Pressure Dependence of Anomalous Diffusion of Zirconium in β-Titanium

HIDEKI ARAKI, YORITOSHI MINAMINO, TOSHIMI YAMANE, TETSUYA NAKATSUKA, and YOSHINARI MIYAMOTO

The impurity diffusion coefficients of Zr in β-Ti have been determined at temperatures from 1173 to 1773 K under pressures of 0.1 MPa and 1.0, 2.1, and 3.0 GPa using Ti/Ti-3.06 at. pct Zr diffusion couples. The Arrhenius plots of the diffusion coefficients exhibit strong curvature, and their degree becomes larger with increasing pressure. The activation volumes, ΔV, evaluated from the isothermal pressure dependence of the diffusion coefficient are 0.22 to 0.36 Ω, where Ω is the atomic volume of the host metal. The values of $\Delta V/\Omega$ are very close to the ratio of 0.33 for self-diffusion in β-Ti reported by Jeffery and the ratios of 0.28 to 0.41 for W and Sn diffusion in β-Ti reported by Araki *et al.*, whereas they are considerably smaller than that normally expected for diffusion in bcc metals *via* "simple" monovacancy mechanism. The increase in degree of curvature in the Arrhenius plot by pressure and the small values of $\Delta V/\Omega$ can be interpreted in terms of the model of phonon-assisted diffusion jumps *via* monovacancies.

I. INTRODUCTION

THE self- and impurity diffusion of some elements in β-Ti have unusual features: (a) nonlinear Arrhenius plots and (b) very low values of the apparent frequency factor, D_0, and the apparent activation energy, Q, at low temperature.[1–4] This anomalous diffusion behavior has also been found in diffusion in β-Zr,[5,6,7] γ-U, δ-Ce, ε-Pu, and γ-Yb, and various speculative models[1,2,4,8–11] have been proposed to explain it.

Measurement of the diffusion coefficient under high pressures makes it possible to evaluate the activation volume, ΔV, which represents the isothermal change in volume of a real and finite crystal associated with an actual diffusive jump.[12] The comparison between the experimental values of ΔV and the theoretically calculated values of volumes of formation and migration of various defects in metals is one of efficient approaches to elucidate diffusion mechanism. However, there are still only a few experimental determinations[13–16] of ΔV for the anomalous diffusion in β-Ti.

Jeffery[13] measured the self-diffusion coefficient in β-Ti at 1273 K under pressures to 700 MPa and obtained the $\Delta V/\Omega$ of 0.33, where Ω is the atomic volume of host metal. In this case, Ω is 10.6 × 10^{-6} m^3/mol for pure titanium at room temperature and atmospheric pressure. As shown in Table I, the value of $\Delta V/\Omega$ is appreciably smaller than those[17–20] measured for self-diffusion in Na and interdiffusion in the Fe-V system, whose diffusion coefficients do not exhibit strong curvature in the Arrhenius plots. Lazarus[21] theoretically estimated the volumes of formation and migration of monovacancy, ΔV_0^F and ΔV_0^M, in "normal" bcc metals to be 0.4 and 0.2 Ω, respectively. The calculated results show that the magnitude of $\Delta V/\Omega$ for the self-diffusion in β-Ti is only 55 pct of that normally expected for diffusion in bcc metals *via* "simple" monovacancy mechanism. Jeffery, therefore, concluded that the short-dislocation-path diffusion mechanism[22,23] is operative in addition to the monovacancy diffusion mechanism in β-Ti at the low temperature of 1273 K. However, LeClaire[1] and Graham[24] claimed that the dislocation density of about 10^{10} to 10^{15} m^{-2} required to account for the diffusion coefficients in terms of the short-dislocation-path diffusion mechanism is too high to be acceptable.

Buescher *et al.*[14] have measured the diffusion coefficient of ^{95}Zr in the Ti-50 at. pct Zr alloy at 1003 and 1493 K in the pressure range up to 1.44 GPa and evaluated the $\Delta V/\Omega$ to be 0.31 and 0.35, respectively, which are very close to $\Delta V/\Omega$ of self-diffusion in β-Ti reported by Jeffery.[13] They claimed that the difference in $\Delta V/\Omega$ between 1003 and 1493 K is within the limits of error, and only the monovacancy diffusion mechanism is operating in the whole temperature range of the bcc phase, although the Arrhenius plot of the diffusion coefficient shows strong curvature. However, they did not quantitatively explain why the magnitude of $\Delta V/\Omega$ is considerably small in comparison with those measured for other bcc systems and estimated for the diffusion *via* simple monovacancy mechanism.

Araki *et al.*[15,16] recently measured the impurity diffusion coefficients of W and Sn in β-Ti in the wide temperature ranges of 1323 to 1673 K and 1173 to 1773 K, respectively, under pressures to 2.8 GPa, and found that $\Delta V/\Omega$ for the W and Sn diffusion is in the range of 0.28 to 0.41, which is close to $\Delta V/\Omega$ for the self-diffusion in β-Ti and the ^{95}Zr diffusion in the Ti-50 at. pct Zr alloy. They succeeded in quantitatively explaining the small magnitude of ΔV for the diffusion in terms of a model of phonon-assisted diffusion jumps *via* monovacancies. However, the diffusion model cannot be confirmed, because the ΔV for the impurity diffusion of other elements in β-Ti has never been reported. A systematic study of ΔV for β-Ti is required to thoroughly understand the mechanism of the anomalous diffusion.

HIDEKI ARAKI, Research Associate, YORITOSHI MINAMINO, Assistant Professor, TOSHIMI YAMANE, Professor, and TETSUYA NAKATSUKA, Graduate Student, are with the Department of Materials Science and Engineering, Faculty of Engineering, Osaka University, Suita 565, Japan. YOSHINARI MIYAMOTO, Associate Professor, is with the Institute of Scientific and Industrial Research, Osaka University, Ibaraki 567, Japan.

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Table I. The Activation Volume, ΔV, Evaluated from Pressure Dependence of Diffusion Coefficients of Elements in Bcc Metals at the Atmospheric Pressure

		T (K)	$\Delta V/\Omega$*	Reference
"Anomalous" bcc metals				
β − Ti	self-diffusion	1273	0.33	13
Ti−50 at. pct Zr	diffusion of Zr	1003	0.31	14
		1493	0.35	
β − Ti	diffusion of W	1323	0.31	15
		1373	0.28	
		1423	0.28	
		1473	0.33	
		1523	0.31	
		1573	0.34	
		1623	0.41	
		1673	0.41	
β − Ti	diffusion of Sn	1173	0.28	16
		1223	0.29	
		1273	0.28	
		1373	0.30	
		1473	0.32	
		1573	0.34	
		1673	0.41	
		1773	0.41	
Normal bcc metals				
Na	self-diffusion	223 to 231	0.41	17
Na	self-diffusion	363	0.52	18
Na	self-diffusion	288	0.46	19
		364	0.54	
Fe-V	interdiffusion	1250 to 1540	0.69	20

*Ω the atomic volume of the host metal.

Zirconium is added to many (α + β)-type and β-type commercial titanium alloys in order to strengthen them. The accumulation of data on Zr diffusion in β-Ti and an understanding of its mechanism hence are essential for studying various phenomena in the relevant alloys, *e.g.*, creep, aging, sintering, grain growth, *etc.* However, there is no previous research on the impurity diffusion even under atmospheric pressure (0.1 MPa) except for the article of Pavlinov.[25] The experimental data of Pavlinov fall on one straight line in the Arrhenius plot, although the impurity diffusion coefficients of many other elements in β-Ti exhibit continuous upward curvature. It is hence necessary to reinvestigate the temperature dependence of the impurity diffusion coefficient at 0.1 MPa.

In this article, we have measured the impurity diffusion coefficient of Zr in β-Ti in the wide temperature range from 1173 to 1773 K under 0.1 MPa using Ti/Ti-3.06 at. pct Zr diffusion couples. Furthermore, the impurity diffusion coefficients have also been measured under the high pressures of 1.0, 2.1, and 3.0 GPa in the same wide temperature range as the atmospheric pressure experiment in order to determine the ΔV.

II. PROCEDURE

The pure titanium and Ti-3.06, 24.50, 47.73, and 74.99 at. pct Zr alloy ingots were prepared by repeated arc melting of sponge titanium and zirconium in high purity argon atmosphere. The impurity levels of the starting materials are listed in Table II. The ingots were annealed for 172.8 ks at 1373 K, 0.1 MPa in argon atmosphere for homogenization and grain growth. After this annealing, the average grain sizes of the titanium and Ti-3.06 at. pct Zr alloy samples are about 2 mm, and their oxygen concentrations are less than 670 and 520 ppm, respectively. The titanium and Ti-3.06 at. pct Zr alloy samples were cut into blocks 7-mm long, 7 mm-wide, and 4-mm high and cylinders in 4 mm in diameter and 2.5-mm high. They were metallographically polished and rinsed with acetone.

A diffusion couple for the atmospheric experiment was assembled by placing blocks of titanium and Ti-3.06 at. pct Zr alloy between two thin plates of tungsten (99 mass pct) and clamping them with bolts, nuts, and plates of stainless steel. The tungsten plates prevented the diffusion couple and the plates of stainless steel from reacting with each other during diffusion annealing. The diffusion couple and a broken piece of titanium (99.5 mass pct) were sealed with argon into a quartz capsule. The pressure of argon gas was 0.1 MPa at the diffusion annealing temperature. The quartz capsule was annealed in an electric furnace, and the temperature was controlled within ±1 K. After diffusion annealing, the quartz capsule was broken in ice water to quench the diffusion couple.

Two cylinders of titanium and Ti-3.06 at. pct Zr alloy were put into a high pressure cell to serve as a diffusion couple for a high pressure experiment. As shown in Figure 1, the high pressure cell is composed of a capsule for a diffusion couple, a cube of pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), a graphite tubular heater, a thermocouple, and two copper caps. The capsule is made of boron nitride which has good lubricity and thermal stability. The cubic pyrophyllite served as a pressure medium and a gasket. The caps were used for passing an electric current to the graphite heater. The high-pressure equipment consists of a 12 MN press machine and an apparatus with six anvils of tungsten carbide. The apparatus is designed to convert a unipress generated by the 12 MN press machine into six equal presses from the six anvils. The six anvils compress the cubical cell and produce a hydrostatic high pressure on the diffusion couple. Under high pressure, the diffusion couple was heated to the prescribed annealing temperature within 120 seconds with the internal tubular heater and held at the temperature for the prescribed diffusion time. The annealing temperature was measured with the Pt/Pt-13 pct Rh thermocouple placed on the capsule and controlled within ±2 K. The diffusion couple was cooled to room temperature within 60 seconds, and the average cooling rate during the first 5 seconds was larger than 50 K/s. After cooling, the diffusion couple was released from the high pressure. The calibration of annealing temperature was carried out using a method similar to that of Hanneman and Strong.[29] The pressure was calibrated through the measurements of the transitions of bismuth I–II (2.55 GPa), bismuth II–III (2.70 GPa), and thallium II–III (3.67 GPa) at room temperature.

A dummy experiment was carried out in order to estimate the change of impurity level of diffusion couple caused by diffusion anneal at high temperature under high pressure. Chemical analysis of titanium samples after anneal for 7.2 ks at 1623 K under 2.0 GPa gave oxygen concentrations less than 700 ppm. The results indicate that the

Table II. Impurities (Mass Ppm) in the Starting Materials

(a) Sponge Titanium

Fe	Ni	Cr	Al	Sn	N	Cl	0	C	Mn	Si	Mg	H	Ti
44	16	9	6	<10	10	610	280	30	2	<10	210	10	bal

(b) Sponge Zirconium

Al	B	Cl	Cr	Co	Fe	Hf	Mn	N	Ni	O	Pb	Si	Ti	V	Cd	Cu	C	Mg	W	U	Zr
56	<0.5	<30	83	<5	497	42	12	10	<10	430	<20	<30	<10	<10	<0.5	<10	22	<200	<10	<1	bal

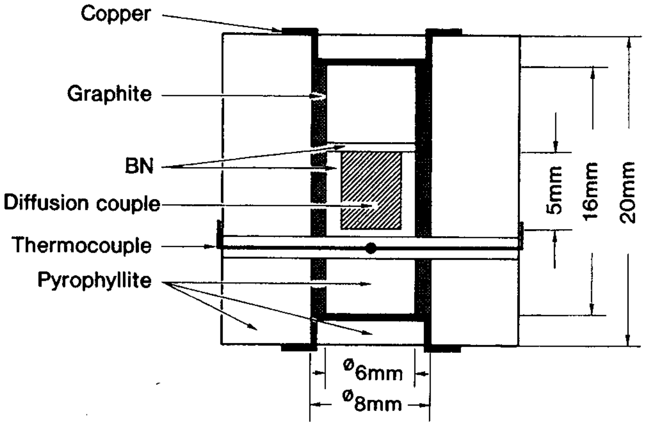

Fig. 1—Schematic illustration of high pressure cell.

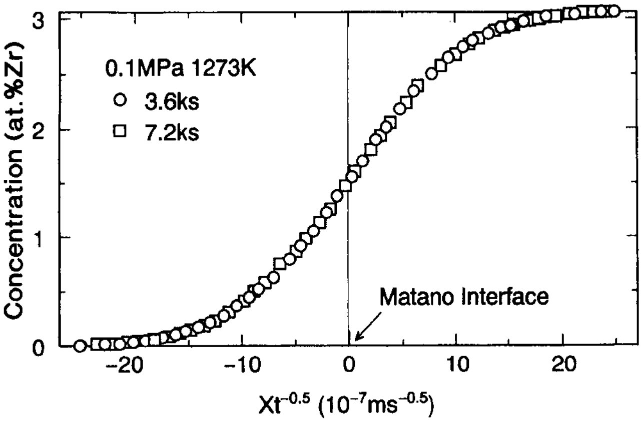

Fig. 2—Diffusion profiles in the diffusion couples annealed for 3.6 and 7.2 ks at 1273 K under 0.1 MPa.

diffusion anneal at high temperature under high pressure causes no significant increase in the oxygen concentration of diffusion couple.

The diffusion couples annealed at various pressures were mounted in epoxy resin, ground, and metallographically polished. They were analyzed with an electron probe microanalyzer to determine the penetration profiles. The measured relative intensities of ZrL_α radiation were converted to concentrations through a calibration curve experimentally established from the four alloys of Ti-3.06, 24.50, 47.73, and 74.99 at. pct Zr with the method described by Ziebold and Ogilvie.[30] The interdiffusion coefficients were determined with the Boltzman–Matano[31] and Hall[32] methods.

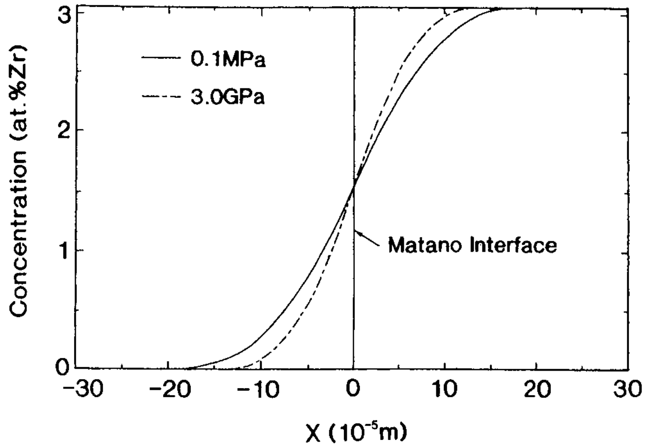

Fig. 3—Diffusion profiles in the diffusion couples annealed for 14.4 ks at 1173 K under 0.1 MPa and 3.0 GPa.

III. RESULTS

Figure 2 shows a plot of the atomic fraction of Zr, N_{Zr}, against $xt^{-0.5}$ for the diffusion couples annealed for 3.6 and 7.2 ks at 1273 K under 0.1 MPa, where x is the distance from the Matano interface and t is the diffusion annealing time. The two penetration profiles are directly together. The interdiffusion coefficient, $\tilde{D}$, can be determined through the analysis of penetration profiles with the Boltzman–Matano[31] and Hall[32] methods.

The penetration profiles in the diffusion couples annealed for 14.4 ks at 1173 K under 0.1 MPa and 3.0 GPa are shown in Figure 3. The penetration distance of Zr at 3.0 GPa is shorter than that at 0.1 MPa, and the high pressure suppresses the Zr diffusion in β-Ti.

Figure 4 shows the concentration dependence of interdiffusion coefficients at 1573 K under 0.1 MPa and 2.1 and 3.0 GPa. At all the pressures, the interdiffusion coefficients determined in the intermediate concentration ranges by the Boltzmann–Matano method[31] slightly increase with Zr concentration and smoothly link to those determined at the terminal compositions by the Hall method.[32]

Darken[33] proposed the following relationship between the interdiffusion, $\tilde{D}$ (N_B), and the impurity diffusion coefficients, D_A^*, D_B^*, for an A-B binary system:

$$\tilde{D} (N_B) = \{D_A^* N_B + D_B^* (1 - N_B)\} m \qquad [1]$$

$$m = 1 + d \ln \gamma_B / d \ln N_B \qquad [2]$$

where N_B is the atomic fraction and γ_B the activity coefficient, with the subscripts referring to the components.

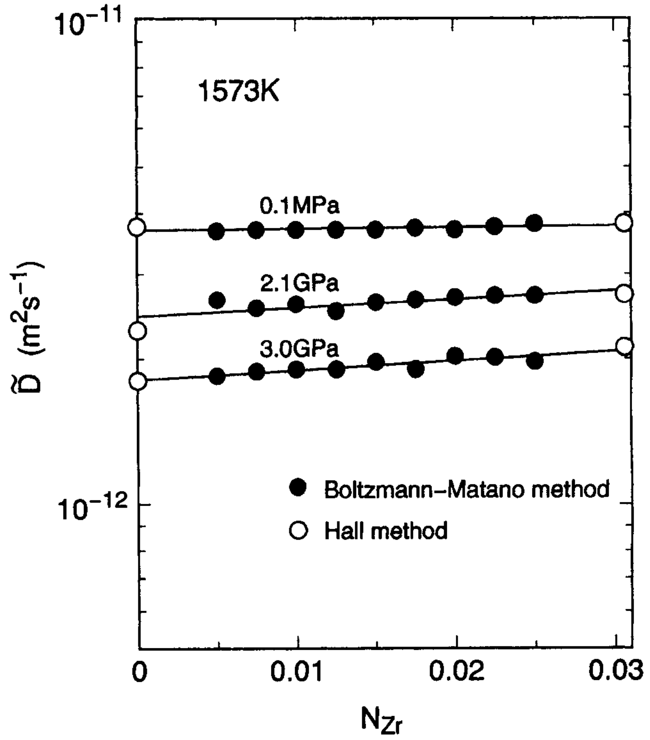

Fig. 4—Concentration dependence of interdiffusion coefficients, $\tilde{D}$, at 1573 K under 0.1 MPa and 2.1 and 3.0 GPa.

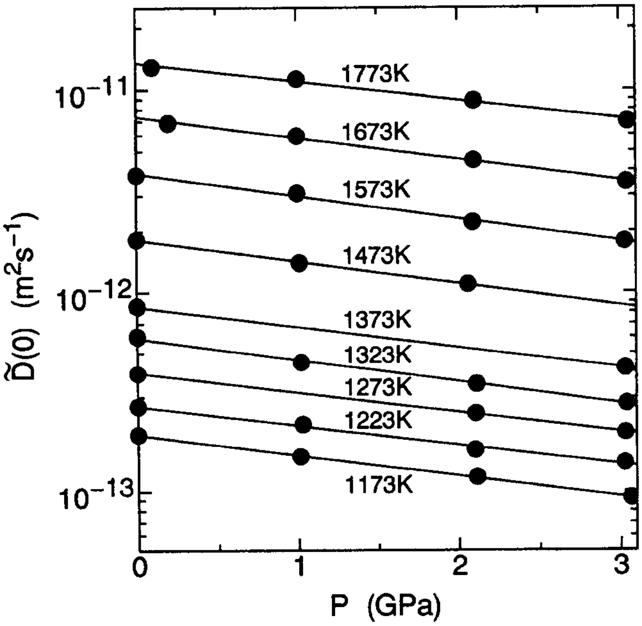

Fig. 5—Isothermal pressure dependence of impurity diffusion coefficients of Zr in β-Ti, $\tilde{D}$ (0).

When N_B approaches zero, the thermodynamic factor m goes to one, and consequently, the following relation is obtained:

$$\lim_{N_B \to 0} \tilde{D}(N_B) = D^*_B \qquad [3]$$

The interdiffusion coefficient at $N_{Zr} = 0$, which is symbolized by $\tilde{D}$ (0), can hence be regarded as the impurity diffusion coefficient of Zr in β-Ti, D^*_{Zr}.

Table III. The Experimental Values for the Activation Volume of Impurity Diffusion of Zr in β-Ti, ΔV

Temperature (K)	ΔV ($\times 10^{-6}$ m³/mol)	$\Delta V/\Omega$*
1173	2.4	0.22
1223	2.4	0.23
1273	2.7	0.25
1323	2.9	0.28
1373	2.7	0.26
1473	3.3	0.31
1573	3.5	0.33
1673	3.8	0.36
1773	3.4	0.32

*Ω: the atomic volume of Ti at room temperature and atmospheric pressure.

Figure 5 shows the isothermal pressure dependence of $\tilde{D}$ (0). The logarithm of $\tilde{D}$ (0) linearly decreases with pressure at all temperatures. The ΔV for diffusion can be determined[12] from the isothermal pressure dependence of $\tilde{D}$ (0):

$$\Delta V = -RT\,(d \ln D/dP)_T + \gamma_G\, K_T RT \qquad [4]$$

where T is the diffusion annealing temperature, R the gas constant, γ_G the Grueneisen constant, and K_T the isothermal compressibility. For β-Ti, γ_G and K_T were reported to be 1.04 and 1.10×10^{-11} Pa^{-1}, respectively.[13] The second term of Eq. [4] ranges from 1.12×10^{-7} to 1.69×10^{-7} m³/mol in the temperature range of this work and is considerably smaller than the first term. The values of ΔV and $\Delta V/\Omega$ obtained in this work are summarized in Table III. They are considerably smaller than the $\Delta V/\Omega$ estimated for diffusion in bcc metals *via* simple monovacancy mechanism, whereas it is close to $\Delta V/\Omega$ for the ^{95}Zr diffusion in the Ti-50 at. pct Zr alloy and the self- and impurity diffusion of W and Sn in β-Ti.

$\tilde{D}$ (0) at the pressures of 0.1 MPa and 1.0, 2.1, and 3.0 GPa was obtained by extrapolating and interpolating the experimental data on $\tilde{D}$ (0) at various pressures. The $\tilde{D}$ (0) is plotted against the reciprocal of absolute temperature, $1/T$, in Figure 6. The Arrhenius plots of $\tilde{D}$ (0) at all the pressures decrease nonlinearly with $1/T$. The diffusion coefficients of ^{95}Zr in β-Ti, D^*_{Zr}, measured in vacuum at temperatures from 1193 to 1753 K by Pavlinov[25] do not exhibit strong curvature in the Arrhenius plot, and their temperature dependence is represented using the following simple Arrhenius equation:

$$D^*_{Zr} = 4.70 \times 10^{-7}\ (\text{m}^2/\text{s}) \exp\{-148\ (\text{kJ/mol})/\text{R}T\} \qquad [5]$$

The equation is denoted by the broken line in Figure 6. Near 1273 K, the line intersects the experimental data of this work at 0.1 MPa, and at the higher temperature, D^*_{Zr} is larger than the experimental data of this work.

IV. DISCUSSION

Attempts have been made to interpret the non-Arrhenius-type diffusion behavior in β-Ti. Kidson[9] attributed the anomalous diffusion behavior to an enhancement of the vacancy concentration by oxygen-vacancy complexes at low temperature. However, the explanation was rejected by the

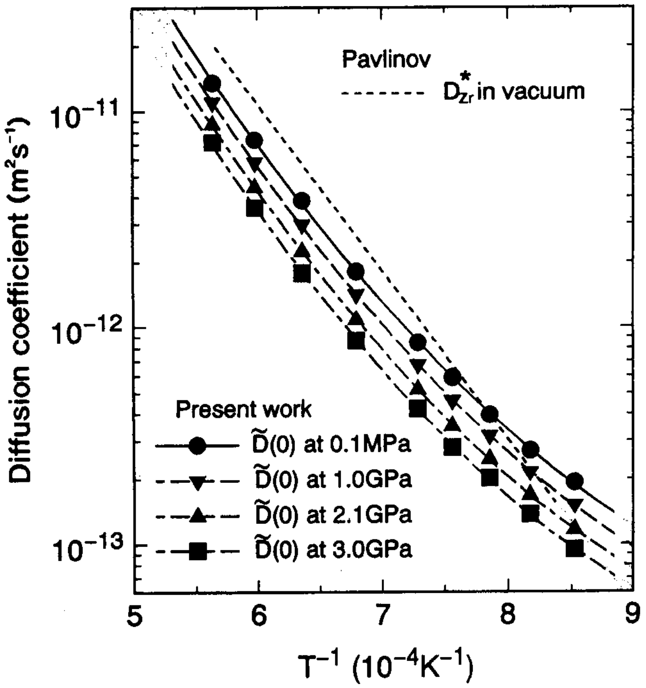

Fig. 6—Isobaric temperature dependence of impurity diffusion coefficients of Zr in β-Ti, $\tilde{D}$ (0).

experiments by Askill[34] and Herzig and Eckseler.[5] Askill and Gibbs[8] interpreted the nonlinear Arrhenius plots in terms of the monovacancy plus divacancy diffusion model. However, this model cannot explain very small experimental values[13–16] of activation volume for the anomalous diffusion in β-Ti.

The recent measurement[35] of phonon dispersion in β-Ti by means of quasielastic neutron scattering shows that the longitudinal $L(2/3)(1, 1, 1)$ mode and the transverse $T_1(1/2)(1, 1, 0)$ mode with $[1\ \bar{1}\ 0]$ polarization are of very low energy at low temperature. The softening of these phonons is interpreted as a dynamical precursor of martensitic phase transformation into α-Ti and ω-Ti in the bcc structure. Koehler and Herzig[11] proposed that the displacement of lattice caused by the phonons decreases the effective migration energy of monovacancy with decreasing temperature, resulting in the curvature of the Arrhenius plot. They assumed simple temperature dependence of the free energy of migration of monovacancy and thereby expressed the free energy of diffusion, G^D, and the diffusion coefficient, D, by the following equations:

$$G^D = G_0^F + G_0^M (1 - T_0/T) \qquad [6]$$

$$D = D_0 \exp\{-Q/(\mathrm{R}T)\} \exp\{G_0^M T_0/(\mathrm{R}T^2)\} \qquad [7]$$

where D_0, Q, G_0^F, and G_0^M are, in the absence of any phonon-induced lattice instabilities, the frequency factor, the activation energy, free energies for formation of monovacancy, and migration of monovacancy, respectively. The term T_0 is the hypothetical temperature where the bcc lattice becomes instable for atomic displacements in the $\langle 111 \rangle$ direction.

The $\tilde{D}$ (0) for 0.1 MPa obtained in this work were fitted to Eq. [7] with the least-squares technique to give the values for D_0, Q, and $G_0^M T_0$. The fitted curve is shown by the solid line in Figure 6, and the values of D_0, Q, and $G_0^M T_0$ are listed in Table IV, together with those for diffusion of other elements in β-Ti at vacuum and 0.1 MPa. The $G_0^M T_0$ for Zr diffusion in β-Ti is larger than that for self-diffusion in β-Ti, and it appears that the phonon softening of β-Ti influences the Zr diffusion more seriously than the self-diffusion.

The experimental data of $\tilde{D}$ (0) for 1.0, 2.1, and 3.0 GPa are denoted by ▼, ▲, and ■ in Figure 6. The experimental data at the high pressures scatter more than those at 0.1 MPa, owing mainly to difficulties in controlling the annealing temperatures at high pressures. The simple monovacancy model describes the temperature dependence of the diffusion coefficient only with the two parameters of the frequency factor, D_0', and the activation energy, Q', whereas the model of phonon-assisted diffusion jumps *via* monovacancy describes it with the three parameters of D_0, Q,

Table IV. The Values of D_0 ($\times 10^{-4}$ m²/s), Q (kJ/mol), $G_0^M T_0$ (MJK/mol), and G_0^M (kJ/mol) of Impurity Diffusion of Elements in β-Ti

	P	D_0	Q	$G_0^M T_0$	G_0^M	Reference
Zr	0.1 MPa	1.59	316	136	209	*
	1.0 GPa	1.60	322	140	211	*
	2.1 GPa	1.62	329	145	213	*
	3.0 GPa	1.64	334	148	214	*
Ti	vacuum	3.5	328	129	198	11
W	0.1 MPa	180	431	176	271	15
Sn	0.1 MPa	2.69	329	126	194	16
	1.0 GPa	2.72	336	131	197	16
	2.0 GPa	2.75	342	135	199	16
	2.8 GPa	2.77	348	139	201	16
Sn	0.1 MPa	0.690	301	111	171	26
Si	0.1 MPa	0.422	259	78.9	121	26
Ge	0.1 MPa	0.792	282	95.1	146	26
Cu	0.1 MPa	0.570	241	72.6	112	27
Ag	0.1 MPa	10.8	353	142	218	27
Cr	0.1 MPa	0.084	208	36.6	56	28
Pd	0.1 MPa	5.70	310	99.7	153	28
Sc	vacuum	2.46	298	108	166	28

*Present work.

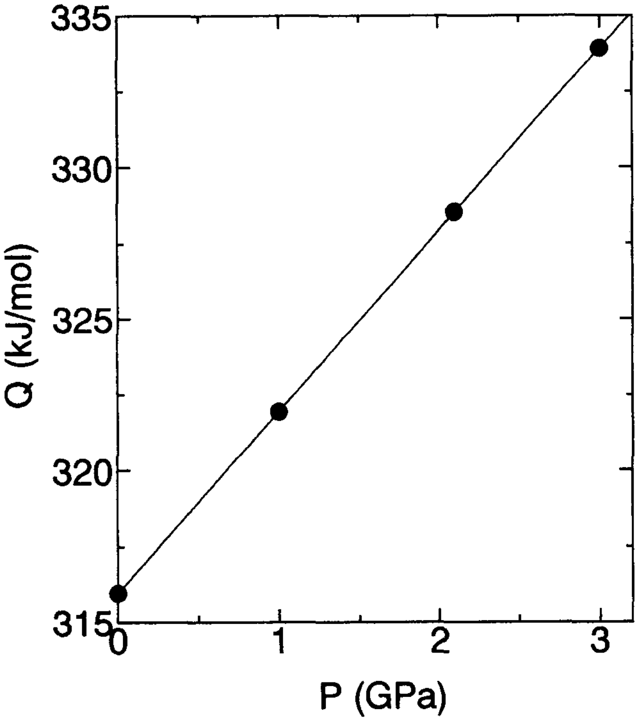

Fig. 7—Pressure dependence of activation energy for impurity diffusion of Zr in β-Ti *via* monovacancy mechanism in the absence of any phonon-induced lattice instabilities, Q.

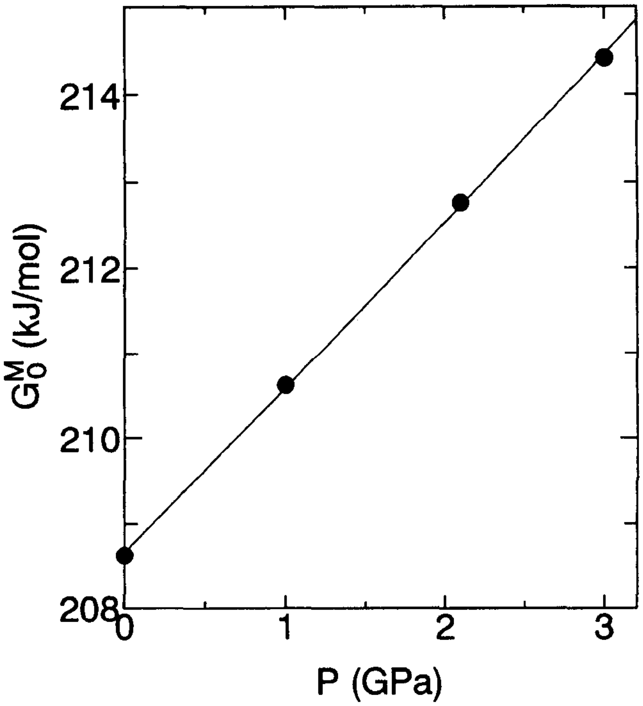

Fig. 8—Pressure dependence of free energy for migration of monovacancy in the absence of any phonon-induced lattice instabilities, G_0^M, responsible for impurity diffusion of Zr in β-Ti.

and $G_0^M T_0$. The values of D_0, Q, and $G_0^M T_0$ are, consequently, easily influenced by the scatter of experimental data, compared with D_0' and Q'. Therefore, only the Q and $G_0^M T_0$ at high pressures are determined with the least-squares technique from the experimental data at high pressures, and D_0 values at high pressures are estimated from D_0 at 0.1 MPa

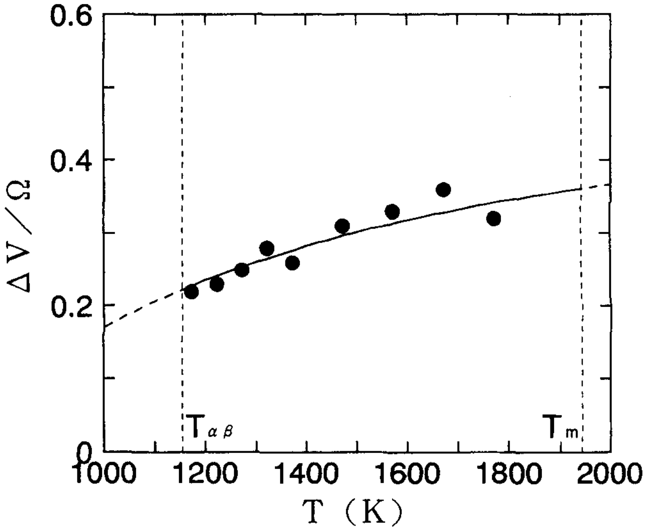

Fig. 9—The experimental and calculated results for the activation volume of the impurity diffusion of Zr in β-Ti, $\Delta V/\Omega$. Ω: the molar volume of Ti at room temperature and atmospheric pressure.

on the basis of the following equation:

$$D_{0\,(P=P)} = D_{0\,(P=P_0)} \exp\{\gamma_G K_T (P - P_0)\} \qquad [8]$$

where $D_{0\,(P=P_0)}$ and $D_{0\,(P=P)}$ are the frequency factors at atmospheric pressure, P_0, and high pressure, P. The values of D_0, Q, and $G_0^M T_0$ at high pressure determined in this work are listed in Table IV, and the curves represented by these values of D_0, Q, and $G_0^M T_0$ are shown by dot-dash lines in Figure 6. The good agreement between the lines and the experimental data in the whole experimental temperature range warrants validity of these values of D_0, Q, and $G_0^M T_0$ at the high pressures.

Figure 7, shows the pressure dependence of Q. The Q increases linearly with pressure. The slope of the straight line in Figure 7 indicates that the activation volume for Zr diffusion in β-Ti in the absence of any phonon-induced lattice instabilities is 0.56 Ω. This value is nearly equal to that for Sn diffusion in β-Ti[16] and agrees remarkably well with the sum of volumes of the formation and motion of monovacancy in bcc metals, $\Delta V_0^F + \Delta V_0^M$, theoretically estimated without consideration of phonon softening of bcc lattice by Lazarus.[21]

As shown in Table IV, the $G_0^M T_0$, which represents the extent of deviation from linearity in the Arrhenius plot of the diffusion coefficients, increases with pressure. This suggests that the diffusion enhancement caused by the phonons increases with pressure.

Lee *et al.*[4] reported T_0 to be 650 K on the basis of the diffusion data of the 13 elements in β-Ti. Araki *et al.*[16] estimated dT_0/dP to be 14 K/GPa from the experimental data on ΔV for the self- and impurity diffusion of W and Sn in β-Ti. On the basis of these values, the G_0^M at pressures of 0.1 MPa and 1.0, 2.1, and 3.0 GPa is evaluated from the values of $G_0^M T_0$. As shown in Table IV and Figure 8, the G_0^M depends linearly upon pressure according to the following equation:

$$G^M_{0\,(P=P)} = G^M_{0\,(P=P_0)} + \Delta V_0^M (P - P_0) \qquad [9]$$

The activation volume of migration of monovacancy in the absence of any phonon-induced lattice instabilities, ΔV_0^M, responsible for Zr diffusion in β-Ti, is estimated to be 0.18Ω. This value is nearly equal to ΔV_0^M responsible for Sn diffusion in β-Ti[16] and is in good agreement with ΔV_0^M theoretically estimated without consideration of phonon softening of bcc lattice by Lazarus.[21] To our regret, the volume of migration of monovacancy in any normal bcc metals has never been determined experimentally, but it is interesting that this value of ΔV_0^M is very close to the experimental values of volume of migration of monovacancy in Au[36] and Al.[37]

In consideration of phonon softening of bcc lattice, the activation volume for diffusion *via* monovacancy, ΔV, is estimated through the differentiation of Eq. [6] with respect to pressure.

$$\Delta V = \Delta V_0^F + \Delta V_0^M - \Delta V_0^M\, T_0/T - (G_0^M/T)\,(dT_0/dP) \qquad [10]$$

where ΔV_0^F and ΔV_0^M, respectively, are the activation volumes for formation and migration of monovacancy in the absence of any phonon-induced lattice instabilities. The ΔV_0^F and ΔV_0^M are estimated to be 0.38 and 0.18Ω, respectively, on the basis of both the pressure dependence of Q and G_0^M and the theoretical calculation by Lazarus.[21] From the literature, the T_0 and dT_0/dP were taken to be 650 K[4] and 14 K/GPa,[16] respectively.

The $\Delta V/\Omega$ calculated for Zr diffusion in β-Ti on the basis of Eq. [10] is denoted by the solid line in Figure 9, the $T_{\alpha\beta}$ and T_m symbolize the α to β phase transformation temperature and the melting point, respectively. The experimental values of $\Delta V/\Omega$ for $\tilde{D}$ (0) are shown by ● in Figure 9. The calculated $\Delta V/\Omega$ is 0.22 at $T_{\alpha\beta}$ and increases to 0.36 with increasing temperature to T_m. The calculated results are in good agreement with the experimental data. This indicates that the very small magnitude of $\Delta V/\Omega$ for the impurity diffusion of Zr in β-Ti, as well as those for the self- and impurity diffusion of W and Sn in β-Ti, can be interpreted in terms of the model of phonon-assisted diffusion jumps *via* monovacancies.

The sum of the first and second terms of Eq. [10], $\Delta V_0^F + \Delta V_0^M$, corresponds to 0.56 Ω of the activation volume normally expected for the diffusion in bcc metals *via* monovacancy mechanism, and the third and fourth terms reduce the ΔV to the very small values of 0.22 to 0.36 Ω. The third term of $-\Delta V_0^M T_0/T$ physically represents the reduction of migration volume by phonons and varies from -0.10 to -0.06 Ω in the range between $T_{\alpha\beta}$ and T_m. The fourth term of $-(G_0^M/T)$ (dT_0/dP) ranges from -0.24 to -0.14 Ω in the same temperature range, and its contribution to ΔV is considerably larger than that of the third term. This fourth term physically represents the contribution of pressure dependence of phonon softening to the activation volume. In β-Ti, the phonon-induced lattice instabilities become softer with increasing pressure, and T_0 accordingly rises at the rate of 14 K/GPa. This suggests that the diffusion enhancement caused by the phonons increases with increasing pressure, and the degree of curvature in the Arrhenius plot becomes larger. The suppression of formation and migration of monovacancy by pressure reduces the diffusion rate in β-Ti, whereas the increase of diffusion enhancement induced by the softening of phonons at high pressure weakens the reduction of diffusion rate, resulting in the small values of $\Delta V/\Omega$.

V. CONCLUSIONS

In this work, the diffusion coefficients of Zr in β-Ti have been determined at temperatures from 1173 to 1773 K under pressures of 0.1 MPa and 1.0, 2.1, and 3.0 GPa using the Ti/Ti-3.06 at. pct Zr diffusion couples. The interdiffusion coefficients at Zr concentration $N_{Zr} = 0$, $\tilde{D}$ (0), which can be regarded as the impurity diffusion coefficients, exhibit upward curvature in the Arrhenius plot for each of the pressures, and its degree becomes larger with increasing pressure. The diffusion coefficients can be represented by the following equations on the basis of the model of phonon-assisted diffusion jump *via* monovacancies:

at 0.1 MPa,

$$\tilde{D}\,(0) = 1.59 \times 10^{-4}\ (\mathrm{m^2/s})\ \exp\{-316\ (\mathrm{kJ/mol})/RT\}\ \exp\{136\ (\mathrm{MJK/mol})/RT^2\}$$

at 1.0 GPa,

$$\tilde{D}\,(0) = 1.60 \times 10^{-4}\ (\mathrm{m^2/s})\ \exp\{-322\ (\mathrm{kJ/mol})\mathrm{R}T\}\ \exp\{140\ (\mathrm{MJK/mol})/RT^2\}$$

at 2.1 GPa,

$$\tilde{D}\,(0) = 1.62 \times 10^{-4}\ (\mathrm{m^2/s})\ \exp\{-329\ (\mathrm{kJ/mol})/RT\}\ \exp\{145\ (\mathrm{MJK/mol})/RT^2\}$$

at 3.0 GPa,

$$\tilde{D}\,(0) = 1.64 \times 10^{-4}\ (\mathrm{m^2/s})\ \exp\{-334\ (\mathrm{kJ/mol})/RT\}\ \exp\{148\ (\mathrm{MJK/mol})/RT^2\}$$

The values of activation volumes, ΔV, evaluated from the isothermal pressure dependence of diffusion coefficients are in the range between 0.22 and 0.36 Ω. The values of $\Delta V/\Omega$ are very close to 0.33 for self-diffusion in β-Ti reported by Jeffery[13] and 0.28 to 0.41 for impurity diffusion of W[15] and Sn[16] in β-Ti reported by Araki *et al.* However, these values are appreciably smaller than those measured for diffusion in other bcc metals whose diffusion coefficients do not exhibit strong curvature in the Arrhenius plots, and approximately half of that estimated for diffusion in bcc metals *via* simple monovacancy mechanism.

We applied the model of phonon-assisted diffusion jump *via* monovacancies to the impurity diffusion of Zr in β-Ti under high pressure and estimated ΔV as $dT_0/dP = 14$ K/GPa. The value of dT_0/dP is derived from the experimental results for ΔV of the self- and impurity diffusion of W and Sn in β-Ti. The estimate is in very good agreement with the experimental results for ΔV of the impurity diffusion of Zr in β-Ti obtained in this work.

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