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A mathematical model of hydrogen permeation in pure iron

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A one-dimensional problem of hydrogen permeation through thin plates is analysed. The permeation process is considered as a two-stage transient process. The first stage is assumed to be transportation, and the second diffusion. The non-linear time-dependent diffusion equation is then solved by employing a finite difference scheme. The result shows that the lag time is a quadratic function of the plate thickness. Also, the square of the hydrogen concentration asymptotically tends to be linear across the plate thickness.

1. Introduction

The diffusion of hydrogen in iron and steel has been studied extensively both theoretically and experimentally by many investigators [1–6]. The measured diffusion coefficient of hydrogen is obtained from linear differential equations for diffusion. For linear diffusion models the hydrogen permeation is obtained, in a thin membrane, by using the assumption that the diffusion coefficient does not depend upon pressure. The present work introduces a non-linear model to simulate the hydrogen permeation process.

2. Experimental details

2.1. Equipment and experimental technique

The electrochemical permeation technique used in this work was described by McCright [7]. The permeation cell is composed of two 1000 ml three-necked pyrex flasks connected by glass joints which are grooved to take O-rings. A clamp holds the joints with the sample membrane between them. The exposed specimen area is $3.0\,\text{cm}^2$. The experimental apparatus is shown in Fig. 1 and the electrical circuit is shown in Fig. 2. A 0.1 N NaOH solution was used for the anodic side and a 1 N H_2SO_4 solution was used for the cathodic side. Both solutions were deoxygenated to reduce background current arising from the reduction of oxygen.

The entry side of the sample membrane (specimen) was exposed to hydrogen by cathodic polarization. On the exit side, the amount of hydrogen that permeates through was measured as a function of time. The hydrogen was measured electrochemically by maintaining the exit side of the specimen at a constant anodic potential of + 250 mV (SCE). At this potential, any hydrogen reaching the exit side would be ionized. A potentiostat supplies the current necessary for hydrogen ionization without changing the potential of the sample. The potentiostatic current, i_p, is a direct measure of the amount of hydrogen leaving the exit side of the specimen. This current was recorded as a function of time with a Hewlett Packard Model Moseley 680 strip chart recorder. Since the sample has constant cross-sectional area, the recorded current could be equated to current density.

2.2. Material

The material chosen for this study is VP (vacuum processed) iron. The composition is listed in Table I. The VP iron and analysis was furnished by Materials Research Corporation.

Specimens were cut from a round bar and machined to 25 mm diameter and varying thicknesses from 0.2 to 2.0 mm. The specimens were ground with SiC grinding paper down to 600 grit. The specimen

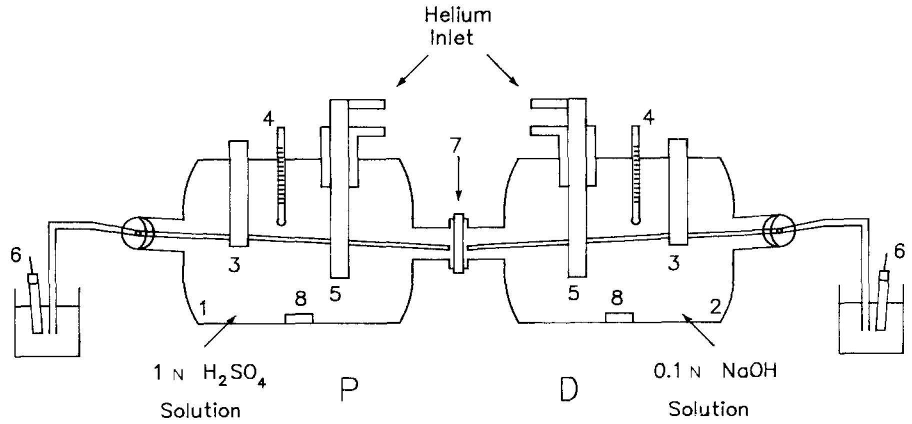

Figure 1 Schematic diagram of experimental apparatus. (1) permeation cell (P); (2) determination cell (D); (3) counter electrode; (4) thermometer; (5) gas dispersion tube; (6) saturated calomel electrode with a Luggin capillary; (7) specimen; (8) magnetic bar.

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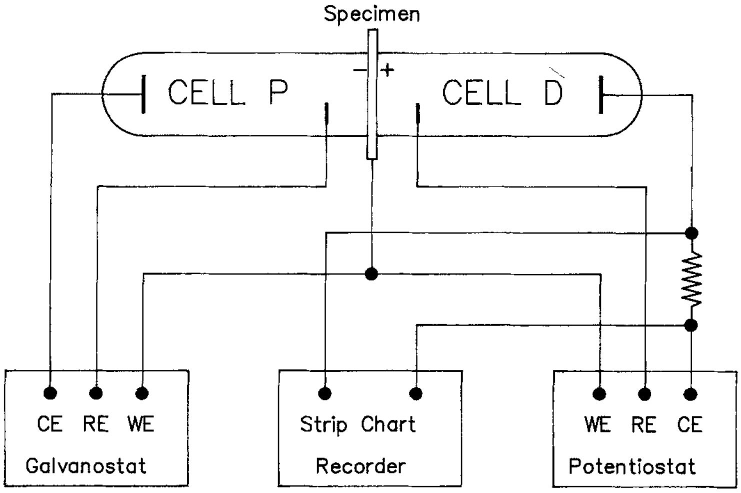

Figure 2 Block diagram of the circuit employed for the measurement of hydrogen permeation.

surfaces were subsequently polished with γ-Al_2O_3 to 0.3 μm. This was followed by a rinse with acetone. All specimens were austenitized at the same temperature and vacuum furnace cooled.

Prior to permeation measurement, each specimen was palladium plated on the anodic side to eliminate surface effects. The thickness was about 100 nm.

The test cells were immersed in a container which was filled with distilled water. This container which held recirculating water was maintained at ± 0.2° C by an external controller/heat source.

Successive absorption and evolution transients showed good reproducibility after an initial charging run was made on the sample. Deep trapping is not operative after the first hydrogen charge. Similar reproducibility has been demonstrated by Xie and Hirth [1] using electrochemical charging.

3. Theoretical analysis

3.1. Formulation

Consider a thin membrane of porous matrix with a high gas pressure, $\mathscr{P}_H$, externally applied at the entering side from left and a zero gas pressure maintained at the exit side from right as shown in Fig. 3.

The permeation process is considered as a two-stage transient process. The first stage is assumed to be pure transportation due to the fact of thin membrane and high pressure difference.

In the initial time period t_1, we assume that the hydrogen wave front travels at a limit velocity V_0 and the pressure distribution in the membrane is linear. The pressure distribution of the first stage is

$$\mathscr{P} = \mathscr{P}_H(1 - V_0 tx/L), \qquad 0 < t < L/V_0 = t_1. \qquad (1)$$

The second-stage transient process follows immediately after the first-stage process. Thus, in the subsequent time period $t_1 < t < \infty$, the transient process in the membrane is assumed to be pure diffusion. The diffusion equation can be given by Darcy's Law [8] as

$$\frac{\partial \mathscr{P}}{\partial t} = \frac{k}{\eta\varepsilon}\frac{\partial}{\partial x}\left(\mathscr{P}\frac{\partial \mathscr{P}}{\partial x}\right),$$

here $\mathscr{P}$ is the pressure, η is the viscosity, k is the permeability, ε is the effective porosity. Introducing the non-dimensional variable $\mathscr{P} = \mathscr{P}_H P$, $x = LX$, $t = t_2 T$ (t_2 is the transient time constant), and $\alpha = k\mathscr{P}_H t_2/\eta\varepsilon L^2$, the non-dimensional equation becomes

$$\frac{\partial P}{\partial T} = \frac{\partial}{\partial X}\left(\alpha P \frac{\partial P}{\partial X}\right), \qquad \text{for } 0 < X < 1, \text{ and } T > 0. \qquad (2)$$

TABLE I Chemical analysis of VP iron

Element	p.p.m.	Element	p.p.m.
C	8.0	Cr	30.0
O	33.0	Ni	< 10.0
H	< 1.0	Zn	ND
N	< 1.0	Ca	ND
Al	60.0	Zr	ND
Na	ND	Nb	ND
P	ND	Pd	ND
Mg	< 10.0	Ag	< 5.0
S	40.0	In	ND
Cl	ND	Sn	< 30.0
K	ND	Sb	ND
Ca	< 10.0	Ta	ND
Ti	< 10.0	W	ND
Fe	MAJOR	Pt	ND
Cu	30.0	Au	ND
Si	50.0	Pd	< 30.0
Other	0.1%		

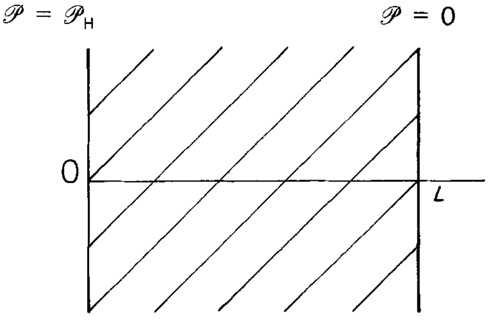

Figure 3 Geometry of system.

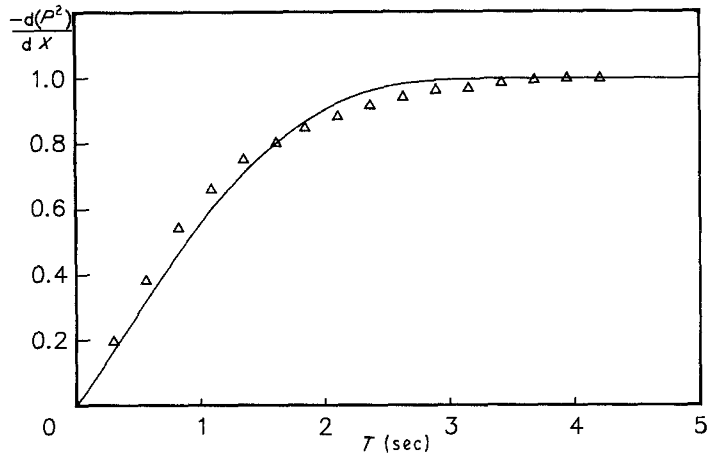

Figure 4 Hydrogen permeation against time at the exit wall. (△) Experimental data, (——) present theory. Thickness of 0.93 mm, and temperature of 25° C.

The appropriate boundary conditions are

$$\begin{aligned} P &= 1 &\text{at } X &= 0,\\ P &= 0 &\text{at } X &= 1,\\ P &= (1 - X) &\text{at } t &= 0. \end{aligned} \quad (3)$$

3.2. Numerical method

The solution for differential Equation 2 and boundary conditions, Equation 3, is obtained by employing a finite difference scheme. The implicit finite difference equation used is

$$\frac{P^{2\,n+1}_{i} - P^{2\,n}_{i}}{\Delta T} = \alpha P^{n+1}_{i}\left[\frac{P^{2\,n+1}_{i+1} + P^{2\,n+1}_{i-1} - 2P^{2\,n+1}_{i}}{\Delta X^2}\right] \quad (4)$$

For a fixed value of α the pressure evolution function at every location X is obtained by using a point SOR (Successive Over-relaxation) iteration method [9] to solve Equation 4. The flux $-\partial P^2/\partial X$ at the exit wall ($X = 1$) is integrated with respect to T and then T_2,

$$T_2 = \int_0^\infty \left[1 - \left(\frac{\partial P^2}{\partial X}\right)\Big/\left(\frac{\partial P^2}{\partial X}\right)_{T=\infty}\right] \mathrm{d}T,$$

is the normalized transient time constant which must be equal to 1. In the calculation the value of α is adjusted such that $T_2 = 1$. The normalized value of T_2 corresponds to $\alpha = 0.17$. This implies that, when we take transient time constant t_2 as a reference time, the present model demands that

$$\alpha = 0.17 = k\mathscr{P}_{\mathrm{H}} t_2/\eta\varepsilon L^2.$$

4. Discussion of results

The evolution of hydrogen permeation in the diffusion stage at the exit wall surface is compared with an experimental curve. A fair agreement is shown in Fig. 4.

The squared pressure distribution and the hydrogen flux varying with time at locations across the membrane are shown in Figs 5 and 6. The distribution of the squared hydrogen concentration asymptotically tends to be linear in the membrane. The hydrogen flux changes from an initial linear distribution to a final constant distribution. At the entering wall the flux decays asymptotically from 2 to 1, while at the exit wall the flux grows asymptotically 0 to 1. The lag time,

$$t_l = t_1 + t_2 = L/V_0 + (0.17\eta\varepsilon/k\mathscr{P}_{\mathrm{H}})\, L^2,$$

is a quadratic function of L as $t_1 = aL + bL^2$. A remarkable feature for this type of function is that the lag time will decrease asymptotically to zero as the membrane thickness decreases asymptotically to zero. The experimental data can be curve-fitted to this function with least square errors. The result with good agreements is shown in Fig. 7.

5. Conclusions

A non-linear model may be used to simulate the physical hydrogen permeation process. The distribution of the squared hydrogen concentration

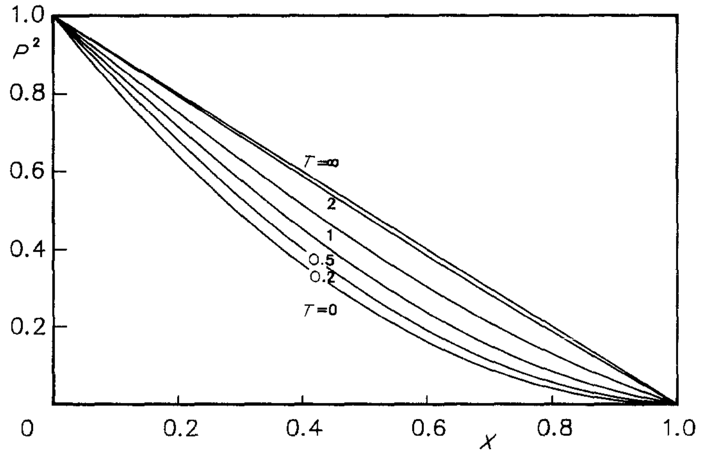

Figure 5 Square of hydrogen pressure for various time in the membrane.

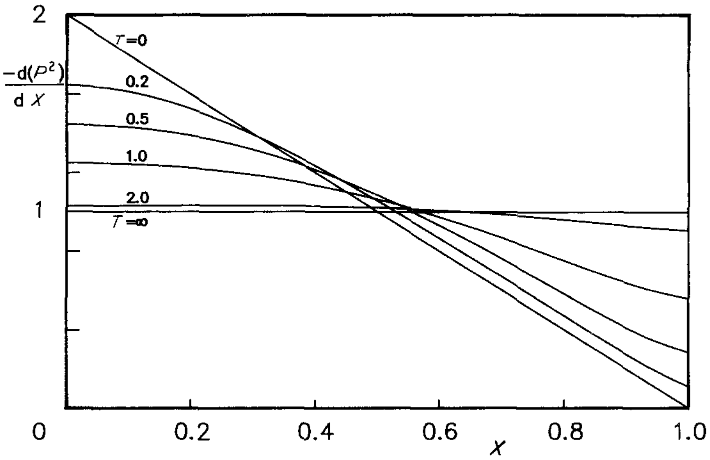

Figure 6 Hydrogen permeation for various time in the membrane.

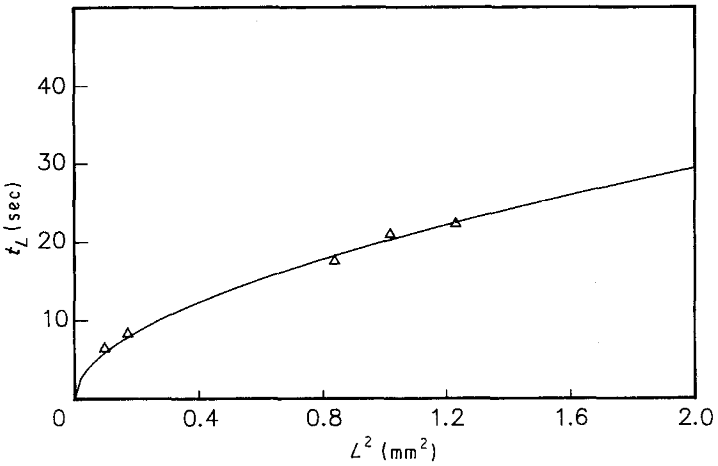

Figure 7 Lag time against L^2 by curve fitting with least square errors. (△) Experimental data, (——) present theory. $t_L = 1.824L + 1.826C^2$.

asymptotically tends to be linear in the membrane. The lag time followed from the model yields good agreement with the experimental data. The lag time will decrease asymptotically to zero as the membrane thickness decreases to zero.

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