Effect of Mechanical Deformation on Permeation of Hydrogen in Iron

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Rate of hydrogen permeation was measured under static as well as dynamic mechanical deformation conditions. Cylindrical tensile test specimens were used for the study and hydrogen permeation was measured electrochemically. It was observed that the hydrogen diffusivity decreased as plastic deformation increased for the static deformation experiments while elastic deformation had no significant effect on diffusivity but increased the steady state permeation flux. For the dynamic loading experiment, an elastic deformation increased the hydrogen permeation rate almost linearly. Onset of plastic deformation led a sudden decrease of permeation rate and the reduced rate was rapidly recovered when the plastic deformation ceased. These rapid changes in the permeation rates were explained that the absorbed hydrogen was trapped by dislocations and creation rate and density of dislocations changed drastically when plastic deformation started and stopped.

KEY WORDS: hydrogen permeation; hydrogen trap; diffusivity; mobile dislocation; hydrogen absorption; plastic deformation.

1. Introduction

Corrosion fatigue cracking (CFC) and stress corrosion cracking (SCC) associated with hydrogen embrittlement are problems that exist in engineering structures. The influence of strain on hydrogen transport through metals is one of the most important and interesting aspects among them. A resolution would provide a substantial understanding of some of the mysteries of CFC and SCC mechanisms. Since the idea that mobile dislocations might carry hydrogen1) was suggested, the role of plastic deformation in affecting hydrogen transport was the subject of studies. Past works yield conflicting conclusions. Some experimental results support the concept of hydrogen transport by moving dislocations, while others do not. It was observed that plastic deformation accelerates the release of tritium from various metals such as iron, AISI 304L stainless steel, nickel, Inconel 718, and aluminum.2) Louthan et al.3) found that tritium penetrates more deeply into AISI 304L during plastic deformation than that of purely elastic. Kurkela and Latanision4) found an increase of the apparent diffusivity by up to five orders of magnitude for nickel. Otsuka and Isaji5) also observed similar phenomena for nickel. Frankel et al.6) observed direct evidence for dislocation transport of hydrogen in the easy glide region of deformation for single crystals of nickel. As for poly-crystals, they concluded that the trapping effect was the dominant process of deformation.7) If certain conditions were met, the increased permeation flux can be observed.7) Kang et al.8) obtained increased diffusivity by analyzing the decaying permeation flux during deformation for 3.3Ni–1.6Cr steel. Permeation experiments conducted by Kurkela et al.9) with a 2.25Cr–1Mo steel and by Berkowitz and Heubaum10) with an AISI 4130 steel as well as Zakroczymski11) with pure iron subjected to simultaneous hydrogen charging and straining, indicated that dislocations acted as traps for hydrogen and thus decreased the total hydrogen transport. While others12) showed that the effect of dislocation resulted from plastic deformation is directly related to the boundary condition of the experiment. The conflicting results by different researchers suggest that the hydrogen transport behavior during deformation is far from clear. As Johnson and Hirth predicted,13) a larger effect could be expected in face-centered cubic (fcc) metals and alloys than in body-centered cubic (bcc) ones because of the much higher lattice hydrogen diffusivity in the latter case. However, even for the same kind of materials, the conclusions deduced from the individual results obtained by researchers are different.4,5,7)

When the materials are deformed, two competing effects, namely, enhanced trapping and enhanced transport by dislocation can both play a role, but one may overcome another. In this paper, the results of an experimental study on the effect of straining on hydrogen transport in iron were reported and a reasonable discussion was given.
2. Experimental

2.1. Materials and Preparation
The material for the study was commercial pure iron after annealing. A tube type specimen of 8.6 mm in outer diameter and 0.3 mm in wall thickness was used. The specimen was heat treated again after machining at 973 K in vacuum for one hour to reduce the residual stress, and then coated with thin layer of palladium using commercial solution.

2.2. Test Solution
0.2 mol/l NaOH was used both as anodic solution and hydrogen charging solution prepared with analytical grade chemicals and double distilled water.

2.3. Experimental Setup
Devanathan–Stachurski \(^{(14)}\) double cell method was used for the hydrogen permeation measurement with one side of the tube as hydrogen detecting side and the other as charging side. A multi-channel Potentiostat/Galvanostat (Toho Giken, Model PS-08) was used for the control of ionizing potential and charging current of hydrogen. A uniaxial tensile machine (Tensilon, Model UTM-4L) was used for the static and continuous loading.

2.4. Test Procedures
After cleaning and degreasing, the specimen was mounted on the loading machine. The anodic side was filled with 0.2 mol/l NaOH and polarized potentiastically at 150 mV vs. HgO/Hg/0.2 M NaOH. When the static passive state was reached (more than 24 h, the remaining current was less than 0.1 \(\mu\)A/cm\(^2\)) under various constant loading levels, the cathodic side was filled with the charging solution and galvanostatically polarized immediately with a cathodic current of 2 mA/cm\(^2\). The permeation current was recorded using a computer simultaneously. For the dynamic loading experiment, load was applied at a strain rate of \(1.1 \times 10^{-5}/s\) after quasi-static permeation current was reached. In order to differentiate the permeation current from passive current, an experiment was performed to measure the background current change at the same strain rate.

3. Results
3.1. Hydrogen Permeation Behavior under Static Loading Conditions
Figure 1 is a hydrogen permeation build up curve for iron free of stress with hydrogen charging current density of 2 mA/cm\(^2\). It was reported that the plot of \(\log(P_t/P_0)\) against time, where \(P_0\) is the steady state permeation current, and \(P_t\) is that at time \(t\), for the rise transient, is a straight line.\(^{(15,16)}\) The slope of the line \(1/t_0\) can be described as:

\[
1/t_0 = \pi^2 D/L^2
\]

where \(D\) is diffusivity, \(L\) is thickness of the specimen. By calculating the slope, the diffusivity \(D\) can be estimated.

Figure 2 shows the plot of logarithmic dependence of the permeation flux on time derived from Fig. 1. The calculated diffusivity is \(2.5 \times 10^{-5}\) cm\(^2\) s\(^{-1}\) for the unstressed specimen. This method was adopted to assess the effect of static loading on apparent diffusivity. All the measurements were repeated for three times and the average value was given. An example of hydrogen permeation build up curve under loading is shown in Fig. 3 and the corresponding logarithmic dependence of the permeation flux on time is shown in Fig. 4.

Figure 5 shows the results of diffusivity measurements and the corresponding stress–strain curve. The elastic deformation had no significant effects on diffusivity, while plastic deformation decreased the apparent diffusivity of
hydrogen. The change of steady state hydrogen permeation current with strain under static state loading conditions is shown in Fig. 6. The stress–strain curve is overlaid on the figure. The permeation current $P$ increased with the increase of loading.

The permeation current decay was also recorded after the shut off of the charging current. Figure 7 shows current decay curves at different strain levels while Fig. 8 shows the normalized ones. When the strain was increased, it took longer time for the hydrogen to diffuse out of the specimen completely. This means the specimen absorbed more hydrogen when it was stretched. The integration of the area in Fig. 7 below each decaying curve can be roughly regarded as the hydrogen dissolved in the specimen. This is not accurate, because it is not a closed system, but can work as an indication of total hydrogen concentration increased. Suppose this value is $Q_0$. Since the concentration $C$ varies linearly throughout the specimen when the hydrogen permeation reaches steady state, the quantity of hydrogen required to saturate the same specimen to a uniform concentration $C_0$ will be $2Q_0$, and $C_0 = 2Q_0/L$, where $L$ is the thickness of the specimen.

Figure 9 shows the estimated total hydrogen concentration $C_0$ at the surface of the specimen against strain curve.

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Fig. 4. Logarithmic transient of buildup permeation flux for iron stressed at 231 MPa.

Fig. 5. Change in apparent hydrogen diffusivity in iron with static stress conditions.

Fig. 6. Change in steady permeation current and stress with static strain.

Fig. 7. Decay curves of hydrogen permeation current at different static strain levels.

Fig. 8. Normalized decay curves of permeation current at different static strain levels.

Fig. 9. Estimated hydrogen concentration on the surface of entry side at different strain level.
together with the curve of stress–strain. The concentration \( C_0 \) increased with the increase of deformation.

### 3.2. Hydrogen Permeation Behavior under Dynamic Loading Condition

Under dynamic loading condition, a portion of the total current change was due to the change in the background passive current as a result of the emergence of slip steps at the surface, which expose the fresh metal area to the anodic solution. In order to separate this effect, experiment was performed to measure directly the increase in passive current during deformation in the absence of hydrogen, and then the background current was subtracted from the total current change. **Figure 10** shows the typical background current change during an elastic loading, plastic loading, stop loading and a unloading cycle. Elastic deformation did not influence the passive current while the plastic deformation could increase the current to a certain value.

The hydrogen permeation current change with deformation is shown in **Fig. 11**. The hydrogen permeation current increased with stress under elastic deformation range, while decreased with the onset of plastic deformation and then reached a critical point after which increased. When the deformation was stopped, a sudden increase in permeation current occurred. The experiment was repeated several times and resulted in similar phenomenon.

### 4. Discussion

#### 4.1. Effect of Static Loading on Hydrogen Permeation

Mechanisms of hydrogen entry into metals were recently reviewed by Protopopoff and Marcus.\(^{17}\) McNabb and Foster\(^{18,19}\) made a mathematical analysis for diffusion accompanied by trapping and untrapping. According to their model, the apparent diffusivity \( D \) is related to the lattice-dissolved hydrogen \( C \), the concentration of trap \( N \), and the kinetic parameters of trapping \( (k) \) and untrapping reactions \( (p) \) as follows:

\[
D = D_L \left\{ \left[ \frac{1}{N(k/p)} \right]^{1/2} \right. \left[ \frac{2}{N(k/p)} \right] + \cdots \right. ...
\]

where \( D_L \) is lattice diffusivity. When trapping does not occur, that is either \( N=0 \) or \( k/p=0 \), the measured diffusivity will be equal to the lattice diffusivity. Elastic deformation is not supposed to increase the concentration of trap, so the diffusivity does not change under elastic deformation. The dislocations generated by plastic deformation were regarded as traps. With the increasing of plastic deformation, the density of dislocation increases and so the concentration of trap, as a result, the apparent diffusivity decreases with plastic deformation.

The increase in permeation current was observed under static loading condition. This phenomenon is in agreement with that observed by Beck et al.\(^{20}\) Under elastic loading condition, the increase in permeation current is explained as the lattice expansion.\(^{11}\) In fact, the expansion is a result of applied stress, and the stress can increase the lattice energy. Since the dissolution of hydrogen into the lattice is endothermic, the increase in lattice energy with stress would account for the increase in hydrogen solubility. In the elastic region, the energy is

\[
\Delta E = \frac{\sigma^2}{2Y} \tag{3}
\]

Where \( \sigma \) is stress, \( Y \) is Young’s modulus. According to Beck et al.,\(^{20}\) in iron, each iron atom is directly associated with six metal atoms in the octahedral position of the metal lattice, then the ratio of the solubilities in the stressed and unstressed condition is:

\[
C_\sigma/C_0 = \exp(6\sigma^2V/2YRT) \tag{4}
\]

where \( V \) is the molar volume of iron. Equation (4) can be rewritten as follows,

\[
\log(C_\sigma/C_0) = (6V/2YRT)\sigma^2 \tag{5}
\]

**Figure 12** shows the log \((C_\sigma/C_0)\) against \( \sigma^2 \) curve which is
a straight line as predicted by Eq. (5).

As shown in Fig. 6, the permeation current also increases under static plastic deformation condition. At a steady state, the permeation current can be written as

\[ P_n = D_L C_0 / L \]  \hspace{1cm} (6)

Where \( C_0 \) is the hydrogen concentration just below the charging surface, \( L \) is the specimen thickness, \( D_L \) is lattice diffusivity. The diffusivity decreases with the increase of deformation, so the increase in \( P_n \) must be due to the increase of \( C_0 \) or the decrease of \( L \). As the maximum deformation is only 0.14, the contribution of thickness decrease is no more than 16\%, while the actual increase of \( P_n \) is 56\%. It seems likely that deformation also results in an increase in hydrogen entry. The active sites generated on a deformed surface act to enhance both the reduction of hydrogen ions and also the entry of hydrogen into the lattice.\(^6\) The enhanced entry of hydrogen results in an increase in the input concentration and then the measured permeation current.

4.2. Effect of Dynamic Loading on Hydrogen Permeation

Although there are some contradictions among literatures about the role of dislocations on the transport of hydrogen, the enhanced transport in nickel is the dominant result,\(^2\)–\(^6\) while enhanced trapping in bcc materials is the main phenomenon.\(^9\)–\(^11\) In fact, when a material is deformed, enhanced trapping and enhanced transport by dislocation can both play a role, no matter it is fcc or bcc, but one may overcome another. As Johnson and Hirth predicted,\(^13\) a larger effect could be expected in fcc metals and alloys than that in bcc ones because of the much higher lattice hydrogen diffusivity in the latter case.

It is found in the literatures that the hydrogen permeation behavior is directly related with the straining rate.\(^11\)–\(^12\) The higher the straining rate, the higher the trapping effect would be. In order to avoid the overwhelming trapping of hydrogen by dislocation, a relatively lower strain rate was selected in this paper. The onset of plastic deformation resulted in a drop in permeation current, and then began to increase after reaching a critical point. Zakroczymski\(^11\) also observed similar results, but comments were not given.

During the plastic deformation, the lattice could no longer expand. Instead, dislocations were generated. Before loading the existing traps were already being saturated by hydrogen, so the change in permeation current mainly reflected the behavior of newly generated dislocations. When plastic deformation occurred, the dislocations trapped some hydrogen atoms and the measured hydrogen current decreased. In the meantime, the trapped hydrogen in the dislocation began to move with it. When the dislocation reached to the surface of the anodic side, the hydrogen carried by the moving dislocation would strip from the dislocation and resulted increase in permeation current.

It can be supposed that the estimated increase in total hydrogen concentration shown in Fig. 9 after plastic deformation is a result of dislocation trapping. If the hydrogen concentration level before plastic deformation is subtracted from the curve, the change can be regarded as a reflection of concentration trapped by dislocation. Figure 13 shows the curve of trapped hydrogen concentration by dislocation with time deduced from Fig. 9 if the specimen was elongated at a strain rate of 1.1×10\(^{-5}\)/s.

The trapping of hydrogen will reduce the hydrogen concentration in the lattice. For simplification, the hydrogen concentration changes linearly from the charging side to the anodic side as shown in Fig. 14. In this case, the measured current change will be:

\[ P = DC_1 / L - DC_0 / L = DC_1 - DC_0 = -DC_0 / L \]  \hspace{1cm} (7)

Where \( D \) is lattice diffusion constant, \( C_1 \) and \( C_0 \) are lattice hydrogen concentration after and before straining of the specimen. The reported lattice diffusion constant for pure iron is 8.25×10\(^{-5}\) cm\(^2\)/s. The estimated permeation current change against time curve obtained from Fig. 13 and Eq. (7) is shown in Fig. 15 together with the measured change after onset of plastic deformation. The estimated value fits the earlier current change well considering experimental error, which means the permeation current decrease was a result of dislocation trapping.

While the trapped hydrogen in the dislocation is increasing, the hydrogen transport by dislocation began. Again for simplification, the following assumptions are reasonable refer to Frankel et al.\(^7\)

1. Dislocations are assumed to be created at the surfaces and can sweep through the grain boundary, then travel completely through the specimen.
2. Dislocations immediately obtain an atmosphere in equilibrium with the local lattice concentration at each surface.
3. The dislocations carry this initial atmosphere of hydrogen through the specimen without interacting with the lattice.

The flux of hydrogen at the exit surface due to dislocation transport, \(J_{DT}\) (number of H/cm\(^2\) s), can be written as follows since dislocations move in both directions.

\[
J_{DT}=J_{D+}-n_{+}J_{D-n} \quad \text{...............(8)}
\]

Where \(J_{D}\) (cm/cm\(^2\) s) is the dislocation flux, \(n\) (number of H/cm) is the concentration of hydrogen along the length of a dislocation, \(+\) and \(-\) in the subscripts indicate motion toward and away from the exit surface respectively.

The flux of dislocations can be represented by the product of the dislocation density at the surfaces, \(p\), and the average dislocation velocity, \(v\).

\[
J_{DT}=(n_{+}-n_{-})pv \quad \text{...............(9)}
\]

According to the second assumption stated above, dislocations carry an atmosphere that is in equilibrium with the local lattice concentration at each surface, \(i.e., n_{+}\) at the input side and \(0\) at the exit side. Then the flux as a result of dislocation transport is

\[
J_{DT}=n_{+}pv \quad \text{...............(10)}
\]

From the well known Orowan relationship, \(\dot{\gamma}=pr\mathbf{b}\), where \(\dot{\gamma}\) is the shear strain rate and \(\mathbf{b}\) is Burger’s vector,

\[
J_{DT}=p(\dot{\gamma}/\mathbf{b})n_{+} \quad \text{...............(11)}
\]

According to Frankel \textit{et al.,}\(^7\) \(n_{+}\) can be estimated as the product of the concentration of hydrogen in an atmosphere \(C_{H+}\), and the effective area \(A\),

\[
J_{DT}=p(\dot{\gamma}/\mathbf{b})A_{H+} \quad \text{...............(12)}
\]

\(C_{H+}\) may be estimated from the local lattice concentration \(C_{L}\), and the binding energy \(E_{b}\) using following relation,\(^7\)

\[
C_{H+}=C_{L}\exp(E_{b}/RT) \quad \text{...............(13)}
\]

where \(R\) is the gas constant and \(T\) is temperature. The effective area \(A\) estimated to be \(12.5\pi \mathbf{b}^{2}\), a semicircle of radius \(5\mathbf{b}\).\(^7\)

\[
J_{DT}=(\dot{\gamma}/\mathbf{b})(12.5\pi \mathbf{b}^{2})C_{L}\exp(E_{b}/RT)=12.5\pi \mathbf{b}^{2}C_{L}\exp(E_{b}/RT) \quad \text{...............(14)}
\]

\(C_{L}\) may be estimated as the hydrogen concentration beneath the input side before the onset of plastic deformation under the charging condition of this paper. \(C_{L}=1.02\times10^{-7}\) mol/cm\(^3\) from Fig. 7. Considering that \(\dot{\gamma}=2\dot{e}\), where \(\dot{e}\) is the tensile strain rate, \(b=0.248\) nm,\(^{21}\) \(E_{b}=28.5\) kJ/mol,\(^{21}\) \(R=8.31\) J/mol K, under the strain rate of \(\dot{e}=1.1\times10^{-5}/s\), the calculated value of the contribution by dislocation transport is 0.02 \(\mu\)A/cm\(^2\).

The oversimplifications made here result in an overestimation of the flux due to dislocation transport. Dislocations moving from the input surface toward the exit surface will leak hydrogen to the lattice, and conversely, dislocations moving from the exit surface toward the input surface will pick up hydrogen from the lattice. Moreover, not all the dislocations are movable, the actual amount of hydrogen transported by dislocations would be lower than the estimated value. Even the overestimated value is too small, therefore can not counteract with the increasing trapping current. The enhanced transport of hydrogen by dislocation can not explain the current increase shown in Fig. 11 after critical point.

The compensation of hydrogen input as well as the enhanced entry from the charging surface as a result of deformation can act as a reason for explaining the behavior shown in Fig. 11. With the depletion of hydrogen from lattice as a result of trapping, the driving force for the compensation increases. While a breakthrough time is required for any change in concentration at the input surface to have an effect on the diffusional flux measured at the exit surface.\(^7\) The deviation from quasi-linear line of trapping process shown in Fig. 11 is a reflection of the compensation input of hydrogen. The time between the onset of deformation and the deviation of the curve from quasi-linear line is about 60 s, which agrees with the breakthrough time recorded for the strained specimen of this study as shown in Fig. 3. The competition between trapping and compensation resulted in a critical point shown in Fig. 11.

When the loading stopped, the competing processes also stopped and the permeation current recovered. The recovered permeation current is higher than that before plastic deformation, which is in agreement with the results of static loading experiments. The permeation current decreased with unloading which was a reverse process of loading.

5. Conclusion

Hydrogen permeation in iron was studied under static and dynamic loading condition in this paper. The following conclusions are obtained.

1. Hydrogen diffusivity decreases with the increase of plastic deformation while elastic deformation has no significant effect.
2. The increase in permeation current under static loading condition can be explained as a result of enhanced hydrogen entry and the reducing specimen thickness after deformation.
3. Hydrogen trapping by dislocation is the dominant process in plastic deformation. Enhanced transport of hydrogen by dislocation may also occur, but too small to overcome the effect of trapping.
4. The competition between dislocation trapping and enhanced compensation of hydrogen at the charging surface...
resulted a critical point after onset of plastic deformation.

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