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Hydrogen diffusion in Fe–Ni alloys around room temperature

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ABSTRACT

We have revisited hydrogen behavior in Fe–Ni alloys with the tritium evolution technique. Applying a 3D analytical solution of Fick's diffusion equation to the tritium evolution curve from disk shaped samples, hydrogen retention and apparent diffusion coefficients in Fe–Ni alloys with Ni content from 6 to 50 at.% are determined around RT. In γ phase region, diffusion coefficients were not appreciably changed and increased with lattice parameter. In the α' phase region, two diffusion components were distinguished: For fast diffusion components, diffusion coefficients have quite good agreement with the literature value and decreased with increase of lattice parameter. The slower diffusion components are likely attributable to retained γ phase precipitates or Ni_3Fe dispersed in the α' matrix and must be very important to understand hydrogen embrittlement and tritium safety handling.

1. Introduction

Ferritic/martensitic and austenitic steels are going to be used in fusion reactor devices. However, there are still concerns to hold back from their long term usage due to hydrogen embrittlement of ferritic/martensitic steels [1,2] and tritium retention in austenitic steels. These phenomena were originally derived from the hydrogen properties in the ferrite (α)/martensite (α') and austenite (γ) phase. This work is devoted to understanding the effect of lattice structure and chemical composition on hydrogen diffusion in those steels by employing various Fe–Ni alloys which is a base alloy for all stainless steels and is suitable for understanding hydrogen behavior in them. We have applied tritium (T) tracer technique which is one of powerful tools to detect very tiny amount of hydrogen and extensively examine their release (evolution) behaviors from the Fe–Ni alloys.

2. Experimental

Samples used here were Fe–Ni alloys with Ni contents of 0 (pure Fe), 6, 12, 20, 40, 50 and 100 (pure Ni) at.%, hereafter denoted as pure Fe, Fe–6Ni, Fe–12Ni, Fe–20Ni, Fe–40Ni, Fe–50Ni and pure Ni, respectively. These samples were prepared by forging and solution treatment followed by annealing at temperatures lower than the transformation temperature from α to γ, except for an electrolytically purified Fe. The crystallographic microstructures in the samples were examined by X-ray diffraction analysis (XRD) showing fully distorted bcc structure, i.e. martensite (α') phase, for Ni content up to 20 at.% and γ phase for higher Ni content. Lattice parameters were determined by an extrapolation method in the d-spacing vs. Nelson–Riley function plot. Disk shaped sample of 10 mm in diameter and 2 or 4 mm in thickness was prepared. Each sample surface was mechanically polished to a mirror.

Hydrogen including tritium ($T/H = 10^{-6}$) was loaded by gaseous absorption at 1.3 kPa and 673 K for 24 h, followed by rapid cooling at liquid N_2 temperature. Subsequently, the sample was immersed in a liquid scintillation cocktail kept at a constant temperature ranging from 273 to 323 K. T was evolved into the scintillation cocktail and continuously measured by a scintillation counter with a certain time interval.

3. Results and discussion

3.1. Apparent hydrogen diffusion coefficient and hydrogen retention in the Fe–Ni alloys

Fig. 1(a) and (b) shows tritium evolution curves for Fe–40Ni and pure Ni (γ phase) and Fe–12Ni (α' phase), respectively. Note that the evolution time until saturation was much shorter in (b) as compared with (a). In the case of γ phase region, an apparent diffusion coefficient was evaluated from the least squares fitting according to analytical solution of Fick's diffusion equation for 3D disk geometry [3–5] given by

$$Q^T(t) = Q^T_\infty\left(1 - \frac{32}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\frac{-(2n+1)^2\pi^2 D^T_{a_a} t}{a^2}\right.$$
$$\left.\times\sum_{n=1}^{\infty}\frac{1}{\beta_n^2}\exp\frac{-4\beta_n^2 D^T_a t}{b^2}\right), \qquad (1)$$

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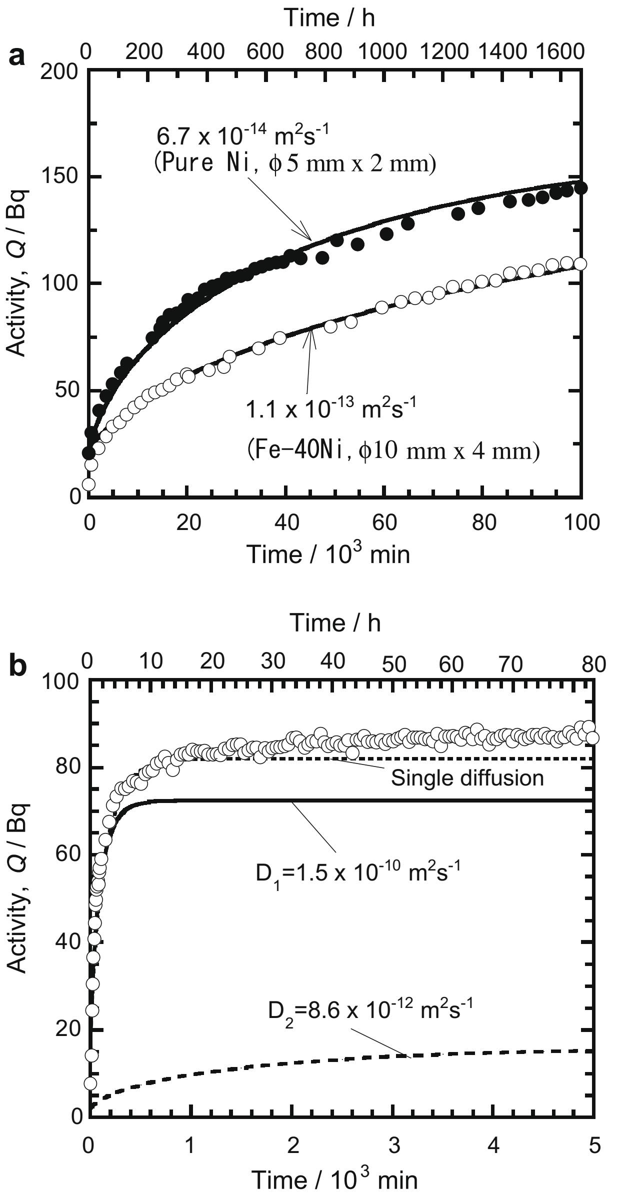

Fig. 1. Tritium evolution curves for (a) Fe–40Ni and pure Ni (γ phase) and (b) Fe–12Ni (α′ phase) alloy.

where $Q^T(t)$ is the amount of released T at a time t; Q_∞^T, the total T evolved; D_a^T, an apparent diffusion coefficient of T; βn_i, roots of zero order Bessel function; a and b, the thickness and diameter of the disk, respectively. The apparent hydrogen diffusion coefficients, D_a, were thus obtained as a product of the T diffusion coefficients multiplied by $\sqrt{3}$. The least squares fitting curves (solid lines) reproduced the data for Fe–40Ni and pure Ni quite well, and apparent diffusion coefficients and Q_∞/(Hydrogen atoms/Metals atoms, H/M) were successfully evaluated as given in Fig. 1(a) and Table 1, respectively. In the case of α′ phase region, on the other hand, the fitting was not successful suggesting the existence of some slower release component as depicted in Fig. 1(b). We simply assume that the evolution is constructed with two independent diffusing components,

$$Q^T(t) = Q_1^T(t, D_1^T) + Q_2^T(t, D_2^T), \tag{2}$$

where $Q_1^T(t)$ and D_1^T, $Q_2^T(t)$ and D_2^T represent the amount of released T for each component at a time t and an apparent T diffusion coefficient for each component, respectively. Applying the least squares fitting, D_1 and Q_1, and D_2 and Q_2 were determined as given in Table 1. The appearance of the slower component was appreciable only for Fe–6Ni and Fe–12Ni.

Table 1
Hydrogen retention in the sample, $Q_1(Q_\infty)$ and Q_2 at RT.

Sample	Phase	$Q_1(Q_\infty)$[H/M]	Q_2 [H/M]
Pure Fe	α′	–	–
Fe–6Ni	α′	1.3×10^{-7}	4.9×10^{-8}
Fe–12Ni	α′	1.7×10^{-7}	1.4×10^{-7}
Fe–20Ni	α′	6.7×10^{-7}	–
Fe–40Ni	γ	4.2×10^{-7}	–
Fe–50Ni	γ	3.9×10^{-7}	–
Pure Ni	γ	4.4×10^{-6}	–

The apparent hydrogen diffusion coefficients at 298 K were plotted against the Ni content in Fig. 2. In the figure, previously reported data [6,7] for the same alloys showing quasi-equilibrium two-phase (α + γ) behavior determined by the electrolytic permeation technique are given for comparison. In α′ phase region, the apparent diffusion coefficients, D_1, significantly decrease from the value for pure Fe to Fe–20Ni by three orders of magnitude with increasing Ni content. The apparent diffusion coefficients for the faster diffusion components agree quite well with the reported data. This suggests that the microstructure would not play important role for the faster diffusing components in this particular alloy. An important difference is the appearance of the slower diffusing component which could not be detected in the previous works. Although the total evolution of the slower diffusion component Q_2 is much smaller than the faster diffusing component Q_1, it remains for longer and could have an influence on mechanical properties in the long term.

In the γ phase, variation of the apparent diffusion coefficients with Ni content is not so appreciable. Nevertheless they seem to decrease with Ni content following to α′ phase but has a local minimum for Fe–40Ni. Such a local minimum around 40 at.% Ni was also reported by Dresler et al. [7].

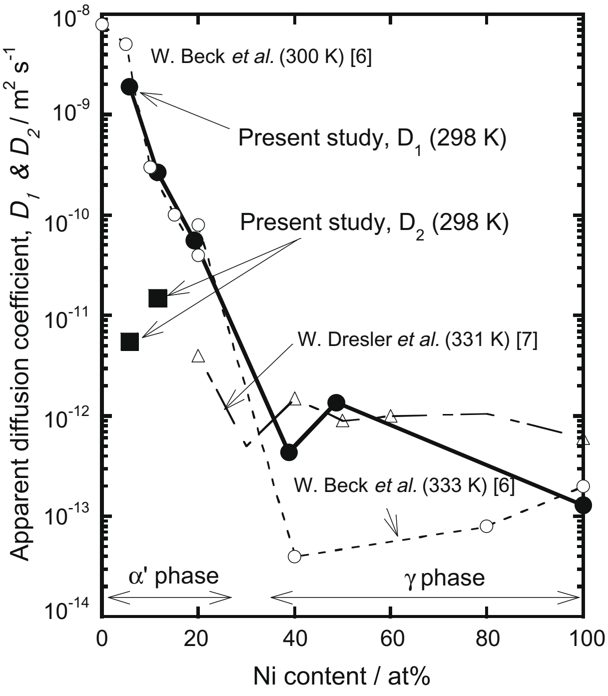

Fig. 2. The plot of H diffusion coefficient against the Ni content.

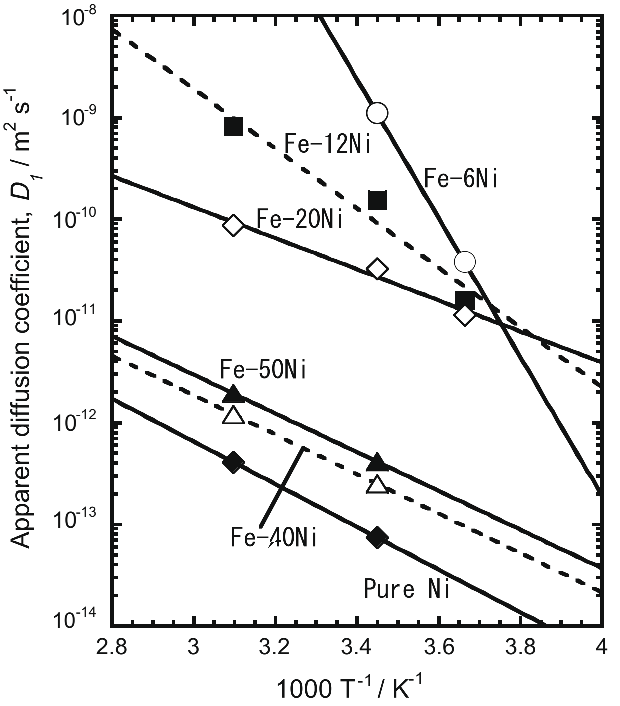

Fig. 3. Temperature dependence of H diffusion coefficient.

Fig. 3 is the temperature dependence of D_1 from 273 to 323 K. The activation energies for the alloys in the γ phase region are nearly constant (0.1 eV), whereas those for the α' phase appreciably decrease from 0.4 to 0.1 eV with increasing the Ni content.

3.2. The relationship between apparent diffusion coefficient and lattice parameter

As depicted in Fig. 2, the apparent diffusion coefficients change with Ni content. Here we have tried to correlate them to the lattice parameters of the alloys and results are shown in Fig. 4(a) and (b) for α' and γ phase, respectively. Note that the reported value [8] is used in Fig. 4(a) for hydrogen diffusion coefficient in pure Fe. Interestingly, the relationship is opposite between α' phase and for γ phase. In the γ phase region, the diffusion coefficients seem to increase with the lattice parameters. Considering nearly same activation energies for the γ phase alloys, the increase of the lattice parameter would weaken the bonding force of H atoms to interstitials, resulting in larger diffusion coefficients. The appearance of the local minimum at Fe–40Ni is attributed to the appearance of Invar (Fe–36%Ni) which shows quite different magnetic and electronic structure from other Fe–Ni alloys [7]. In the α' phase region, the variation of the apparent diffusion coefficients for the faster diffusing components is well correlated inversely to the change of their lattice parameters. As seen in Fig. 3, one can note that the activation energies also change with the similar way. As already noted in the previous section, the agreement of the present data with the previously determined ones strongly suggests that the microstructure would not play important role for the faster diffusing components in this particular alloy. Still the reason for the decrease of the apparent diffusion coefficient with decreasing the lattice parameter or with increasing the Ni contents is not clear. The fast diffusing component might not have important role on hydrogen embrittlement compared to the slower diffusing component. There may be slower components but Q_i must be very small and hard to detect.

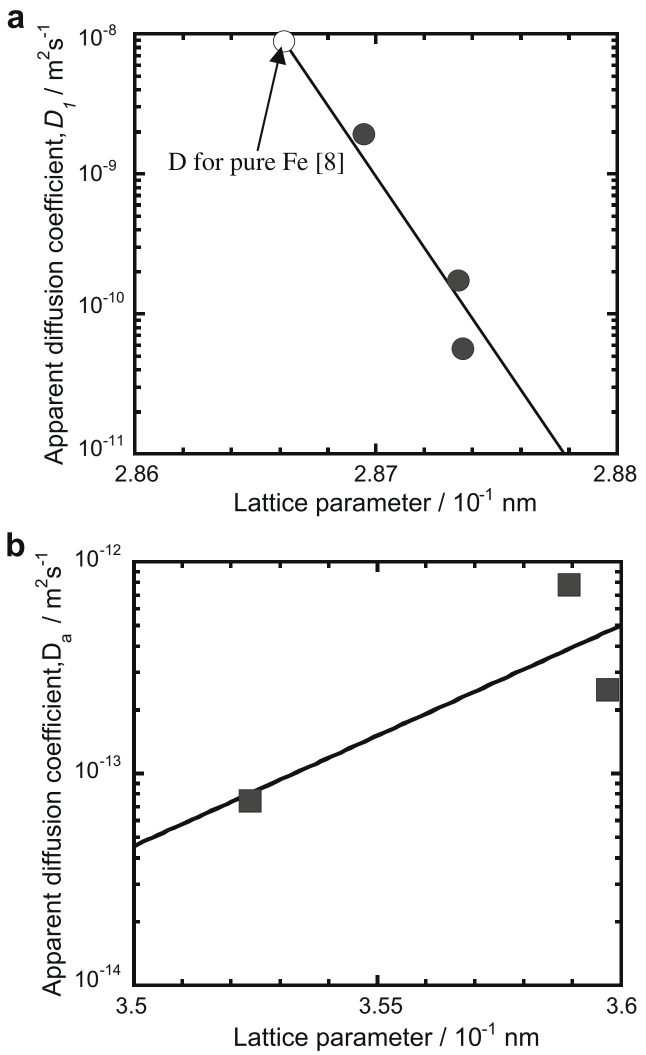

Fig. 4. The relationship between H diffusion coefficient and lattice parameter, (a) α' and (b) γ phase regions.

As the possible origin of the slower diffusion component, one can think of a second phase having high hydrogen solubility and lower diffusivity, such as a retained γ phase particle or Ni_3Fe dispersed in the α' matrix. However, such precipitates must be very tiny and dispersed homogeneously [5] and were not observed in the present alloys by XRD and electron back-scattering diffraction analysis in a scanning electron microscopy. The origin of the slower diffusion component is not clear but it must be strongly correlated to hydrogen embrittlement and safety concerns on tritium retention of stainless steels.

4. Conclusions

We have revisited hydrogen behavior in Fe–Ni alloy with the tritium tracer technique. Applying a 3D analytical solution of Fick's diffusion equation to the T evolution curve for disk shaped samples, hydrogen retention and apparent diffusion coefficients are determined around RT. The results are summarized as follows:

(1) In the γ phase region, the release behaviors for the alloys are similar to that for pure Ni. As the lattice parameter increases, the apparent diffusion coefficient is likely to increase. The

lattice expansion weakens the bonding force of H to interstitials, which could results in larger diffusion coefficients.

(2) In the α' region, the hydrogen release behavior is not well described by a single diffusion component but includes an additional component with much slower diffusion. The apparent diffusion coefficients at RT for the faster diffusing component agree well with the reported values and their variation with alloy components is well correlated inversely to the change of their lattice parameters. The activation energies for diffusion also decrease with increase of the lattice parameters or Ni content in the alloys. It is suggested that the faster diffusion coefficients could be attributed to normal diffusion for hydrogen in the α' matrix. Since the faster diffusion component dominates the total evolution, it might have been difficult to observe the slower diffusing component which is clearly seen in the present work. The origin of the slower diffusion component is not clear at the moment but it could be strongly correlated to hydrogen embrittlement of steels and tritium safety handling.

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