

Isotope effect in the diffusion of hydrogen and deuterium in titanium, $\text{Ti}_{88}\text{Al}_{12}$ and Ti_3Al

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Diffusion coefficients of hydrogen and deuterium in titanium, titanium–aluminium alloy $\text{Ti}_{88}\text{Al}_{12}$ and intermetallic Ti_3Al have been measured in the temperature range 873–1298 K. The activation energy for diffusion has been found to be almost the same for hydrogen and deuterium and to increase, as the aluminium content in the metals increases, from *ca.* 0.44 eV for titanium to *ca.* 0.85 eV for Ti_3Al . The ratio of the measured diffusion coefficient of deuterium to that of hydrogen also increases from the classical value $1/\sqrt{2}$ for titanium to *ca.* 0.8 for Ti_3Al . An application of the classical rate theory to the measured ratio shows that the hydrogen atom at the saddle point of the diffusion path is more tightly bound to the metal atoms and has a larger vibration energy in Ti_3Al than in titanium.

Diffusion of hydrogen in titanium–aluminium alloys and intermetallics plays a key role in the understanding of their hydrogen absorption–desorption properties required for use as hydrogen-storage materials¹ and of their potential susceptibility to hydrogen embrittlement.² A characteristic of the diffusion is that hydrogen atoms migrate in a metal composed of titanium, which exothermically absorbs hydrogen, and aluminium, which endothermically does so.³ This characteristic suggests that the diffusion behaviour in the titanium–aluminium alloys and intermetallics is different from that in titanium and aluminium. In fact, the measured activation energy is *ca.* 0.5 eV for both titanium^{4–7} and aluminium,⁸ but is as large as 0.84 eV for Ti_3Al .^{9,10} Different diffusion behaviour in titanium–aluminium alloys and intermetallics is expected to appear also in an isotope effect of diffusion. The purpose of the present paper is to find experimentally such an isotope effect and to discuss it in terms of the mechanism of hydrogen diffusion in the metals, particularly in the titanium–aluminium intermetallics.

Measurements of diffusion coefficients have been reported for hydrogen in titanium^{4–7} and in aluminium,⁸ and in their alloy $\text{Ti}_{88}\text{Al}_{12}$ ¹⁰ and intermetallic Ti_3Al .^{9,10} For these metals, however, no report is found for diffusion coefficients of deuterium and tritium and for the isotope effect of diffusion. Previous theoretical study³ shows that the classical rate theory,^{11,12} if it is modified so as to include quantized vibration of hydrogen atoms, is applicable to the diffusion of hydrogen in hcp metals such as titanium and Ti_3Al .^{13,14} Since hcp metals have a larger potential barrier for hydrogen diffusion than bcc metals, a quantum effect, *i.e.*, tunnelling of hydrogen atoms through the barrier, does not play an important role in determining the diffusion rate. The classical rate theory can give an expression of the isotope effect of diffusion.^{12,15,16}

In the present study we report the result of measurements of diffusion coefficients of hydrogen and deuterium in titanium, $\text{Ti}_{88}\text{Al}_{12}$ and Ti_3Al . The classical rate theory is applied to the measured ratio of the diffusion coefficient of deuterium to that of hydrogen. We then mention the effect of the presence of

constituent aluminium atoms on the vibration of hydrogen atoms at the saddle point of their diffusion paths.

Experimental

Diffusion coefficients (D_{H} and D_{D}) have been obtained from the rate at which hydrogen and deuterium gases were absorbed by samples. Hereafter the subscripts H and D denote hydrogen and deuterium, respectively. The apparatus and procedure to obtain the diffusion coefficients,^{16–18} the samples and their heat treatment¹⁰ and the measurement ranges of temperature and hydrogen concentration¹⁰ were almost the same as those described previously. The samples and the measurement ranges are shown here again in Table 1. We have chosen the measurement ranges so that the metals remain in the hcp structure.^{13,14} Measurements were made for hydrogen and deuterium at an identical pressure (p , 6.25 Pa) and the deuterium concentration (θ_{D} , atomic ratio) was therefore *ca.* 15% smaller than the hydrogen concentration (θ_{H}).

We took precautions of correcting the measured rate by removing from it the effect of the surface process that influences the absorption rate, *e.g.* dissociative adsorption of hydrogen molecules on the sample surface^{16–18} and of eliminating, as completely as possible,¹⁵ the small amount of hydrogen (deuterium) remaining in the sample and on the surface of the apparatus when measuring the rate of deuterium (hydrogen) absorption.

Results and Discussion

Experimental results

Fig. 1 shows the Arrhenius plot of D_{H} and D_{D} measured for titanium, $\text{Ti}_{88}\text{Al}_{12}$ and Ti_3Al . A previously reported value of D_{H} is also shown for titanium⁵ by the thick solid line. Other reported results^{4,6,7} give similar values of D_{H} and are not shown for clarity of the figure. The solid and dashed lines are the result of least-square fits of the equation

$$D = D_0 \exp(-E_d/k_B T) \quad (1)$$

to the measured values of D_{H} and D_{D} , respectively, with D_0 and E_d as parameters. Here D_0 is the prefactor of the diffusion coefficient, E_d is the activation energy, k_B is the Boltzmann

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Table 1 Diameters and purity of the samples, measurement ranges of temperature and hydrogen concentration, reported heat of hydrogen solution, prefactor and activation energy of the measured D_H ^a and D_D , and energy-level spacings ($h\nu_H$ and $h\nu_H^\ddagger$) for vibration of a hydrogen atom, which is regarded as a harmonic oscillator, in the interstitial site and at the saddle point

	titanium	Ti ₈₈ Al ₁₂	Ti ₃ Al
diameter/mm ^b	8.5	9.4	10.2
purity(%)	99.97	>99.9	>99.9
temperature/K	873–1123	873–1273	973–1273
hydrogen concentration, θ_H ^c	3.8×10^{-3} – 1.3×10^{-2}	8.7×10^{-4} – 5.1×10^{-3}	7.1×10^{-4} – 3.1×10^{-3}
E_s /eV	0.48 ^d	0.47 ^e	0.56 ^f
$\log D_0/\text{m}^2 \text{ s}^{-1}$			
hydrogen	–6.33 ± 0.40	–5.90 ± 0.39	–5.21 ± 0.52
deuterium	–6.56 ± 0.47	–5.98 ± 0.43	–5.36 ± 0.38
E_d /eV			
hydrogen	0.45 ± 0.08	0.57 ± 0.09	0.86 ± 0.11
deuterium	0.43 ± 0.09	0.58 ± 0.09	0.84 ± 0.08
$h\nu_H/\text{eV}^g$	0.14 ^h	0.14 ⁱ	0.14 ^j
$h\nu_H^\ddagger/\text{eV}^g$	0.17 ± 0.04	0.20 ± 0.03	0.24 ± 0.02

Errors added to D_0 , E_d and $h\nu_H^\ddagger$ are statistical errors with 95% confidence limits. ^a Most of the D_H values shown in the present study are the same as those reported previously.¹⁰ ^b Spherical samples are used in the present study. ^c Deuterium concentration (θ_D) is ca. 15% smaller than θ_H at the same hydrogen and deuterium pressures. ^d Ref. 19. ^e Ref. 10. ^f Ref. 20–22. ^g For deuterium, the relationships $h\nu_D = h\nu_H/\sqrt{2}$ and $h\nu_D^\ddagger = h\nu_H^\ddagger/\sqrt{2}$ have been used. ^h Ref. 21–23. ⁱ See the text. ^j Ref. 21 and 22.

constant and T is the temperature. Table 1 shows the result for D_0 and E_d .

We see from Table 1 that the values of D_0 and E_d increase as the aluminium content in the metal increases. The trend of the E_d values has been discussed^{9,10} in terms of the large difference in the heats of hydrogen solution (E_s) in aluminium and titanium, i.e., endothermic solution in aluminium and exothermic solution in titanium, and the regularly distributed aluminium atoms along the diffusion path in Ti₃Al and the randomly distributed aluminium atoms along the diffusion path in Ti₈₈Al₁₂. The trend of the D_0 values has also been discussed¹⁰ on the basis of the jump length of diffusing hydrogen atoms. It has been suggested that the presence of aluminium atoms increases the jump length, i.e., the distance

between the potential barriers that correspond to the activation energy.

We can see no appreciable difference in the values of E_d for hydrogen and deuterium. The difference in the values of D_H and D_D , however, is not the same for titanium, Ti₈₈Al₁₂ and Ti₃Al; the difference is the largest for titanium and the smallest for Ti₃Al (see also Fig. 3). In the next section we discuss a possible cause of this difference.

Isotope effect of diffusion

We discuss within the framework of the rate theory^{11,12} possible causes of the values of D_D/D_H observed for titanium and Ti₃Al (See Fig. 3) paying attention to the fact that the heat of hydrogen solution (E_s) is almost the same for titanium and Ti₃Al^{20–22} and the value for E_d for Ti₃Al is about twice that for titanium.^{9,10} To do so, we first show that the classical rate theory is applicable to the diffusion of hydrogen and deuterium in titanium and Ti₃Al at high temperatures. In the present study, the word classical is used for the regime of over-barrier jump of hydrogen atoms. There are some reasons for justifying its application. First, all the measured D_H and D_D fit into eqn. (1). The classical rate theory gives the diffusion coefficient of hydrogen in metals the same form as eqn. (1),^{3,11,12} although the over-barrier jump coupled with thermally activated and metal–phonon assisted tunnelling of hydrogen atoms can also lead to a similar form of diffusion coefficient.³ Secondly, titanium and Ti₃Al have the hcp structure in the ranges of T and θ in the present study.^{13,14} In the hcp lattice, the distance between interstitial sites for hydrogen occupation and the height of the potential barrier between them are, as in the fcc lattice,³ large enough for most hydrogen atoms to jump over the barrier rather than to tunnel through it. Thirdly, titanium and Ti₃Al exhibit the same magnitude of Debye–Waller factors²⁴ and no anomalous metal phonons are likely to assist with the tunnelling of hydrogen atoms through the barrier in Ti₃Al. For these reasons it is reasonable to assume that the classical rate theory is applicable to the jump rate for hydrogen atoms. However, the vibration of hydrogen atom in the metal has to be quantized even in the formulation within the framework of the classical rate theory. This is because, according to the classical rate theory, the jump rate depends mainly on the thermal vibration of the hydrogen atom and its small mass makes it invalid to regard the energy level of the vibration as continuous when computing the partition functions that include the vibration.

We now formulate an expression of D_D/D_H . For comparison with the experimental result it is convenient to use D_D/D_H

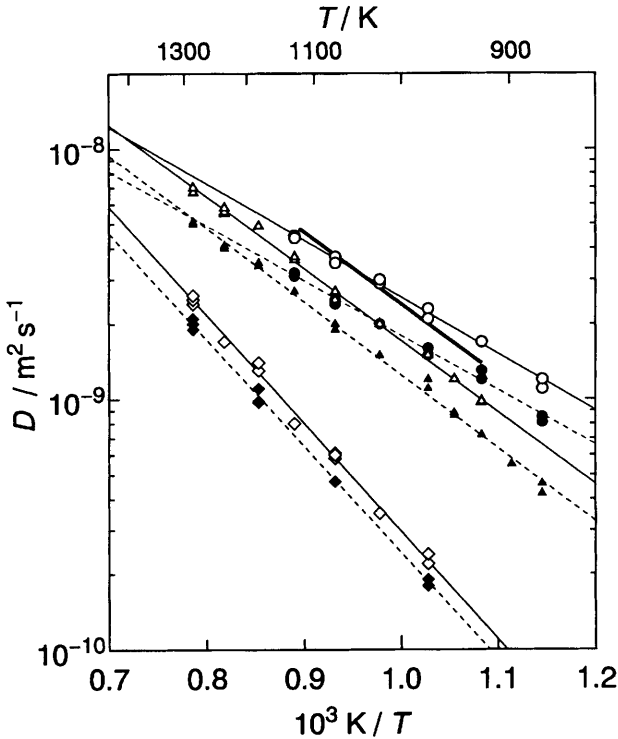


Fig. 1 Arrhenius plot of D_H and D_D measured for titanium (circles), Ti₈₈Al₁₂ (triangles) and Ti₃Al (squares). Open symbols are for hydrogen and filled symbols for deuterium. The thick solid line is the reported value of D_H for titanium.⁵ The solid and dashed lines are the result of the fits of eqn. (1) to the measured D_H and D_D , respectively.

because it includes only the terms that differ for hydrogen and deuterium, and those common to D_H and D_D , such as the term related to the electronic contributions, are dropped from it. According to the classical rate theory the diffusion coefficient is given by¹¹

$$D = \frac{k_B T}{h} \frac{f^\ddagger}{f} \exp(-E_d/k_B T) \quad (2)$$

where f is the partition function for hydrogen or deuterium atom in the interstitial site and f^\ddagger at the saddle point (Fig. 2). It should be noted that E_d in eqn. (2) is not the same as that in eqn. (1); E_d in eqn. (1) comprises a set of differences between the energy levels occupied by the thermally activated hydrogen atom in the interstitial site and at the saddle point whilst E_d in eqn. (2) is the difference between the energies at the bottom of the potentials shown in Fig. 2. E_d in eqn. (1) is therefore isotope-dependent whilst E_d in eqn. (2) is isotope-independent. The two definitions of E_d , however, cause no serious problem in determining the values of E_d from the measured D_H and D_D . In fact, the results of least-squares fits of eqn. (2) to the measured D_H and D_D coincides almost completely with the lines in Fig. 1 if the E_d values are taken to be a little smaller than those listed in Table 1. The result of the fits of eqn. (2) is not shown in Fig. 1 for clarity. Assuming that the hydrogen atom is a three-dimensional harmonic oscillator in the interstitial site and a two-dimensional harmonic oscillator at the saddle point, we have from eqn. (2)¹⁵

$$\frac{D_D}{D_H} = \left[\frac{\sinh(h\nu_D/2k_B T)}{\sinh(h\nu_H/2k_B T)} \right]^3 \left[\frac{\sinh(h\nu_H^\ddagger/2k_B T)}{\sinh(h\nu_D^\ddagger/2k_B T)} \right]^2 \quad (3)$$

where $h\nu$ and $h\nu^\ddagger$ are the energy-level spacings, per degree of freedom, for vibration of a hydrogen or deuterium atom in interstitial sites and at the saddle point, respectively. We can modify eqn. (3) to include the effect of a possible large entropy at the saddle point. The hydrogen atom at the saddle point may have various modes of motion in addition to the single two-dimensional harmonic oscillation. As a simplest example, we can regard the hydrogen atom as a multi-dimensional harmonic oscillator and replace the power of 2 in the last term of eqn. (3) by a larger power. This modification, however, was

found only to reproduce poorer the measured D_D/D_H than without the modification. We use below eqn. (3) without modification.

Fig. 3 shows the values of D_D/D_H obtained experimentally and the result of least-squares fits of eqn. (3) to the D_D/D_H . The D_D/D_H value increases from the classical value $1/\sqrt{2}$ to ca. 0.8 for Ti_3Al as the aluminium content in the metal increases. The D_D/D_H values obtained in the present study are reasonable compared with those reported previously, e.g. ca. 0.8 for nickel^{25,26} and for copper²⁶ and ca. 0.7 for hafnium¹⁶ and yttrium,¹⁸ for the same temperature range as in the present study. For the fits we used the reported values of $h\nu_H = 0.14$ eV for titanium obtained by inelastic neutron scattering²³ and $h\nu_H = 0.14$ eV for Ti_3Al obtained from the solubilities of hydrogen and deuterium in it.^{21,22} The value of $h\nu_H$ for $Ti_{88}Al_{12}$ has been assumed to be 0.14 eV because $h\nu_H = 0.14$ eV for the random alloy $Ti_{94}Al_6$ ²¹ as well as for titanium and Ti_3Al . In addition, it has been assumed that $h\nu_D = h\nu_H/\sqrt{2}$ and $h\nu_D^\ddagger = h\nu_H^\ddagger/\sqrt{2}$, and that $h\nu^\ddagger/h\nu$ is the same for hydrogen and deuterium. We can thus regard $h\nu_H^\ddagger$ as a parameter. The result of the fits is listed in Table 1 together with the values of E_d ^{19–21} for convenience. From Fig. 3 and Table 1 we see that $h\nu^\ddagger > h\nu$ for hydrogen and deuterium and for all the metals used in the present study. This implies that hydrogen and deuterium atoms are more tightly bound to the metal atoms at the saddle point than in the interstitial site. The values of $h\nu^\ddagger/h\nu$ obtained in the present study are reasonable compared with previously reported values of $h\nu^\ddagger/h\nu = 1.7$ for nickel,^{25,26} 1.8 for copper,²⁶ 1.3 for hafnium¹⁶ and 1.1 for yttrium,¹⁸ although these values have been obtained by assuming hydrogen and deuterium atoms are anharmonic oscillators. We can also see that the ratio $(h\nu^\ddagger \text{ for } Ti_3Al)/(h\nu^\ddagger \text{ for titanium}) = 1.47$ for both hydrogen and deuterium. This implies that hydrogen and deuterium atoms at the saddle point are more tightly bound to the metal atoms in Ti_3Al than in titanium in contrast to those atoms in the interstitial sites, in which they have the same vibration energies (0.14 eV for hydrogen and 0.10 eV for deuterium in titanium and Ti_3Al . See Table 1).^{21,22} For a harmonic oscillator the value of the ratio 1.47 results in the ratio of force constants (force constant between a hydrogen atom and titanium and aluminium atoms)/(force constant between a hydrogen atom and titanium atoms) = 1.99, i.e., in Ti_3Al the hydrogen and deuterium atoms at the saddle point

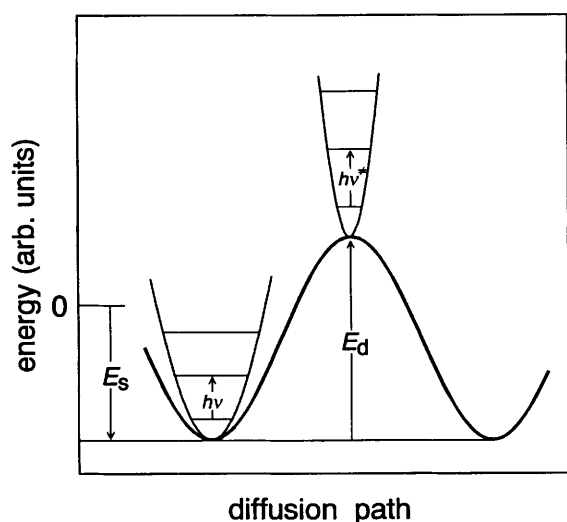


Fig. 2 Schematic diagram of potential energy along the diffusion path of a hydrogen atom. E_s is the heat of hydrogen solution and E_d the activation energy for diffusion. The energy of the hydrogen atom in the molecule has been taken as the zero of the vertical axis. Potentials for the hydrogen atom in the interstitial site and at the saddle point and the corresponding energy-level spacings for its vibration ($h\nu$ and $h\nu^\ddagger$) are also shown.

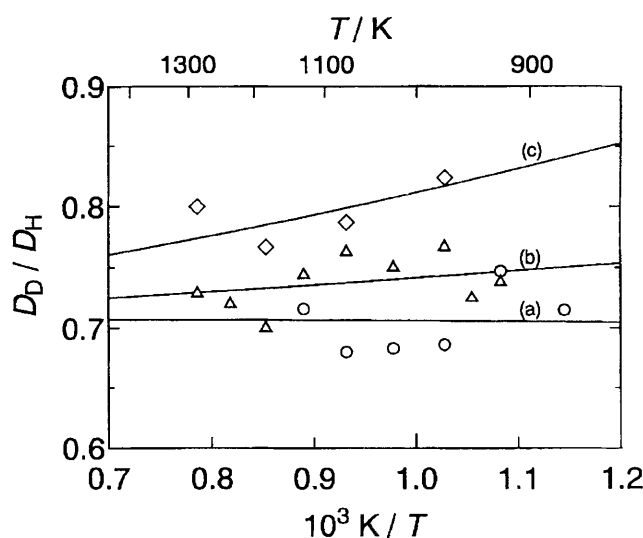


Fig. 3 Temperature dependence of D_D/D_H obtained from D_H and D_D measured for titanium (circles), $Ti_{88}Al_{12}$ (triangles) and Ti_3Al (squares). The solid lines are the result of the fits of eqn. (3) to the obtained D_D/D_H . The values of $h\nu^\ddagger/h\nu$ are (a) 1.23 for titanium, (b) 1.41 for $Ti_{88}Al_{12}$ and (c) 1.72 for Ti_3Al .

are bound to the metal atoms with a force constant 1.99 times that in titanium. In $\text{Ti}_{88}\text{Al}_{12}$ the value of $h\nu^\ddagger/h\nu$ falls between those of titanium and Ti_3Al (Table 1) owing to the random distribution of aluminium atoms. It is almost impossible to formulate a detailed discussion of the value of $h\nu^\ddagger/h\nu$ for the random alloy $\text{Ti}_{88}\text{Al}_{12}$, similar to that formulated for the prefactor and the activation energy for diffusion,¹⁰ because the accuracy of the measured D_{H} and D_{D} values is insufficient to do so.

The reason for the larger value of $h\nu$ at the saddle point than in the interstitial site may be as follows. Since the saddle point is on or near a triangle composed of three titanium atoms or of two titanium and one aluminium atoms and the triangle is a face of the tetrahedron in which a hydrogen atom normally occupies its interstitial site,^{9,10} the space available for vibration of the hydrogen atom is smaller at the saddle point than in the interstitial site. The hydrogen atom may vibrate in a potential corresponding to a larger force constant at the saddle point than in the interstitial site and may have a larger value of $h\nu$. It does not seem straightforward to find microscopic origins leading to the larger value of $h\nu^\ddagger$ at the saddle point in Ti_3Al than that in titanium. We should note that although E_{d} is larger for Ti_3Al than for titanium (see the values of E_{d} and E_{s} in Table 1) and the hydrogen atom at the saddle point is at a higher energy in Ti_3Al , it does not necessarily follow that the hydrogen atom in Ti_3Al has a larger value of $h\nu^\ddagger$. It seems that from *e.g.* the electronic structures calculated for Ti_3Al ²⁷ we can guess a potential for a hydrogen atom placed at the saddle point. A considerable electron redistribution² caused by addition of the hydrogen atom, however, makes it difficult to guess the potential correctly. In addition, relaxation of the metal atoms around the added hydrogen atom may give an effect on the potential. The effect of the relaxation can be so large as to reduce the value of E_{d} , *e.g.* in the palladium–hydrogen system,²⁸ to less than half that without it and is expected to change considerably the value of $h\nu$ as well. More precise knowledge of the electronic structures is needed to make clear the microscopic origins of the motion of hydrogen atoms in titanium–aluminium–hydrogen systems.

Conclusions

D_{D} and D_{H} in titanium, $\text{Ti}_{88}\text{Al}_{12}$ and Ti_3Al have been measured. E_{d} and $D_{\text{D}}/D_{\text{H}}$ have been found to increase as the aluminium content in the metals increases, but E_{d} is the same for hydrogen and deuterium in each metal. The classical rate theory, in which vibration of hydrogen atoms is quantized, has been applied to the measured $D_{\text{D}}/D_{\text{H}}$ and it has been shown that hydrogen and deuterium atoms are more tightly bound to the metal atoms at the saddle point than in the interstitial site. Clarification of possible microscopic origins of the tighter binding requires precise knowledge of the elec-

tronic structures of the titanium–aluminium–hydrogen systems.

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