Diffusion of hydrogen in titanium, $Ti_{88}Al_{12}$ and Ti_3Al

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Diffusion coefficients for hydrogen in titanium, its alloy $Ti_{88}Al_{12}$ and the intermetallic Ti_3Al have been measured in the temperature range 873–1298 K. It has been found that the activation energy for diffusion in Ti_3Al (0.84 eV) is nearly twice that in titanium (0.45 eV), and in $Ti_{88}Al_{12}$ (0.57 eV) it is closer to that in titanium than that in Ti_3Al. The prefactor of the diffusion coefficient has been found to increase as the aluminium content increases. The activation energy and prefactor obtained for Ti_3Al are explained by the presence of ordered aluminium atoms in Ti_3Al as well as by the large difference in the heats of solution of hydrogen in titanium and aluminium. The diffusion coefficient of $Ti_{88}Al_{12}$ is modelled, assuming distributions of the prefactor and activation energy resulting from the disordered aluminium atoms.

Titanium–aluminium alloys exhibit excellent mechanical properties and corrosion resistance. However, they suffer, potentially, from hydrogen embrittlement[1,2] when used as structural materials. They are also candidates for light hydrogen-storage materials,[3,4] which must be able to absorb and desorb hydrogen rapidly. In both cases of hydrogen embrittlement and hydrogen storage, diffusion of hydrogen is known to play a crucial role. In addition to technological interest, the titanium–aluminium system offers a good opportunity of studying the hydrogen diffusion mechanism in metals. Since the titanium–aluminium system includes disordered alloys and intermetallics, we can study in a single system the effect of ordering of the constituent titanium and aluminium atoms on the diffusion. An added interest is that titanium and aluminium have different electronic interactions with hydrogen,[2,5,6] and we can therefore expect to see the effect of this difference on the hydrogen diffusion.

There have been several reports on the measurement of hydrogen diffusion in titanium.[7–11] Many experimental studies have been reported for hydrogen diffusion in alloys and intermetallics other than in the titanium–aluminium system.[12–15] No report, however, is available on disordered titanium–aluminium alloys, and only a brief report is available for the intermetallic, Ti_3Al.[16] The observed large activation energy for hydrogen diffusion in Ti_3Al has been ascribed to the difference in the heats of hydrogen solution in titanium and aluminium and to the presence of ordered aluminium atoms in Ti_3Al.[17]

Various models of hydrogen diffusion in disordered alloys and amorphous metals have been proposed.[14,15,18–24] The models incorporate the distribution of prefactors of diffusion coefficients as well as of activation energies for diffusion and site energies for hydrogen atoms. Brief discussions have been reported concerning a relationship between hydrogen diffusion and the arrangement of the constituent atoms of alloys and intermetallics, including a critical discussion of evidence for the distribution.[14,21] No detailed discussion, however, seems available that successfully leads to an explanation of the difference in diffusion coefficients between the titanium–aluminium alloy and intermetallics.

In the present study, we report measurements of diffusion coefficients for hydrogen in pure titanium, the disordered alloy $Ti_{88}Al_{12}$ and intermetallic Ti_3Al. The origin of the difference in the diffusion coefficients measured for titanium and Ti_3Al is discussed. We then consider distributions of the prefactor and activation energy of the diffusion coefficient and estimate the diffusion coefficient for $Ti_{88}Al_{12}$ using the prefactors and activation energies for titanium and Ti_3Al. We also discuss briefly a possible origin of the distributions.

Experimental

The diffusion coefficients (D) have been obtained by measuring the rate of absorption of hydrogen gas by titanium, $Ti_{88}Al_{12}$ and Ti_3Al samples. The apparatus and procedure for measurements were the same as those reported previously.[25–27] We used spherical polycrystalline samples. Their diameter and purity were as follows: 8.5 mm and 99.97% for titanium, 9.4 mm and >99.9% for $Ti_{88}Al_{12}$ and 10.2 mm and >99.9% for Ti_3Al. Chemical analysis showed that the main impurities were oxygen, carbon and nitrogen. The precise composition of Ti_3Al was $Ti_{75.8}Al_{24.2}$. The samples were subjected to a heat treatment at 1323 K under a vacuum of *ca.* 5×10^{-7} Pa for *ca.* 48 h. This heat treatment resulted in the Ti_3Al sample having a $D0_{19}$ structure[28] and a degree of long-range ordering better than 0.95.[29]

Measurements were made at a constant hydrogen pressure (p) of 6.25 Pa and over the following range of temperature (T) and hydrogen concentration (θ, atomic ratio): 873–1123 K and 3.8×10^{-3}–1.3×10^{-2} for titanium, 923–1298 K and 7.8×10^{-4}–4.3×10^{-3} for $Ti_{88}Al_{12}$ and 973–1273 K and 7.1×10^{-4}–3.1×10^{-3} for Ti_3Al. At these values of T and θ, all the samples retain the hcp structure.[3,28–30] We found no appreciable p dependence of the measured D down to 6.25×10^{-2} Pa, provided a correction was made for the effect of dissociative adsorption of hydrogen molecules at the surfaces of the samples.[25–27]

To interpret the activation energy obtained from the measured D, we need the value of the heat of hydrogen solution, q_s. No report of q_s was available for $Ti_{88}Al_{12}$. We therefore obtained the value of q_s for $Ti_{88}Al_{12}$ from the measured values of T, p and θ at which absorption of hydrogen had been completed.

Results and Discussion

Experimental results

Fig. 1 shows the Arrhenius plot of D measured for titanium,

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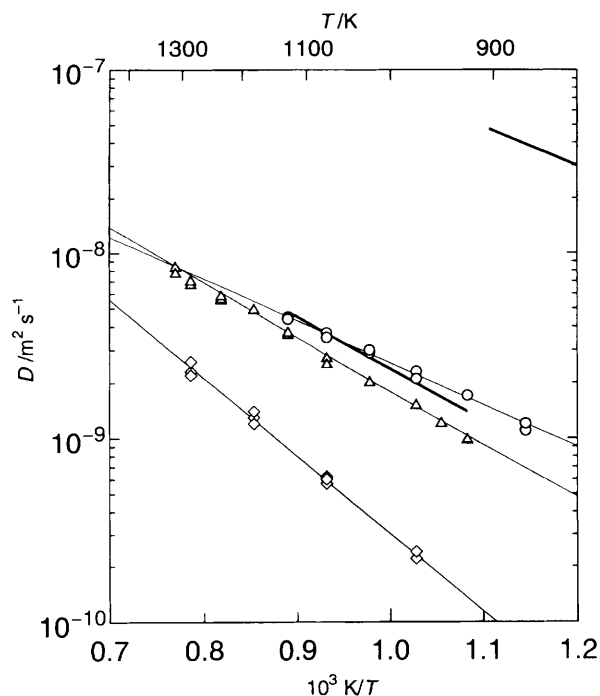
Fig. 1 Arrhenius plot of D measured for titanium, $Ti_{88}Al_{12}$ and Ti_3Al. ($\bigcirc$) Titanium, ($\triangle$) $Ti_{88}Al_{12}$ and ($\diamondsuit$) Ti_3Al. The upper thick solid line is for aluminium[31] and the lower thick solid line for titanium.[9] The thin solid lines are the result of the fits of eqn. (2)–(6).
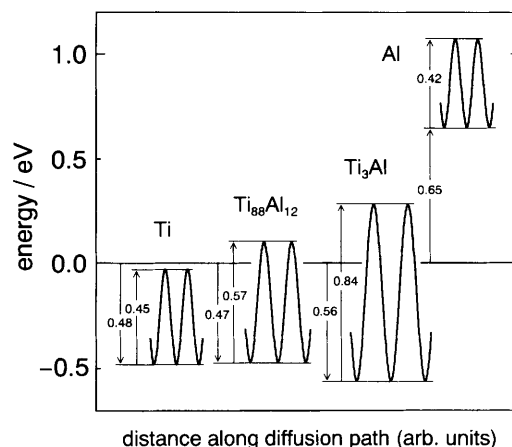

Fig. 2 Schematic potential-energy diagram for the diffusion of hydrogen atoms in titanium,[16,17,29] $Ti_{88}Al_{12}$, Ti_3Al[3,16,17,29] and aluminium.[31] The zero of energy is taken to be that of the hydrogen atom in a hydrogen molecule. The figures on the arrows indicate the values of q_s and E_d.

$Ti_{88}Al_{12}$ and Ti_3Al. Previously reported values of D for titanium[9] and aluminium[31] are also shown for comparison. We have determined D by fitting the expression

$$D = D_0 \exp\left(-\frac{E_d}{k_B T}\right) \quad (1)$$

to the measured D with the prefactor D_0 and the activation energy E_d as parameters. The result of the fit of eqn. (1) is not shown in Fig. 1 for clarity. The values of D_0 and E_d determined are shown in Table 1 together with the values reported for aluminium.[31] The errors added to the values in Table 1 are statistical errors with 95% confidence limits. The value of D for titanium is in fairly good agreement with the reported value (Fig. 1) while the values of D_0 and E_d only approximately agree with the reported values $D_0 = -5.84$ and $E_d = 0.553$ eV.[9] The value of E_d for Ti_3Al is in agreement with the reported value, $E_d = 0.89$ eV.[16]

We can see from Fig. 1 and Table 1, three trends in D_0 and E_d. First, the value of E_d increases as the aluminium content increases. For Ti_3Al, the value of E_d is almost twice that for titanium despite the similar values of E_d for titanium and aluminium (Table 1). A possible reason for the large value of E_d for Ti_3Al has been discussed previously.[16] We briefly discuss it here again and, to do so, consider the heats of solution of hydrogen (q_s) for titanium and aluminium and possible diffusion paths for a hydrogen atom in Ti_3Al. Fig. 2 schematically

shows the values of q_s experimentally obtained for titanium,[16,17,29] $Ti_{88}Al_{12}$, Ti_3Al[3,16,17,29] and aluminium.[31] The value for $Ti_{88}Al_{12}$ has been obtained in the present study from the Arrhenius plot of k in the relationship $p = k\theta^2$ (Fig. 3), which the measured p and θ are assumed to obey when θ is small. The value of q_s has been found to be 0.466 ± 0.020 eV. There may be a distribution of q_s, but it must be small, as expected from the standard deviation of the distribution obtained for $Ti_{96}Al_6$, *i.e.* 0.01 eV,[32] and can safely be neglected in the present study. Note the similar values for titanium and Ti_3Al and the value for aluminium, which is much different from those for titanium and Ti_3Al. Fig. 4 shows tetrahedral (T) and octahedral (O) sites of the hcp structure accessible to hydrogen atoms and diffusion paths through these sites. We note that in the long-range diffusion of hydrogen in Ti_3Al, the hydrogen atom must make a T–T or T–O–T jump, in which the hydrogen atom 'sees' an aluminium atom or two, respectively, on its nearest neighbours.[16] It is not unreasonable to assume, according to the result of electronic structure calculation on hydrogen in $Ti_{1-x}Al_x$,[2] that the hydrogen atom during the jump, has an energy not much different from the large energy of a hydrogen atom in aluminium

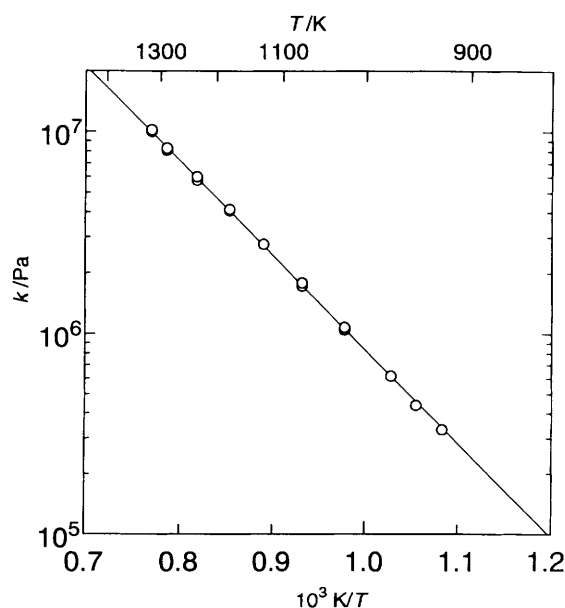**Table 1** Prefactor D_0 and activation energy E_d of the diffusion coefficients measured for titanium, $Ti_{88}Al_{12}$, Ti_3Al and aluminium

sample	$\log D_0/m^2\ s^{-1}$	E_d/eV
Ti	-6.33 ± 0.40	0.449 ± 0.078
$Ti_{88}Al_{12}$	-5.88 ± 0.37	0.572 ± 0.083
Ti_3Al	-5.30 ± 0.58	0.838 ± 0.128
Al	-5.0^a	0.424^a

[a] Ref. 31. Errors shown are statistical errors with 95% confidence limits.

Fig. 3 Arrhenius plot of k in the relationship $p = k\theta^2$ for $Ti_{88}Al_{12}$

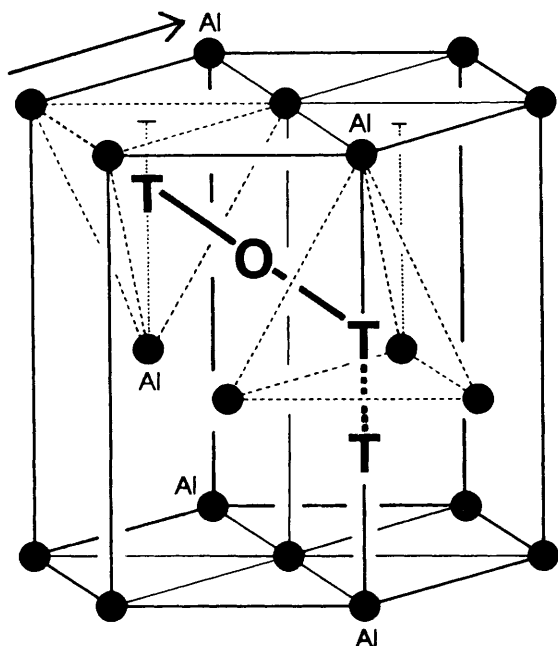**Fig. 4** Hcp structure and the possible diffusion paths for hydrogen atoms. The structure of $Ti_{88}Al_{12}$ is obtained by replacing the solid circles (titanium atoms) by aluminium atoms and the structure of Ti_3Al (DO_{19}) by replacing the solid circles labelled Al by aluminium atoms. (**T**) T sites and (**O**) O sites. The thick solid and dotted lines indicate possible diffusion paths. For Ti_3Al, the T–O–T path shown by the thick solid lines has two aluminium atoms on its nearest neighbours and the T–O–T path obtainable by displacing it in the direction and magnitude indicated by the arrow has only titanium atoms on its nearest neighbours.

(Fig. 2). We can thus expect, from the heats of hydrogen solution and diffusion paths for hydrogen atoms, the large value of E_d for Ti_3Al. In disordered titanium–aluminium alloys with the aluminium content less than 0.25, a probability that the hydrogen atom on its diffusion path finds aluminium atoms on its nearest neighbours increases as the aluminium content increases. On the other hand, the heat of hydrogen solution in these alloys practically remains constant (Fig. 2). We thus have the value of E_d increasing with increasing aluminium content.

Secondly, the value of E_d for $Ti_{88}Al_{12}$ is nearer to that for titanium than for Ti_3Al, despite the fact that the aluminium content of $Ti_{88}Al_{12}$ lies between those of titanium and Ti_3Al. A likely reason for this is the presence of disordered aluminium atoms in addition to the smaller aluminium content than in Ti_3Al. A hydrogen atom in $Ti_{88}Al_{12}$ can more frequently find T–T or T–O–T paths with only titanium atoms on their nearest neighbours (Fig. 4) and the average value of E_d therefore tends to be close to that for titanium. In $Ti_{88}Al_{12}$, a variety of diffusion paths, and therefore of values of E_d, is expected owing to the presence of disordered aluminium atoms. We will formulate in the next section an expression of D with a distribution of E_d.

Thirdly, the prefactor D_0 increases as the aluminium content increases. D_0 is mainly determined by the effective frequency associated with a hydrogen atom enclosed with potential barriers due to the presence of aluminium atoms and by the length of the jump that the hydrogen atom makes over the barriers.[33,34] Since the hcp structure is retained in the metals under discussion, the number of directions of the jumps is unlikely to differ much from that for titanium, even if some titanium atoms are replaced by aluminium atoms. For the estimation of the jump length for titanium, the T–T path must be considered as well as the T–O–T path, because the hydrogen atom can probably move almost freely between the two T

sites in the T–T path (Fig. 4) as evidenced for yttrium, for example.[35] The jump length is therefore a vector sum of the T–T and T–O–T paths. For Ti_3Al, the jump length corresponds to the distance the hydrogen atom can travel without seeing aluminium atoms on its nearest neighbours. Since one fourth of the whole T–T paths and one half of the whole T–O–T paths in Ti_3Al have no aluminium atoms on their nearest neighbours (Fig. 4), they can contribute to the jump length. We can see that the resulting jump length would be larger than that in titanium because one half of all the T–O–T paths, each of which has a length $ca.$ five times that of the T–T path, contribute greatly to the resulting jump length, and thus compensate the decrease due to the decreased number of the T–T paths without aluminium atoms on their nearest neighbours compared with the situation for titanium. No great change in effective frequency is expected from the similar vibrational-energy levels observed for the hydrogen atom in titanium[36] and Ti_3Al.[17,29] We can thus expect the larger value of D_0 for Ti_3Al than for titanium. For $Ti_{88}Al_{12}$, the relative number of aluminium atoms, which lies between that for titanium and for Ti_3Al, and the presence of disordered aluminium atoms, imply a value of D_0 between those for titanium and Ti_3Al. We note here that the above discussion is intended only to give a rough estimate of values of D_0 and E_d. A more realistic estimate requires $e.g.$ a molecular dynamics calculation, coupled with an electronic structure calculation of the titanium–aluminium–hydrogen system.

Calculation of D for $Ti_{88}Al_{12}$

We have calculated D for $Ti_{88}Al_{12}$ using the values of D_0 and E_d for titanium and Ti_3Al. We can formally regard a predominant process of hydrogen diffusion in hcp metals as a jump of hydrogen atoms over a potential barrier[15] created by the array of metal atoms. Such models have been proposed for the over-barrier jump diffusion of hydrogen in disordered alloys and amorphous metals.[14,15,18–24] In these models, the distribution of site energies for hydrogen atoms and activation energies for hydrogen diffusion have been considered to characterize the effect of the structure of the metals on hydrogen diffusion.

We have formulated an expression of D_0 for $Ti_{88}Al_{12}$ using a considerably simpler model than the above-mentioned models, in that it involves the distribution of E_d and no distribution of site energies. This model has been used because we found that a large difference in E_d for titanium and Ti_3Al and a distribution of E_d is likely to exist in the disordered alloy $Ti_{88}Al_{12}$. In contrast, the observed heats of hydrogen solution in titanium, $Ti_{88}Al_{12}$ and Ti_3Al (Table 1) show only a small difference between them and no distribution of site energies seems to be needed in the model. We will, however, consider a similar distribution of D_0, as previously carried out.[24] This distribution is necessary because, in addition to the fact that $Ti_{88}Al_{12}$ is a disordered alloy, the jump length in $Ti_{88}Al_{12}$ is contributed to by those in titanium and Ti_3Al, which differ significantly, as discussed in the previous section. Since the presence of disordered aluminium atoms is a main cause of the distributions, we have assumed that D_0 and E_d are functions of the aluminium content x and represent them as

$$D_0 = D_0^{Ti} + \frac{x}{x^{Ti_3Al}} (D_0^{Ti_3Al} - D_0^{Ti}) \qquad (2)$$

$$E_d = E_d^{Ti} + \frac{x}{x^{Ti_3Al}} (E_d^{Ti_3Al} - E_d^{Ti}) \qquad (3)$$

where x is expressed in the units of (number of aluminium atoms)/(number of titanium and aluminium atoms). Obviously $x^{Ti} = 0$, $x^{Ti_{88}Al_{12}} = 0.12$ and $x^{Ti_3Al} = 0.25$. We have used, for

the distribution of both D_0 and E_d, a modified Gaussian distribution of the form

$$f = A \exp\left[-\frac{(x - x_M)^2}{2\sigma^2}\right] \qquad (4)$$

for $x^{Ti} \leqslant x \leqslant {}^{Ti_3Al}$ and $f = 0$ otherwise. Here, A is a constant normalized to unity within the range x^{Ti}–x^{Ti_3Al}. The mean x_M is selected so that the average of x over the range x^{Ti}–x^{Ti_3Al} coincides with the aluminium content of the alloy under consideration and in the case of $Ti_{88}Al_{12}$, with x^{Ti_3Al}. It can be taken outside the range x^{Ti}–x^{Ti_3Al}. The standard deviation, σ, is assumed to have the form

$$\sigma = \sigma_0 \min(|x_M - x^{Ti}|, |x_M - x^{Ti_3Al}|) \qquad (5)$$

where σ_0 is a constant and the symbol $\min(,)$ means that $\min(a, b) = a$ when $a < b$ or b when $a > b$. Eqn. (5) implies that the alloys with $x \approx x^{Ti}$ and x^{Ti_3Al} show narrow distributions of D_0 and E_d as in titanium and Ti_3Al, while the alloys with $x \approx (x^{Ti} + x^{Ti_3Al})/2$ show wide distributions corresponding to disordered alloys. We note here that the use of the Gaussian distribution [eqn. (4)] for the titanium–aluminium alloys must be made with care. Distributions of site energies quite different from a simple Gaussian distribution have been experimentally found in some amorphous alloys.[14,21] For the titanium–aluminium alloys, however, no experimental evidence for or against eqn. (4) is available in the literature. In the present study, we have contented ourselves with the use of eqn. (4) as it has successfully reproduced the measured D. We can now write down the diffusion coefficient for the titanium–aluminium alloy with $x^{Ti} \leqslant x \leqslant x^{Ti_3Al}$:

$$D = \int_{x^{Ti}}^{x^{Ti_3Al}} f^{D_0} D_0\, f^{E_d} \exp\left(-\frac{E_d}{k_B T}\right) dx$$

$$\equiv \int_{x^{Ti}}^{x^{Ti_3Al}} f^{D} D_0 \exp\left(-\frac{E_d}{k_B T}\right) dx \qquad (6)$$

where f^{D_0} and f^{E_d} are representations of f for D_0 and E_d, respectively, and $f^D \equiv f^{D_0} f^{E_d}$. Eqn. (6) suggests that we can regard f^D as the distribution of the diffusion coefficient. If $f^{D_0} = f^{E_d}$, then f^D has the same form as eqn. (4) and so eqn. (4) can be used for f^D.

The thin solid lines in Fig. 1 represent the result of least-squares fits of eqn. (2)–(6) to the measured D. The computation has been made for $f^{D_0} = f^{E_d}$ mainly because we found it difficult to determine uniquely the parameters for $f^{D_0} \neq f^{E_d}$. To compute the values of D for $Ti_{88}Al_{12}$, we used the values of D_0 and E_d for titanium and Ti_3Al (Table 1) and those of x^{Ti}, $x^{Ti_{88}Al_{12}}$ and x^{Ti_3Al}. From the result of the fit for $Ti_{88}Al_{12}$, we have found $\sigma = 0.29^{+0.01}_{-0.28}$ and $x_M = 0.037^{+0.082}_{-0.031}$. The errors come from the restriction that the average of x must equal $x^{Ti_{88}Al_{12}}$ and the statistical error corresponding to the 95% confidence limit is larger. The value of σ indicates a rather wide distribution of D_0 and E_d, spreading nearly equally over the range x^{Ti}–x^{Ti_3Al}. This wide distribution makes it possible for hydrogen atoms to follow the diffusion paths with small E_d and results in the apparent value of E_d for $Ti_{88}Al_{12}$ being closer to that for titanium rather than to that for Ti_3Al, as conjectured in the previous section. In addition, the small value of the mean x_M obtained for $Ti_{88}Al_{12}$ implies that the diffusion behaviour resembles that for titanium. The fits for titanium and Ti_3Al have also been made for $\sigma = 10^{-4}$ considering single values of D_0 and E_d. The result is shown in Fig. 1. This result is the same as the result of the fits of eqn. (1) to the measured D.

Conclusions

We have measured the diffusion coefficient of hydrogen in titanium, $Ti_{88}Al_{12}$ and Ti_3Al. The prefactor and activation energy of the diffusion coefficient have been found to increase

as the aluminium content increases. The observed large prefactor and activation energy for Ti_3Al are due to the ordered aluminium atoms and also to the fact that the heats of hydrogen solution are different for titanium and aluminium and almost the same for titanium and Ti_3Al. The diffusion coefficient for $Ti_{88}Al_{12}$ has been calculated using the distributions of the prefactor and activation energy. The calculated result shows that the diffusion coefficient measured for $Ti_{88}Al_{12}$ can be well reproduced by the wide distribution reflecting the presence of disordered aluminium atoms.

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