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HYDROGEN PERMEATION THROUGH ANNEALED
ZONE-REFINED IRON BY USING ELECTROCHEMICAL
CHARGING AT ROOM TEMPERATURE

by

Hsiuan-Ming Shih

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ABSTRACT

Room temperature permeation of cathodically produced hydrogen through annealed zone-refined Ferrovac-E was measured by the electrochemical technique. The dependence of the steady state flux and the effective hydrogen diffusivity on charging current density and specimen thickness were investigated.

The steady state flux was found to be linearly proportional to the square root of the charging current density for current densities below 10^{-3} Amp/cm² and inversely proportional to the specimen thickness. At room temperature, the magnitude of the steady state flux was observed to depend on the hydrogen evolution reaction on the entrance surface.

The decrease of effective hydrogen diffusivity with decreasing specimen thickness and decreasing charging current density was explained on the basis of hydrogen trapping.

A correlation of electrochemical and gas-phase chargings was established using steady state flux measurements. For charging current densities below 10^{-3} Amp/cm², where the steady state flux depends linearly on the square root of charging current density, the relationship between the charging current density and its effective charging fugacity was found to be:

$$P(\text{atm.}) = 6,700 i \left(\text{Amp/cm}^2 \right); i < 10^{-3} \text{ Amp/cm}^2.$$

A method to analyze the entrance surface boundary condition during hydrogen evolution in electrochemical method was suggested.

CHAPTER I

INTRODUCTION

A. General Remarks

The process of brittle fracture in structural materials can be separated into three stages⁽¹⁾; (1) crack nucleation, (2) slow crack growth, and (3) rapid, unstable fracture. Hydrogen makes steels brittle by affecting the first two of these stages. Therefore, it is important to determine accurately the hydrogen transport parameters in order to understand thoroughly those phenomena.

Steels embrittled by hydrogen exhibit characteristic dependences on strain rate and temperature⁽²⁾. Similar dependences has been observed^{(3),(4),(5)} in both steels embrittled in a bulk environment of molecular hydrogen and those by electrochemical charging, pickling, or prior exposure to hydrogen at high temperature or perhaps pressure. At low strain rates, the absorbed hydrogen has a pronounced embrittling effect. If the strain rate is sufficiently large, the hydrogenated steel exhibits the same ductility as the unhydrogenated steel. Also, hydrogen embrittling effect is most pronounced at temperatures near 300°K, completely disappearing at both lower and higher temperatures. At lower temperatures, the diffusivity of hydrogen is too low to allow significant crack growth before

failure. At higher temperatures, either hydrogen diffuses out of materials completely or maybe the "traps" are emptied by thermolization. All these observations suggest that hydrogen transport through material is an integral feature of the embrittlement mechanism.

Hydrogen embrittlement is a complicate phenomenon and its explanation has been quite controversial. Zapffe⁽⁶⁾ first proposed the "pressure theory" which was then subsequently modified by many other researchers including Tetelman and Robertson^{(7),(8)}. This theory proposes that hydrogen embrittlement results from the precipitation of hydrogen gas at defects such as inclusions, and the expansion of microcracks and voids due to the gas pressure. However, Troiano, Morlet and Johnson^{(9),(10),(11)} postulate that hydrogen atoms diffuse from the crack to positions in the iron lattice ahead of it which are subject to high tri-axial stress, and that embrittlement then results from the weakening of atomic bonds due to the presence of dissolved hydrogen. Recently, Johnson⁽¹²⁾ proposes a model of diffusion controlled subcritical crack growth for exterior hydrogen embrittlement on the basis of a favorable agreement between the velocity of subcritical crack growth in the metal lattice and that of hydrogen transport through the metal lattice.

Tiller and Schrieffer⁽¹³⁾ postulate a new concept of hydrogen embrittlement which occurs from redistribution of electrons as a result of tensile stress and lattice expansion, making the stressed region cathodic with respect to the neighboring region. This cathodic potential is calculated to be

high enough so as to cause appreciable hydrogen evolution and ingress into the metal.

No matter how controversial the theories to explain hydrogen embrittlement, it is important to note that hydrogen has a maximum embrittling effect in the same temperature range where anomalies in both hydrogen solubility and diffusivity have been reported. This perhaps indicates the necessity of detailed study of hydrogen permeation through ferritic iron and iron alloys as a basis to understand the mystery of hydrogen embrittlement.

B. Hydrogen-Iron System

Many reports on the solubility and diffusivity in the hydrogen-iron system have been published. Because of the differences in experimental techniques and in material composition and history, results are often not easily compared or generalized and a clear and concise characterization over a wide range of temperatures and pressures of the system has not been obtained.

Sievert's⁽¹⁴⁾ law, which is expressed below, holds for the hydrogen-iron system at temperatures extending to as low as 400°C and at pressures up to 100 atmospheres,

$$C = SP^{\frac{1}{2}} \quad (1)$$

where C = concentration of dissolved hydrogen in equilibrium

with gaseous hydrogen at pressure P

S = proportionality constant which is temperature dependent.

This $P^{1/2}$ dependence of hydrogen concentration indicates that hydrogen enters the iron lattice in the atomic or dissociated rather than molecular form and is distributed as a random solute.

There is substantial evidence that hydrogen in solid solution of iron occupies interstitial lattice sites. The partial molal volume of hydrogen in iron is $2.0 \text{ cm}^3/\text{g atom}$ and the diameter of hydrogen atom is $1.06 \text{ \AA}$ (15). At $1.06 \text{ \AA}$, hydrogen atom is much smaller than an iron atom, which is $2.52 \text{ \AA}$, and it is improbable for hydrogen atom to have such a large partial molal volume if it exists on substitutional lattice site. Furthermore, the pre-exponential term D_0 in the expression for the diffusivity has been calculated by Wert and Zener (16) for hydrogen in iron to be $1.6 \times 10^{-3} \text{ cm}^2/\text{sec}$ by assuming interstitial diffusion. Also, if hydrogen jumps interstitially, the lattice dilatation resulting from this jump will be small and this results in lower activation energy for hydrogen diffusion. McNeil (17) calculated this value to be 1.3 Kcal/mole . Both these values of D_0 and activation energy compare reasonably well with the high temperature experimental values shown in fig. 1.

The observation (29), (30) of Snoek relaxation peaks for hydrogen in b.c.c. iron is also an evidence that hydrogen is interstitially dissolved in α -iron. The characteristic of Snoek peaks of hydrogen is quite similar to that of carbon, which is generally agreed to be octahedral lattice site in iron. This suggests that both species occupy the same type

Fig. 1 : Log D of Hydrogen in Iron

Note :

- a Geller and Sun (ref. 18)
- b Sykes, Burton and Gregg (ref. 19)
- c Stross and Tompkins (ref. 20)
- d Johnson and Hill (ref. 21)
- e Heumann and Primas (ref. 22)
- f Barrer (ref. 23)
- g Beck, Bockris, McBreen and Nanis (ref. 24)
- h Kumnick (ref. 25)
- i Quick (ref. 26)
- j Nelson and Stein (ref. 27)
- k Bryan and Dodge (ref. 28)

of interstitial site. However, there are still some doubts⁽³¹⁾ about the identification of the site for carbon in α -iron and, hence, same for hydrogen.

Finally, Mamontov and Toshkin⁽³²⁾ found that not only hydrogen is present at interstitial sites, but the experimental result reveals a steady change in the internal friction with large applied stress amplitudes in aged, hydrogen charged electrolytic iron. They claimed that this steady change is due to the accumulation of hydrogen in "traps".

In short, hydrogen is believed to be present in interstitial lattice sites in α -iron and the determination of which kind of interstitial sites at which hydrogen is present requires much works to be done.

C. Observed Anomalies

Despite those general agreements of physical aspects of hydrogen-iron system, conflicting data on both the diffusivity and the solubility of hydrogen in iron have been reported in the low temperature range.

Hill and Johnson⁽³³⁾ observed a positive deviation from Sievert's law and showed that at low temperatures measured solubilities were substantially greater than the values predicted by extrapolation of high temperature data shown in fig. 2. Chang and Bennett⁽³⁴⁾ also observed the same deviation.

The results of experimental studies⁽¹⁸⁾⁻⁽²⁸⁾ of the diffusivity of hydrogen in iron are summarized in fig. 1, in which the values of apparent diffusivity D are plotted against the

Figure 2: Solubility of hydrogen in iron.

reciprocal temperature. The degree of divergence of diffusivity increases as temperature decreases. The scatter at low temperature is greater than simple experimental error and can't be accounted for on the basis of composition variation of materials tested. Furthermore, there are some contradictory results about the anomalous break. Hill and Johnson et al observed an anomalous break at approximately 200°C , whereas Stross and Tompkins⁽²⁰⁾ did not observe the same break by using a similar method. Bryan and Dodge⁽²⁸⁾, using a quite different technique, didn't observe the break also. Quick⁽²⁶⁾ observed this anomaly at approximately 70°C by using vacuum method with charging pressure 0.8 atom and specimen thickness 0.0127 cm. In addition, the diffusivities recorded by experimentalists using evolution rate methods^{(20),(21)} are lower than those using permeability methods^{(25),(26)}. This suggests that some "trapping" barrier, which will be discussed in later section, to hydrogen transport is in existence in the iron at these low temperatures.

D. Concepts of Low-Temperature Anomalies

The low-temperature anomaly of hydrogen diffusion in iron or steel has often been attributed to surface control of the evolution or permeation rate, but this explanation is not supported by experimental data. Dünwald and Wagner⁽³⁵⁾ have pointed out that the observed time constant of a diffusion-controlled process is proportional to the thickness squared. Hill and Johnson⁽²¹⁾ could conform their data to this relation

and concluded that the evolution is diffusion controlled. Also, Kumnick⁽²⁵⁾ and Quick⁽²⁶⁾ found that the steady state flux of hydrogen permeating through α -iron is inversely proportional to the thickness of specimen. Finally, the concept of surface-controlled process can't explain the high residual hydrogen concentration in iron observed during evolution studies at low temperatures⁽²¹⁾.

The foregoing argument concerning surface-controlled process then suggests that a trapping of hydrogen at preferential bulk sites contribute to the low temperature anomaly of hydrogen diffusion. Kumnick⁽²⁵⁾ and Hancock⁽³⁶⁾ have well documented the trapping phenomenon and related theory. For briefness only recent developments(dealing with the characterization of trap) relevent to the present work are summarized.

All structural irregularities including grain boundaries, dislocations, voids and interfaces can be possible candidates for trapping sites. By assuming local equilibrium between trapped and diffusing populations, Oriani⁽³⁷⁾ used the same approach employed by Frank and Turnbull⁽³⁸⁾ in semiconductor and obtained the effective diffusivity as follows:

$$D_{\text{eff}} = D_L \frac{C_L}{C_L + C_X(1 - \theta_X)} \quad (2)$$

D_L = lattice diffusivity of hydrogen

C_L = lattice concentration of hydrogen

θ_X = fractional occupancy of traps

C_X = trapped concentration of hydrogen

This equation allows for the asymmetry in effective diffusivities by absorption and evolution when θ_x is not small and also for the concentration dependence of D_{eff} .

McNabb and Foster⁽³⁹⁾ developed the diffusion equation which includes trapping as

$$\frac{\partial C_L}{\partial t} + N_x \frac{\partial \theta_x}{\partial t} = D_L \nabla^2 C_L \quad (3)$$

N_x = trap density

By considering the trap as potential well and using probability of trapping and releasing, the rate equation for trapping is

$$\frac{\partial \theta_x}{\partial t} = k C_L (1 - \theta_x) - p \theta_x \quad (4)$$

k = the kinetic trapping parameter

p = the kinetic releasing parameter

An exact solution of equations (3), (4) for the time lag, when subjected to suitable permeation boundary conditions, is as follows⁽³⁹⁾,

$$t = \frac{a^2}{D_L} \left\{ \frac{1}{6} + \frac{\alpha}{2\beta} + \frac{\alpha}{\beta^2} - \frac{\alpha}{\beta^3} (1 + \beta) \ln(1 + \beta) \right\} \quad (5)$$

a = jump distance

$\alpha = N_x \frac{k}{p}$ = trapping parameter

$\beta = C_o \frac{k}{p} = \frac{\theta_x}{1 - \theta_x}$ = activity of hydrogen in traps

C_0 = lattice concentration at input surface of the permeation membrane

With the effective diffusivity D_{eff} defined as $a^2/6t$, we have two limiting cases:

i) trap occupancy are sparingly, $\beta \ll 1$, then

$$D_{eff} = D_L (1 + \alpha)^{-1} \quad (6)$$

This expression for D_{eff} does not depend on the lattice concentration and the same effective diffusivity should be measured by both absorption and evolution experiment.

ii) traps are heavily occupied, $\beta \gg 1$, and

$$D_{eff} = D_L \left(1 + \frac{3N_x}{C_L} \right)^{-1} \quad (7)$$

From eq. (7), the effective absorption diffusivity is concentration dependent and larger than the effective evolution diffusivity when traps are heavily occupied.

Since thick specimen requires less deformation prior annealing and the traps are rather thermally stable⁽⁴⁰⁾ during annealing, the trap density N_x of thick specimen will be less than that of thin specimen. Equation (7) then indicates indirectly the thickness dependence of effective diffusivity. It also suggests that chemical reduction and annealing should lead to higher effective diffusivities in thin specimens than reduction by rolling followed by annealing. This has been verified by Kumnick⁽²⁵⁾.

There is another kind of "trap" whose density is con-

trolled by the charging pressure or current density in electrochemical method and is not fixed by microstructure. This concept is proposed by Ono and Rosales⁽⁴¹⁾ who assume that the hydrogen di-interstitials are immobile. These di-interstitials are then the "traps". Quick⁽²⁶⁾ gives detailed considerations of their concept and shows that their concept should lead to the inverse dependence of effective diffusivity on charging pressure at low temperatures. When comparing this prediction to his experimental results, Quick et al didn't observe this phenomenon. Furthermore, to make agreement of anomaly between calculated and experimental values, they assigned a positive value of 10-11 Kcal/mole for binding energy of di-interstitial; which has not been confirmed by experiment.

In short, the phenomena of trapping are necessarily accompanied by the dependence of effective diffusivity on both lattice concentration and specimen thickness. Nanis⁽⁴²⁾ confirms the dependence of effective hydrogen diffusivity in iron on concentration while Dillard, Talbot-Besnard⁽⁴³⁾ and others show that the effective hydrogen diffusivity in iron depends on specimen thickness.

E. Hydrogen Fugacity in Electrochemical Charging

At room temperature the atomic hydrogen resulting from cathodic reaction which occurs when steel is exposed to aqueous media, is by far, the most significant source of hydrogen in steels. This reaction can occur in service when steel surfaces are exposed to aqueous environments or to

gaseous environments from which aqueous condensates may form, or in processing operations such as pickling, cleaning, or electroplating.

The high saturation hydrogen contents or the high steady-state permeation fluxes which can be attained by cathodic charging often indicate a hydrogen solubility value which would be in equilibrium with a very high-pressure hydrogen environment. Hence, some aqueous environments can be considered as exerting an effective pressure (or fugacity) of hydrogen that is very high. Borelius and Lindblom⁽⁵⁵⁾ found from the experiment relation for the effective hydrogen pressure (atm) and the charging current density (Amp/cm²) for iron in a 2% NaOH solution:

$$P_{H_2} = 17,000 i \quad (8)$$

For acid solutions, and particularly in those containing poisons, the proportionality factor in eq.(8) would be much higher than 17,000.

Bockris and Subramanyan⁽⁴⁴⁾ formulate extensively the hydrogen fugacity as a function of over-potential for various mechanisms of the hydrogen evolution reaction. They then can differentiate which mechanism has the most embrittling power in metals. However, there are no experimental data to evaluate their theory. Nonetheless, the importance of determining hydrogen fugacity in the cathodic reaction as a basis for an improved understanding of the mechanism of hydrogen embrittlement can easily be seen in their theory.

Previously effective hydrogen fugacities for electro-

chemical charging were either not known or only roughly estimated. Further work has to be done to establish quantitative relationships which would permit the application of laboratory studies of cathodically charged steels to investigations of the behaviors of steels for pressure vessels to be used for the storage of high-pressure hydrogen.

F. Purpose

The purpose of this work is to study both concentration and thickness dependences of hydrogen diffusivity in iron at room temperature with electrochemical charging and to better understand the characteristics of hydrogen trapping and of the electrochemical charging procedure.

In order to fulfill this purpose, a new type of permeation cell coupled with sensitive electrochemical technique is designed. This allows for the possibility of charging with higher current density by removing the problem of temperature instability and reduction of permeating area due to the formation of hydrogen bubbles at higher current densities.

A comparison study of steady state and transient characteristics by both gas-phase and electrochemical charging techniques was undertaken. A correlation between charging pressure and current density is established through steady state flux measurements.

CHAPTER II

EXPERIMENTAL

A. Material Composition

The material chosen for this study is FerrovacE, supplied by Crucible steel, subject to 4-pass zone refinement by using electron beam in vacuum(8×10^{-6} torr). This zone-refined high purity iron is in 0.5 in.-diameter-rod form and has the following composition:

Element	%
Aluminium	0.01
Chromium	0.001
Cobalt	0.001
Copper	0.0003
Lead	*0.002
Manganese	0.003
Molybdenum	0.002
Nickel	0.05
Silicon	0.007
Tin	0.005
Tungsten	*0.05
Vanadium	0.004
Carbon	0.026
Sulfur	0.002

Element	%
Nitrogen	0.0005
Hydrogen	0.0001
Oxygen	0.0013

* ----- less than value shown

B. Method

Hydrogen is introduced by cathodic polarization at the entry side of the iron membrane; the amount of hydrogen that comes through the exit side is measured as a function of time. Hydrogen is measured electrochemically by maintaining the exit side of the membrane at a constant anodic potential of +100 mV versus standard calomel reference electrode with the aid of the Wenking electronic potentiostat. Any hydrogen reaching the exit side of the membrane will be ionized at the above potential. This ionized hydrogen current is a direct measure of the quantity of the hydrogen that comes through the specimen and is recorded as a function of time with a Keithley Electrometer and Esterline Angus strip chart recorder. The measured current divided by the permeating area of the specimen is current. From Faraday's law of electrolysis, we can express this current density as hydrogen flux through the following relation:

$$10^{-6} \text{ amp/cm}^2 = 1.04 \times 10^{-11} \text{ moles H/cm}^2 \text{ sec.}$$

Fluxes can be measured accurately for values as low as 10^{-13} moles H/cm²sec. The schematic of the permeation cell and electrical circuit is shown in fig. 3 in which hydrogen is produced by cathodic polarization.

- 1. Reference Electrode
- 2. Connecting Probe
- 3. Specimen
- 4. Pt Electrodes

Figure 3: Permeation cell and electrical circuit.

The specimen is in horizontal position in order to remove the effect of bubble gathering due to the recombination effect of adsorbed hydrogen atoms which would increase the temperature and reduce the effective permeating area of the specimen. The permeation cell is composed of two flasks of different shapes. The upper(or cathodic) cell is a 3-necked, spherical pyrex flask which has a volume of 200 ml. The lower(or anodic) cell is a cylinder-shaped pyrex flask with a comparable capacity. The whole permeation cell is sitting on a brass stand with a cylindrical slot which allows the lower cell to slide into stable position. Cells are connected to the specimen by using flanged tubing with Viton O-rings. The exposed area of the specimen is about 1.2 square cm. Nitrogen gas is introduced to stir and de-aerate the solutions in each cell. Temperature is always controlled at 25°C with variation of approximate $\pm 0.5^{\circ}\text{C}$.

The solution used in the anodic and cathodic cells was 0.1 N sodium hydroxide. This solution was made with analytical reagent grade sodium hydroxide pellets and Fisher double distilled water. The solutions were always deaerated with pre-purified nitrogen gas for 24 hrs. before use.

C. Specimen Preparation

The received FerrovacE was in 0.5 in.-diameter-rod form. It is then zone-refined by using electron beam with zone rate 2 ins./hr under atmosphere of 8×10^{-6} torr. Electron beam

passed the rod four times.

After zone refinement, rod was cut into 1.25 in. lengths and then cold-rolled across the diameter to the required thickness without intermediate annealings. They were then sheared to 1" x 1" pieces and then cleaned by first using ethyl alcohol to degrease and then using 1 to 2 mixture by volume of hydrogen peroxide and phosphorous acid to remove the adsorbed surface impurities during rolling and get a very bright surface. After degreasing and polishing, sheets were annealed at 850°C for 12 hrs under atmosphere of 5×10^{-6} torr.

After the heat treatment, the specimen was chemically polished using a one to two mixture by volume of hydrogen peroxide(30%) and phosphorous acid for 90 sec. The specimen was then rinsed uniformly and quickly with distilled water to remove all the residuals of chemicals and get a very shining surface. It was then electroplated with palladium on either both sides or one side of specimen and rinsed with distilled water. Specimen treated under these procedures is ready to use in the permeation experiment.

D. Electroplating Palladium on The Iron Surfaces

The palladium film on anodic(or exit) side of the specimen is necessary to prevent the surface from severe corrosion resulting from applied anodic potential to ionize hydrogen coming through the specimen. The palladium film on the cathodic(or entry) side of the specimen is not necessary for electrochemical charging. When electroplating, the film will

serve as a protective coating which tends to prevent iron surface from oxidation and make the experimental results to be volume-controlled and reproducible. However, when not, the permeation process is still volume-controlled (as will be seen in Chapter III Results and Discussions) but with more scatter. Furthermore, the steady state flux of one-side Pd plated specimen is higher than that of 2-side Pd plated specimen under same charging condition.

The electroplating solution is Sel-Rex Palladex VI and the temperature of solution should be kept between 32-38°C. The PH value of this solution lies between 8.5-9.0. Area ratio between plating electrodes and specimen should be greater than 2 to ensure the uniformity of current density. Cathodic current density is 140 mA/in² and the plating time is about 10 sec.. Under these conditions the palladium film(s) is uniformly plated and the thickness of it is about 0.05μ, measured by Beta back scatter technique.

1. 2-Side Pd Plating

When plating palladium at both sides of the specimen, the electroplating set-up is shown in fig. 4.

Specimen prepared for electroplating is connected to higher potential of D.C. supply and is a cathode while platinum electrodes are anodes. The electroplating solution is stirred gently by a magnetic stirrer. After the specimen is chemically treated and the electroplating conditions are satisfied as in section 1, the specimen is dipped into the solution for about 10 sec.

Figure 4: Electroplating set-up for plating Pd film on both sides of specimen.

Figure 5: Electroplating set-up for plating Pd film on one side of specimen.

2. 1-Side Pd Plating

The electroplating set-up for plating Pd on one side of specimen is shown in fig. 5.

Specimen prepared for electroplating is flanged in between two flasks. It is better to have the plated area be greater than the hydrogen permeating area. This avoids the aligning problem of the set-up of permeating cells.

The flask on the right hand side(as we see from fig. 5) is filled with sodium hydroxide to keep the oxidation of iron surface minimum. The left-hand-side flask is filled with electroplating solution and is also stirred gently with magnetic stirrer. Before electroplating, it is better to remove all the bubbles sticking on specimen surface to have the electroplating as uniform as possible.

CHAPTER III

RESULTS AND DISCUSSION

A. Experimental Parameters

1. Data Recorded and Reproducibility

All permeation curves carried out in this experiment have three distinct regions, typical of those recorded, shown in fig. 6. The first is the breakthrough region, whose magnitude depends on diffusivity, the sensitivity of the measuring system, and the thickness of the specimen. The following region is the so-called transient region, in which the hydrogen flux increases with time. The third is the steady state region which is associated with a constant flux and a time independent hydrogen concentration profile within the bulk material. The magnitude of the steady state flux,

$$J_{\infty} = D_L \frac{C_o}{L} \quad (9)$$

is dependent on the lattice diffusivity, D_L , concentration of the lattice hydrogen at the entry surface C_L , and the thickness of the specimen L . When the charging current is turned off, the evolution behavior at exit surface is as recorded in fig. 7. Further discussion of the evolution behavior will be given in a later section.

Figure 6: Typical absorption transient.

Figure 7: Typical evolution transient.

It is important to check reproducibility by charging two or more specimens with different current densities from the lowest up to the highest value and returning to the lowest. Fig. 8 and 9 show steady state flux and effective absorption diffusivity versus current density, respectively, for two specimens with same thickness at same temperature. Reproducibility is obvious and excellent only for charging from the lowest to the highest current density.

2. Volume Versus Surface Control

In diffusion experiments, especially when using electrochemical charging, it is important to consider the possibility of surface impedance. A suitable and critical test is the measurement of the steady state hydrogen flux as a function of thickness L of the specimen; for the volume-controlled permeation the steady state flux should be linearly dependent on the inverse of the specimen thickness, as shown in eq. (9). This relationship is demonstrated for annealed zone-refined iron in figs. 10 and 11, which are the plots of J_{∞} vs. $1/L$ for the specimens with Pd film on both sides and on one side, respectively. Both show the linear dependence of the steady state flux on the inverse of the specimen thickness; the permeation process in each case is diffusion (or volume) controlled. However, data points in fig. 11 show more scatter than those in fig. 10. Surface reaction may still be an important process for the specimen with Pd film on one side by varying the concentration C_0 .

Figure 8: Reproducibility of steady state flux versus current density.

Figure 9: Reproducibility of effective diffusivity versus current density.

Figure 10: Steady state flux as a function of inverse thickness for specimen with Pd film on both sides.

Figure 11: Steady state flux as a function of inverse thickness for specimen with Pd film on one side

3. Method of Data Analysis

a. Absorption and Evolution Transients

Since the permeation process is diffusion controlled, the effective diffusivity can be calculated on the assumption that the hydrogen transport obeys Fick's law. McBreen's⁽⁴⁵⁾ analysis for hydrogen absorption can be used in this experiment. The permeation process can be characterized by Fick's second law for constant diffusivity as

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D} \frac{\partial c}{\partial t} = 0 ; 0 < x < L \quad (10)$$

The boundary and initial conditions for this experimental set-up for absorption transient are shown below⁽⁴⁵⁾:

$$\begin{aligned} c &= c_0 & ; & & x &= 0 & ; & t \geq 0 \\ c &= 0 & ; & & x &= L & ; & t \geq 0 \\ c &= 0 & ; & & 0 < x < L & ; & t < 0 \end{aligned}$$

Using the method of Laplace transform on eq. (10) for the above initial and boundary conditions, a series solution of the transient hydrogen flux is obtained, i.e.

$$J_t = \frac{2DC_0}{\pi^{1/2}L} \frac{1}{(\tau)^{1/2}} \sum_{n=0}^{\infty} (-1)^n \exp \left[-(2n+1)^2 / 4\tau \right] \quad (11)$$

$$\text{where } \tau = Dt/L^2 \quad (12)$$

Noting $J_{\infty} = DC_0/L$, we have

$$\frac{J_t}{J_{\infty}} = \frac{2}{\pi^{1/2}} \frac{1}{\tau^{1/2}} \sum_{n=0}^{\infty} (-1)^n \exp \left[-(2n+1)^2 / 4\tau \right] \quad (13)$$

The first term in eq. (13) gives results valid up to 96.5% attainment of the steady state permeation, i.e.

$$\frac{J_t}{J_\infty} = \frac{2}{\pi^{1/2}} \frac{1}{\tau^{1/2}} \exp\left(-\frac{1}{4\tau}\right); \quad 0 < \tau < 0.5 \quad (14)$$

Using eq. (13), it is possible to calculate the effective absorption diffusivity of hydrogen in iron by finding the time required to attain any fraction of the steady state permeation through eq. (12), i.e.

$$D_{\text{eff}} = \frac{\tau L^2}{t}$$

where t is the time to attain any fraction of the steady state permeation.

For example, we see⁽⁴⁵⁾ that when $\tau=0.25$, $J_t/J_\infty=0.83$; $\tau=0.15$, $J_t/J_\infty=0.55$; $\tau=0.1$, $J_t/J_\infty=0.29$. Effective diffusion coefficients obtained from these three different times, i.e., $t_{0.83}$, $t_{0.55}$, $t_{0.29}$, are called the long-time, intermediate-time, and short-time diffusivities, respectively. The term effective diffusivity is used because in later section it will appear that the value determined this way will increase with increasing current density and the specimen thickness.

The same analysis can be applied to analyze the evolution transients and get similar values to those predicted from absorption transients. However, it should be noted here that because the boundary condition at the entrance surface is not known when electrochemical charging is turned off, the evolution transient is somewhat more complicated. The two extremes for this boundary condition are that the concentration becomes

zero immediately on the entrance surface, or that there is no flux of hydrogen across the entrance surface. The first of these extremes predicts a faster decay than the second one and its hydrogen flux is the complement⁽⁴⁵⁾ of hydrogen flux of the absorption transient at certain charging current density. For example, when $\tau=0.25$, $J_t/J_\infty = 0.83$ for absorption transient and hence, $J_t/J_\infty = 0.17$ for this fast decay transient. An effective decay diffusivity can be calculated this way.

However, in later section, it is shown experimentally that the evolution transients occur more slowly than predicted by either boundary condition. Hence all the information obtained from the evolution transient are in doubt unless proper and definite boundary condition is known when the electrochemical charging is turned off. Even though the concept of hydrogen trapping can explain, ideally, part of the slower decay than those predicted, there is still a question of how to separate the contribution of trapping to the slower decay from that of boundary condition of entry surface when the charging is turned off.

b. Electrochemical Kinetics of Hydrogen Evolution

Reaction on Iron and Palladium Surfaces

The electrochemical reactions which produce adsorbed hydrogen on iron and palladium surfaces in alkaline solution are as follows⁽⁴⁶⁾:

Water molecule is discharged by an electron from the metal to form atomic hydrogen, which remained adsorbed on the metal surface.

The rate of these hydrogen evolution reactions can be expressed, in terms of current⁽⁴⁶⁾, as follows:

$$\bar{i} = F(1-\theta) K e^{-\beta VF/RT} \quad (16)$$

where F = Faraday constant = 96500 coulombs/electrochemical equivalent

θ = hydrogen coverage of the metal surface

$K = K \exp(-Q/RT)$ = rate constant

Q = activation energy for the reaction

R = gas constant

β, k = constants

$V = V_E - V_{rev}$ = hydrogen overpotential

The reverse reaction can occur also and has a reverse current $\bar{i}$. However, when the metal electrode is much more negative to the reversible electrode, the reverse reaction can be neglected. In the case of electrochemical reaction at the reversible potential, there is no net current flow. Both the forward and reverse reactions occur at equal rates, i.e.

$\bar{i} = \bar{i} = i_0$. This rate current i_0 is called the exchange current and is an important parameter in that it is a rate constant for a particular electrochemical reaction. If the metal electrode at which hydrogen evolves is more negative to the reversible electrode, the rate expression for a particular electrochemical reaction is as follows:

$$i = i_0 \exp(-\beta VF/RT) \quad (17)$$

$$\text{or } V = \frac{RT}{\beta F} \ln i_0 - \frac{RT}{\beta F} \ln i \quad (17a)$$

$$= a - b \ln i \quad (17b)$$

Eq. (17b) is the famous Tafel's equation. The value of i_0 varies from metal to metal. Typical values are given in Table 1.

Table 1 (46) -

Metal	i_0 Amp/cm ²
Hg	10^{-13}
Fe	$\sim 10^{-7}$
Ni	$\sim 10^{-7}$
Pd	10^{-3}
Pt	5×10^{-3}

From Table 1, we can see that at same hydrogen overpotential V the hydrogen evolution rate is over four orders of magnitude greater on palladium than it is on iron. This means that the surface coverage of adsorbed hydrogen on iron surface is much greater than that on palladium surface. Part of adsorbed hydrogen atoms will then form molecular hydrogen through two probable mechanisms: either the adsorbed hydrogen atoms combine directly⁽⁴⁶⁾

or a water molecule discharges near an adsorbed hydrogen atom and gives molecular hydrogen⁽⁴⁶⁾

Reaction(18) is commonly called "catalytic desorption", since its rate is generally believed to depend upon the catalytic activity of the metal surface for recombination of hydrogen atoms into molecules. Reaction(19) is called "electrochemical desorption". Another part of adsorbed hydrogen atoms change themselves from the adsorbed to the absorbed state and then diffuse through the metal.

Bonhoeffer⁽⁴⁷⁾ studied the ability of different metals to affect recombination of adsorbed hydrogen atoms and arranged metals in the following order⁽⁴⁸⁾;

$$\text{Pt} > \text{Pd} > \text{W} > \text{Fe} > \text{Cr} > \text{Ag} > \text{Cu} > \text{Pb}$$

decreasing efficiency .

The effect of palladium surface on the recombination of H_{ads} is greater than that of iron surface.

When the permeation process is diffusion controlled, the surface-to-bulk reaction at the entry surface, which is the reaction that hydrogen atoms change themselves from the adsorbed state to the absorbed state, can be taken to be in equilibrium, i.e.,

$$\overline{K}\theta \left(1 - \frac{N_o}{N_s}\right) = \overline{K} C_o (1 - \theta) \quad (20)$$

where $\overline{K}, \overline{K}$ = rate constants of surface-to-bulk reaction

N_o = number of occupied interstitial sites/cm³

N_s = number of available interstitial sites/cm³

$$C_o = \frac{\overline{K}}{K} \frac{\theta}{1-\theta} \left(1 - \frac{N_o}{N_s} \right) \quad (21)$$

Hence,

$$J_\infty = \frac{D_L}{L} C_o = \frac{D_L}{L} \frac{\overline{K}}{K} \frac{\theta}{1-\theta} \left(1 - \frac{N_o}{N_s} \right) \quad (22)$$

The magnitude of steady state flux of hydrogen transport through metal depends on the concentration of absorbed hydrogen atoms at the entry surface which in turn depends on the surface coverage of the adsorbed hydrogen atoms and rate constants of surface-to-bulk reactions. Since the hydrogen evolution mechanism will determine the surface coverage of H_{ads} , it is obvious that the various mechanisms for hydrogen evolution can give different permeation-current and permeation-potential relationships.

4. Effect of Palladium Film on Hydrogen Transport through Iron Surface

It is important to show that the existence of palladium film on iron surface exerts no limiting effect on the hydrogen transport during electrochemical charging. This is equivalent to showing that bulk iron is the limiting material of hydrogen transport.

Barrie and others⁽⁴⁹⁾ analysis of diffusion through composite membranes can be used to demonstrate that the volume diffusion through bulk iron is the rate limiting step. From Barrie et al the appropriate equation for permeation through a Pd-Fe-Pd specimen is

$$\frac{L}{P_T} = \left(\frac{L_{Fe}}{D_{Fe} S_{Fe}} + \frac{2L_{Pd}}{D_{Pd} S_{Pd}} \right) \quad (23)$$

and

$$\frac{L}{P_T} = \left(\frac{L_{Fe}}{D_{Fe} S_{Fe}} + \frac{L_{Pd}}{D_{Pd} S_{Pd}} \right) \quad (23a)$$

for Fe - Pd specimen.

P_T = Permeability through composite membrane = $J_{\infty} L/P_O^{\frac{1}{2}}$

D_{Fe} = Lattice diffusivity of hydrogen in iron

D_{Pd} = Lattice diffusivity of hydrogen in palladium

S_{Fe} = Lattice solubility of hydrogen in equilibrium with 1 atm. hydrogen pressure

S_{Pd} = Lattice solubility of hydrogen in equilibrium with 1 atm. hydrogen pressure

L_{Fe} = Thickness of iron layer

L_{Pd} = Thickness of palladium layer

L = Total thickness of membrane = $L_{Fe} + 2L_{Pd}$

or = $L_{Fe} + L_{Pd}$.

At 25°C the lattice diffusivities of hydrogen in iron and palladium are estimated respectively as $3.2 \times 10^{-5} \text{ cm}^2/\text{sec}$ (15)

and $3.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ (50). The ratio of the lattice solubilities of hydrogen in iron and palladium can be estimated from Oriani (15) and Salmon (51) at 25°C as

$$\frac{S_{Pd}}{S_{Fe}} = 1.4 \times 10^6.$$

For the thinnest specimen used in this study, $L_{Fe} = 1.5 \times 10^{-2} \text{ cm}$ and $L_{Pd} = 5 \times 10^{-6} \text{ cm}$. Substitution in equation (23) shows that the overall permeation process is controlled by the bulk iron

to within about 3 parts in 10^7 . With increasing iron thickness the influence of palladium on hydrogen transport is even less.

B. Steady State Flux

For hydrogen transport in the presence of traps, it can be shown that the steady state flux, J_α , is equal to $D_L C_O / L$ and is independent⁽²⁵⁾ of the microstructure of the materials if the permeation process is diffusion controlled. From figs. 10 and 11, we know that the permeation process is diffusion controlled both in specimen with Pd films on both sides and specimen with Pd film on one side. Hence, $J_\alpha L$ of specimen of either kind of electroplating should be a constant under any given charging condition and is independent of trap density. This is shown in figs. 12 and 13. The scatter in both figures may probably be due to the variation of history from specimen to specimen or of the catalytic activity of the entry surface. Fig. 13 for specimens with Pd on one side shows more scatter.

Note that in fig. 13, the steady state flux at any given current density for specimen with Pd film on one side is higher than that for specimen with Pd films on both sides. This may be due to the higher concentration of absorbed hydrogen atom just beneath the entry surface for specimen with Pd film only on anodic side. During the experiment of charging specimen with Pd film on anodic side, the hydrogen bubbles coming up to the surface of electrolytic solution are much less than that of charging specimen with Pd films on both sides at the same

Figure 12: Product of steady state flux and thickness as a function of current density for specimen with Pd film on both sides.

Figure 13: Product of steady state flux and thickness as a function of current density for specimen with Pd film on one side.

current density.

Bonhoeffer et al observed that the efficiency of Pd to catalyze the recombination of adsorbed hydrogen atoms is higher than that of iron. Furthermore, from eqs. (16), and table 1, we know that the surface coverage of the adsorbed hydrogen atoms on iron surface is greater than that on palladium surface. This makes qualitatively the higher value of steady state flux for specimen with Pd film on anodic side possible through eq. (22). Completely quantitative agreement warrants further study.

Kumnick⁽²⁵⁾ observed the opposite phenomenon to the present ones. However, his Pd film was plated by dipping the specimen into pallarmorse solution. This makes the surface condition of his Pd film different from that of electroplated Pd film. The condition of the entry surface is an important factor on the magnitude of hydrogen flux at given current density.

Figs. 14 and 15 show the dependence of the steady state flux on the square root of current density for both 1-side and 2-side specimens, respectively. Figs. 16 and 17 are plotted for the product of steady state flux and the thickness versus the square root of current density for both 1-side and 2-side specimens. The linear relation of J_{∞} vs $i^{1/2}$ holds for 2-side specimen at current densities below 1 mA/cm^2 and for 1-side specimen at current densities below 0.5 mA/cm^2 . According to McBreen and Genshow et al, above these critical values, the steady state flux of hydrogen through iron is no longer to be directly proportional to the coverage of the metal surface with the adsorbed hydrogen atoms and a more complicated rela-

Figure 14: Steady state flux as a function of square root of current density for specimen with Pd film on one side.

Figure 15: Steady state flux as a function of square root of current density for specimen with Pd films on both sides.

Figure 16: Product of steady state flux and thickness as a function of square root of current density for specimen with Pd film on one side.

Figure 17: Product of steady state flux and thickness as a function of square root of current density for specimen with Pd film on both sides.

tion exists between steady state flux and current density. Raczynski⁽⁵²⁾ found that the full plot of steady state flux versus current density has four regions in which the permeation rate has different dependence on the current density. Figs. 16 and 17 seem to suggest that they agree with Raczynski's et al b and c regions qualitatively, i.e., in b region J_{α} is directly proportional to $i^{1/2}$ and in c region the relation of J_{α} vs. i is more complicated.

C. Correlation between Gas-Phase and Electrochemical Chargings

It is possible to correlate these results with the gas-phase charging carried out by Kumnick⁽⁵³⁾, based on the steady state properties of the hydrogen transport, i.e., figs. 10 and 12 for specimen with Pd films on both sides. This is shown in fig. 18. The straight line is the least square fit of gas-phase charging data⁽⁵³⁾. For any given value of $J_{\alpha} L$ for 2-side specimens in fig. 12, it is always possible to find an effective pressure for the current density which gives this value of $J_{\alpha} L$. Since the corresponding effective pressure can be quite high, up to 30 atms, it is important to check whether under this high pressure hydrogen behavior will deviate from ideality or not. From Darken and Gurry⁽⁵⁴⁾, at 100 atm fugacity, the deviation from ideality is only 4.5%, well within experimental error. Therefore, hydrogen in the range of effective pressure behaves as ideal gas at room temperature and no correction has to be made when carrying out the correlation. Fig. 19 is a plot of the corresponding

Figure 18: Correlation between gas-phase and electrochemical chargings-- Product of steady state flux and thickness as a function of square root of effective pressure.

Figure 19: Effective pressure as a function of current density for a larger range of current density.

effective pressure vs. charging current density at room temperature and in 0.1 N NaOH. This curve will vary as the charging condition is changed. Note that this curve is obtained from the steady state data and hence it is an empirical one. Borelius and Lindblom⁽⁵⁵⁾ found that the relation between effective pressure(atm) and current density(Amp/cm²) is

$$P_{H_2} = 17,000 i \quad (8)$$

at temperature 90°C and in 2% NaOH solution. However, their finding is only valid for the condition that the permeation rate is directly proportional to the square root of current density and therefore is invalid when this relation is not satisfied. In the present work, when the permeation rate is directly proportional to $i^{1/2}$ for specimen with Pd films on both sides, the relationship between pressure(atm) and current density(Amp/cm²) is, as shown in fig. 20,

$$P_{H_2} = 6700 i \quad ; \quad i < 10^{-3} \text{ Amp/cm}^2 \quad (24)$$

at room temperature. The difference of factor of about 2.5 can't be explained by the effect of temperature on lattice diffusivity alone. Since from Kumnick and Johnson's⁽⁵³⁾ result,

$$\begin{aligned} J_{\alpha} L &= P^{1/2} = D_0 K_0 \exp(-Q/RT) P^{1/2} \\ &= 2.6 \times 10^{17} \exp(-8500/RT) P^{1/2} \text{ atoms H/cm sec} \end{aligned} \quad (25)$$

As temperature increases from 25°C to 90°C, $J_{\alpha} L$ will increase, according to eq. (25), by an order of magnitude at same charging pressure, and is higher than 2.5. In fact, as temperature increases, the coverage of adsorbed hydrogen atoms on cathodic surface will also change and, hence, also the absorbed hydro-

Figure 20: Effective pressure as a function of current density for a smaller range of current density.

gen concentration on the entry surface.

The relationship between pressure and current density is hence affected by the magnitude of current density, temperature, material used, and the electrolytic solution.

Furthermore, when the correlation is made, the agreement of the transient property between gas phase and electrochemical charging can be seen in fig. 21. Although there is some scatter, the plot exhibits a rather continuous curve in this plot. This trend is a supporting evidence for the correlation between gas phase and electrochemical chargings in terms of steady state fluxes.

D. Evaluation of Analyses of Absorption and Evolution Transients

The best way to test the agreement of boundary conditions between the experimental situation and the theoretical consideration is to compare both the normalized absorption and evolution transients between gas-phase and electrochemical chargings which give the same value of J_{∞} . Figs. 22 and 23 show these comparisons. The normalized absorption transients behave approximately the same, at least when taking account of the specimen variation and 7% difference of $J_{\infty} L$ values. However, the normalized evolution transient of electrochemical charging falls off much slower than that of gas-phase charging⁽⁵³⁾.

In gas-phase charging, the boundary condition on the entrance surface, when hydrogen gas is removed away by pure high-speed helium gas, is very close to zero. Its evolution transient falls off rapidly as expected from the theoretical

Figure 21: Effective diffusivity as a function of square root of effective pressure.

Figure 22: Comparison of normalized absorption transients between gas-phase and electrochemical chargings.

Figure 23: Comparison of normalized evolution transients between gas-phase and electrochemical chargings.

fast decay equation. The experimental observation of evolution transient suggests that there is still no hydrogen through before charging. Hence, the boundary condition on the entrance surface when current is turned off in the electrochemical process is apparently not zero and hence there is a slower evolution of hydrogen. As current density is increased, the decay transient will fall off more rapidly. This is what we would expect since the contribution of boundary condition of the entrance surface to the evolution transient can probably be neglected at higher current density. Absorption and evolution diffusivities agree better at higher current densities and the amount of hydrogen coming through when current is off is not dependent on the prior charging current density. These are depicted in figs. 32 and 24.

All the following analyses of evolution transients are then only valid qualitatively by neglecting the boundary-condition contribution to the evolution transient, since at present it is not possible to determine this contribution. If one wants to find accurate information on hydrogen transport by using evolution transient in electrochemical charging, he should first separate the contribution of boundary condition of the entrance surface to the evolution transient from the experimental evolution transient and then analyze the rest by trapping concept.

E. Thickness Anomaly of Effective Diffusivity

Normalized absorption and evolution curves for various

Figure 24: Ratio of effective absorption and evolution diffusivities as a function of current density for various thickness.

thickness at given charging condition are shown in figs. 25 and 26. The rise and decay times for transient fluxes to reach or decay down to some fraction of the steady state flux are always larger for the thicker specimen. However, when eq. (12) is used to calculate the effective diffusivity at different times, its value increases with increasing thickness. For example, figs. 27,28,29 show that thickness anomaly for the effective absorption diffusivity calculated at the times when $J_t/J_\alpha = 0.83$, 0.55 and 0.29, respectively. Surface control is not responsible for this anomaly, since we have volume controlled process.

This anomaly can be explained by trapping theory⁽³⁷⁾. From fig. 24, we know that, according to McNabb and Foster⁽³⁹⁾, the traps are heavily occupied if we neglect all the contribution of boundary condition of entrance surface of zero current density to the evolution transient. For heavily occupied traps,

$$D_{\text{eff}} = D_L \frac{C_L}{C_L + 3N_X} \quad (7)$$

At constant temperature and current density, D_L and C_L are constant. Since the thick specimen has probably less N_X than thin specimen due to the less rolling prior to annealing, we would expect to see higher value of D_{eff} for thicker specimen. Note that in plot of figs.27 etc, the diffusivity increases very rapidly initially and then seems to approach a saturation value. Dillard and Talbot-Besnard⁽⁴³⁾ also found this phenomenon and the saturation value of D_{eff} is $8.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ for thickness on the order of 2 mm and for current densities greater than 9 mA/cm^2 . However, in the present work, this

Figure 25: Normalized absorption transients at $\text{C.D.} = 5.67 \text{ mA/cm}^2$ for various thickness.

Figure 26: Normalized evolution transients at $\text{C.D.} = 5.67 \text{ mA/cm}^2$ for various thickness.

Figure 27: Effective absorption diffusivity ($\tau = 0.25$) as a function of thickness for various current densities.

Figure 28: Effective absorption diffusivity ($\tau = 0.15$) as a function of thickness for various current densities.

Figure 29: Effective absorption diffusivity ($\tau = 0.1$) as a function of thickness for various current densities.

saturation value perhaps will occur for thickness greater 2.5 mm and for current densities greater than 22.5 mA/cm^2 .

Since the magnitude of the trap density determine the value of effective absorption diffusivity, it is suggested that specimen thinned by chemical thinning followed by annealing has higher effective absorption diffusivity than specimen thinned by mechanical rolling and annealing. This is depicted in fig.30. Kumnick⁽²⁵⁾ also found this result for Armco iron. The result is not what we really expect. Perhaps during chemical thinning, hydrogen produced by the chemical reaction may enter the metal and make some structural damage inside the metal.

F. Concentration Dependence of Effective Absorption Diffusivity

Figs. 31 and 32 show the normalized absorption and evolution curves for a specimen charged by three different current densities. The rise and decay times for the lower current density are always larger than those of higher ones. By the analysis of McBreen, i.e., eq. (12), the effective absorption diffusivity increases with charging current density.

Figs. 33,34 and 35 show experimental data of effective absorption diffusivities obtained by fitting at different times as a function of current density for various thickness. One has to note here that the rate of effective absorption diffusivity increase with current density depends on the thickness of specimen in each figure. The thinner the specimen, the larger the rate of increase. This phenomenon may be due to either surface process or the trapping of hydrogen inside the metal.

Figure 30: Effective diffusivity as a function of thickness.

Figure 31: Normalized absorption transients for specimen of 0.127 cm by varying current density.

Figure 32: Normalized evolution transients for specimen of 0.127 cm by varying current density.

Figure 33: Effective absorption diffusivity ($\tau = 0.1$) as a function of current density for various thickness.

Figure 34: Effective absorption diffusivity ($\tau = 0.15$) as a function of current density for various thickness.

Figure 35: Effective absorption diffusivity ($\tau = 0.25$) as a function of current density for various thickness.

Again, since we have diffusion controlled process, it seems impossible that surface process plays role here. Hence we might turn to explain the concentration dependence of effective absorption diffusivity and thickness dependence of the rate of effective absorption diffusivity increase in terms of trapping of hydrogen within bulk iron.

Tables 2 and 3 are lists of trap density of specimens with various thickness, where D_L is taken to be the effective diffusivity of the thickest specimen and C_L is calculated from Oriani's⁽³⁷⁾ equation, i.e.,

$$C_L = 3.7 P^{\frac{1}{2}} \exp(-6500/RT) \text{ cm}^3 \text{H}_2 / \text{cm}^3 \text{Fe} . \quad (26)$$

Note that tables 2 and 3 are just crude estimations. However, it can be used to explain the present situation. From table 2, we know that at the lowest current density, the lattice concentration is much less than the trap density of the thinnest specimen and comparable with that of the thicker specimen.

Hence, let

$$D_{\text{eff}} = D_L \frac{C_L}{C_L + 3N_x} \quad \text{for thick specimen} \quad (7)$$

and
$$D_{\text{eff}} = D_L \frac{C_L}{3N_x} \quad \text{for thin specimen} . \quad (27)$$

Since N_x is fixed for a given thickness, the rate of effective absorption diffusivity increase is determined by the relative magnitudes of numerator and denominator in both eqs. (7) and (27). In eq. (7), both numerator and denominator increase with increasing current density. Hence the increase in numerator tends

Table 2

Trap Density Data for Zone-Refined Iron

C.D. ($\frac{\text{mA}}{\text{cm}^2}$)	$P^{\frac{1}{2}}(\text{atm})^{\frac{1}{2}}$	L(cm)	$D_L^*(\frac{\text{cm}^2}{\text{sec}})$	$D_{\text{eff}}(\frac{\text{cm}^2}{\text{sec}})$	$C_L^{**}(\frac{\text{H atom}}{\text{Fe atom}})$	$N_x^{***}(\frac{\text{no.}}{\text{Fe atom}})$
0.7	1.9	0.015	7.5×10^{-5}	6.5×10^{-7}	7.3×10^{-8}	2.8×10^{-6}
		0.025		2.2×10^{-6}		8.1×10^{-7}
		0.051		1.5×10^{-5}		9.6×10^{-8}
		0.132		2.9×10^{-5}		4.0×10^{-8}
		0.188		4.5×10^{-5}		1.6×10^{-8}
3.6	3.2	0.015	9.5×10^{-5}	2.6×10^{-6}	1.2×10^{-7}	1.5×10^{-6}
		0.025		7.1×10^{-6}		5.1×10^{-7}
		0.051		4.0×10^{-5}		5.6×10^{-8}
		0.132		6.1×10^{-5}		2.3×10^{-8}
		0.188		8.5×10^{-5}		4.8×10^{-9}

Table 3

Trap Density Data for Zone-Refined Iron

C.D. ($\frac{\text{mA}}{\text{cm}^2}$)	$P^{1/2}(\text{atm})^{1/2}$	L (cm)	$D_L^* (\frac{\text{cm}^2}{\text{sec}})$	$D_{\text{eff}} (\frac{\text{cm}^2}{\text{sec}})$	$C_L^{**} (\frac{\text{H atom}}{\text{Fe atom}})$	$N_x^{***} (\frac{\text{no.}}{\text{Fe atom}})$
7.6	4.0	0.015	9.7×10^{-5}	5.7×10^{-6}	1.6×10^{-7}	8.3×10^{-7}
		0.025		1.6×10^{-5}		2.7×10^{-7}
		0.051		5.0×10^{-5}		4.9×10^{-8}
		0.132		7.3×10^{-5}		1.7×10^{-8}
		0.188		9.0×10^{-5}		4.4×10^{-9}
22.5	5.8	0.015	1.0×10^{-4}	1.5×10^{-5}	2.2×10^{-7}	4.4×10^{-7}
		0.025		2.6×10^{-5}		2.1×10^{-7}
		0.051		6.2×10^{-5}		4.5×10^{-8}
		0.132		8.4×10^{-5}		1.4×10^{-8}
		0.188		9.5×10^{-5}		3.9×10^{-9}

* Taken to be the effective diffusivity of the thickest specimen

(L = 0.259 cm)

** $C_L = 3.7 P^{1/2} \exp(-6500/RT) \text{ cm}^3 \text{H}_2 / \text{cm}^3 \text{Fe}$

*** Calculated from

$$D_{\text{eff}} = \frac{D_L C_L}{C_L + 3N_x}$$

to be reduced by the increase in denominator and the rate of effective absorption diffusivity increase in thicker specimen is very small. However, in eq. (27), since N_x is fixed for a given thickness and numerator increases with increasing current density, the rate of effective absorption diffusivity increase for thin specimen is larger.

Namboodhiri and Nanis⁽⁴²⁾ and others^{(26), (43), (53)} also observed the concentration dependence of effective diffusivity. Nowever, Nanis et al argue that this phenomenon is a real "concentration dependence" of effective diffusivity and not a effect of trapping of hydrogen. His argument relies on a doubtable experimental analysis of fitting the short time portion of the absorption transient with the theoretical absorption equation and fitting the long time portion of the decay transient with the theoretical fast decay equation. Kumnick, Johnson⁽⁴⁰⁾ and Quick⁽²⁶⁾ can explain satisfactorily their concentration dependence by the trapping concept that is also used in the present work.

Figs. 36-41 are plots of the effective absorption hydrogen diffusivity of different time fitting versus charging current density over varied thickness. For the thinnest specimen the effective absorption diffusivity of short time fitting is greater than those of longer time fittings. As the specimen thickness is increased, the values of effective diffusivity of different time fitting are getting closer. For specimen with thickness greater than 0.13 cm, the effective absorption diffusivity of short time fitting is smaller than those of longer

Figure 36: Effective absorption diffusivities of different-time fitting versus charging current density for $L=0.015\text{ cm}$.

Figure 37: Effective absorption diffusivities of different-time fitting versus charging current density for $L=0.027 \text{ cm}$.

Figure 38: Effective absorption diffusivities of different-time fitting versus charging current density for $L=0.051\text{ cm}$.

Figure 39: Effective absorption diffusivities of different-time fitting versus charging current density for $L=0.13 \text{ cm}$.

Figure 40: Effective absorption diffusivities of different-time fitting versus charging current density for $L = 0.19 \text{ cm}$.

Figure 41: Effective absorption diffusivities of different-time fitting versus charging current density for $L = 0.26\text{ cm}$.

time fittings. In fact it is safe to say that for specimen thickness greater than 0.13 cm, the effective absorption diffusivity will be about the same no matter where we fit the normalized experimental absorption curve to the normalized theoretical curve. Qualitatively, the present work for specimen thickness greater than 0.13 cm agrees well with Oriani's⁽³⁷⁾ prediction(i.e. equation (2) in this thesis). However, for specimen thickness less than 0.13 cm, the opposite result is obtained. The reason why this is so is not clear yet. This warrants further study.

CHAPTER IV

CONCLUSIONS

1. Hydrogen trapping occurs in annealed zone-refined iron at room temperature. The thickness and concentration dependences of effective diffusivity of hydrogen are associated with hydrogen trapping in iron.
2. The steady state flux of hydrogen permeation through iron specimen with Pd plated only on the anodic side is higher than that through iron specimen with Pd plated on both sides of specimen. This is probably caused by the different electrochemical kinetics of the hydrogen evolution reaction on the iron and palladium surfaces.
3. A correlation between gas-phase and electrochemical chargings was established. The effective pressure associated with an electrochemical charging cell is determined from the comparison of the steady state flux with that of gas-phase charging.
4. A method is suggested to test the boundary condition of evolution transient in electrochemical method. This is to compare the absorption and evolution transients of electrochemical method with those of gas-phase charging. At lower charging current density, the contribution of this boundary condition to the evolution transient can not be neglected.

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