JOURNAL OF MATERIALS SCIENCE 19 (1984) 2633–2638

Effect of cathodic charging current density on the apparent hydrogen diffusivity through pure iron

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The dependence of the apparent hydrogen diffusivity in pure iron on the cathodic charging current density has been measured using an electropermeation cell, establishing the relationship

$$D_A\,(\mathrm{cm^2\,sec^{-1}}) = -3.48 \times 10^{-9} + 1.25 \times 10^{-9}\, i^{1/2}\,(\mu\mathrm{A\,cm^{-2}})$$

This cathodic charging current dependence is explained in terms of trap theory and the basic electrochemical model. This explanation is totally different from the general concept of a concentration dependence of diffusivity. A double plateau in the permeation curve is detected in this experiment at low charging current density.

1. Introduction

The apparent hydrogen diffusivity through iron and steel at room temperature has two typical characteristics. One is that experimentally measured hydrogen diffusivity (apparent hydrogen diffusivity) at room temperature is much smaller than the lattice hydrogen diffusivity calculated from high temperature extrapolated data, and the other is that apparent hydrogen diffusivity is markedly affected by the amount of defects in the specimen [1].

These phenomena have been explained by the trapping theory where interaction between the hydrogen and defects changes the mobility of hydrogen [1, 2]. Subsequently, many researchers [3–5] have studied the effect of trap density and trap character on the hydrogen apparent diffusitivity, since the resistance to hydrogen embrittlement could be improved by the availability of uniformly distributed and sufficiently abundant traps. Up to now, however, it has not been known that apparent hydrogen diffusivity and permeation flux characteristic can be changed by the cathodic charging current density.

In this work, the effect of cathodic charging current density on hydrogen movement was studied in order to understand more clearly the phenomena of hydrogen entrapment in defects. An electropermeation cell was used to measure the hydrogen flux through iron membranes.

2. Rearrangement of McNabb–Foster theory

The theory of McNabb and Foster [1] is adapted to the case of hydrogen diffusion through a metal medium of thickness, a. It is assumed that there are N traps per unit volume in the medium, and of these, a fraction n are filled at any time; the equilibrium lattice solubility of hydrogen is C_L and hydrogen diffusivity through a perfect lattice is D_L. The traps are described in their overall effect by two parameters P and K; the parameter P is the rate constant for release of trapped hydrogen from traps, the rate constant K is the rate at which hydrogen is captured by the traps.

The diffusion equation and trapping equation can be written as

$$N\frac{\partial n}{\partial t} + \frac{\partial C_L}{\partial t} = D\frac{\partial^2 C_L}{\partial x^2} \qquad (1)$$

$$\frac{\partial n}{\partial t} = KC_L\,(1-n) - Pn. \qquad (2)$$

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The ratio of lattice hydrogen diffusivity (D_L) to apparent hydrogen diffusivity (D_A) can be expressed as in Equation 3 by solving Equations 1 and 2 in the boundary condition of the hydrogen permeation test.

$$D_L/D_A = 1 + 6fR(r) \qquad (3)$$

where $R(r) = \frac{1}{2} + r[1 - (1 + r)\ \ln\ (1 + 1/r)]$, $f = N/C_L$ and $r = P/(KC_L)$. Because $\partial n/\partial t = 0$ at equibrium, Equation 2 can be rearranged to give:

$$r = P/(KC_L r) = \frac{1 - n_{eq}}{n_{eq}} \qquad (4)$$

where n_{eq} is the fraction of traps occupied at equilibrium. When the value of n_{eq} is close to 1, the value of r is much smaller than 1 and the value of $R(r)$ is close to 0.5 [6]. In the case of a reversible trap, the value of n_{eq} at room temperature is close to 1, because the binding energy between the trap and hydrogen is much bigger than the thermal energy at room temperature [10]. A limiting value of $R(r)$ is used to simplify Equation 3 leading to Equation 5:

$$D_L/D_A = 1 + \frac{3N}{C_L} \qquad (5)$$

From this, it can be seen that D_L/D_A increases as N is increased or C_L is decreased. Dependence of the apparent hydrogen diffusivity on the trap density has already been widely studied whereas solubility dependence has not.

3. Experimental procedure

Ferrovac iron was used for the specimens, in two conditions, 40% cold-rolled and fully annealed. After mechanically polishing to 0.006 to 0.01 cm thickness, chemical polishing was employed to remove any surface mechanical damage.

All the permeation experiments were carried out using an electrochemical cell originally developed by Devanathan and Stachursky [7] in which hydrogen was introduced by cathodic charging on one side of a metal membrane with hydrogen leaving on the side oxidized. A schematical diagram of the electropermeation cell is shown in Fig. 1. Palladium was plated on to both sides of the membrane to prevent the anodic dissolution of iron and to give similar hydrogen entry conditions on the cathodic side [3]. The potentiostate current necessary to maintain the oxidizing potential of the exiting hydrogen was a direct measure of the output flux of hydrogen.

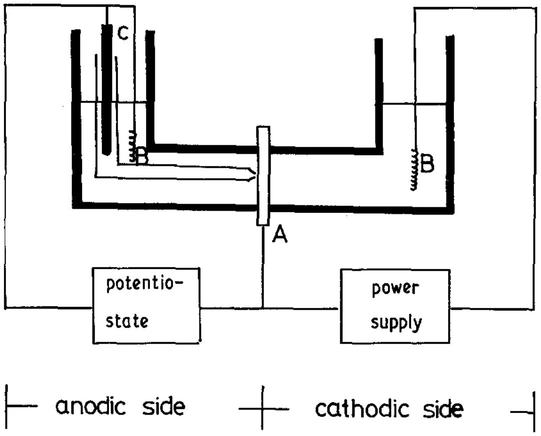

Figure 1 A schematic diagram of the electropermeation cell. a, specimen; b, platinum electrode; c, calomel reference electrode.

Both cathodic and anodic solutions were 0.1 N NaOH solution and cathodic charging current density was changed from 10 to 2340 μA cm^{-2} to test the charging current density effect on the permeation flux characteristic and apparent hydrogen diffusivity. In order to test the trap character of the specimen, the experiments were repeated on iron which had been cold-rolled to a 40% reduction.

Three different apparent hydrogen diffusivities can be calculated from each permeation curve using the following different diffusion equations [7];

$$D_A^b = \frac{a^2}{15.3 t_b} \qquad (6)$$

where t_b is the breakthrough time, and D_A^b is the apparent hydrogen diffusivity calculated from breakthrough time;

$$D_A^L = \frac{a^2}{6 t_L}; \qquad (7)$$

where t_L is the lag time which is simply obtained by observing the time at which the rate of permeation is 0.6299 times the steady-state value, and D_A^L is the apparent hydrogen diffusivity calculated from lag time;

$$\ln\left(\frac{J - J_t}{J}\right)_{x+0} = \ln[1 - \exp(-3t/t_0) + \exp(-8t/t_0) \ldots] + \ln 2 - t/t_0], \qquad (8)$$

where t_0, the rising time constant, is related to the apparent diffusion constant by the

TABLE I The three different apparent hydrogen diffusivities and other experimental data

	40% cold-rolled pure iron					Annealed pure iron				
Current density (μA cm^{-2})	Thickness (10^3 cm)	t_b (min)	$D_A^b \times 10^9$ (cm^2 sec^{-1})	$D_A^L \times 10^9$ (cm^2 sec^{-1})	$D_A^r \times 10^9$ (cm^2 sec^{-1})	Thickness (10^3 cm)	t_b (min)	$D_A^b \times 10^9$ (cm^2 sec^{-1})	$D_A^L \times 10^9$ (cm^2 sec^{-1})	$D_A^r \times 10^9$ (cm^2 sec^{-1})
10	7.6									
15	8.9	58	1.48	2.68	7.95					
20	5.8	23	1.49	2.62		8.4	16.6	4.6	1.91	
30	7.6	22	2.88							
40	8.6	26.5	3.07	5.58	29.37					
100	8.9	14.6	5.90	10.87	22.2	7.6	4.2	15.1	9.49	8.40
500	8.9	3.2	26.9	42.2	126.15					
1000	8.9	1.95	44.2	73.2	234	7.1	0.5	110.19	76.8	107.6
2340	10.2	2.2	51.1	83.8						

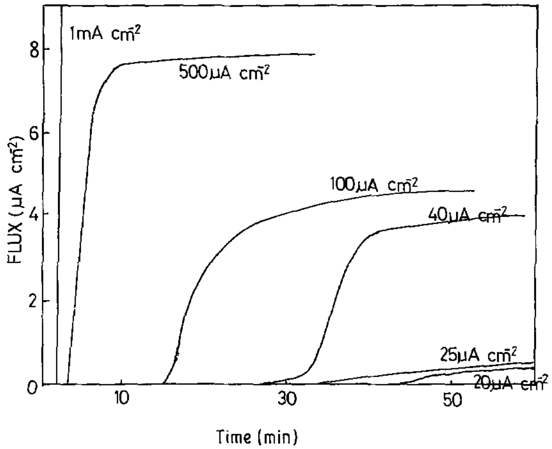

Figure 2 Hydrogen permeation curves of 40% cold-rolled pure iron at different charging current densities.

equation:

$$t_0 = L^2/\pi^2 D_A^r \quad (9)$$

where D_A^r is the apparent hydrogen diffusivity calculated from rising transient method.

4. Results

The hydrogen permeation curves at each cathodic charging current density are shown in Figs. 2 and 3. Breakthrough time becomes shorter as the cathodic current density increases. The breakthrough time of the 40% cold-rolled specimen varies about 30 fold as a result of changing the cathodic charging current density from $15\,\mu$A cm^{-2} to 1 mA cm^{-2}. This also means that the apparent hydrogen diffusivity is similarly different.

The experimental results are shown in Table I. The apparent hydrogen diffusivity of cold-rolled iron calculated from breakthrough time (D_A^b) is about two or three times smaller than that of fully annealed iron. Defect density, dislocation and microvoid, are increased by cold rolling and these defects act as trapping sites for hydrogen. In general, the apparent hydrogen diffusivity is decreased as the trap density increases. The difference in apparent hydrogen diffusivity between annealed and cold-rolled specimens may be due to the difference in trap density [2, 5]. The apparent hydrogen diffusivity varies somewhat depending on the calculation method, but the trend for the effect of cathodic charging current is much the same in the three different calculation methods.

The shape of the permeation curve at low charging current density (below $40\,\mu$A cm^{-1}) is different from that at high charging current density. Hydrogen permeation curves of 40% cold-rolled specimens charged below $40\,\mu$A cm^{-2} are shown in Fig. 4. Charging at 20 and $25\,\mu$A cm^{-2} gave permeation curves showing a double plateau, not found when charging at high current density. On the other hand, the double plateau was not detected at $15\,\mu$A cm^{-2}, probably due to the small permeation flux and the short experimental time.

In order to characterize the trap sites of 40% cold-rolled material, the specimen charged at a current density of $500\,\mu$A cm^{-2} was recharged at the same charging current density after one week. The two permeation curves are shown in Fig. 5. The apparent hydrogen diffusivity and permeation curve shapes for both are almost

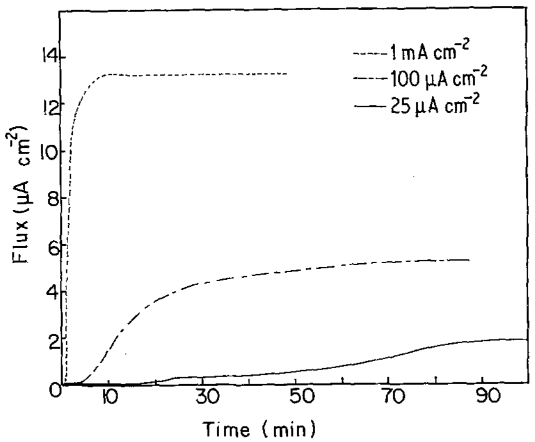

Figure 3 Hydrogen permeation curves of fully annealed pure iron at different charging current densities.

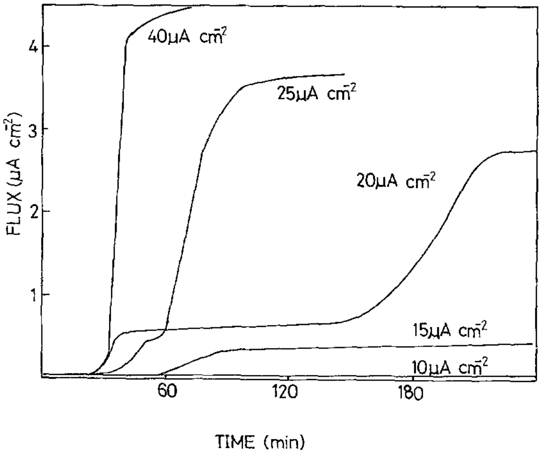

Figure 4 Hydrogen permeation curve of 40% cold-rolled pure iron at low charging current densities. A double plateau is shown in the case of 20 and $25\,\mu$A cm^{-2}.

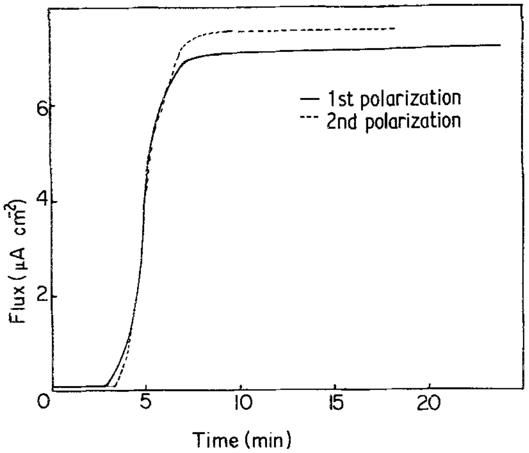

Figure 5 First and second polarization curves of 40% cold-rolled pure iron at 500 μA cm^{-2}.

identical, in spite of the consecutive polarization. This means that the character of traps in this specimen is almost reversible.

5. Discussion

A correlation between apparent hydrogen diffusivity and lattice hydrogen solubility has been shown in Equation 5. In this work, a correlation between apparent diffusivity and cathodic current density has been measured. In order to convert the relation between apparent hydrogen diffusivity and cathodic charging current density to the relation between apparent hydrogen diffusivity and lattice hydrogen solubility, hydrogen entry reaction in the cathodic site is divided into several reactions as follows [8]:

$$\begin{tikzcd}
 & 2\mathrm{FeH_{ads}} \arrow[r, "K_2"] & \mathrm{H_2} + 2\mathrm{Fe} \\
\mathrm{H^+} + \mathrm{Fe} + e^- \arrow[r, "K_1"] & \mathrm{FeH_{ads}} \arrow[u] \arrow[r, shift left, "K_{+3}"] & \mathrm{FeH_{abs}} \arrow[l, shift left, "K_{-3}"]
\end{tikzcd}$$

where $\mathrm{FeH_{ads}}$ refers to adsorbed hydrogen on the metal surface and $\mathrm{FeH_{abs}}$ refers to absorbed hydrogen directly beneath the metal surface. K_1, K_2, K_{+3}, K_{-3} are rate constants for various steps.

Since diffusion through the membrane is the rate-determining step in the permeation process, the surface-to-bulk reaction at the cathodic surface can be in equilibrium:

$$K_{+3}\theta\left[1 - \frac{Y_0}{Y_s}\right] = K_{-3}C_L(1-\theta) \qquad (10)^*$$

where θ is the hydrogen coverage on the cathodic surface of the membrane, Y_0 is the number of occupied intersititial sites per unit cm^3 directly beneath the cathodic surface and Y_s is the number of available interstitial sites per unit cm^3 for hydrogen saturation to occur. In case of low hydrogen coverage and low degree of saturation, Equation 10 can be reduced to Equation 11:

$$K_{+3}\theta = K_{-3}C_L \qquad (11)$$

in this case, then

$$C_L = \frac{K_{+3}}{K_{-3}}\theta \qquad (12)$$

From Equation 12 it is clear that lattice hydrogen solubility (C_L) is directly proportional to surface coverage (θ).

Cathodic current density can be related to θ as in Equation 13, from the assumption that equilibrium is maintained between $\mathrm{FeH_{ads}}$ and $\mathrm{FeH_{abs}}$:

$$i = K_1 a_{H^+}(1-\theta)\exp(-\beta VF/RT) = K_2\theta^2 \qquad (13)$$

where β is a transmitted coefficient, V is the overvoltage and F is the Faraday constant. By combining Equations 12 and 13,

$$C_L = \frac{K_{+3}}{K_{-3}}\left(\frac{1}{K_2}\right)^{1/2} i^{1/2}. \qquad (14)$$

By inserting Equation 14 into Equation 5, the apparent diffusivity can be related to current density:

$$D_A = \left(\frac{D_L}{3N}\right)\left[\frac{K_{+3}}{K_{-3}}\left(\frac{1}{K_2}\right)^{1/2}\right] i^{1/2} = Bi^{1/2} \qquad (15)$$

where B is a constant.

Equation 15 shows that the apparent hydrogen diffusivity is linearly related to the square root of current density. The apparent diffusivity (D_A^b) of 40% cold-rolled iron is plotted against $i^{1/2}$ in Fig. 6 which shows that apparent hydrogen diffusivity varies linearly with the square root of current density. The best line calculated from the least square method is in Equation 16:

$$D_A(\mathrm{cm^2\,sec^{-1}}) = -3.48 \times 10^{-9} + 1.25 \times 10^{-9} \times i^{1/2}\ (\mu\mathrm{A\,cm^{-2}}) \qquad (16)$$

Equation (16) strongly shows that apparent hydrogen diffusivity is changed according to the

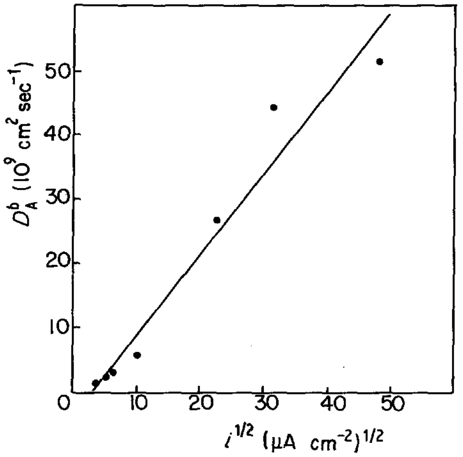

Figure 6 Linear dependence of apparent hydrogen diffusivity of 40% cold-rolled iron on square root of cathodic charging current density.

cathodic charging current density, i.e. the apparent hydrogen diffusivity is changed depending on the amount of dissolved hydrogen in the lattice.

The origin of the dependence of apparent diffusivity on the cathodic charging current density is different from the dependence of diffusivity on solute concentration. The concentration dependence of diffusivity is related to the interaction between diffusing atoms. In this work, the cathodic current dependence of apparent diffusivity is shown to arise from the interaction of hydrogen with traps.

Another interesting point is that a double plateau on permeation curve occurred at low cathodic current density but not at high cathodic current density. A double plateau in the permeation curve has been observed elsewhere [9] in the case of specimens which have both reversible and irreversible type traps. This does not apply to the present work where the major trap character is reversible.

The relationship between apparent diffusivity and lattice hydrogen solubility, as in Equation 5 can be used to predict the apparent hydrogen diffusivity when the direct measurement is difficult for experimental reasons, i.e. very low permeability or diffusivity [11].

6. Conclusions

1. The apparent hydrogen diffusivity varies linearly with the square root of cathodic charging current density. The best fit line calculated from least squares method is

$$D_A(\text{cm}^2\ \text{sec}^{-1}) = -3.48 \times 10^{-9} + 1.25 \times 10^{-9} \times i^{1/2}\ (\mu\text{A cm}^{-2})$$

2. The dependence of the apparent hydrogen diffusivity on cathodic charging current density is explained in terms of a trap theory and a simple electrochemical model.

3. A double plateau on the permeation curve at low cathodic charging current density is shown in this experiment.

Acknowledgement

This study was supported by Korea Science and Engineering Foundation and Carnegie–Mellon University.

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Received 27 June
and accepted 29 November 1983