Diffusion of Chromium and Palladium in β -Titanium

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Interdiffusion coefficients in the β phase of Ti-Cr and Ti-Pd alloys have been determined by Matano's method in the temperature range between 1173 and 1823 K with (pure Ti)-(Ti-4.62 at% Cr alloy) and (pure Ti)-(Ti-1.84 at% Pd alloy) couples. The impurity diffusion coefficients of Cr and Pd in β -Ti have been determined by extrapolating concentration dependence of the interdiffusion coefficient to the infinite dilution of solute, and the following results have been obtained. In the whole temperature range, the diffusion coefficient of Cr, D_{Cr} , in β -Ti is about twice as large as the self-diffusion coefficient in β -Ti, D_{Ti}^* . The magnitude of diffusion coefficient of Pd, D_{Pd} , in β -Ti lies in the range between D_{Cr} and D_{Ti}^* , that is, at higher temperatures D_{Pd} is nearly of the same magnitude as D_{Cr} and at lower temperatures it is nearly equal to D_{Ti}^* . Both the Arrhenius plots of D_{Cr} and D_{Pd} indicate an upward curvature showing the behavior of so-called anomalous diffusion in b.c.c. metals, but the curvature of D_{Cr} is much looser than those of D_{Pd} and D_{Ti}^* . The curved Arrhenius plots have been explained by the monovacancy mechanism taking into account a temperature dependent migration energy of a vacancy due to the softening of the longitudinal acoustic $LA_{\frac{2}{3}}\langle 111 \rangle$ phonon in β -Ti. It has been recognized that the activation energy estimated for the monovacancy mechanism in the impurity diffusion of Cr and Pd and self-diffusion in β -Ti is proportional to the square of radius of the diffusing atom. This suggests that the size effect is dominant in the impurity diffusion in β -Ti.

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I. Introduction

To explain the deviation from linearity in the Arrhenius plot of self-diffusion coefficients in the so-called anomalous b.c.c. metals⁽¹⁾, Herzig and Köhler⁽²⁾⁻⁽⁴⁾ have recently proposed a model based on the experimental evidence of significant lattice softening of the longitudinal acoustic phonon in $\langle 111 \rangle$ direction at reduced wave vector $\frac{2}{3}$, $LA_{\frac{2}{3}}\langle 111 \rangle$ phonon, in β -Zr⁽⁵⁾. According to this model, the free energy of atomic migration G^M in the anomalous b.c.c. metals is expressed by

$$G^M = G_0^M(1 - T_0/T), \quad (1)$$

where G_0^M is the free energy of migration of a monovacancy in the monovacancy mechanism, and T_0 is the hypothetical temperature defined as the lowest temperature for the metal to have the b.c.c. structure. G^M would diminish to zero in the completely softened lattice at T_0 where the frequency of $LA_{\frac{2}{3}}\langle 111 \rangle$ would diminish to zero. Thus, the temperature dependence of the self-diffusion coefficient, D , in the anomalous b.c.c. metals should be expressed by

$$D = D_0 \exp(-Q/RT) \exp(G_0^M T_0/RT^2), \quad (2)$$

where D_0 and Q are the frequency factor and the activation energy, respectively, for the monovacancy mechanism in the lattice without the softening. The extent of deviation from the linearity in the Arrhenius plot

of diffusion coefficients is represented by the term $\exp(G_0^M T_0/RT^2)$ in eq. (2). An equation similar to eq. (2) has been obtained by Sanchez and de Fontaine⁽⁶⁾ on the basis of the ω embryo model where the ω embryo in the transition from the β phase to the ω phase has the same structure as the activated complex, and the ω embryo is also regarded as a lattice in significantly softened state of $LA_{\frac{2}{3}}\langle 111 \rangle$. Herzig and Köhler⁽⁴⁾ have shown that eq. (2) holds for the self-diffusion not only in the anomalous b.c.c. metals but also in the normal b.c.c. metals where deviation from linearity in the Arrhenius plot is very slight. Thus, the $LA_{\frac{2}{3}}\langle 111 \rangle$ phonon softening model appears to be the most suitable one among the models proposed for the diffusion mechanisms in the b.c.c. metals, so far.

In our previous work on the impurity diffusion of Cu and Ag in β -Ti⁽⁷⁾, eq. (2) has been confirmed to hold, and it has been recognized that the activation energy estimated for the monovacancy mechanism in the impurity diffusion of Cu and Ag and self-diffusion in β -Ti is proportional to the square of the atomic radius of the diffusing atom. In the present work, to confirm such a size effect for other impurities with different electronic structure from the noble metals, impurity diffusion of transition metals, Cr and Pd, in β -Ti has been investigated.

Although impurity diffusion of Cr in β -Ti has been studied by the autoradiography⁽⁸⁾⁽⁹⁾, the experimental data are insufficient to analyze the temperature dependence of the diffusion coefficients. Impurity diffusion of Pd in β -Ti has not been studied, so far.

In the present work, in addition to the new experimental data on diffusion of Cr and Pd in β -Ti, the experimental data on impurity diffusion coefficients of Sc⁽¹⁰⁾, V⁽¹¹⁾ and Ta⁽¹²⁾ in β -Ti have been referred to confirm the validity of eq. (2) and to determine the parameters of D_0 , Q

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and $G_0^M T_0$ in eq. (2). The atomic radii of Cr(0.1248 nm), V(0.1310 nm) and Pd(0.1339 nm) are smaller than that of Ti(0.1422 nm), while those of Ta(0.1427 nm) and Sc(0.1596 nm) are larger than that of Ti⁽¹³⁾, thus it has been possible to examine the size effect for the impurity diffusion in β -Ti over a wide range of atomic radius of the diffusing atom.

In the present work, interdiffusion experiments with the couples of pure Ti and dilute binary Ti alloys containing Cr and Pd have been carried out. Impurity diffusion coefficient of the solute atom in β -Ti has been determined by extrapolating concentration dependence of the interdiffusion coefficient to the infinite dilution of solute. This method is especially effective in determining impurity diffusion coefficient of the element, such as Cu and Pd for which the tracer diffusion experiment with radioactive isotope is not easy.

II. Experimental Procedure

Pure Ti rods 12 mm in diameter and 100 mm in length were machined from a pure Ti bar 160 mm in diameter supplied by Kobe Steel Ltd. The main impurities in this material were Fe: 0.046, N: 0.0032 and O: 0.0041 mass%. The rods were polished chemically, then sealed in quartz tubes with high purity argon gas and annealed at 1373 K for 172.8 ks (48 h) to cause grain growth. Alumina rings (more than 99% purity) were fitted up at both ends of the rod to prevent reaction with the quartz tube. The resultant grain size was about 3 mm. The rod was cut to make the disc specimens 5 mm in thickness. To obtain fully flat surface, the specimen was set in a stainless steel holder 50 mm in diameter and ground on abrasive paper and polished on a buff with fine alumina paste.

Buttons of Ti-4.62 at% Cr and Ti-1.84 at% Pd alloys were made by argon arc-melting the pure Ti blocks with Cr flakes of 99.4% purity and Pd plates of 99.7 % purity. To homogenize the buttons, the arc-melting was repeated a few times. Finally, the buttons were cast into a copper boat water-cooled to make an ingot 10 mm in diameter and 80 mm in length. The resultant grain size after the same grain growth treatment as described above was about 2 mm. The alloy rods were cut to make disc specimens 5 mm in thickness. The cut surface of the alloy specimen was ground and polished in the same way as the pure Ti specimen.

To make the semi-infinite interdiffusion couple the pure Ti and the alloy discs were put in a stainless steel holder with two screws, pressed by the screws and wrapped by a vanadium foil and surrounded by titanium sponges, and then diffusion-welded by heating at 1073 K for 3.6 ks in a stream of high purity argon gas. After the diffusion-welding, the couple was removed from the holder and put into an alumina tube with high purity argon gas. By putting the quartz tube in a furnace, diffusion annealing was carried out at temperatures in the range from 1173 to 1823 K for 2.4 ks to 2.16 Ms. For diffusion above 1673 K, the couple was sealed in double

tubes of quartz, keeping the inner tube from crushing by adjusting the pressure of argon gas between the inner and outer tubes. The diffusion temperature was controlled within ± 1 K at 1173–1473 K and ± 3 K at 1673–1823 K.

After the diffusion, the couple was cut parallel to the diffusion direction, and the cut surfaces were polished on a buff with fine alumina paste to examine the concentration-penetration profiles by an electron probe microanalyzer (Shimadzu ARL-II), operated under the conditions; accelerating voltage, 20 kV; take-off angle of Cr- $K\alpha$ and Pd- $L\alpha$ X-rays, 0.916 rad; specimen current, 50 nA; line scanning speed, 100 $\mu\text{m}/\text{min}$. In the case of Ti-Cr system, the calibration curve was obtained by the aid of the standard specimens for which chemical analyses were carried out. It showed that the relative intensity of Cr- $K\alpha$ X-ray emitted from the specimen was proportional to the mole fraction of Cr. In the case of the Ti-Pd system for which the concentration of Pd in the present work was low, it could be reasonably assumed that the relative intensity of Pd- $L\alpha$ X-ray was proportional to the mole fraction of Pd. This was confirmed with the calculation by Philibert's method⁽¹⁴⁾ and Pool and Thomas's method⁽¹⁵⁾. The interdiffusion coefficient was determined as a function of solute concentration by Matano's method⁽¹⁶⁾. The molar volume of Ti-Cr alloys⁽¹⁷⁾ has been shown to be proportional to the mole fraction of Cr, indicating that both the partial molar volumes of Cr and Ti are independent of concentration of Cr. The experimental data on the molar volume of Ti-Pd alloys are not available, but it may be reasonable to assume that the partial molar volumes of Pd and Ti are constant because of the diluteness of the Ti-Pd alloys studied in the present work. Therefore, the mole of solute (Cr and Pd) per cubic meter could be used as the unit of concentration in the analysis of diffusion.

III. Results and Discussion

Figure 1 shows the concentration dependence of the interdiffusion coefficient, $\bar{D}$, in Ti-Cr alloys determined with (pure Ti)-(Ti-4.62 at% Cr alloy) couples in the temperature range between 1173 and 1823 K. Interdiffusion coefficients determined for different diffusion times are shown distinguishably from each other by different marks ($\circ$, $\bullet$ and $\triangle$). As shown in Fig. 1, at each temperature $\bar{D}$ is independent of diffusion time. According to Darken's relation⁽¹⁸⁾, the extrapolated value of $\bar{D}$ to the infinite dilution of Cr can be regarded as the impurity diffusion coefficient of Cr, D_{Cr} , in β -Ti. The values of D_{Cr} determined in this way are listed in Table 1 with the marks corresponding to those in Fig. 1. If the impurity diffusion coefficient is perfectly independent of concentration of solute, it can be also determined from the slope of a straight line in the plot of probability function of concentration of solute versus distance⁽¹⁹⁾. However, the plot of the present data does not show a fully single straight line. This may be due to slight dependence of $\bar{D}$ on concentration of solute. Then, in the present work Matano's method has been employed to determine the interdiffu-

Table 1 Impurity diffusion coefficient of Cr in β -Ti.

Diffusion temperature T/K	Diffusion time t/s	Diffusion coefficient $D_{Cr}/m^2 s^{-1}$	Mark
1823	2.40×10^3	$(3.44 \pm 0.21) \times 10^{-11}$	○
1773	3.60×10^3	$(2.48 \pm 0.14) \times 10^{-11}$	○
1723	5.40×10^3	$(1.74 \pm 0.11) \times 10^{-11}$	○
1673	7.20×10^3	$(1.33 \pm 0.11) \times 10^{-11}$	○
	1.08×10^4	$(1.35 \pm 0.07) \times 10^{-11}$	●
1623	9.00×10^3	$(9.01 \pm 0.47) \times 10^{-12}$	○
	1.44×10^4	$(9.31 \pm 0.91) \times 10^{-12}$	●
1573	1.44×10^4	$(5.99 \pm 0.24) \times 10^{-12}$	○
	2.16×10^4	$(5.94 \pm 0.28) \times 10^{-12}$	●
	2.88×10^4	$(6.00 \pm 0.37) \times 10^{-12}$	△
1523	2.88×10^4	$(4.24 \pm 0.27) \times 10^{-12}$	○
	4.32×10^4	$(4.18 \pm 0.27) \times 10^{-12}$	●
1473	2.88×10^4	$(2.66 \pm 0.13) \times 10^{-12}$	○
	4.32×10^4	$(2.67 \pm 0.21) \times 10^{-12}$	●
	6.48×10^4	$(2.51 \pm 0.04) \times 10^{-12}$	△
1423	4.32×10^4	$(1.74 \pm 0.12) \times 10^{-12}$	○
	7.92×10^4	$(1.73 \pm 0.09) \times 10^{-12}$	●
1373	2.16×10^4	$(1.05 \pm 0.08) \times 10^{-12}$	○
	4.32×10^4	$(1.08 \pm 0.06) \times 10^{-12}$	●
	8.64×10^4	$(1.03 \pm 0.06) \times 10^{-12}$	△
1323	1.73×10^5	$(6.44 \pm 0.35) \times 10^{-13}$	○
	2.59×10^5	$(6.28 \pm 0.44) \times 10^{-13}$	●
1273	1.73×10^5	$(3.69 \pm 0.28) \times 10^{-13}$	○
	2.59×10^5	$(3.48 \pm 0.21) \times 10^{-13}$	●
1223	6.91×10^5	$(2.04 \pm 0.15) \times 10^{-13}$	○
1173	4.32×10^5	$(1.16 \pm 0.07) \times 10^{-13}$	○
	6.91×10^5	$(1.10 \pm 0.08) \times 10^{-13}$	●

sion coefficient as a function of concentration of solute.

Figure 2 shows the concentration dependence of the interdiffusion coefficient $\tilde{D}$ in Ti-Pd alloys determined with (pure Ti)-(Ti-1.84 at% Pd alloy) couples in the temperature range between 1173 and 1823 K. Also in this alloy, $\tilde{D}$ is recognized to be independent of diffusion time. The impurity diffusion coefficients of Pd, D_{Pd} , in β -Ti determined in the same way as D_{Cr} are listed in Table 2 with marks corresponding to those in Fig. 2.

Figure 3 shows the temperature dependence of D_{Cr} and D_{Pd} in β -Ti determined by the present experiments, in comparison with that of the tracer diffusion coefficient of Cr, D_{Cr}^* , in β -Ti determined by Mortlock and Tomlin⁽⁸⁾ and that of the tracer selfdiffusion coefficient D_{Ti}^* by Köhler and Herzig⁽³⁾. The magnitude of D_{Cr} is nearly equal to that of D_{Cr}^* , as predicted by Darken's relation⁽¹⁸⁾. In the whole temperature range of β -Ti, D_{Cr} is about twice as large as D_{Ti}^* . On the other hand, the magnitude of D_{Pd} lies in the range between D_{Cr} and D_{Ti}^* , that is, at higher temperatures D_{Pd} is nearly of the same magnitude as D_{Cr} and at lower temperatures the magnitude of D_{Pd} is nearly equal to that of D_{Ti}^* . In the Arrhenius plot of D_{Cr} and D_{Pd} an upward curvature is recognized as in the case of D_{Ti}^* , but the curvature of the plot of D_{Cr} is much looser than those of D_{Pd} and D_{Ti}^* . Fitting the experimental values of D_{Cr} and D_{Pd} into eq. (2), the parameters, D_0 , Q and $G_0^M T_0$, and the probable errors are calculated as listed in Table 3 together with those for Cu and Ag calculated

Fig. 1 Concentration dependence of interdiffusion coefficient $\tilde{D}$ in Ti-Cr alloys.

Fig. 2 Concentration dependence of interdiffusion coefficient $\tilde{D}$ in Ti-Pd alloys.

Table 2 Impurity diffusion coefficient of Pd in β -Ti.

Diffusion temperature T/K	Diffusion time t/s	Diffusion coefficient $D_{Pd}/m^2 s^{-1}$	Mark
1823	2.40×10^3	$(2.59 \pm 0.07) \times 10^{-11}$	○
1773	3.60×10^3	$(1.94 \pm 0.12) \times 10^{-11}$	○
1723	5.40×10^3	$(1.26 \pm 0.06) \times 10^{-11}$	○
1673	7.20×10^3	$(9.00 \pm 0.51) \times 10^{-12}$	○
	1.08×10^4	$(9.06 \pm 0.29) \times 10^{-12}$	●
1623	9.00×10^3	$(6.11 \pm 0.43) \times 10^{-12}$	○
	1.44×10^4	$(6.22 \pm 0.49) \times 10^{-12}$	●
1573	1.44×10^4	$(3.89 \pm 0.27) \times 10^{-12}$	○
	2.16×10^4	$(3.82 \pm 0.39) \times 10^{-12}$	●
	2.88×10^4	$(3.89 \pm 0.29) \times 10^{-12}$	△
1523	3.78×10^4	$(2.40 \pm 0.12) \times 10^{-12}$	○
	6.48×10^4	$(2.38 \pm 0.15) \times 10^{-12}$	●
1473	2.88×10^4	$(1.49 \pm 0.11) \times 10^{-12}$	○
	5.76×10^4	$(1.41 \pm 0.08) \times 10^{-12}$	●
	8.64×10^4	$(1.38 \pm 0.10) \times 10^{-12}$	△
1423	8.64×10^4	$(8.96 \pm 0.37) \times 10^{-13}$	○
	1.44×10^5	$(8.58 \pm 0.33) \times 10^{-13}$	●
1373	8.64×10^4	$(5.32 \pm 0.29) \times 10^{-13}$	○
	5.18×10^5	$(5.27 \pm 0.27) \times 10^{-13}$	●
1323	4.32×10^5	$(3.10 \pm 0.17) \times 10^{-13}$	○
	6.91×10^5	$(3.16 \pm 0.24) \times 10^{-13}$	●
1273	6.05×10^5	$(1.77 \pm 0.11) \times 10^{-13}$	○
	9.50×10^5	$(1.80 \pm 0.13) \times 10^{-13}$	●
	1.30×10^6	$(1.82 \pm 0.10) \times 10^{-13}$	△
1223	8.64×10^5	$(1.07 \pm 0.08) \times 10^{-13}$	○
	1.47×10^6	$(1.07 \pm 0.10) \times 10^{-13}$	●
1173	8.64×10^5	$(5.63 \pm 0.23) \times 10^{-14}$	○
	1.47×10^6	$(5.55 \pm 0.37) \times 10^{-14}$	●
	2.16×10^6	$(5.38 \pm 0.21) \times 10^{-14}$	△

Fig. 3 Temperature dependence of diffusion coefficients of Cr and Pd in β -Ti.

previously by the present authors⁽⁷⁾.

Temperature dependence of the impurity diffusion coefficients of Sc⁽¹⁰⁾, V⁽¹¹⁾ and Ta⁽¹²⁾ in β -Ti is shown in Fig. 4 in comparison with that of self-diffusion⁽³⁾ in β -Ti. Here, it is recognized that $D_{Sc}^* > D_V^* \approx D_{Ti}^* > D_{Ta}^*$. The parameters of D_0 , Q and $G_0^M T_0$ for diffusion of Sc, V and Ta in β -Ti are also calculated and listed in Table 3.

If eq. (2) is applicable, the softening of $LA_{\frac{2}{3}}\langle 111 \rangle$ phonon increases the diffusion coefficient D by the factor $\exp(G_0^M T_0 / RT^2)$. In Table 3, values of this factor at the melting temperature of Ti ($T_m = 1943$ K) and at the β - α transformation temperature of Ti ($T_{\beta-\alpha} = 1155$ K) are also listed for the impurity diffusion of the seven elements in β -Ti and the self-diffusion in β -Ti. At T_m , the factor ranges from 3.2 to 92, depending on the diffusing

element, however, at $T_{\beta-\alpha}$ it ranges much more widely, from 27 to 3.6×10^5 .

Since Q is the sum of enthalpy of the formation H_0^F and the migration H_0^M of a monovacancy, $G_0^M T_0$ can be written as

$$G_0^M T_0 = (H_0^M - TS_0^M) T_0 = (Q - H_0^F) T_0 - T_0 S_0^M T, \quad (3)$$

where S_0^M is the entropy of migration of a monovacancy. According to Sanchez⁽²⁰⁾, the term $T_0 S_0^M$ is negligible compared with $H_0^M (= Q - H_0^F)$. Because we are concerned with β -Ti, $T_{\beta-\alpha} (= 1155 \text{ K}) < T < T_m (= 1943 \text{ K})$, and T_0 is 657 K, as estimated below. Thus, the second term of the right hand side in eq. (3) is much smaller than the first

Table 3 Parameters for the anomalous diffusion in β -Ti.

	$D_0/m^2 s^{-1}$	$Q/kJmol^{-1}$	$G_0^M T_0/MJmol^{-1} K$	$\exp\left(\frac{G_0^M T_0}{RT_m^2}\right)$	$\exp\left(\frac{G_0^M T_0}{RT_{\beta-\alpha}^2}\right)$	$r/10^{-10} m$
Ti→Ti	3.5×10^{-4}	328 ± 25	129 ± 18	61	1.1×10^5	1.422
Cr→Ti	$(8.41^{+6.39}_{-2.63}) \times 10^{-6}$	208 ± 9	36.6 ± 6.4	3.2	27	1.248
Pd→Ti	$(5.70^{+3.47}_{-2.16}) \times 10^{-4}$	310 ± 11	99.7 ± 7.9	24	8.0×10^3	1.339
Sc→Ti	$(2.46^{+7.00}_{-2.38}) \times 10^{-4}$	298 ± 77	108 ± 52	31	1.7×10^4	1.596
V→Ti	$(3.17^{+5.07}_{-1.95}) \times 10^{-3}$	352 ± 23	124 ± 17	52	7.2×10^4	1.310
Ta→Ti	$(1.09^{+6.82}_{-0.94}) \times 10^{-4}$	334 ± 49	135 ± 36	74	1.9×10^5	1.427
Cu→Ti	$(5.70^{+2.34}_{-1.66}) \times 10^{-5}$	241 ± 8	72.6 ± 5.6	10	7.0×10^2	1.244
Ag→Ti	$(1.08^{+1.25}_{-0.58}) \times 10^{-3}$	353 ± 18	142 ± 13	92	3.6×10^5	1.406

Fig. 4 Temperature dependence of diffusion coefficients of Sc, V and Ta in β -Ti.

term. Then $G_0^M T_0$ increases in proportion to T_0 with increasing activation energy Q . This is confirmed by the present and previous experimental results^{(7)(10)–(12)}, as shown in Fig. 5, where for diffusion of all the eight elements in β -Ti, a single straight line can be drawn, indicating that H_0^F is constant independent of the element. The value of H_0^F is estimated to be 142 kJmol^{-1} by extrapolating Q to $G_0^M T_0 = 0$ in Fig. 5. From the slope of the straight line in Fig. 5, T_0 is estimated to be 657 K. This means that the activation energy Q for the impurity diffusion in β -Ti is controlled by the value of H_0^M rather than H_0^F .

According to Sanchez and de Fontaine⁽⁶⁾, the free energy of formation of the ω embryo (or the activated complex), G_ω , is correlated with the transforming parameter from the β phase to the ω phase, ε , by

$$G_\omega = A(T, p)\varepsilon^2 - B(T, p)\varepsilon^3, \quad (4)$$

where $A(T, p)$ and $B(T, p)$ are the functions of both temperature, T , and pressure, p . ε is proportional to the atomic displacement in the β phase lattice which participates in the formation of the ω embryo⁽²¹⁾. $\varepsilon = 0$ in the perfect b.c.c. structure, but $\varepsilon = 1$ in the perfectly transformed lattice (ω phase). The driving force for the transformation expressed by the second term $B(T, p)\varepsilon^3$ is negligible at higher temperatures but increases with decreasing temperature. On the other hand, in the temperature range much higher than T_ω , which is the highest temperature for the ω phase to exist, only the first term

Fig. 5 Plot of $G_0^M T_0$ versus Q for diffusion in β -Ti. G_0^M : the free energy of migration of a monovacancy, T_0 : the hypothetical temperature defined as the lowest temperature for the metal to have the b.c.c. structure, Q : activation energy estimated for diffusion via the monovacancy mechanism.

$A(T, p)\varepsilon^2$ is significant, and the normal monovacancy mechanism operates for the diffusion, then

$$G_\omega(T \gg T_\omega) \approx A\varepsilon^2 = G_0^M = H_0^M - TS_0^M. \quad (5)$$

By the theoretical considerations⁽²⁰⁾, it has been supposed that $T_{\beta-\alpha} > T_\omega > T_0$. In the process of formation of the ω phase of the h.c.p. structure from b.c.c. β -Ti by the lattice displacement in the $\langle 111 \rangle$ direction, the intrinsic strain due to an activated configuration contributing to the transformation to the ω phase comes about 3.4% in the direction $[1\bar{2}1]$ in the β phase. However, if the atomic radius of one of the two atoms located on the unit cell of the ω phase is larger by 1.7% than that of the other atom, the intrinsic strain in the ω phase must be just canceled out, and the value of ε becomes unity. Furthermore, in the activated configuration the frequency of $LA\frac{2}{3}\langle 111 \rangle$ is zero and the b.c.c. structure becomes completely unstable, thus the migration energy of an activated atom to the nearest neighbor vacancy becomes to be maximum. If the radius of diffusing impurity atom r is smaller than 1.017 times the radius of solvent atom r_m , the parameter ε can be represented by

$$\varepsilon = r/1.017r_m \quad (r \leq 1.017r_m) \quad (6)$$

and for the impurity atom larger than $1.017r_m$

$$\varepsilon = 1 - (r - 1.017r_m)/1.017r_m \quad (r \geq 1.017r_m). \quad (7)$$

From eqs. (5)–(7), it can be concluded that the migration enthalpy of an impurity in the direction $[1\bar{2}1]$ is pro-

Fig. 6 Plot of the activation energy Q estimated for diffusion via the monovacancy mechanism versus the square of radius r^2 of diffusing atom in β -Ti.

portional to the square of the radius of the impurity atom. As the coordination number in the b.c.c. structure of the β -Ti is eight, the atomic radius of the metal of different structure from the b.c.c. is converted for the coordination number eight by the conversion relation⁽¹³⁾ and shown in the last column of Table 3. As shown in Fig. 6, for $r < 1.017r_m$, Q increases linearly with increasing r^2 , and for $1.017r_m < r$, Q decreases with increasing r^2 . This is consistent with the prediction that $H_0^M (= Q - H_0^F)$ is proportional to r^2 , as deduced from eqs. (5)–(7). Thus, it must be emphasized that the size effect is dominant in the impurity diffusion in β -Ti.

IV. Conclusions

The present experimental results show that the Arrhenius plots of the impurity diffusion coefficients of Cr and Pd in β -Ti in the temperature range 1173 to 1823 K exhibit an upward curvature. This can be explained by a monovacancy mechanism with a temperature dependent

migration energy due to the softening of the $LA_{\frac{1}{2}}\langle 111 \rangle$ phonon in β -Ti. The activation energy estimated for the monovacancy mechanism in the impurity diffusion of Cr and Pd and the self-diffusion in β -Ti is proportional to the square of radius of the impurity atom.

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