Dissolution of Hydrogen and Deuterium in Titanium, Ti$_{94}$Al$_6$ and Ti$_3$Al

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The solubility of hydrogen and deuterium in α-, α,β- and β-titanium, Ti$_{94}$Al$_6$ and in α$_2$-Ti$_3$Al has been volumetrically measured in the ranges of temperature 623–1323 K and hydrogen concentration (atomic ratio) 0.001–0.25. The equilibrium hydrogen pressure at a given temperature and hydrogen concentration has been found to increase greatly as the aluminium content increases. This is explicable on the assumption that aluminium atoms block some of the sites available to hydrogen atoms. In contrast, the heat of solution of hydrogen only slightly increases with the aluminium content and in α-titanium, α-Ti$_{94}$Al$_6$ and α$_2$-Ti$_3$Al, the ratio of the deuterium pressure to the hydrogen pressure at identical hydrogen and deuterium concentrations is almost independent of the aluminium content. A possible cause of the small dependence of the measured heat and ratio on the aluminium content is discussed and occupation of the tetrahedral site by hydrogen atoms is suggested for α-titanium, α-T$_{94}$Al$_6$ and α$_2$-Ti$_3$Al. The origin of the sloping plateaus observed in the pressure–composition isotherms for α,β-Ti$_{94}$Al$_6$ is also briefly discussed.

Alloys and intermetallics in the titanium–aluminium system[1] have excellent mechanical properties and corrosion resistance at high temperatures. However, they also have the potential problem of hydrogen embrittlement because they contain titanium, which easily reacts with hydrogen and forms hydrides.[2] The solubility of hydrogen in the titanium–aluminium system is therefore a quantity of crucial importance to the understanding of hydrogen embrittlement. In addition to the practical interest, the system attracts research interest owing to the variety of crystal structures it takes depending on the aluminium content, *e.g.* hcp (α-titanium and α$_2$-Ti$_3$Al), bcc (β-titanium) and fcc (TiAl, TiAl$_3$ and aluminium) structures with randomly and regularly distributed aluminium atoms.[1] The titanium–aluminium system thus provides a good opportunity to study the solubility of hydrogen in a variety of crystal structures within a single system. Since this system consists of titanium, which exothermically absorbs hydrogen,[2] and aluminium, which endothermically does so,[2] a large effect of the aluminium atoms on the solubility is expected. The purpose of the present paper is to elucidate the effects of aluminium atoms on the solubility of hydrogen in the alloys and intermetallics in the titanium–aluminium system and to estimate the kind and number of interstitial sites occupied by hydrogen atoms in these alloys and intermetallics.

Much work has been reported on the solubility of hydrogen and deuterium in α- and β-titanium.[3–10] Hydrogen atoms have been found to occupy tetrahedral sites of hcp α-titanium[2,11,12] and bcc β-titanium.[12] Some investigators[5,8] have discussed the difference in the measured solubility of hydrogen and deuterium in α-titanium on the basis of a harmonic oscillator model of hydrogen atoms. In contrast, few reports are found on the solubility of hydrogen in the titanium–aluminium alloys.[7] Since aluminium atoms form less-stable bonds with hydrogen atoms than titanium atoms do, the aluminium atoms in the alloys and intermetallics are

expected to block some of the sites available to hydrogen atoms[2,13] and the equilibrium hydrogen pressure to increase as the aluminium content increases. No reports on the sites for hydrogen occupation have been made for the titanium–aluminium alloys. The solubility of hydrogen and deuterium in α$_2$-Ti$_3$Al has been reported by several investigators.[14–16] The increased equilibrium hydrogen pressure due to the presence of aluminium atoms was discussed from the viewpoint of blocking of interstitial sites by substitutional additions.[14] The heat of solution of hydrogen and deuterium in Ti$_3$Al has been found to be close to that in α-titanium.[14–16] The sites available to hydrogen atoms have been reviewed[17] for intermetallics other than Ti$_3$Al, and in Ti$_3$Al it was estimated from the measured ratio of *p* (the equilibrium pressure) for hydrogen and deuterium to be tetrahedral.[16]

In the present paper we measure the solubility of hydrogen and deuterium in α-, α,β- and β-titanium and Ti$_{94}$Al$_6$ and in α$_2$-Ti$_3$Al. From the measured equilibrium hydrogen and deuterium pressures and heats of solution we estimate for each phase the kinds of site available to hydrogen atoms and the number of sites relative to that for titanium. We will briefly mention the sloping plateaus observed in the pressure–composition isotherm for α,β-Ti$_{94}$Al$_6$. The sloping plateaus occurring in the mixed-phase regions in some intermetallics have been discussed[18,19] with practical applications in mind. Models of the sloping plateaus applicable also to amorphous metals have been presented.[2,20,21] We briefly and critically discuss the origin of the sloping plateaus.

Experimental

The solubility was obtained by measuring the amount of hydrogen and deuterium gases absorbed by titanium, Ti$_{94}$Al$_6$ and Ti$_3$Al samples. The apparatus and procedure for the measurements were essentially the same as those reported previously.[22–25] We describe here only minor changes made and some precautions taken in the present study. To ensure that a precise amount of hydrogen is absorbed by the samples, we used a bakeable quartz chamber in which the

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sample reacted with hydrogen, making its volume as small as possible. The sample was heated from the outside of the chamber by an electric furnace. We detected a very small amount of hydrogen and oxygen originating from water molecules which evaporated from the surface of the heated quartz chamber and were then decomposed by reaction with the surface of the sample. However, it made no appreciable difference to the measured solubility.

The samples were *ca.* 500 mm³ cubes of polycrystalline titanium, $Ti_{94}Al_6$ and Ti_3Al with titanium content of 94.0 atom% and 75.8 atom% for $Ti_{94}Al_6$ and Ti_3Al, respectively. They were prepared as plasma-arc-melted ingots and cut into the cubes. Chemical analysis of the samples showed that their purity was better than 99.9%, the main impurities being 300 ppm oxygen, 70 ppm carbon and 50 ppm nitrogen. To increase the degree of ordering of aluminium atoms in the intermetallic Ti_3Al, we heated the sample to 1323 K for 48 h under a vacuum of *ca.* 5×10^{-7} Pa. The crystal structure of Ti_3Al was determined by X-ray diffraction. A powder of average grain diameter *ca.* 10 μm was prepared by filing the sample; in order to remove strains, it was annealed at 1323 K in a vacuum (*ca.* 10^{-6} Pa). To obtain good diffraction patterns and a precise crystal structure we adopted step scanning with a step width of $\Delta 2\theta = 0.04°$ and the Rietveld analysis[26] by the use of the computer program RIETAN.[27] The degree of long-range ordering was found to exceed 0.95 for the heat-treated sample, indicating the correct DO_{19} structure.[1]

Measurements were made within the ranges of temperature 623–1323 K and hydrogen and deuterium pressures 10^{-1}–10^4 Pa, which correspond to the range of hydrogen and deuterium concentrations (atomic ratio) 0.001–0.25. The time needed to obtain equilibrium hydrogen pressure varied from 0.5 h for titanium at 1323 K to 24 h for Ti_3Al at 823 K. It was longer for the samples with larger aluminium contents because the diffusion coefficient is smaller for these samples.[28] In addition, for the samples in the mixed α,β-phase it was *ca.* 10 times that for the sample with a single phase, probably because of the slow $\alpha \rightarrow \beta$ phase change.[29] We also examined the partial reversibility of the equilibrium hydrogen pressure, *i.e.* whether the same equilibrium hydrogen pressure was reached or not after the temperature fluctuated by ± 50 K without changing the amount of the hydrogen gas in the quartz chamber. The difference between the equilibrium pressures before and after applying the temperature fluctuation turned out to be within 1%.

Results and Discussion

Expressions of Solubility and its Isotope Effects

Sievert's Law is a relationship between the equilibrium hydrogen pressure, p, and the hydrogen concentration, θ (equal to the number of hydrogen atoms/number of metal atoms), applicable to many metal–hydrogen systems when $\theta \ll 1$ and no phase change occurs in this range of θ. The simplest extension of this relationship to the case where θ is not much smaller than unity is to include the restriction that no more than one hydrogen atom can occupy a site available to hydrogen atoms in the metal at any one time. A possible form can thus be written as[2,30]

$$p = k\left(\frac{\theta/r}{1 - \theta/r}\right)^2 \qquad (1)$$

where k is a constant dependent on temperature and independent of θ, and r is a factor that converts θ into units of (number of hydrogen atoms)/(number of sites available to hydrogen atoms). It should be remembered that this equation can often reproduce only poorly the observed pressure–

concentration relationship when θ/r approaches unity because other factors such as the electronic energy-band effects come into play as θ increases. In the present study we will apply this equation to the solubility of hydrogen in the single α- and β-phases of the metal–hydrogen systems.

We note here the estimate of r for the metals considered in the present study. In α-titanium, hydrogen atoms are believed to occupy tetrahedral (T) sites[2,11,12] although octahedral-site occupation by some of them has been reported.[31] There are two T sites per titanium atom in the hcp structure. The distance between the nearest-neighbour tetrahedral sites, however, is $c/4 = 0.12$ nm[1,30] (c is the lattice constant along the c axis) and is too small for two hydrogen atoms to occupy them simultaneously. The maximum number of sites available to hydrogen atoms is therefore unity per titanium atom and $r = 1$ for α-titanium. In the alloys and intermetallics, values of r are expected to be less than those for titanium for the following reason. Aluminium atoms form less-stable bonds with hydrogen atoms than titanium atoms do as can be seen from the smaller heat of solution of hydrogen for aluminium[32] than for titanium[3–10] and from the smaller bonding state in the aluminium hydride[33] than in the titanium hydride.[34] The increase in less-stable aluminium–hydrogen bonds results in a decrease in titanium–hydrogen bonds, thus reducing the number of interstitial sites available to hydrogen atoms in α-$Ti_{94}Al_6$ and Ti_3Al. If all sites are blocked by aluminium atoms then $r \rightarrow 0$ and therefore $p \rightarrow \infty$ from eqn. (1). In β-titanium, hydrogen atoms occupy T sites in the bcc structure;[2,12] six per titanium atom. The T sites actually occupied in β-titanium and their maximum number per titanium atom, however, are not clear at present. We assume here $r = 2$ (two sites per titanium atom) simply because there exists the β-phase at $\theta > 1$.[35] If the hydrogen atoms occupy four T sites[2] then $r = 1.5$. The two values of r, *i.e.* 2 and 1.5, cause no appreciable difference in the result obtained. When there are substitutional aluminium atoms in the metals, $r < 2$. We rewrite k in eqn. (1) as

$$k = k' \exp\left(-\frac{2\varepsilon_s}{k_B T}\right) \qquad (2)$$

so that the effect of the difference in r on p may easily be compared at different temperatures. Here k' is a constant and ε_s is the heat of solution per hydrogen atom, k_B is the Boltzmann constant and T is the temperature.

To discuss the isotope dependence of the solubility we rewrite k in eqn. (1) as[22,24,25]

$$k = k''T \frac{f_{H(g)}}{f_{H(i)}^2} \exp\left(-\frac{2\varepsilon_s}{k_B T}\right) \qquad (3)$$

where k'' is a constant independent of T, $f_{H(g)}$ is the partition function for a hydrogen molecule and $f_{H(i)}$ is the partition function for a hydrogen atom in the metal. Note, especially when comparing eqn. (3) with the experimental results, that ε_s in this equation is slightly different from ε_s in eqn. (2) because the temperature-dependent terms $T, f_{H(g)}$ and $f_{H(i)}$ are separated out in eqn. (3) and ε_s is isotope independent. The following assumptions have been made for $f_{H(g)}$ and $f_{H(i)}$, where H(g) and H(i) indicate hydrogen gas and hydrogen atom in the metals, respectively. $f_{H(g)}$ includes translational, rotational and vibrational motions of hydrogen atoms and $f_{H(i)}$ includes only harmonic vibration along three directions. Electronic contributions, which are included in k'' in eqn. (3), are the same for hydrogen and deuterium. Thus we have from eqn. (3)[16,23–25]

$$\frac{k_D}{k_H} = \left(\frac{m_D}{m_H}\right)^{5/2} \frac{\sinh(\hbar\omega_{H(g)}/2k_B T)}{\sinh(\hbar\omega_{D(g)}/2k_B T)} \prod \left[\frac{\sinh(\hbar\omega_{D(i)}/2k_B T)}{\sinh(\hbar\omega_{H(i)}/2k_B T)}\right]^2$$

$$(4)$$

where the subscripts H and D indicate hydrogen and deuterium, respectively, m is the mass of hydrogen isotopes, ω is the angular frequency of vibration of hydrogen and deuterium atoms in the molecule and in the metal and Π denotes the product with respect to x, y and z directions. When comparing eqn. (4) with the experimental results we put $\omega_{D(g)}/\omega_{H(g)} = \omega_{D(i)}/\omega_{H(i)} = (m_H/m_D)^{1/2} = (1/2)^{1/2}$. We can estimate the value of ω, and therefore the sites occupied by hydrogen atoms, by comparing eqn. (4) with the measured p for hydrogen and deuterium, as will be shown below.

Measured Solubility and its Interpretation

α-Titanium

Fig. 1 shows the plot of p measured for hydrogen (open circles) and deuterium (filled circles) against θ at various temperatures. The values of the measured p are in general agreement with those reported previously,[3,5,8,10] which are not shown for clarity in the figure. The values of ε_s and k'/r^2 obtained by fitting eqn. (1) and (2) with $r = 1$ to the measured p are shown in Table 1. The least-squares fit has been carried out with ε_s and k' as parameters and p, θ and T as variables. No significant difference has been found in the values of ε_s for hydrogen and deuterium. The value $\varepsilon_s = 0.48$ eV lies within the ranges of reported values 0.42–0.55 eV[3,5,8,10] for hydrogen and 0.40–0.55 eV[5,8,10] for deuterium. In Fig. 1 the values of p computed using eqn. (1) and (3) with $r = 1$ are also plotted for hydrogen (thick solid lines) and deuterium (thin
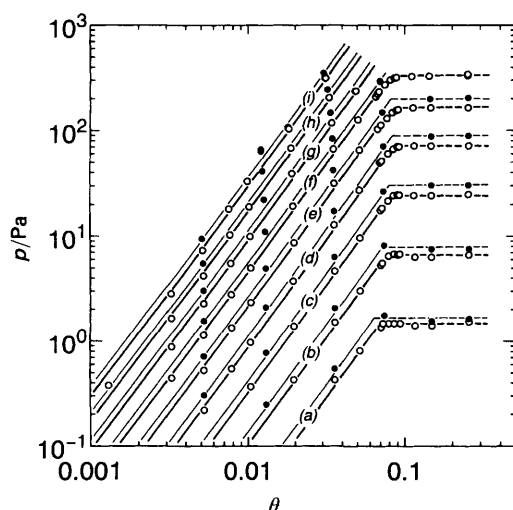
solid lines). In the computation $\varepsilon_s = 0.50$ eV and $\hbar\omega_{H(i)} = 0.14$ eV have been used. As noted in the previous section, ε_s in eqn. (3) is isotope independent and its value is slightly larger than that listed in Table 1. The $\hbar\omega_{H(i)}$ value has been obtained from inelastic neutron scattering (INS) and found to correspond to the spacing of the vibrational energy of hydrogen atoms in the T sites in α-titanium.[2,12] Since the values of p computed using eqn. (1) and (2) with the values of r, $k'(= k'/r^2)$ and ε_s listed in Table 1 almost completely coincide with those computed above, they are not plotted in Fig. 1.

In order to show the quality of the fit, $p \exp(2\varepsilon_s/k_BT)$ with $\varepsilon_s = 0.48$ eV are plotted against θ for measured p and θ values and compared with $p \exp(2\varepsilon_s/k_BT)$ computed using eqn. (1) and (2) for the values of ε_s, r and k'/r^2 in Table 1 (Fig. 2). For clarity we have not plotted in Fig. 2 the values of $p/(Tf_{H(g)}/f_{H(i)})\exp(2\varepsilon_s/k_BT)$ computed, in the same way as in Fig. 1, for eqn. (1) and (3) because they differ only slightly from those computed for eqn. (1) and (2). (The slight difference is due to the temperature dependence of the term $Tf_{H(g)}/f_{H(i)}$, whose appreciable effect on Fig. 2 is to make the two solid lines thicker.) For the same reason, the values of p computed for eqn. (1) and (3) are not shown later in Fig. 5 (α-Ti$_{94}$Al$_6$), Fig. 7 (α$_2$-Ti$_3$Al), Fig. 9 (β-titanium) or Fig. 11 (β-Ti$_{94}$Al$_6$).

Fig. 3 shows the ratio, k_D/k_H, of p measured for deuterium to that for hydrogen plotted against $1/T$. To reduce systematic errors, which consist mainly of those in the hydrogen-pressure measurement and those dependent on the experimental procedure, we took the ratio of k measured at identical hydrogen and deuterium concentrations. The ratio at a given temperature in Fig. 3 is the average of those at two or more different θ (see Fig. 1). Scatter of the k_D/k_H values has
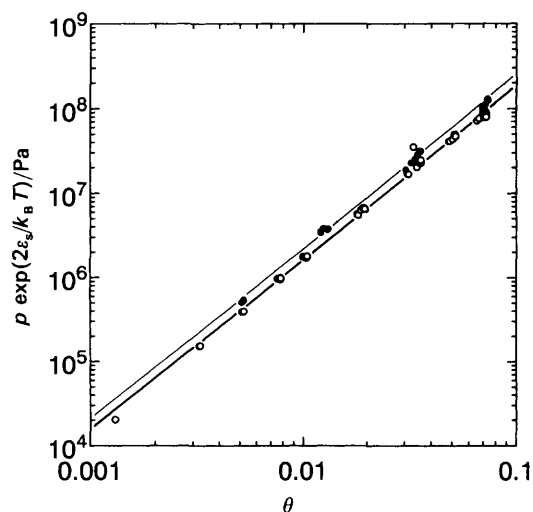

Fig. 1 Measured p vs. θ for α-titanium at (a) 623, (b) 673, (c) 723, (d) 773, (e) 823, (f) 873, (g) 923, (h) 973 and (i) 1023 K. (○) Hydrogen and (●) deuterium. Eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.14$ eV and $\varepsilon_s = 0.50$ eV are shown by the thick (hydrogen) and thin (deuterium) solid lines. The dashed lines correspond to the α,β-phase region.

Fig. 2 $p \exp(2\varepsilon_s/k_BT)$ vs. θ for α-titanium. (○) Hydrogen and (●) deuterium. The thick (hydrogen) and thin (deuterium) lines show eqn. (1) and (2) computed for the values of ε_s, r and k'/r^2 in Table 1.

Table 1 Measured heats of solution of hydrogen and deuterium and blocking of interstitial sites by aluminium atoms

| metal | ε_s/eV | | r | | $(10^{-10}k'/r^2)$/Pa | |
	H	D	H	D	H	D
α-titanium	0.48[a]	0.48[a]	1	1	1.6 ± 0.1	2.1 ± 0.2
α-Ti$_{94}$Al$_6$	0.48 ± 0.01	0.48 ± 0.04	0.8 ± 0.1	0.9 ± 0.4	2.4 ± 0.6	2.7 ± 2.5
α$_2$-Ti$_3$Al	0.56 ± 0.01	0.56 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	60 ± 13	78 ± 17
β-titanium	0.57 ± 0.02	0.57 ± 0.02	2	2	3.1 ± 1.0	3.5 ± 1.2
β-Ti$_{94}$Al$_6$	0.60 ± 0.02	0.60 ± 0.03	1.3 ± 0.3	1.3 ± 0.4	7.0 ± 5.3	8.3 ± 7.3

[a] Errors are less than ± 0.005.
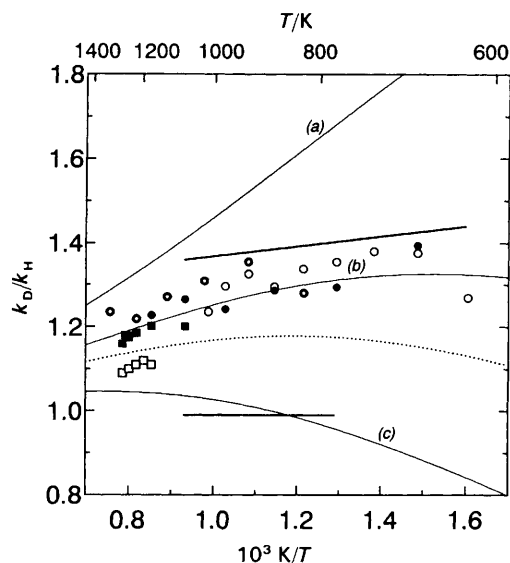
Fig. 3 Temperature dependence of k_D/k_H. (O) α-Titanium, ($\bullet$) α-$Ti_{94}Al_6$, (O) α_2-Ti_3Al, ($\square$) β-titanium and ($\blacksquare$) β-$Ti_{94}Al_6$. The reported values are shown by the upper[5] and lower[8] thick solid lines. The thin solid lines show eqn. (4) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} =$ (a) 0.10, (b) 0.14 and (c) 0.18 eV and the dotted line for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.12$ and 0.17 eV. Scatter of the k_D/k_H values is within ± 0.08 for α-titanium, ± 0.18 for α-$Ti_{94}Al_6$, ± 0.22 for α_2-Ti_3Al, ± 0.05 for β-titanium and ± 0.07 for β-$Ti_{94}Al_6$.

thus been found to be within ± 0.08. Two results of earlier measurements are also plotted. One result[5] (upper thick solid line) is in agreement with the result in the present study; the other one[8] (lower thick solid line) gives much smaller values at all T at which the measurements were made. No reason can be found at present for this difference. The thin solid lines in Fig. 3 indicate k_D/k_H computed using eqn. (4) for $\hbar\omega_{H(i)} = 0.10$, 0.14 and 0.18 eV. The value $\hbar\omega_{H(i)} = 0.14$ eV, which corresponds to the T-site occupation in α-titanium, gives the best fit to the measured k_D/k_H. The relationship between k_D/k_H and $\hbar\omega$ makes it possible to estimate from the measured values of k_D/k_H the site occupied by hydrogen atoms if the estimate is less direct compared with the estimate in terms of methods[2] such as channelling (which, however, does not give so straightforwardly the positions of hydrogen atoms in hcp metals as in cubic metals), and neutron scattering techniques like INS and neutron diffraction.

α-$Ti_{94}Al_6$

In this alloy, aluminium atoms are randomly distributed in the hcp structure.[1] Fig. 4 shows the plot of p measured for hydrogen (open circles) and deuterium (filled circles) against θ at various temperatures. The measured p are in agreement with those reported previously.[7] Table 1 lists the values of ε_s, r and k'/r^2 obtained by fitting eqn. (1) and (2) to the measured p, θ and T. The fit has been carried out with ε_s and r as parameters, p, θ and T as variables and the values of k' kept the same as for α-titanium. Fig. 5 shows the result of the fit. The values for deuterium include relatively large errors (Table 1) owing to smaller numbers of p and θ measured. The values of p measured and ε_s obtained for hydrogen are in agreement with the reported p values and $\varepsilon_s = 0.49$ eV,[7] respectively. The values of ε_s are found to be identical to those for α-titanium. $r = 0.8$ for hydrogen indicates that the 6 atom% substitutional aluminium atoms can block 20% of the sites available to hydrogen atoms and p increases accordingly. Since the value of ε_s is identical to that for α-titanium, p for hydrogen is $ca.$ 1.5 times that for α-titanium at a given θ and T (see k'/r^2 in Table 1). The solid lines in Fig. 4 show the
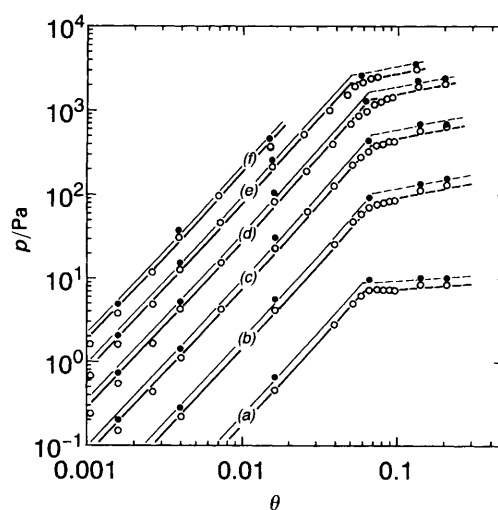
Fig. 4 Measured p vs. θ for α-$Ti_{94}Al_6$ at (a) 673, (b) 773, (c) 873, (d) 973, (e) 1073 and (f) 1173 K. (O) Hydrogen and ($\bullet$) deuterium. Eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.14$ eV and $\varepsilon_s = 0.50$ eV are shown by the thick (hydrogen) and thin (deuterium) lines. The dashed lines correspond to the α,β-phase region.

plot of eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = 0.14$ eV and $\varepsilon_s = 0.50$ eV. The filled circles in Fig. 3 show the measured values of k_D/k_H. In spite of the presence of aluminium atoms and the resulting increase in p, the curve of k_D/k_H computed for $\hbar\omega_{H(i)} = 0.14$ eV and $\varepsilon_s = 0.50$ eV, which are identical to those for α-titanium, gives the best fit to the measured k_D/k_H.

α-Ti_3Al

This intermetallic compound has an ordered hcp structure DO_{19}.[1,16] Fig. 6 shows the plot of p against θ measured for hydrogen (open circles) and deuterium (filled circles). This plot is essentially the same as that reported previously.[16] Small upward deviations from eqn. (1) and (2) at $\theta > 0.05$ imply the limit of applicability of eqn. (1) mentioned above. The values of ε_s and r have been determined in the same way as in α-$Ti_{94}Al_6$ by fitting eqn. (1) and (2) to the measured p, θ and T, and are listed in Table 1. Fig. 7 shows the result of the fit. $\varepsilon_s = 0.56$ eV for hydrogen is in good agreement with the reported value of 0.55 eV.[14] The value $r = 0.16$ suggests more site blocking due to the larger fraction of aluminium atoms in Ti_3Al compared with the case of α-$Ti_{94}Al_6$. This value compares well with the reported 88% blocking in this metal.[14]
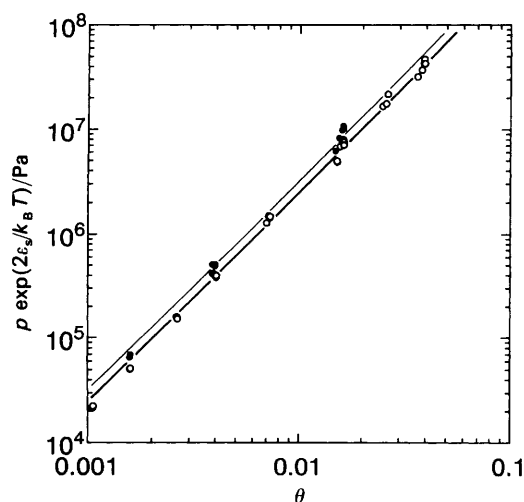

Fig. 5 $p \exp(2\varepsilon_s/k_BT)$ vs. θ for α-$Ti_{94}Al_6$. Symbols are the same as in Fig. 2.
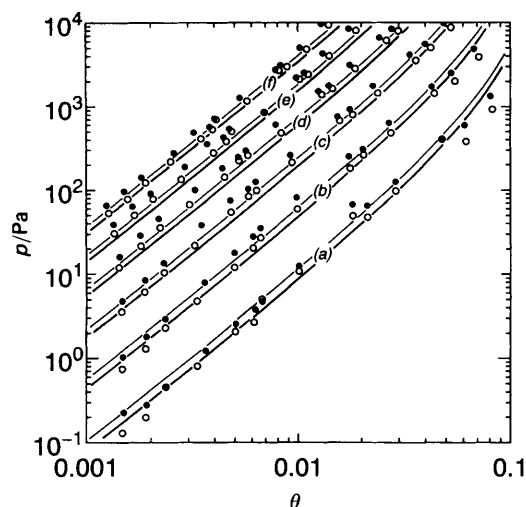
Fig. 6 Measured p vs. θ for α_2-Ti$_3$Al at (a) 823, (b) 923, (c) 1023, (d) 1123, (e) 1223 and (f) 1323 K. (○) Hydrogen and (●) deuterium. Eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.14$ eV and $\varepsilon_s = 0.58$ eV are shown by the thick (hydrogen) and thin (deuterium) lines.

We can also apply Sievert's Law to the p–θ relationship measured for $\theta \ll 1$ as was done previously.[16] The ε_s value obtained was 0.57 eV, which agrees well with the value obtained in the present study, i.e. 0.56 eV. The solid lines in Fig. 6 have been computed by using eqn. (1) and (3) with $\hbar\omega_{H(i)} = 0.14$ eV and $\varepsilon_s = 0.58$ eV. We note the large difference in p for α-titanium and Ti$_3$Al in contrast with the small difference in ε_s for these metals. The thick open circles in Fig. 3 indicate the measured k_D/k_H. They are roughly reproduced by eqn. (4) computed for $\hbar\omega_H(i) = 0.14$ eV, which is the energy of vibration of hydrogen atoms in the T site in α-titanium.

The great increase in p and small change in ε_s with the aluminium content is a characteristic of the result obtained above. We now make a brief comment on a possible origin of this characteristic. The results of electronic-structure calculations show that dissolution of hydrogen into titanium and aluminium causes a low-lying band composed mainly of the hydrogen s state hybridized with the titanium d state[34,36] and a low-lying band composed of the hydrogen s and aluminium p states,[33] respectively, to form below the Fermi levels. The difference in the electronic density of states (DOS)
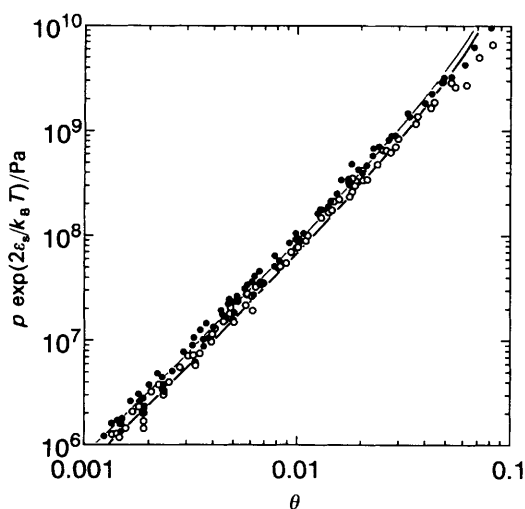
of titanium[34,37] and TiH[34] in the energy range corresponding to the low-lying band is larger than the difference in those of aluminium[38] and AlH.[33] Since this difference is a measure of the strength of the metal–hydrogen bond, titanium atoms are expected to make stronger bonds with hydrogen atoms as mentioned before. The DOS of Ti$_3$Al has some resemblance to that of titanium,[39] although hybridized features due to the interaction between titanium and aluminium atoms in the region that corresponds to the low-lying band of TiH are seen. In Ti$_3$Al, therefore, hydrogen atoms are expected to form titanium–hydrogen bonds similar to those in titanium, suggesting a smaller change in ε_s with aluminium addition. This, together with the observed $\hbar\omega$ value that is almost independent of the aluminium content (Fig. 3), suggests that hydrogen atoms in α-Ti$_{94}$Al$_6$ and Ti$_3$Al occupy the T site. The larger value of ε_s in Ti$_3$Al than in titanium and Ti$_{94}$Al$_6$ is not explicable simply from the discussion given above. On the other hand, the decrease in the fraction of titanium, and therefore the decrease in the number of titanium–hydrogen bonds, with increasing aluminium content suggests a decrease in the number of sites available to hydrogen atoms, hence the increase in p. The number of sites blocked by aluminium atoms estimated from the measured p, however, is not the same as the number of the substitutional aluminium atoms (see the values of r in Table 1). Electronic structure calculations of the Ti$_3$Al–hydrogen system seem to be necessary to explain quantitatively the slight increase in ε_s and great increase in p. They will also clarify whether hydrogen atoms really form stronger bonds with titanium atoms than with aluminium atoms; it has been found that in TiFeH, contrary to the expectation that hydrogen atoms would form bonds with titanium atoms rather than with iron atoms, the low-lying band involves mainly hydrogen s and iron d states.[36] Unfortunately it is impossible to discuss, on the basis of the electronic structures available at present, possible effects of the difference in the ordered (α_2-Ti$_3$Al) and disordered (α-Ti$_{94}$Al$_6$) structures on ε_s.

β-Titanium

Fig. 8 plots the measured p against θ for hydrogen (open circles) and deuterium (filled circles). The measured p are in agreement with those reported previously,[3,4,6–10] which are not shown for clarity. The values of ε_s and k'/r^2 obtained by

Fig. 7 $p \exp(2\varepsilon_s/k_B T)$ vs. θ for α-Ti$_3$Al. Symbols are the same as in Fig. 2.

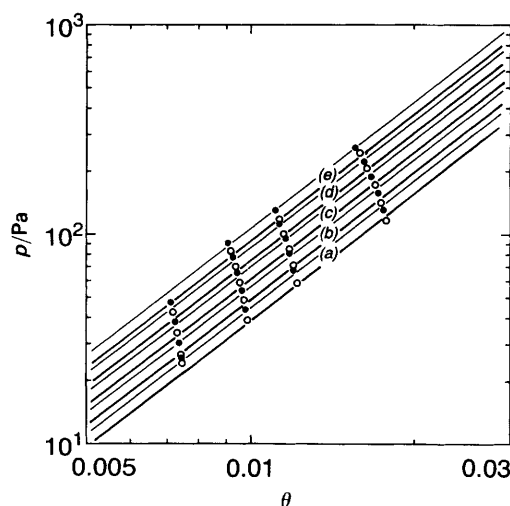**Fig. 8** Measured p vs. θ for β-titanium at (a) 1173, (b) 1198, (c) 1223, (d) 1248 and (e) 1273 K. (○) Hydrogen and (●) deuterium. Eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.12$ and 0.17 eV and $\varepsilon_s = 0.57$ eV are shown by the thick (hydrogen) and thin (deuterium) lines.
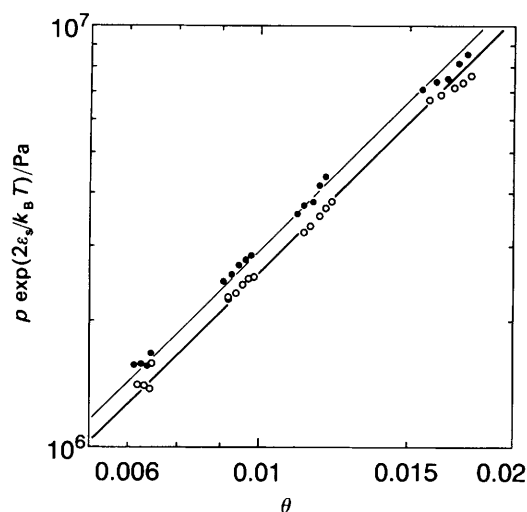
Fig. 9 $p \exp(2\varepsilon_s/k_B T)$ *vs.* θ for β-Ti. Symbols are the same as in Fig. 2.

fitting eqn. (1) and (2) with $r = 2$ to the measured p, θ and T are listed in Table 1. Fig. 9 shows the result of the fit. $\varepsilon_s = 0.56$ eV lies in the range of reported values 0.56–0.63 eV,[3,4,6,7,9,10] but it is smaller than the reported values 0.62[8] and 0.70 eV.[7] The origin of this difference cannot readily be found. Possible reasons may be the θ dependence of ε_s and the influence of the $\alpha \to \beta$ phase change on the solubility of hydrogen. The solid lines in Fig. 8 show eqn. (1) and (3) computed for $r = 2$, $\varepsilon_s = 0.57$ eV and $\hbar\omega_{H(i)} = 0.12$ and 0.17 eV. Hydrogen atoms in bcc titanium have been found to occupy the T site of a distorted tetrahedron and to have split energy levels of 0.12 and 0.17 eV with the latter doubly degenerated[12] as in other bcc metals.[40] In Fig. 3 the measured k_D/k_H (open squares) are plotted against $1/T$. The dotted line indicates k_D/k_H computed for eqn. (4) for $\hbar\omega_{H(i)} = 0.12$ and 0.17 (doubly degenerate) eV. The measured ratios are largely in agreement with those computed.

β-Ti$_{94}$Al$_6$

In this alloy, aluminium atoms are randomly distributed in the bcc structure.[1] Fig. 10 shows the plot of the measured p for hydrogen (open circles) and deuterium (filled circles) against θ at various temperatures. The measured p for
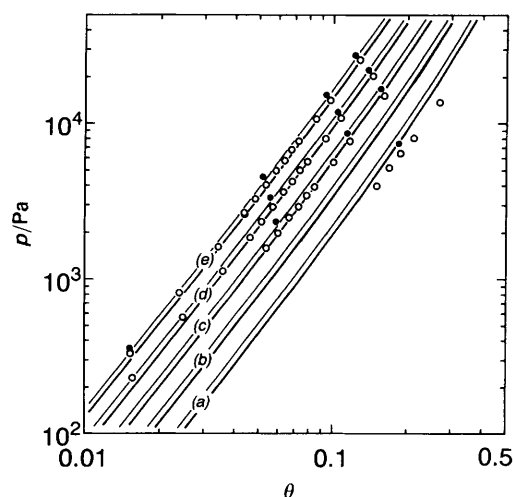
$\theta < 0.15$ at 1073 K, $\theta < 0.05$ at 1173 K and $\theta < 0.01$ at 1223 K have been excluded from the figure because the α,β-phase was found to form at these θ. We measured p at 1248, 1253 and 1263 K as well, but for clarity the result is not plotted in the figure. A small upward deviation from eqn. (1) and (2) at $\theta > 0.2$ implies the limit of applicability of eqn. (1). The measured p are in agreement with those reported previously.[7] Table 1 lists the values of ε_s, r and k'/r^2 obtained by fitting to the measured p, θ and T, eqn. (1) and (2) with the same value of k' as that used for β-titanium. Fig. 11 shows the result of the fit. The rather large errors in k'/r^2 (Table 1) are due to the errors in k' for β-titanium and the resulting errors in r for β-Ti$_{94}$Al$_6$. The value of $\varepsilon_s = 0.60$ eV is smaller than the reported value $\varepsilon_s = 0.70$ eV[7] and is slightly larger than those for β-titanium. $r = 1.3$ indicates that the 6 atom% substitutional aluminium atoms can block *ca.* 35% of the sites available to hydrogen atoms and p greatly increases (see the values of k'/r^2 in Table 1). The solid lines in Fig. 10 show the plot of eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = 0.12$ and 0.17 eV (doubly degenerated) and $\varepsilon_s = 0.61$ eV. The filled squares in Fig. 3. indicate the measured values of k_D/k_H. Agreement between the measured and computed (dotted line) values is rather poor, but not so poor as to imply a site completely different from the T site. Since the T site and the octahedral (O) site in the bcc structure are geometrically near to each other,[2] O-site occupation may be a possibility. We can say that hydrogen atoms in β-Ti$_{94}$Al$_6$ occupy the sites energetically similar to the T site of β-titanium. To discuss further the cause of this rather poor agreement, we need precise knowledge about the distribution of the sites occupied by hydrogen atoms in this random alloy.

The result obtained above implies that as the aluminium content increases, ε_s slightly increases and p increases more greatly than in the α-phase. A reasonable explanation for the difference from the case of the metals in the α-phase seems difficult because at present almost no knowledge is available about *e.g.* the electronic structure of hydrogen in bcc titanium and Ti$_{94}$Al$_6$.

α,β-*Titanium and* α,β-Ti$_{94}$Al$_6$

We consider here only the α,β-phase to which the α-phase in the titanium–aluminium phase diagram[1] is transformed by absorbing hydrogen. The α,β-phase that occurs in Ti$_{94}$Al$_6$ at temperatures between 1220 and 1235 K without hydrogen in it, is not considered. The measured p for hydrogen and deuterium are plotted against θ up to *ca.* 0.25 for titanium (Fig. 1)
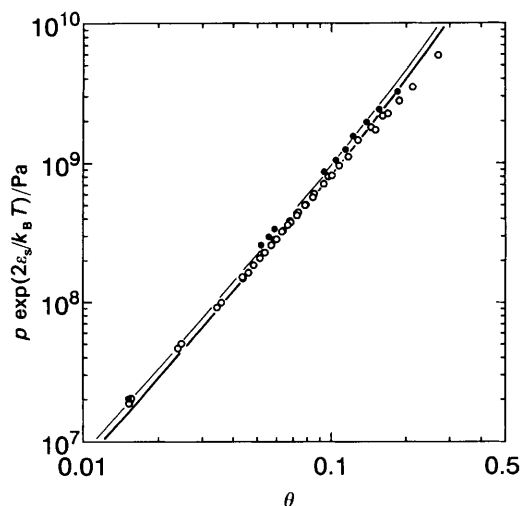

Fig. 10 Measured p *vs.* θ for β-Ti$_{94}$Al$_6$ at (*a*) 1073, (*b*) 1123, (*c*) 1173, (*d*) 1223 and (*e*) 1273 K. (○) Hydrogen and (●) deuterium. Eqn. (1) and (3) computed for $\hbar\omega_{H(i)} = \sqrt{(2)}\hbar\omega_{D(i)} = 0.12$ and 0.17 eV and $\varepsilon_s = 0.61$ eV are shown by the thick (hydrogen) and thin (deuterium) lines.

Fig. 11 $p \exp(2\varepsilon_s/k_B T)$ *vs.* θ for β-Ti$_{94}$Al$_6$. Symbols are the same as in Fig. 2.

and $Ti_{94}Al_6$ (Fig. 4). The dashed lines, which are drawn only to guide the eye, correspond to the α,β-phase regions. The pressure–composition isotherms for titanium show almost horizontal plateaus in the α,β-phase region. In $Ti_{94}Al_6$, however, the plateaus slope, *i.e.* p increases as θ increases in the α,β-phase region. Horizontal plateaus have been interpreted in terms of the lattice-gas model with a hydrogen–hydrogen interaction incorporated into it.[41,42] Sloping plateaus have been reported for some alloys and intermetallics[18,19,43] and discussed on the basis of the distribution of site energies.[2,20,21] Application of the lattice-gas model is straightforward when the sites occupied by hydrogen atoms and the site energies do not change as in the case of the palladium–hydrogen system, where both α- and β-palladium have fcc structures with only slightly different lattice constants.[42] In titanium and $Ti_{94}Al_6$, however, the change of the crystal structure (hcp $\rightarrow$ bcc) and the resulting change in the site energy ($\hbar\omega_{H(i)} = 0.14$ eV $\rightarrow \hbar\omega_{H(i)} = 0.12$ and 0.17 eV) accompany the $\alpha \rightarrow \beta$ phase change. More data for the plateau region are needed to modify the model and apply it to the sloping plateaus in titanium and $Ti_{94}Al_6$. The details will be discussed elsewhere.

The phase boundary between the α- and α,β-phases occurs at slightly smaller θ for deuterium than for hydrogen in both titanium and $Ti_{94}Al_6$, as can be seen from the points at which the solid and dashed lines meet (Fig. 1 and 4). This is consistent with the report that for titanium almost no difference was found in the $\alpha/\alpha,\beta$ phase boundaries for hydrogen and deuterium.[44] We can see from Fig. 1 and 4 that the ratio of p for deuterium to that for hydrogen, p_D/p_H ($= k_D/k_H$), in the α,β-phase is, at low temperatures in particular, smaller than in the α-phase. This may be due to the $\alpha/\alpha,\beta$ phase boundary occuring at smaller θ for deuterium.

Conclusions

The equilibrium pressures and concentrations of hydrogen and deuterium in titanium, $Ti_{94}Al_6$ and Ti_3Al were measured. It has been found that the pressures greatly increase and the heats of hydrogen solution only slightly increase as the aluminium content increases. The great increase in p has been explained as being due to blocking of the sites available to hydrogen atoms by substitutional aluminium atoms. The ratios of hydrogen and deuterium pressures and the heats of hydrogen solution were discussed and it has been suggested that hydrogen atoms in α-titanium, α-$Ti_{94}Al_6$ and α_2-Ti_3Al occupy the tetrahedral sites. The origin of the sloping plateaus observed for α,β-$Ti_{94}Al_6$ was also mentioned.

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