are^{7,8)},

Cr	Mn	Fe	Co	Ni	P
1.6	2.0	2.6	3.6	1.7	0.66.

The trend, $D_\parallel > D_\perp$, is common for the transition metal elements, while it is opposite for P. Similar anisotropy has been observed for noble metal elements in Ti¹⁴⁾ and Cu in α -Zr.¹⁵⁾ Hood and Schultz¹⁵⁾ favoured an interstitial mechanism for Cu in α -Zr, and ascribed the above trend to the difference in volume of saddle point configurations for interstitial jumps in the two directions, parallel and perpendicular to the c -axis. Since the c/a ratio of Ti, 1.586, is almost the same as that of Zr, 1.594, the interpretation also holds for titanium.

The opposite trend observed for P may be related to the difference in the nature of bonds; semi-metallic phosphorus would interact with host titanium atoms in a different manner from that of metallic elements.⁹⁾

(3) Atomic Size Effect

Hood^{16,17)} has demonstrated a correlation between atomic size and impurity diffusion in Pb and in α -Zr; smaller sized atoms diffuse faster. Similar correlation seems to hold as shown in **Fig. 3**, where the diffusivities of various impurities in α -Ti and α -Zr are plotted as a function of atomic size. Here, we adopted, as representing atomic size, "metallic radii for the coordination number 12" after Teatum *et al.*¹⁸⁾ Numerical values are given in tabulated form in the monograph by Pearson.¹⁹⁾ The radii were calculated by assuming a rigid sphere model from lattice spacings of the respective elements. For the case of non fcc crystals, the radius for the coordination number 12 was deduced by appropriate processing of original data. These radii are said to be the most suitable

Fig. 3. Diffusivity vs. atomic radius at 1100 K in α -Ti and α -Zr. The single crystal data are indicated by the bars; the upper limit value is for diffusion parallel to the c -axis and the lower limit value for that perpendicular to the axis.

set to use for metallic alloys.¹⁹⁾ As seen in the figure, the trend that smaller atoms diffuse faster is evident. In particular, Co, Fe and Ni are the smallest and the fastest in α -Ti.

In discussion of fast metallic impurity diffusion in metals, Bakker²⁰⁾ pointed out that the atomic size estimated from the molar volume of pure metal is not sufficient description. He applied the Miedema-Niessen model²¹⁾ of the volume effect on alloying to the interpretation of fast diffusion in Pb and several other metals. By adopting the same model, we have calculated the molar volume of various elements when alloyed in α -Ti or α -Zr, as shown in Fig. 4. Unlike the case of fast diffusion in Pb, the two figures, Figs. 3 and 4, exhibit qualitatively similar trends.⁷⁾

(4) Solubility vs. Diffusivity

It is known that fast diffusers have generally very low solubility. In Fig. 5 is plotted the solubility of various elements in α -Ti and α -Zr at 1100 K vs. the diffusivity at 1100 K, indicating some correlation between the two quantities. It is interesting to recall the 15% empirical rule for the formation of solid solution proposed by Hume-Rothery *et al.*²²⁾; extended solid solution can only be formed if the difference in atomic sizes of the two elements is less than about 15%. In terms of molar volume, the critical value is 38.6%; solute atoms with a relative volume less than 61.4% of the solvent would not form an extensive solid solution. In α -Ti, the elements Co, Fe and Ni are smaller than the critical value, as seen

Fig. 4. Diffusivity vs. molar volume in α -Ti and α -Zr. D_{imp} and D_{self} are, respectively, impurity and self-diffusivity. V_{imp} and V_{self} are, respectively, partial molar volume of impurity and molar volume of pure metal. The single crystal data are indicated by the bars; the upper limit value is for diffusion parallel to the c -axis and the lower limit value for that perpendicular to the c -axis.⁸⁾

Fig. 5. Diffusivity vs. solubility of various elements in α -Ti and α -Zr ($T=1100$ K). For the data points for single crystals, the diffusivity is indicated by bars; the upper limit value is for diffusion parallel to the c -axis and the lower limit value to that perpendicular to the c -axis, except for P. For the latter, $D_{\perp} > D_{\parallel}$.⁸⁾

Fig. 6. Temperature dependence of self- and impurity diffusivities in β -Ti.

in Fig. 3. It is tempting to speculate that these elements are too small to occupy the stable substitutional position, and some fraction would occupy interstitial sites.⁷⁾

2.2. Self-diffusion and Metallic Impurity Diffusion in β -Ti

The temperature dependence of the self-diffusivity and impurity diffusivities in β -Ti are shown in Fig. 6.²³⁻²⁸⁾ The impurity diffusivities of Fe, Co and Ni are more than one order of magnitude larger than the self-diffusivity, while the diffusivities of Mn and Cr are only two to five times larger than the self-diffusivity. Further investigations are required to conclude whether both Mn and Cr diffusion occur with an interstitial-type or a vacancy mechanism.

In the α -phase the self-diffusion and the diffusion of any impurity are described by single rectilinear plots corresponding to an Arrhenius relation with temperature-independent parameters, the pre-exponential factor D_0 and the activation energy Q . On the other hand, in the β -phase the self-diffusion and the impurity diffusion exhibit marked upward curvatures in the Arrhenius plots, which are known as anomalous diffusion.

2.3. Effect of Oxygen on Impurity Diffusion in α -Ti

Titanium is a reactive metal. Commercially available pure titanium contains a few thousand ppm oxygen. Therefore, it is important to know how oxygen affects the diffusivity. The present authors have investigated the effect of oxygen on the diffusion of Fe,²⁹⁾ Ni,⁶⁾ Mn⁷⁾ and P⁹⁾ in polycrystalline α -Ti. Figures 7 and 8 show the temperature dependence of the diffusivities as a function of oxygen concentration.

As shown in Fig. 7, the addition of oxygen only slightly reduces the diffusivities of Fe, Ni and Mn. The Arrhenius

Fig. 7. Temperature dependence of diffusivities of Ni, Fe and Mn in α -Ti and oxygen-doped Ti.

Fig. 8. Temperature dependence of diffusivities of P in α -Ti and Ti-2.35at.%O alloy.⁹⁾

plot of the diffusivity is virtually linear and the diffusion coefficient in the Arrhenius plot seems to be shifted downwards with increasing oxygen concentration, indicating that the binding energy of these elements to oxygen is smaller than that of P to oxygen. In other words, the activation energy remains unchanged, but the

value of D_0 decreases. Such a trend may be understood in terms of the blocking effect: the diffusivity of oxygen is about one to three orders of magnitudes smaller than Fe, Ni and Mn, so that we have regarded the sites occupied by oxygen as immobile blocking sites.⁷⁾ The idea is as follows:

Oxygen and diffusers (Fe, Ni or Mn) share a common lattice formed by the interstices of the hexagonal close-packed lattice of titanium. Oxygen exerts no chemical attraction on diffusers, and yet reduces the diffusivity by its own presence; the sites occupied by oxygen are no longer available for diffuser.

On the other hand, the phosphorus diffusivity is significantly reduced by the oxygen addition particularly at lower temperatures; the Arrhenius plot of the diffusion coefficient exhibits a marked curvature. Such a trend is usually explained in terms of the trapping theory. Trapping effects in diffusion have been discussed by several investigators, mainly in connection with hydrogen diffusion in bcc metals.³⁰⁾ One of the present authors³¹⁾ has derived the following expression for the apparent diffusivity, D_a ,

$$D_a = D[1 - f_t + f_t \exp(B/RT)]^{-1}, \dots\dots\dots(1)$$

where D is the normal diffusion coefficient in the absence of trapping sites, f_t is the fraction of the number of trapping sites, and B the binding energy. The situation in hexagonal lattices is rather complicated because of the existence of multiple-jump frequencies, even in the perfect lattice. Since the essential feature of the trapping effect is expected to be not very much different for different lattices, the above expression is tentatively applied to analyse the data for P diffusion in α -Ti. In the present analysis, oxygen atoms are regarded as immobile, since the oxygen diffusivity is very small in comparison with that of phosphorus ($\sim 10^{-2}$). The binding energy B can be estimated as follows. By transforming Eq. (1), one obtains

$$\ln[(D/D_a - 1 + f_t)/f_t] = B/RT. \dots\dots\dots(2)$$

Assuming that the temperature dependence of D and the value of f_t are known, the experimental data of the diffusivity D_a can be plotted according to Eq. (2) as a function of $1/T$, which should yield a straight line with slope B/R . A least-mean-squares analysis of the data yields the binding energy of about 230 kJ mol⁻¹.

Suppression of the diffusion of Fe, Ni and Mn may be also interpreted as trapping effect of oxygen as McLellan and Brotzen³²⁾ have suggested. However, the present authors' suggestion is that even if oxygen exerts no chemical interaction on diffusers (the binding energy is zero), it can reduce the diffusivity by its own presence. The details are reported elsewhere.^{7,33)}

We remark the reason why no trapping effect is observed in the diffusion of Fe, Co, Ni, Mn and Cr in α -Ti over the same temperature range. The Gibbs free energies for the formation of oxides of these metals at 873 K are listed in Table 1 together with that for P. Because of the difference in the type of oxides, a direct comparison is not possible. If one compares the free

Table 1. Gibbs energies of formation of metal oxides at 873 K.

Reaction	Gibbs energy (kJ mol ⁻¹)
Fe + 2/3 O ₂ = 1/3 Fe ₃ O ₄	-276
Fe + 1/2 O ₂ = FeO	-208
Co + 1/2 O ₂ = CoO	-172
Ni + 1/2 O ₂ = NiO	-165
Mn + 1/2 O ₂ = MnO	-322
Cr + 3/4 O ₂ = 1/2 Cr ₂ O ₃	-445
1/2 P ₂ + 5/4 O ₂ = 1/2 P ₂ O ₅	-543
Ti + O ₂ = TiO ₂	-745

energies per metal atom (Fe, Co, Ni, Mn, Cr and P), the value for P is the largest; the affinity to oxygen is the strongest among these elements.⁹⁾

2.4. Effect of Alloying Elements on Diffusion in α - and β -Ti

The data on self-diffusion and impurity diffusion in alloys are compiled in Table 2. It has been reported that in α -type titanium alloys (Ti-Al-Sn) the addition of Al suppresses the Cr diffusion, while Sn hardly affects the diffusion.⁸⁾ The self-diffusion of the constituent elements in Ti-V alloys exhibits anomalous behaviour and both the diffusivities decrease with the increase in vanadium concentration.³⁷⁾ The trapping theory usually deals with the case of relatively low concentrations of impurity atoms (or trapping centers) so that the simple theory cannot be applied for concentrated alloys with solutes more than several atomic per cent.

2.5. Diffusion of Light Interstitial Elements in Ti

Figure 9 shows the temperature dependence of the diffusivities of (a) oxygen,³⁹⁻⁴⁶⁾ (b) nitrogen^{39,47-49)} and carbon,^{50,51)} and (c) hydrogen isotopes⁵²⁻⁵⁶⁾ in α - and β -Ti. Some of the data have been obtained by the radioactive tracer method using tritium and ¹⁴C, but a variety of different methods such as microhardness measurements and vacuum fusion gas extraction methods, *etc.* have been adopted in the evaluation of diffusion coefficients. As seen in the figures, the agreement of different measurements is not satisfactory. Various factors can be responsible for the discrepancy:

(1) Some experimental methods are not accurate enough to yield reliable values of D .

(2) Diffusion coefficients can be strongly concentration dependent, whereas no systematic investigations have been performed on the effect of solute concentration.

(3) A small amount of impurities may affect the interstitial diffusivity considerably. The purity of specimens for individual experiments can be widely different.

It is known that carbon, nitrogen and oxygen diffuse several orders of magnitude faster than metallic elements in normal bcc and fcc metals. However, as shown in Table 3, the diffusivities of these light interstitial atoms in α -Ti are only one to two orders of magnitude larger than the self-diffusivity of Ti. The activation energies for the diffusion in α -Ti are remarkably larger than those in

Table 2. D_0 and Q for diffusion in Ti alloys.

A (at%)	Element	B (at%)	D_{0A} ($\text{m}^2 \text{sec}^{-1}$)	Q_A (kJ mol^{-1})	D_{0B} ($\text{m}^2 \text{sec}^{-1}$)	Q_B (kJ mol^{-1})	Reference
α -phase							
Al	Sn	Ti	Diffusion of ^{51}Cr				8)
7.49			4.1×10^{-8}	144.0			
Sn		Ti	Diffusion of ^{51}Cr				8)
1.00			2.7×10^{-7}	151.8			
Al		Ti	Diffusion of ^{51}Cr				8)
6.39	1.00		1.8×10^{-8}	138.1			
β -phase							
Co		Ti			1.26×10^{-7}	145.2	2)
1.6					1.58×10^{-7}	140.2	
3.3					1.41×10^{-6}	160.3	
4.9					2.50×10^{-6}	162.8	
7.4							
Mn		Ti			1.90×10^{-6}	171.2	2)
9.7					2.06×10^{-6}	172.0	
13.3					2.60×10^{-6}	176.2	
17.9					5.47×10^{-5}	208.0	
20.6							
Cr		Ti					34)
10.0			2.0×10^{-6}	168.3			
18.0			9.0×10^{-6}	186.3			
Mo		Ti			Diffusion of ^{235}U		35)
5					2.6×10^{-5}	206.3	
10					1.45×10^{-4}	237.3	
15					2.88×10^{-4}	249.5	
20					2.69×10^{-4}	270.4	
25					6.03×10^{-4}	288.8	
30					3.30×10^{-3}	313.9	
Fe		Ti			Diffusion of ^{95}Nb		24)
5			9.2×10^{-6}	165.7	1.82×10^{-13}	146.1	
10			2.14×10^{-4}	203.4	2.9×10^{-6}	172.9	
15			5.25×10^{-3}	243.2	9.9×10^{-4}	234.4	
Nb		Ti			Diffusion of ^{55}Fe		24)
5			1.2×10^{-8}	125.1	7.9×10^{-7}	138.5	
10			5.8×10^{-8}	151.1	1.15×10^{-6}	146.1	
15			1.5×10^{-7}	164.5	7.9×10^{-7}	146.5	
Nb		Ti					25)
31			9×10^{-7}	209.3			
54			8×10^{-6}	267.9			
66			1×10^{-5}	301.4			
89			1×10^{-4}	380.9			
Nb		Ti					36)
5.4			1.79×10^{-7}	160.0	1.27×10^{-7}	149.0	
19.6			1.18×10^{-6}	198.1	3.15×10^{-7}	175.6	
35.7			2.98×10^{-5}	258.4	2.51×10^{-5}	247.0	
Nb		Ti			Diffusion of ^{235}U		35)
5					2.2×10^{-6}	170.3	
10					3.5×10^{-6}	182.1	
15					1.1×10^{-5}	200.9	
20					2.6×10^{-5}	215.6	
25					2.5×10^{-6}	226.0	
30					4.2×10^{-5}	235.6	
Ti	V						37)
0-90			Curved Arrhenius plots		Curved Arrhenius plots		
Ti	V				Diffusion of ^{235}U		35)
	5				3.4×10^{-6}	172.4	
	10				6.3×10^{-6}	182.1	
	15				4.7×10^{-6}	182.1	
	20				9.6×10^{-7}	164.5	
	25				2.5×10^{-6}	177.9	
	30				8.9×10^{-6}	195.5	
	40				1.2×10^{-5}	206.8	
	50				6.5×10^{-5}	235.6	
	60				2.7×10^{-4}	288.8	
	70				5.9×10^{-1}	365.0	
Zr	Ti				Diffusion of ^{60}Co		38)
50					2.95×10^{-7}	95.5	

other normal metals.⁵⁷⁾ Such high activation energies suggest the formation of rather strong covalent-like bonds between these interstitial impurity atoms and the

host titanium atoms.

Fig. 9. Temperature dependence of diffusivities of (a) oxygen, (b) nitrogen and carbon, and (c) hydrogen isotopes in α - and β -Ti.

3. Diffusion Mechanism

3.1. Fast Diffusion Mechanism

Although the details of the mechanism of fast diffusion are still controversial, some type of interstitial mechanism is believed to be operative as discussed in Sec. 2. A dissociative diffusion mechanism, or interstitial-substitutional solute diffusion mechanism, was proposed by Frank and Turnbull,⁵⁸⁾ which has been generally accepted by other researchers.

In identifying the mechanism of diffusion, the isotope effect has been considered to be useful. It seems appropriate to give here a brief account on the isotope

effect. The diffusion coefficient D is known to depend on the isotopic mass m of the diffuser. Quantitatively, the isotope effect E is defined by

$$E = \partial(\ln D) / \partial[\ln(m^{-1/2})] \quad \dots\dots\dots(3)$$

Schoen⁵⁹⁾ first pointed out the significance of the isotope effect in relation to the understanding of the diffusion mechanism. For simple situations such as self-diffusion via monovacancies in pure metals, the isotope effect may be expressed as

$$E = f \cdot \Delta K, \quad \dots\dots\dots(4)$$

where f is the correlation factor and ΔK is the so-called

Table 3. Interstitial diffusion data in Ti and some bcc metals (The data in bcc metals are taken from Ref. 57).).

Solvent	Interstitial element	Q (kJ mol ⁻¹)	D_i/D_s at $T_m/2$
α -Ti	C	130	2.03×10^2
	N	225	3.64
	O	200	1.47×10^2
V	C	116	1.24×10^7
	N	148	1.73×10^6
	O	123	1.64×10^7
Nb	C	142	8.95×10^7
	N	145	5.75×10^7
	O	113	2.39×10^9
Ta	C	162	5.74×10^6
	N	158	6.83×10^6
	O	106	2.10×10^8
Fe*	C	80	1.68×10^6
	N	77	3.16×10^6

* D_i/D_s is evaluated at 1 000 K.

Table 4. Summary of isotope effect coefficients in solids.⁶⁰⁾

Mechanism	E value
Interstitial mechanism	
Li, C→Metals	0.9~1
He, Ne→Quartz	0.9~1
H, D→Metals	0.4~1
Vacancy mechanism	
Self-diffusion	
fcc (Cu, Ag, Pd, Au, γ -Fe, Co, etc.)	0.65~0.90
bcc (Na, α -Fe, δ -Fe, etc.)	0.43~0.70
hcp (Zn)	0.67~0.75
Anomalous diffusion (β -Zr, β -Hf)	0.28~0.41
Impurity diffusion	0.1~0.9
Fast diffusion	
Cu, Ag, Au, Cd, Hg→Pb	0.12~0.26
Ag→Sn parallel to c -axis	0.01
perpendicular to c -axis	0.40
Co→ α -Ti parallel to c -axis	0.1
perpendicular to c -axis	0.3

kinetic factor. This relation holds only when the correlation factor has the particular form

$$f = u/(u+v), \quad (5)$$

where v is the jump frequency of the relevant diffuser and u is independent of v . Some researchers seem to have been unaware of or to have forgotten this limitation. This led to an incorrect understanding that the measurement of the isotope effect always yields the value of the correlation factor f , if one assumes the magnitude of ΔK .

For a simple interstitial diffusion, the equation corresponding to Eq. (4) is given by⁶⁰⁾

$$E = \Delta K. \quad (6)$$

As seen in **Table 4**, the values of E are close to unity for simple interstitial diffusion of Li and C in metals, and Ne and He in quartz; smaller values for hydrogen isotopes in metals have been ascribed to the quantum effect. In the case of the fast diffusers, the value of E is fairly small

(cf. Table 4), which is clearly different from the values for normal interstitial diffusers. Thus, the small isotope effect has been considered to be a major difficulty in accepting the interstitial type diffusion as the mechanism of atom movements for fast diffusers.

The present authors have discussed this point in detail, and suggested a possibility that ΔK can be considerably smaller than unity for some type of interstitial diffusion.⁶¹⁾ Further theoretical investigations are required to clarify this point. At the present stage, it is emphasized, at least, that the small isotope effect is not necessarily inconsistent with the interstitial-like diffusion mechanism.

3.2. Anomalous Diffusion Mechanism

The temperature dependence of the diffusion coefficient D is usually given by

$$D = D_0 \exp(-Q/RT). \quad (7)$$

In other words, $\ln D$ vs. $1/T$ forms a single straight line. For various metals,^{62,63)} the activation energy Q is related to the melting point T_m by

$$Q = 0.14T_m \pm 20\%, \quad (8)$$

and D_0 is within a certain range

$$D_0 = (0.1 \sim 10) \times 10^{-4} \text{ m}^2 \text{ sec}^{-1}. \quad (9)$$

As seen in Fig. 6, self- and impurity diffusion in β -Ti exhibit the significant upward curvature, showing deviation from the Arrhenius plot in the wide range of temperature, 1 155 to 1 940 K. Such anomalous diffusion was also observed in β -Zr, β -Hf, β -Pr, γ -U, δ -Ce and ϵ -Pu. If the anomalous diffusion is described with two different thermal activated processes, D can be expressed by

$$D = D_{0L} \exp(-Q_L/RT) + D_{0H} \exp(-Q_H/RT). \quad (10)$$

According to the data analysis for the self-diffusion in β -Ti,²⁴⁾

low temperature range	high temperature range
$D_{0L} = 2.0 \times 10^{-4} \text{ m}^2 \text{ sec}^{-1}$	$D_{0H} = 1.0 \times 10^{-4} \text{ m}^2 \text{ sec}^{-1}$
$Q_L = 125 \text{ kJ mol}^{-1}$	$Q_H = 250 \text{ kJ mol}^{-1}$

The values for high temperature range were in good agreement with that from the empirical relationship (8) and (9), so that the diffusion in the high temperature range was considered to be normal, and therefore, the diffusion in the low temperature range was said to be anomalous diffusion.

There have been several models for the anomalous diffusion. Kidson⁶⁴⁾ attributed the enhanced diffusion at low temperatures to tightly bound impurity-vacancy pairs, which was, however, rejected by the experiments by Askill.⁶⁵⁾ The enhancement in diffusion can be due to short-circuit diffusion along high-density dislocations produced in $\alpha \leftrightarrow \beta$ transformation process. The density required for this model (10^{15} m^{-2}) is too high. Peart and Askill⁶⁶⁾ proposed divacancy mechanism which would be operative at high temperatures, and single vacancy mechanism at low temperatures. This model failed, since Q_L is too small for a single vacancy diffusion.

Fig. 10. Atomic configuration in ω -embryo structure. (a) Body-centered cube showing the ABC (111) plane section, central atom at M . (b) Activated complex or ω embryo: The atom at M has collapsed into ABC triangle creating trigonal bonds.

Sanchez and deFontaine⁶⁷⁾ have suggested that the diffusion enhancement is related to formation of a metastable ω phase with decreasing temperature toward $\beta \rightarrow \alpha$ transformation temperature. A characteristic of the ω phase is the formation of a trigonal bonding between the atoms in two adjacent (111)-planes of the bcc structure, leaving every third (111)-plane unchanged shown in Fig. 10. When an atom M exchanges planes with a nearest neighbour vacancy in the bcc lattice, it passes through two successive triangular atomic configurations at one third (ABC) and two third of the jumping distance, both representing saddle points of the jump process. An increase in embryo concentration with decreasing temperature supplements the thermally activated atom-vacancy exchanges, thereby enhancing the observed diffusion rate. This interpretation was confirmed by the observation of remarkable softening of the $2/3 \langle 111 \rangle$ longitudinal phonon mode in β -Ti.⁶⁸⁾

4. Summary and Conclusions

The salient points described in this review are summarized as follows.

(1) The transition metal elements and phosphorus exhibit extremely fast diffusion; some type of interstitial-like diffusion must be operative.

(2) The small isotope effect, which has been observed for several fast diffusers, is not necessarily inconsistent with the interstitial-like diffusion mechanism.

(3) Self- and metallic impurity diffusion in β -Ti show the anomalous upward curvature in the Arrhenius plot, which is interpreted by the softening of the phonon mode.

(4) Effect of alloying elements on diffusion is discussed in terms of the trapping and blocking effects.

(5) The diffusivities of C, N and O in Ti are relatively small when compared with those in other metals, e.g. vanadium, niobium, tantalum and iron.

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