Effect of Dislocation Trapping on Hydrogen and Deuterium Diffusion in Iron*

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The diffusion coefficients of hydrogen and deuterium in commercially pure iron deformed and annealed under various conditions have been measured at temperatures between 283 and 318 K by an electrochemical permeation method. The temperature dependence of the diffusion coefficients of hydrogen ($D_H$) and deuterium ($D_D$) is discussed on the basis of the trapping theory by Oriani. Two trapping parameters, the binding energy of hydrogen or deuterium with trapping sites and the trap site density are determined by fitting the diffusion coefficient calculated from the trapping theory to the experimental results. The ratio of the diffusion coefficient of hydrogen to that of deuterium, $D_H/D_D$, has been found to be dependent on temperature, but not on the trap site density. This indicates that the trap site density and the binding energy are, within an experimental error, the same for hydrogen and deuterium, although the activation energy of diffusion in a normal lattice is found to be mass dependent. The binding energies with trapping sites (dislocations) for both hydrogen and deuterium are determined as about 27 kJ/mol, which shows a good agreement with those reported by Gibala, Oriani and others.

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I. Introduction

The values of the diffusion coefficient of hydrogen in iron at temperatures below 500 K reported in literature so far show considerable scatter despite much efforts of many workers. Also the magnitude of many of them is found to be smaller than the values extrapolated from the high temperature data. These anomalous behaviors have been attributed to the trapping of hydrogen at lattice imperfections such as dislocations, grain boundaries, voids and impurity atoms. Cold-working of iron specimens has been found to reduce the diffusion coefficient of hydrogen. This has been attributed to the increase in the number of trapping sites, that is, the dislocation density.

In previous papers, we reported that the values of partial molar volumes for hydrogen and deuterium dissolved in iron were the same within an experimental error. If the trapping of hydrogen and deuterium by dislocation is caused only by the elastic interaction and also the binding energies with dislocation depend only on the partial molar volume of hydrogen or deuterium solute, they should have the same value for hydrogen and deuterium.

Johnson and Lin, and Nagano et al. studied the trapping effect of dislocation on the diffusion coefficients of hydrogen and deuterium in cold-worked iron specimens. However, the latter result was different from that of the former with respect to the isotope dependence. Namely, while Johnson and Lin did not find the isotope dependence in the binding energy and the trap site density, Nagano et al. have found them.

In order to study the isotope dependence in the trapping effect, the diffusion coefficients of hydrogen and deuterium were measured by an electrochemical permeation method using specimens with various degrees of deformation. The temperature dependence of the diffusion coefficients and the isotope effect are discussed on the basis of the trapping theory by Oriani which is based on the general modelistic formulation by McNabb and Foster.

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II. Experimental Procedure

1. Specimens

The material used in the present experiment is commercially pure iron, of which the chemical composition is shown in Table 1. Four kinds of specimens were prepared by varying deformation and annealing procedures; (1) annealed at 1173 K for 10.8 ks (referred to afterwards as 1173 K annealed specimens), (2) 9% cold-worked after annealing at 1173 K for 10.8 ks (cold-worked specimens), (3) 9% cold-worked and annealed at 673 K for 10.8 ks (673 K annealed specimens) and (4) 9% cold-worked and annealed at 773 K for 10.8 ks (773 K annealed specimens). A thin layer of palladium was electrodeposited on the anodic side of the membranes to protect it against anodic dissolution. The specimens were 0.2–1.1 mm thick. The average grain diameter of 1173 K annealed specimens was 35 μm.

2. Measurement of permeation curves

The electrochemical cell was separated into two compartments by a specimen membrane. Hydrogen was generated electrolytically at a constant cathodic current density on one side of the membrane (which was called the cathodic surface), while on the other side of the membrane (which was called the anodic surface) permeating hydrogen was potentiostatically ionized. The electrode potential of the anodic surface of the membrane was maintained at 0 V against a Ag/AgCl reference electrode by a potentiostat. The potentiostatic current, which was proportional to the rate of hydrogen permeation, was recorded\(^{(10)}\)\(^{(11)}\).

The cathodic electrolytes were a 0.5 kmol/m\(^3\) \(\text{H}_2\text{SO}_4 + \text{H}_2\text{O}\) solution for hydrogen, and a 0.25 kmol/m\(^3\) \(\text{D}_2\text{SO}_4 + \text{D}_2\text{O}\) solution for deuterium permeation experiments. The anodic electrolyte was a 0.2 kmol/m\(^3\) \(\text{NaOH} + \text{H}_2\text{O}\) solution.

3. Determination of diffusion coefficients of hydrogen and deuterium

The observed permeation curves of hydrogen and deuterium were analyzed using a modified method of transient curve analysis to obtain the diffusion coefficients of hydrogen and deuterium. The method of analysis has been given in the previous papers\(^{(10)}\)\(^{(11)}\).

III. Experimental Results

1. Measurement of diffusion coefficients of hydrogen and deuterium

To obtain reliable data of the diffusion coefficient by the permeation experiment, which is free from the surface effect, the following requirements should be satisfied in the experimental results. Namely the values of the diffusion coefficient obtained should be independent of the cathodic current density \(i_c\) (1) and the specimen thickness \(L\) (2)\(^{(12)}\), and the steady state permeation rate \((i_a(\infty)\) should be proportional to the reciprocal of the specimen thickness \((1/L)\) (3)\(^{(12)}\).

Typical permeation transients of hydrogen through cold-worked specimens at 298 K are shown in Fig. 1 at various cathodic current densities. The thickness of the membrane \(L\) is 0.75 mm. At large cathodic current densities such as 530 A/m\(^2\), the permeation curves have max-

Table 1 Chemical composition (mass%) of test specimens.

| C   | Si  | Mn  | P   | S   | N   | O   |
|-----|-----|-----|-----|-----|-----|-----|
| 0.003 | 0.005 | 0.09 | 0.0070 | 0.0022 | 0.0040 | 0.0010 |

Fig. 1 Permeation transients of hydrogen through a 9% cold-worked specimen at various cathodic current densities \(i_c\).
imum values, while at small cathodic current densities such as 5.3 A/m² it takes a long time for them to reach a steady state $i_a(\infty)$. Figure 2 shows the relation between a normalized time $\tau(=D_H t/L^2)$ and $t$, which is deduced from the transient curves shown in Fig. 1. The linear relation passing through the origin is obtained in the range of $\tau$ less than 0.1, except in the cases in which the cathodic current density is extremely large. A plot of $D_H$ calculated from the tangent of the curves at the origin is shown in Fig. 3 against the cathodic current density ($i_c$). The apparent values ($D_a$) of diffusion coefficient are shown to be independent of $i_c$. This satisfies the requirement (1).

Also the permeation experiments were carried out with varying the thickness of the cold-worked specimen. The apparent values of $D_H$ and $D_D$ were found to be independent of the thickness at each temperature. This satisfies (2).

The steady state permeation rate $i_a(\infty)$ at $i_c=21$ A/m² was found to be inversely proportional to the thickness of the specimen. This satisfies (3).

Therefore, the present experimental procedure is considered to be free from the surface effect. As these three conditions were satisfied, the diffusion coefficients were determined for the four kinds of specimens (1)-(4).

2. Temperature dependence of $D_H$ and $D_D$

The diffusion coefficients determined for the specimens (1)-(4) with $L=0.7-1.1$ mm are shown in Fig. 4.

The temperature dependence of the ratio of the diffusion coefficient of hydrogen $D_H$ to that
of deuterium $D_0$ is shown in Fig. 5 for four specimens with different treatments. Though the experimental values of the ratio $D_{H}/D_0$ show some scattering, the temperature dependence of the ratio is independent of the specimen treatments.

IV. Discussion

1. Binding energy between hydrogen (deuterium) and dislocation

Cold-working of iron specimens has been known to reduce the diffusivity of hydrogen, and this has been explained as the trapping effect of dislocation introduced by plastic deformation(2)(3). The data in the literature on the binding energy between hydrogen and dislocation $E_{B,H}$ are listed in Table 2.

Many of the investigators obtained about 27 kJ/mol for the binding energy, and some reported 48–60 kJ/mol or about 20 kJ/mol. Therefore, all these values were used as tentative values of $E_{B,H}$ and the temperature dependence of the diffusion coefficients was discussed.

The diffusion coefficient of hydrogen ($D_H$) including the trapping effect of dislocations is expressed by Oriani(8) as

$$D_H = \frac{D_{0,H} \exp \left(\frac{-Q_H}{RT}\right)}{1 - K_H + K_H \exp \left(\frac{E_{B,H}}{RT}\right)},$$

where $Q_H$ and $D_{0,H}$ are the activation energy and the pre-exponential factor for diffusion in normal lattice sites, respectively, and $K_H$ is the ratio of the number of trapping sites to that of total lattice sites and is proportional to the dislocation density(8).

Numerous data have been reported on $D_H$, $D_{0,H}$, and $Q_H$, but those values show scattering(1). The scatter in the data seems to be attributed either to the trapping of hydrogen by lattice defects or to the so-called surface effect. As described before, reliable values of the diffusion coefficient of hydrogen can be obtained from the permeation experiments by the procedure used in the present work. The dislocation density in specimens annealed at temperatures much higher than the recrystallization temperature is extremely small, and so the trapping effect of dislocation can be assumed to be negligible(2)(10)(11). Therefore, the values of $D_H$ measured for 1173 K annealed specimens may be regarded as the diffusion coefficient of hydrogen without the influence of trapping. We have the following:

$$Q_H = 8.0 \text{ kJ/mol.}$$

$$D_{0,H} = 2.1 \times 10^{-7} \text{ m}^2/\text{s.}$$

These values of $Q_H$ and $D_{0,H}$ are substituted for eq. (1), and for the value of $E_{B,H}$ three ten-

| Source             | $E_{B,H}$ (kJ/mol) | Method                                      | Ref.  |
|--------------------|--------------------|---------------------------------------------|-------|
| Asano et al.       | 26.4               | temperature dependence of $D_H$            | (2)   |
| Oriani             | 27.2               | temperature dependence of $D_H$            | (8)   |
| Choo & Lee         | 25.6               | temperature dependence of $D_H$            | (13)  |
| Choo & Lee         | 26.8               | thermal spectrum of H$_2$ gas evolution     | (14)  |
| Johnson & Lin      | 48–58              | analysis of permeation curve               | (6)   |
| Kunnick & Johnson  | 59.9               | analysis of permeation curve               | (15)  |
| Gibala             | 27.2               | internal friction                          | (16)  |
| Takita & Sakamoto  | 20.2               | internal friction                          | (17)  |
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tative values were used; i.e., 27, 54 (a representative of 48–60 kJ/mol) and 20 kJ/mol. The value of \( K_H \) was determined in such a way that the difference between the values of \( D_H \) determined by experiments and those calculated from eq. (1) becomes minimum. A choice of \( E_{B,H} = 27 \) kJ/mol gave the best fit in the temperature dependence of the experimental and the calculated value of \( D_H \). The binding energy between hydrogen and dislocation is, therefore, estimated as about 27 kJ/mol. In this case, the values of trap site density \( K_H \) are given in Table 3. The calculated values of \( D_H \) using \( E_{B,H} = 27 \) kJ/mol and these values of \( K_H \) are shown in Fig. 4.

2. Isotope dependence in trapping effect of dislocation

As described above, there has been inconsistency in the isotope effect of dislocation trapping for hydrogen. Johnson and Lin(6) have compared the permeation curves of hydrogen with those of deuterium and reported the same values of the binding energy with dislocation and the trap site density for both hydrogen and deuterium. While Nagano et al.(7) have studied the effect of cold-working on the diffusion coefficients of hydrogen and deuterium and reported that the values of the binding energy and/or the trap site density are different between hydrogen and deuterium.

Johnson and Lin(6) have discussed the isotope dependence, but the value of the binding energy reported by them (48–58 kJ/mol) is different from that determined in the present work (27 kJ/mol). They have obtained the value of the binding energy from the permeation curves under smaller concentration of hydrogen dissolved in iron than that in the present work. Therefore, the difference of the binding energy might indicate the existence of trapping sites with various binding energies in cold-worked iron. On the other hand, because permeation curves measured by using an NaOH solution as a cathodic electrolyte, which has been used in the experiment of Johnson and Lin, are easy to be affected by the surface effect(3), the value of the binding energy determined by them might be unreliable. We have obtained the value of the diffusion coefficient of hydrogen, which is free from the surface effect, by using an H_2SO_4 solution. The cause of the difference between the value reported by Johnson and Lin and that determined in the present work is not clear and it will be examined in future. However, it is important to discuss the isotope effect from the experimental results obtained in the present work.

Nagano et al.(7) have used a D_2SO_4 + D_2O + CH_3OH solution, in which hydrogen and deuterium coexist, for measurement of the diffusion coefficient of deuterium. Because both hydrogen and deuterium may be introduced into an iron specimen by cathodic polarization in the solution(18), the permeation rate measured by them may be for a mixture of deuterium and hydrogen. Therefore, the diffusion coefficient of deuterium determined from the permeation rate might be unreliable. Also they have measured the diffusion coefficient of hydrogen at 222 K, but this temperature is lower than the freezing point of the cathodic electrolyte used in their experiment. Under these experimental conditions an electrochemical permeation experiment cannot be done. This implies that the measured temperature may be unreliable. Because Nagano et al. have discussed the isotope dependence of dislocation trapping on the basis of the temperature dependence of the diffusion coefficients of hydrogen and deuterium determined under the experimental conditions, the conclusion on the isotope dependence might be erroneous.

Therefore, in this work, the experimental procedure was refined for measurement of the diffusion coefficient and determination of the binding energy and the trap site density: The cathodic electrolyte used for deuterium permeation experiments was a D_2SO_4 + D_2O solution in which only deuterium was contained. In addition, the diffusion coefficient obtained in this

| Specimen                | \( K_H \)   |
|-------------------------|-------------|
| 773 K annealed specimen | 2 \times 10^{-6} |
| 673 K annealed specimen | 4 \times 10^{-6} |
| cold-worked specimen    | 1.1 \times 10^{-4} |

Table 3 The values of trap site density \( K_H \) obtained under the condition of \( E_{B,H} = 27 \) kJ/mol.
work is free from surface effect, and its temperature dependence has been found to be expressed by eq. (1). Namely, the binding energy and the trap site density can be determined by the application of eq. (1) to the diffusivity data obtained in the experiment.

We discuss the isotope dependence in the trapping effect of dislocation: The diffusion coefficient of deuterium $D_D$ will also be expressed by a similar equation to that for hydrogen (cf. eq. (1)). The ratio $D_H/D_D$ is given by

$$\frac{D_H}{D_D} = \left(\frac{D_{0,H}}{D_{0,D}}\exp\left(-\frac{Q_H}{RT}\right)\right) \times \left(\frac{1-K_D+K_D\exp\left(E_{B,D}/RT\right)}{1-K_H+K_H\exp\left(E_{B,H}/RT\right)}\right),$$

where $Q_D$, $D_{0,D}$, $K_D$ and $E_{B,D}$ have their corresponding meanings to those in the case of hydrogen.

As can be seen from Fig. 5, the dependence of $D_H/D_D$ upon the dislocation density (i.e., the value of trap site density) is not found. This indicates that the following relation should hold:

$$\left(1-K_D+K_D\exp\left(E_{B,D}/RT\right)\right) \approx 1.$$  

This relationship holds irrespective of temperature and trap site density, so that the following can be deduced:

$$K_H \approx K_D,$$

$$E_{B,H} \approx E_{B,D} \approx 27 \text{ kJ/mol}.$$  

That is, in the present experiments and analysis, the values of trapping parameters (trap site density and binding energy) for hydrogen are the same, within an experimental error, as those for deuterium.

This result is different from that reported by Nagano et al.\(^{(7)}\). However, the cause of the difference is not clear, because the purity of specimen and the experimental procedure are different.

Assuming the value of $D_D$, like that of $D_H$, of 1173 K annealed specimens is the diffusion coefficient of deuterium without the influence of trapping, the following values are obtained:

$$Q_D = 9.0 \text{ kJ/mol}.$$  

The temperature dependence of $D_D$ is calculated using eqs. (1) and (6)-(9). The calculated values of $D_D$ are shown by the solid curves in Fig. 4.

V. Conclusion

The diffusion coefficients of hydrogen and deuterium in iron specimens with various dislocation densities were measured by an electrochemical permeation method, and they were discussed on the basis of the trapping theory by Oriani, referring to the experimental data of previous workers on the trapping of hydrogen and deuterium by lattice defects (dislocations). The following results were obtained:

1. The ratio of the diffusion coefficient of hydrogen to that of deuterium $D_H/D_D$, is temperature dependent, but its dependence upon the dislocation density was not found.
2. The activation energy for diffusion in a normal lattice is mass dependent, but the trap site density and the binding energy are, within an experimental error, independent of the mass of the diffusing atoms.
3. The binding energies of hydrogen and deuterium with dislocation in iron are the same, that is about 27 kJ/mol.

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