Effects of Interstitial Impurities on Dislocation Trapping of Hydrogen in Iron*

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The diffusion coefficient of hydrogen in iron with various interstitial impurity (C, N) contents has been measured at 298 K by an electrochemical permeation method. The diffusivity of hydrogen is significantly reduced by cold-working. In commercially pure iron specimens (high C, N specimens), the diffusivity of hydrogen is slightly restored by aging at room temperature after cold-working. In decarburized-denitrided specimens (low C, N specimens), however, this change by aging is not observed. Annihilation of dislocations by heat treatments causes recovery of the diffusion coefficient. That is, dislocations serve as trapping sites for hydrogen, and the formation of atmosphere of interstitial impurities (C, N) around dislocations weakens the trapping effect of dislocations. The diffusion coefficient of hydrogen has been analyzed on the basis of the trapping theory, and the trap density (i.e., the ratio of the number of the trapping sites to that of total lattice sites) has been calculated. The trap density before the formation of the C, N atmosphere around dislocations is, within experimental error, proportional to the dislocation density.

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I. Introduction

The diffusion coefficient of hydrogen in iron has been measured by many workers. Its values at temperatures below 500 K reported in the literature so far, however, show considerable scatter(1), and many of them are smaller than the values extrapolated from the high temperature data. The anomalous behavior of hydrogen diffusion in iron at such temperatures has been attributed to the trapping effect by lattice defects and surface effects in inadequate experiments(1).

Cold-working of iron has been found to lower the diffusion coefficient of hydrogen. This has been explained as the trapping effect of lattice defects such as dislocations and voids introduced by cold-working(1).

In previous works, we have measured partial molar volumes of hydrogen and deuterium in iron and obtained an equal volume for both(2)-(4). The binding energies with the lattice defects introduced by cold-working for hydrogen and deuterium have been also obtained to be equal(5). We have concluded that the trapping of hydrogen (deuterium) by the lattice defects is mainly caused by elastic interaction(5).

Aging of cold-worked iron containing interstitial impurities (carbon and nitrogen) causes the rise in yield stress, which is attributed to the elastic interaction between the interstitial impurities and dislocations(6). Consequently, both of the interstitial impurities and hydrogen interact elastically with dislocations. Therefore, the existence of the interstitial impurities should have some effects on the trapping effect of hydrogen diffusion. However, few measurements of the diffusion coefficient of hydrogen in cold-worked iron have been done paying attention to the effect of the interstitial impurities(7).

In the present work, the diffusion coefficient of hydrogen has been measured by an electrochemical permeation method after aging at various temperatures using specimens with various impurity contents and various degrees of deformation.
II. Experimental Procedure

1. Specimens

The materials used in the present experiment are commercially pure iron of which chemical composition is shown in Table 1 (this is denoted by high C, N specimen) and decarburized-denitrided iron (C: 0.0006 mass%, N: 0.0045 mass%) prepared by hydrogen treatment; in wet hydrogen for $2.6 \times 10^6$ s at 973 K and in dry hydrogen for $2.6 \times 10^6$ s at 973 K. Specimens with various dislocation densities and different distributions of interstitial impurities were prepared by various combinations of deformation and annealing procedures. A thin layer of palladium was electroplated on the anodic side of the membranes. The thickness of the specimens was about 1 mm.

2. Measurement of permeation curves

Permeation rates of hydrogen were measured by the electrochemical method\(^{8(9)}\). Hydrogen was generated electrolytically at a constant cathodic current density on one side (cathodic side) of the membrane, while on the other side (anodic side) of the membrane permeating hydrogen was potentiostatically ionized. The electrode potential of the anodic side was maintained at 0 V against an Ag/AgCl reference electrode by a potentiostat.

The cathodic electrolyte was an 0.5 kmol/m\(^3\) H\(_2\)SO\(_4\) aqueous solution, and the anodic electrolyte was an 0.2 kmol/m\(^3\) NaOH aqueous solution.

3. Determination of diffusion coefficient of hydrogen

The observed transient curves of hydrogen permeation were analyzed using the method described in the previous papers\(^{5(8)(9)}\), which enabled us to obtain reliable values of the diffusion coefficient of hydrogen ($D_H$). The permeation curves usually show different time dependences depending on the experimental conditions such as cathodic current density ($i_c$) and specimen thickness ($L$). To determine the diffusion coefficient of hydrogen ($D_H$) from the analysis of permeation curves used in the present work, the following requirements were confirmed\(^{10}\): The apparent values of diffusion coefficient obtained have been independent of $i_c$ and $L$, and the steady state permeation rate has been proportional to the reciprocal of the specimen thickness ($1/L$).

4. Measurement of dislocation density

Specimens with various degrees of deformation and annealing procedures were examined by transmission electron microscopy (JEM-1000, HVEM Lab., Kyushu Univ.) and by X-ray diffraction. The dislocation density in the specimens was obtained from the electron microscopic observation: The length of dislocations was measured from the image and the thickness of the specimens was estimated from thickness fringes. The change in dislocation density with cold-working and annealing procedures was also measured from the half-value width of X-ray diffraction peak of Fe(211) with filtered Co-K\(_\alpha\) radiation.

III. Experimental Results

1. Effect of room temperature aging

The diffusion coefficient of hydrogen ($D_H$) at 298 K, the half-value width of X-ray diffraction peak ($B$) and Vickers hardness ($H_v$) were measured for 9% cold-worked high C, N specimens after aging at room temperature (288–303 K). Changes in $D_H$, $B$ and $H_v$ with aging time are shown in Fig. 1. The values of $D_H$ and $H_v$ for high C, N specimens first increase and reach a minimum or a maximum at approximately the same time by room temperature aging, while the value of $B$ does not change.

As shown in Fig. 2, $D_H$ and $H_v$ for 9% cold-worked low C, N specimens do not change with the aging.
2. Effect of cold-working

The diffusion coefficient of hydrogen \( (D_H) \) at 298 K and Vickers hardness \( (H_v) \) for cold-worked high C, N specimens changed with the time of room temperature aging. Therefore, values of \( D_H \) and \( H_v \) were measured soon after cold-working \( (5 \times 10^3 \text{~to~} 2 \times 10^4 \text{~s after cold-working}) \). The dislocation density \( (\rho) \) and half-value width of X-ray diffraction peak \( (B) \) were also measured. As shown in Fig. 3, for high C, N specimens \( \rho \), \( B \) and \( H_v \) increase, and \( D_H \) decreases with increase in the degree of cold-working.

3. Effect of annealing temperature

For high C, N Specimens which were annealed at various temperatures for 28.8 kS after 9% cold-working and cooled in a furnace, and then aged above \( 10^9 \text{~s at room temperature} \), \( D_H \) at 298 K, \( \rho \), \( B \) and \( H_v \) were measured. As shown in Fig. 4, for high C, N specimens annealed at temperatures between room temperature and 550 K, \( \rho \) and \( B \) stay unchanged, while \( D_H \) increases. Annealing above 550 K reduces \( \rho \), \( B \) and \( H_v \), and increases \( D_H \). And the value of \( D_H \) in high C, N specimens annealed above 1100 K is nearly constant \( (8.5 \times 10^{-5} \text{~m}^2/\text{s}) \).
Also for low C, N specimens which were annealed at various temperatures for 28.8 ks after 9% cold-working and then furnace-cooled, $D_H$ at 298 K, $\rho$ and $B$ were measured. As shown in Fig. 5, for low C, N specimens annealed below 500 K, $D_H$, $\rho$ and $B$ are not found to change. Annealing above 500 K reduces $\rho$ and $B$, and increases $D_H$.

IV. Discussion

Various lattice defects are introduced into iron specimens by plastic deformation. The trapping sites are classified in the literature into the following three categories; void and crack$^{(11)-(15)}$, vacancy$^{(16)}$ and dislocation$^{(17)-(20)}$. Details of trapping effect by these lattice defects are not yet clear. The cause seems to be due partly to the difference in the experimental procedure and purity of specimens. When the defects which have a large binding energy with hydrogen exist in the specimen, hydrogen atoms trapped at the defects do not diffuse apparently at low temperature. Namely, the strongly trapped hydrogen atoms may not be detectable by permeation experiments at low temperature. On the other hand, almost all hydrogen atoms in iron are detected by high temperature measurements. Therefore, the difference in experimental method is expected to alter a kind of trapped hydrogen atoms detected. In addition, though the purity of specimens in the literature differs, the influence of the purity on the trapping effect has not been investigated.

Asano et al.$^{(17)}$, Nakai et al.$^{(18)}$ and Nagano$^{(20)}$ have measured the annealing temperature dependence of $D_H$ in cold-worked iron by an electrochemical permeation method. $D_H$ reduced significantly by cold-working is recovered by annealing above the recrystallization temperature. This indicates that dislocations serve as trapping sites for hydrogen. However, they did not measure the dislocation density in the

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Fig. 3 Variation of (a) hydrogen diffusivity at 298 K ($D_H$), (b) trap density ($K_H$), (c) dislocation density ($\rho$), (d) X-ray line broadening ($B$) and (e) Vickers hardness ($H_v$) with degree of cold-working for commercially pure iron specimens (high C, N specimens). The measurements of $D_H$ and $H_v$ were done soon after the cold-working.
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Fig. 5 Variation of (a) hydrogen diffusivity at 298 K ($D_H$), (b) trap density ($K_H$), (c) dislocation density ($\rho$) and X-ray line broadening ($B$) with annealing temperature for the 9% cold-worked specimens of decarburized-denitrided iron (low C, N specimens).

Fig. 4 Variation of (a) hydrogen diffusivity at 298 K ($D_H$), (b) trap density ($K_H$), (c) dislocation density ($\rho$), (d) X-ray line broadening ($B$) and (e) Vickers hardness ($H_v$) with annealing temperature for the 9% cold-worked specimens of commercially pure iron (high C, N specimens).
specimen. And the purity of the specimens differs between their works and the effect of impurity atoms on the experimental results is not clear. The experimental result of Nakai et al. shows that $D_H$ changes in annealing at temperatures even below 500 K at which annihilation of dislocations is not expected.

The recovery of $D_H$ with dislocation annihilation measured by electrochemical permeation\(^{(17)(18)(20)}\) and appearance of a cold-work peak of internal friction by hydrogen charging\(^{(21)(22)}\) assure that dislocations have significant effect on hydrogen diffusion. Furthermore, the abovementioned change in $D_H$ by heat treatment reported by Nakai et al. is impossible to be explained by only the interaction between hydrogen and dislocation.

The diffusion coefficient of hydrogen ($D_H$) in the process including the trapping effect is expressed as the following equation\(^{(23)}\),

$$D_H = D_0 \exp \left( \frac{-Q}{RT} \right) / \left( 1 - K_H + K_H \exp \left( \frac{E_b}{RT} \right) \right),$$  \(1\)

where $D_0$ and $Q$ are the pre-exponential factor and activation energy for diffusion in normal lattice sites, respectively, $K_H$ is the trap density (the ratio of the number of trapping sites to that of total lattice sites), and $E_b$ is the binding energy between hydrogen and lattice defects. All the experimental data of $D_H$ can be fitted to eq. (1) by changing only the value of $K_H$ with the fixed value of $E_b$.

The values of trap density $K_H$ in various specimens are determined from eq. (1) by substitution of the following values of $D_0$, $Q$, and $E_b$ obtained in the previous work\(^{(5)}\).

$$D_0 = 2.1 \times 10^{-7} \text{ m}^2/\text{s}. \quad (2)$$
$$Q = 8.0 \text{ kJ/mol.} \quad (3)$$
$$E_b = 27 \text{ kJ/mol.} \quad (4)$$

The change in $K_H$ with aging time at room temperature, degree of cold-working and annealing temperature is presented in Figs. 1-5.

These results are summarized as follows: (i) In cold-worked high C, N specimens, the room temperature aging does not affect $B$ (i.e., $\rho$), but it reduces $K_H$. The decrease in $K_H$ appears in accordance with the increase in Vickers hardness $H_V$ (Fig. 1). (ii) In cold-worked low C, N specimens, $K_H$ and $H_V$ are not affected by room temperature aging (Fig. 2). (iii) In the high C, N specimens without aging, $K_H$ is nearly proportional to $\rho$ (Fig. 3). (iv) In cold-worked high C, N specimens, even when annealing temperature is lower than the recrystallization temperature, about 550 K, $K_H$ decreases (Fig. 4). (v) In cold-worked low C, N specimens, $K_H$ and $\rho$ show similar dependence on annealing temperature and $K_H$ is nearly proportional to $\rho$ (Fig. 5).

The increase in hardness by strain aging is due to the formation of the atmosphere of impurity atoms around dislocations\(^{(6)}\). As shown in Fig. 4, the increase in $H_V$ caused by the strain aging for high C, N specimens reaches a maximum at about $10^6$ s of aging time at room temperature. The diffusion distance of interstitial impurities (C, N) during the aging time calculated from the diffusivity of them agrees in the order of magnitude with the average interval between dislocations in 9% cold-worked high C, N specimens (about $10^{14}$ m\(^{-2}\)). Because the diffusion coefficients of carbon and nitrogen are considerably smaller than that of hydrogen, it is considered that only hydrogen atoms diffuse during permeation experiments, while carbon and nitrogen atoms are fixed. The result (i) above described indicates that $K_H$ decreases with the formation of the impurity atmosphere around dislocations through long range diffusion of the impurity atoms. The result (ii) implies that if the atmosphere of the impurities is not formed, the value of $K_H$ does not change at room temperature. Consequently, these results suggest that dislocations are effective trapping sites for hydrogen diffusion and interstitial impurities affect remarkably the dislocation trapping of hydrogen. The effect of interstitial impurities on the dislocation trapping is interpreted on the basis of the site occupation of the trapping sites by interstitial impurities or the relaxation of the stress field around dislocations by the formation of the impurity atmosphere. The restoration in $D_H$ in cold-worked high C, N specimens by aging at room temperature is caused by weakening of the dislocation trapping owing to the formation of the impurity atmosphere around dislocations. If the relaxa-
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The interaction between hydrogen and dislocations free from interstitial impurities can be discussed with the results of \( D_H \) in low C, N specimens, in which the formation of the impurity atmosphere is negligible, and \( D_H \) in high C, N specimens before the formation of the atmosphere. The trap density \( K_H \) is expressed as follows (17)(24):

\[
K_H = \pi r_e^2 \rho,
\]

where \( r_e \) is a parameter associated with the number of trapping sites supplied by a dislocation and it is called an effective radius. The results (iii) and (v), which show \( K_H \) to be nearly proportional to \( \rho \), give the following values of \( r_e \):

\[
r_e = \begin{cases} 
1.1 \times 10^{-9} \text{ m (low C, N specimens)} \\
1.0 \times 10^{-9} \text{ m (high C, N specimens)}. 
\end{cases}
\]

Because these values of \( r_e \) are independent of \( \rho \), each dislocation supplies trapping sites independently. These values larger than the size of a dislocation core indicate that hydrogen atoms are trapped also in the region at a slight distance from the dislocation core. Considering the large experimental errors in \( K_H \) and \( \rho \), the values of \( r_e \) are accepted to be equal for high C, N specimens and low C, N specimens.

The annealing temperature dependence of \( K_H \) (the results (iv) and (v)), in which \( K_H \) decreases with dislocation annihilation, also indicates the significance of dislocation trapping. In the annealing temperature dependence of \( K_H \) for cold-worked high C, N specimens described in the result (iv), the decrease in \( K_H \) by annealing below 550 K is explained by the formation of the impurity atmosphere around dislocations, and the decrease in \( K_H \) by annealing above 550 K is caused by both of the decrease in \( \rho \) and the formation of the impurity atmosphere.

V. Conclusion

In order to study the trapping effect of lattice defects in hydrogen diffusion in cold-worked iron, the diffusion coefficient of hydrogen in iron with various impurity contents and various dislocation densities was measured by an electrochemical permeation method, and they were analyzed to obtain the trap density. The following results were obtained:

1. Dislocation has the greatest effect on the diffusion coefficient of hydrogen in iron measured around room temperature.
2. The diffusion coefficient of hydrogen in cold-worked high C, N specimens slightly recovers with increase in Vickers hardness by aging at room temperature. This change in the diffusivity of hydrogen is due to weakening of the dislocation trapping by the formation of the impurity atmosphere around dislocations.
3. The measured trap density is, within experimental error, proportional to the dislocation density for high C, N specimens without aging and low C, N specimens. The effective radius of a dislocation for trap sites is calculated to be about \( 1 \times 10^{-9} \) m from the proportionality. This value indicates that the trap site extends in the region apart from the core of dislocation.
4. Annihilation of dislocations caused by annealing above the recrystallization temperature reduces the trap density. In iron specimens with much impurity contents, the trap density decreases with increase of annealing temperature even when the dislocation density does not change. These annealing temperature dependences of the trap density can be explained by dislocation trapping and impurity effect on it.

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† In the case of a certain annealing temperature, the precipitation of carbides and nitrides may occur at dislocation cores (25). We cannot separate the effects of precipitation and atmosphere formation of impurities. Therefore, both of them are contained in the effect of the atmosphere formation around dislocations in the present work.
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