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FEM Analysis for Sinusoidal Perturbation of Hydrogen Permeation into a Steel Sheet

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Numerical calculation for the diffusion problem of hydrogen absorbed in a steel sheet during hydrogen permeation measurement using a double electrochemical cell was carried out. The finite element method (FEM) was applied to obtain the concentration distribution of hydrogen expressed by one- or two-dimensional Fick's laws in the sheet, assuming that hydrogen concentration at the hydrogen entry interface was perturbed sinusoidally and both the hydrogen entry and exit reactions were in a mass-transport controlled process. From a comparison with experimental results reported previously, in which a phase shift from entry current to exit current waves observed on a single grain of the specimen sheet was at least two-times larger than that on two grains, it was estimated that the diffusion coefficient at a grain boundary located between two grains was five orders in magnitude larger than that on a single grain.

KEY WORDS: hydrogen permeation; Devanathan-Stachurski cell; diffusion; finite element method (FEM); grain boundary.

1. Introduction

In order to prevent hydrogen embrittlement of steel, it is necessary to understand not only the mechanism but also the kinetics of hydrogen adsorption on the steel surface and the following hydrogen permeation into the steel substrate. For investigating hydrogen permeation, a Devanathan-Stachurski (DS) double electrochemical cell[1,2)] has been used to measure the efficiency of hydrogen permeation from the ratio of hydrogen exit current to hydrogen entry current and the diffusion coefficient of hydrogen in the steel from the transient response of exit current.[3)] The DS cell has been modified to obtain special characteristic features of hydrogen permeation into steel. The authors reported previously[4)] that sinusoidal perturbation of the electrolyte flow rate in the hydrogen-entry side of the DS cell induced an exit current wave as well as an entry current wave. A phase shift of the exit current from the entry current observed during the perturbation of the hydrodynamic condition in the modified DS cell was proposed to be a new factor for evaluating hydrogen permeation into steel. In this background, the authors succeeded in observing a phase shift in local measurement using a DS cell combined with a micro-capillary cell and revealed that diffusivity in a region with two single steel grains and a grain boundary was at least two-times larger than that in a region with a single grain.[5)]

Hydrogen permeation measurement is mainly based on the diffusion of hydrogen in the specimen sheet from the entry side to the exit side. In the case of a one-dimensional diffusion problem, which is suitable for uniform permeation of hydrogen in thin sheets, the concentration gradient of hydrogen at the exit side is analytically elucidated and used for the discussion of hydrogen permeation.[6)] In general, however, it is difficult to solve two- or three-dimensional diffusion problems, which is often necessary for local or heterogeneous hydrogen permeation of a non-uniform substrate and/or environment. Therefore, little theoretical discussion of local or heterogeneous hydrogen permeation has been reported.

In this study, a finite element method (FEM) was applied to solve one- and two-dimensional diffusion problems and to simulate the hydrogen concentration gradient in steel. The application to obtain phase shifts as well as hydrogen flux during local permeation measurement with a DS-micro-capillary cell is succeeded for the first time. Moreover, the difference between diffusion coefficients of hydrogen in a single grain and grain boundary is discussed using the results from a series of FEM calculations.

2. Principles

2.1. Diffusion Problem

Assuming that hydrogen atoms are heterogeneously present in a steel sheet, the local concentration gradient leads to a homogeneous distribution of hydrogen atoms due to diffusion according to Fick's laws:

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$$\mathbf{J} = -D\nabla c, \quad \text{..... (1)}$$

$$\partial c/\partial t + \nabla \cdot \mathbf{J} = v, \quad \text{..... (2)}$$

where **J**, D and c are mass flux, diffusion coefficient, and concentration of hydrogen atoms, respectively, in the sheet and v is the mass reaction term for satisfying the saving law of mass. During hydrogen permeation, it is assumed that no chemical reaction occurs other than hydrogen entry reaction on the entry side and hydrogen exit reaction on the exit side. The mass reaction term becomes

$$v = 0. \quad \text{..... (3)}$$

For the system in a steady state, therefore, Eq. (2) can be simplified as follows:

$$\nabla \cdot \mathbf{J} = -D\nabla^2 c = 0. \quad \text{..... (4)}$$

2.2. Geometry and Boundary Conditions

Absorption and desorption of hydrogen at the entry and exit sides are rapid compared with the diffusion of hydrogen in a steel sheet.[7] They are considered to be always in an equilibrium state. During hydrogen permeation measurement with a DS cell, therefore, hydrogen concentrations c_{entry} and c_{exit} at the entry side interface and the exit side interface, respectively, in a mass-transport controlling process can be expressed as follows:

$$c_{\text{entry}} = c_0 + \Delta c \sin\left(2\pi ft\right), \quad \text{.....(5a)}$$

$$c_{\text{exit}} = 0, \quad \text{..... (5b)}$$

where c_0 and Δc are mean concentration and amplitude of concentration perturbation of hydrogen at the entry side interface, respectively, and f is frequency of the sinusoidal perturbation of the hydrogen entry.

Hydrogen diffusion in a uniform sheet can be expressed as a one-dimensional equation as follows:

$$\partial^2 c/\partial z^2 = 0, \quad \text{..... (6)}$$

where z is a coordinate in the direction of sheet thickness. When the sheet is composed of two domains with different diffusivities in the perpendicular direction to the entry surface, however, the diffusion problem is considered to be a two- or three-dimensional problem and a two- or three-dimensional equation is adopted. In one- and two-dimensional diffusion problems, the sheet can be regarded as a line with a length of L and a rectangle with side lengths of L and W, respectively, where L and W are equivalent to the thickness and width of the sheet, respectively. On the other hand, the diffusion coefficient of hydrogen in a pure iron sheet without trapping by dislocations and impurities was reported to be 5.8×10^{-8} m^2 s^{-1} at room temperature.[8] From previous results,[5] moreover, $D = 1.2\times10^{-9}$ m^2 s^{-1} was obtained for the sheet used in experiments. In the following discussion, therefore, the value of 10^{-9} m^2 s^{-1} is basically used for the hydrogen diffusion coefficient of a steel sheet.

While the flux of hydrogen on the entry or exit electrode surface is expressed by Eqs. (1) and (5), no flux passes through the insulating surface or the steel other than electrode surfaces. Any steel sides other than the hydrogen entry or exit side are treated as 'walls' and no flux passes through them, the normal vector of which is **N**.

$$\mathbf{N} \cdot \mathbf{J} = 0 \quad \text{..... (7)}$$

No flux also passes through any symmetric lines, and Eq. (7) is adopted in a periodic boundary condition. Currents flowing through the entry and exit side electrodes are products of fluxes that have passed through the electrodes and a Faraday constant.

2.3. FEM Calculation

Equations (5)–(7) governing the diffusion-controlled permeation of hydrogen in a steel sheet were calculated by FEM. All of the finite element calculations presented in this paper were performed by COMSOL Multiphysics® 5.0 running on a Windows PC equipped with 3.5 GHz Intel® Xeon® CPU E3-1241 v3 and with 32 GB RAM.

3. Results and Discussion

3.1. One-dimensional Diffusion Problem

The theory of the diffusion problem used in this paper was checked by one-dimensional FEM calculation. In the case of one-dimensional diffusion of hydrogen in a homogeneous sheet with a sinusoidal perturbation at the entry side interface, the hydrogen concentration at the exit side interface becomes a function of the following five parameters: mean concentration c_0 and concentration amplitude Δc of hydrogen at the entry side, thickness L of the sample sheet, diffusion coefficient D of hydrogen in the sheet and frequency f of entry perturbation. **Figure 1** shows a series of dependencies of phase shift θ, which is the difference of the exit flux wave from the entry flux wave, on the five parameters used in the calculations. One of them was used as a variable, while the other four parameters were fixed. The defaults used were as follows: c_0 = 1 mol m^{-3}, Δc = 0.1 mol m^{-3}, $L = 10^{-4}$ m, $D = 10^{-9}$ m^2 s^{-1} and f = 0.01 Hz. It is obvious that the phase shift is independent of the values of c_0 and Δc (Figs. 1(a) and 1(b)), though the amplitude of the exit flux wave was strongly dependent on these values. This means that the calculated result of phase shift is also independent of irregular change of the hydrogen entry or signal noise, suggesting that phase shift measurement is useful for investigating hydrogen permeation. On the other hand, the values of L, D and f strongly affect θ as shown in Figs. 1(c)–1(e). The value of θ increases with increases in L and f and with a decrease in D. It is clear that the diffusion phenomenon is dependent on these parameters. In order to normalize these dependencies, the parameter α is defined as follows:

$$\alpha = \left(\pi fL^2 / D\right)^{1/2}. \quad \text{..... (8)}$$

Figure 2 shows the relation between θ and α. θ increases exponentially with increase in α with slopes of 2 at values of α smaller than 1 and of 1 at larger values of α. θ at the cross point of the slopes is 57.29°, which is equivalent to 1 rad, suggesting that the perturbation of hydrogen permeation is governed by some trigonometric functions of physical phenomena, though the details including the reason why two slopes are shown are not clear. In any case, it is obvious that the relation as a function of L, D or f coincides with

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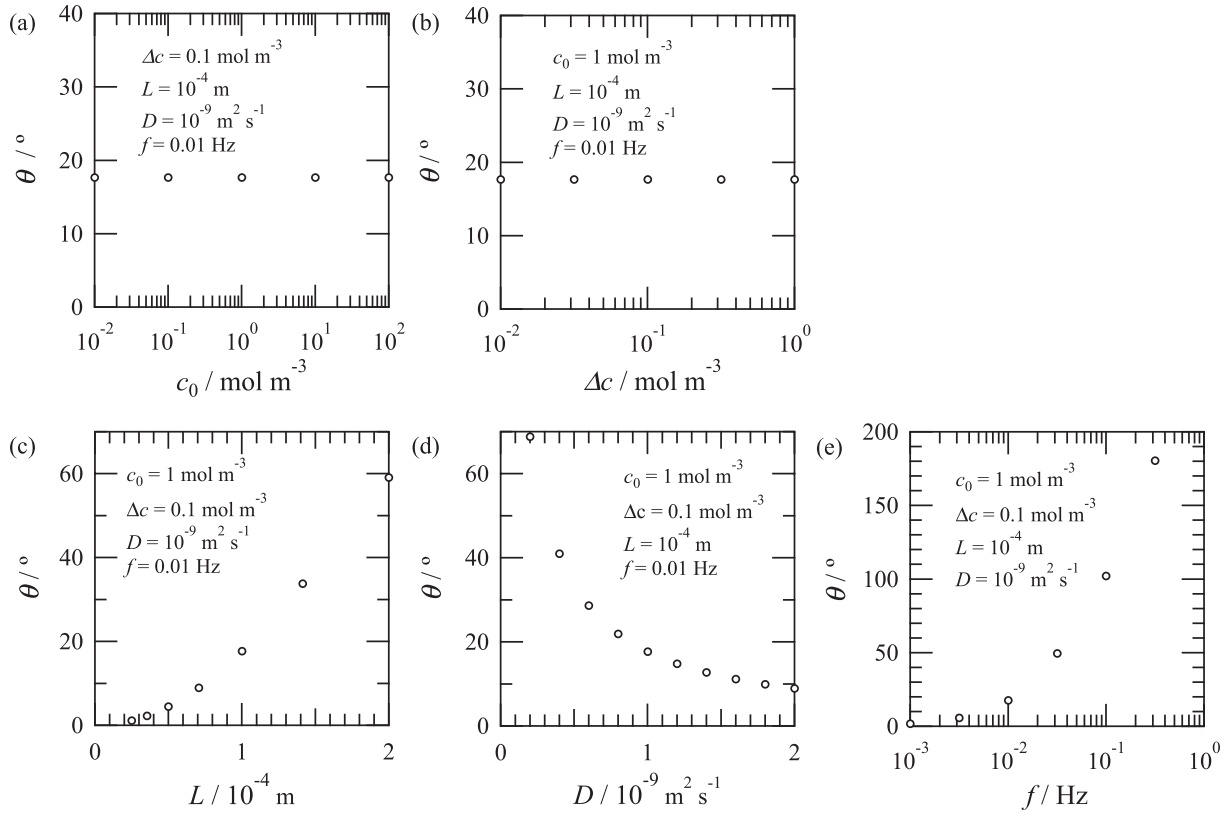


Fig. 1. Dependencies of phase shift θ on (a) mean concentration c_0 and (b) concentration amplitude Δc of hydrogen at the entry side, (c) thickness L of the sample sheet, (d) diffusion coefficient D of hydrogen in the sheet and (e) frequency f of entry perturbation. The values of $c_0 = 1$ mol m^{-3}, $\Delta c = 0.1$ mol m^{-3}, $L = 10^{-4}$ m, $D = 10^{-9}$ m^2 s^{-1} and $f = 0.01$ Hz were used as default values.

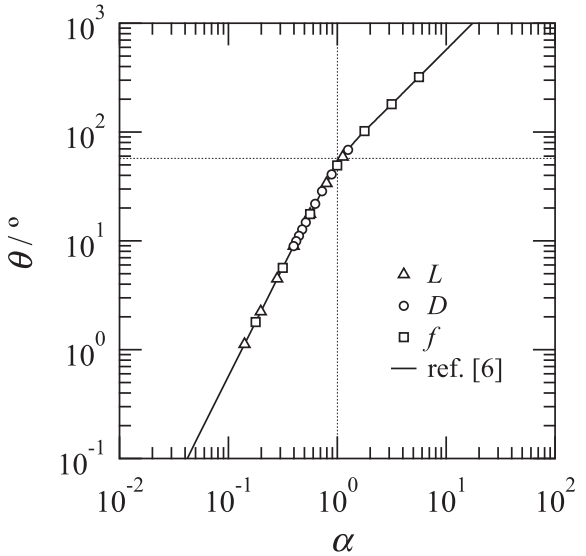


Fig. 2. Relations between θ and α when L, D or f was changed from default values of $L = 10^{-4}$ m, $D = 10^{-9}$ m^2 s^{-1} and $f = 0.01$ Hz. The relation reported by Sekine[6] was also plotted as a solid line. $\alpha = (\pi f L^2/D)^{1/2}$.

the algebraic result reported by Sekine,[6] which is an inverse trigonometric function for the tangent of the product of the tangent and hyperbolic tangent of α as follows:

$$\theta = \tan^{-1}\left(\tan\alpha \tanh\alpha\right). \quad \text{..... (9)}$$

This agreement verifies the results of the FEM calculation for the diffusion problem of hydrogen permeation in this paper. In the following calculations, $c_0 = 1$ mol m^{-3}, $\Delta c = 0.1$ mol m^{-3}, $L = 10^{-4}$ m, $D = 10^{-9}$ m^2 s^{-1} and $f = 0.01$ Hz are used as default parameters.

3.2. Local Measurements with a Micro-capillary Cell

In the previous study,[5] the authors investigated the local permeation of hydrogen in a steel sheet using a DS cell combined with a micro-capillary cell. In that case, the hydrogen exit side of the micro-cell was smaller than that of the hydrogen entry side because the diameters of them were 2.5×10^{-4} m and 8×10^{-3} m, respectively. Hydrogen permeation during local measurement was simulated with FEM calculation in a two-dimensional, axis-symmetrical diffusion problem. A steady-state diffusion of hydrogen in a homogeneous sheet, in which there is no distribution of the diffusion coefficient, can be expressed as a two-dimensional equation with cylindrical coordination as follows:

$$\partial^2 c/\partial z^2 + \partial c/r\partial r + \partial^2 c/\partial r^2 = 0, \quad \text{..... (10)}$$

where r is a coordinate in the radial direction from the cell center. **Figure 3**(a) shows a cross-sectional distribution of hydrogen concentration in the steel. The slope of the gradient of hydrogen concentration means the flux of hydrogen according to Eq. (1). It is confirmed that the diffusion layer (or depletion layer in this case) is mainly formed below the exit side interface. However, local hydrogen flux at the exit edge ($r = 1.25\times10^{-4}$ m) is higher than that at any other exit interface as shown in Fig. 3(b), due to the edge effect, in which the flux of hydrogen is concentrated at the electrode edge. It is indicated that the micro-cell can detect hydrogen

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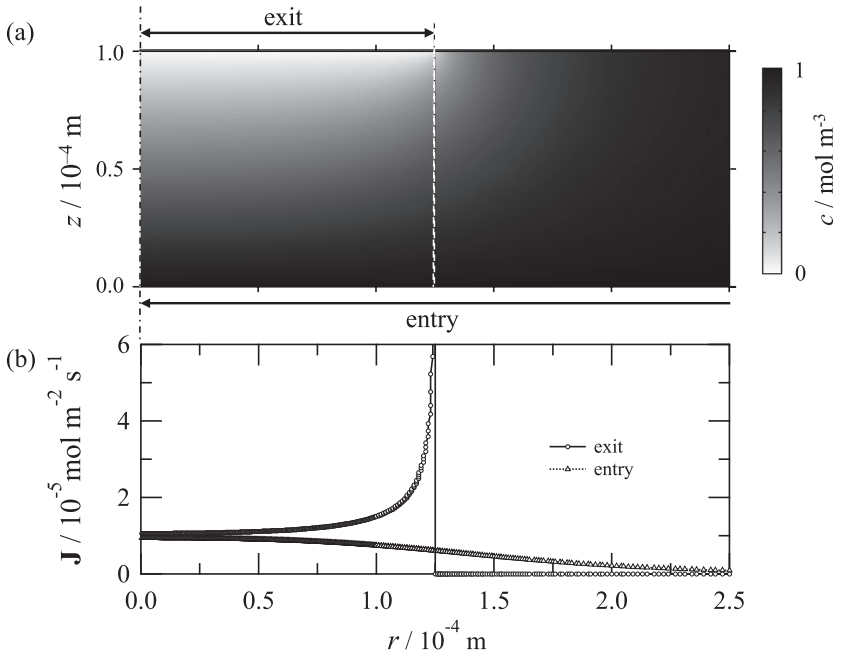


Fig. 3. (a) Cross-sectional distribution of hydrogen in the sheet and (b) local fluxes of the entry and exit sides during permeation measurement when the entry and exit sides were 8×10^{-3} m and 2.5×10^{-4} m in diameter, respectively. The hydrogen diffusion coefficient of the sheet was 10^{-9} m^2 s^{-1}.

diffused not only from just below the exit side but also from the outer part. The resolution of local measurement with the micro-capillary cell, which is a ratio of hydrogen flux from the entry side plane just below the cell to that of the exit side plane, was estimated to be 43.3%.

Though the experiment might be very difficult to carry out, local measurements of hydrogen permeation with an inversed set-up of the micro-capillary cell combined with the DS cell, in which the hydrogen entry was the micro-cell and smaller than that of the hydrogen exit, and with a DS set-up using a double micro-capillary cell, in which the entry and exit cells were two micro-cells with a same diameter, were employed in the FEM calculation. Broadening of hydrogen diffusion from the entry side interface in the steel was confirmed in both the inversed set-up and the double micro-cell set-up as shown in **Figs. 4**(a) and **5**(a), respectively. The hydrogen distribution in the sheet in Fig. 4(a) was as same as that of the reversed distribution in Fig. 3(a). Thus, hydrogen flux in Fig. 4(b) also absolutely coincided with that of the inversed relation in Fig. 3(b). At the entry edge, the flux shows a maximum, indicating active diffusion in the sheet bulk. On the other hand, exit flux in the case of the single micro-cell (Fig. 3(b)) was larger than that of the double micro-cell (Fig. 5(b)) by 30.8%, suggesting that hydrogen diffusion outside of the micro-cell interface decreases the resolution of local measurement. The difference would be decreased with increase in diameter of the capillary cell and with decrease in thickness of the sheet.

3.3. Two-dimensional Diffusion Problem

In general, a steel sheet is polycrystalline and has a heterogeneous structure including a number of single grains and grain boundaries. The diffusion problem of hydrogen in heterogeneously structured sheets has frequently been discussed. However, it is difficult to obtain a rigid solution for hydrogen permeation in a heterogeneous structure even in the case of a sheet with uniform thickness because two- or three-dimensional diffusion problems should be solved. In order to analyze tentatively the permeation in a heterogeneous structured sheet, the geometry of the specimen sheet is simplified perpendicularly as shown in **Fig. 6**. The sheet is a lamella composed of two domains of A and B with diffusion coefficients of D_A and D_B and with widths of $2w_A$ and $2w_B$, respectively. Since the boundary planes of the domains are perpendicular to both the entry and exit surfaces, a periodic boundary condition, in which hydrogen flux becomes symmetric at the center plane, is effective. Thus, a two-dimensional diffusion problem, in which w_A and w_B are the periodic boundary condition, was carried out as shown in **Fig. 7**(a). In the case of $w_B = w_A$, θ calculated at $D_B = D_A$ is 17.62°, which corresponds to the phase shift θ_0 for a homogeneous sheet. θ decreases with increase in D_B, though the value is asymptotically approaching the critical values θ_H and θ_L, which are θ calculated for homogeneous sheet, *i.e.*, $\theta_H = 32.34°$ at smaller D_B and $\theta_L = 0°$ at larger D_B. The value θ_H is strongly dependent on width w_B. When D_B is smaller than D_A, θ_H decreases with a decrease in w_B and approaches the value of θ_0, indicating that the diffusion phenomenon in the sheet is dominated by that of larger domains. When D_B is larger than D_A, however, the value θ at a D_B increases with decrease in width w_B. At $D_B = 10^{-7}$ m^2 s^{-1}, θ is 9.02°, which is almost half of θ_0. This suggests that the presence of a domain with a significantly large diffusivity affects hydrogen diffusion in the sheet. Figure 7(b) is a double logarithmic plot of the relation between D_B and w_B, where the sinusoidal entry perturbation leads to hydrogen permeation with a half phase shift of θ_0. It is obvious that D_B increases with decrease in w_B with a slope of 1 at w_B smaller than 10^{-5} m. The smaller slope at large w_B suggests that the hydrogen diffusion in not only perpendicular direction but also the horizontal direction affects the hydrogen permeation in a sheet with a heterogeneous structure com-

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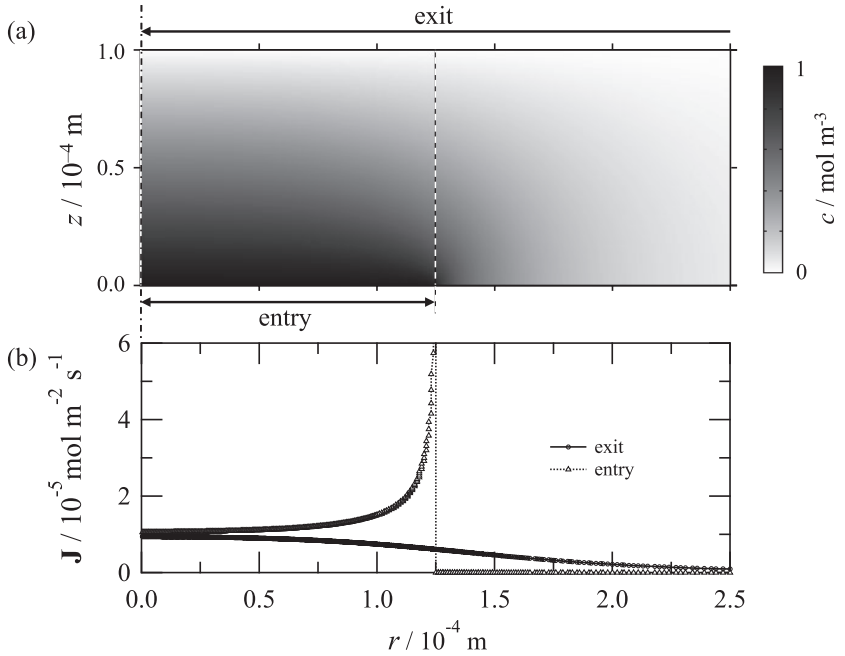


Fig. 4. (a) Cross-sectional distribution of hydrogen in the sheet and (b) local fluxes of the entry and exit sides during permeation measurement when the entry and exit sides were 2.5×10^{-4} m and 8×10^{-3} m in diameter, respectively. The hydrogen diffusion coefficient of the sheet was 10^{-9} m^2 s^{-1}.

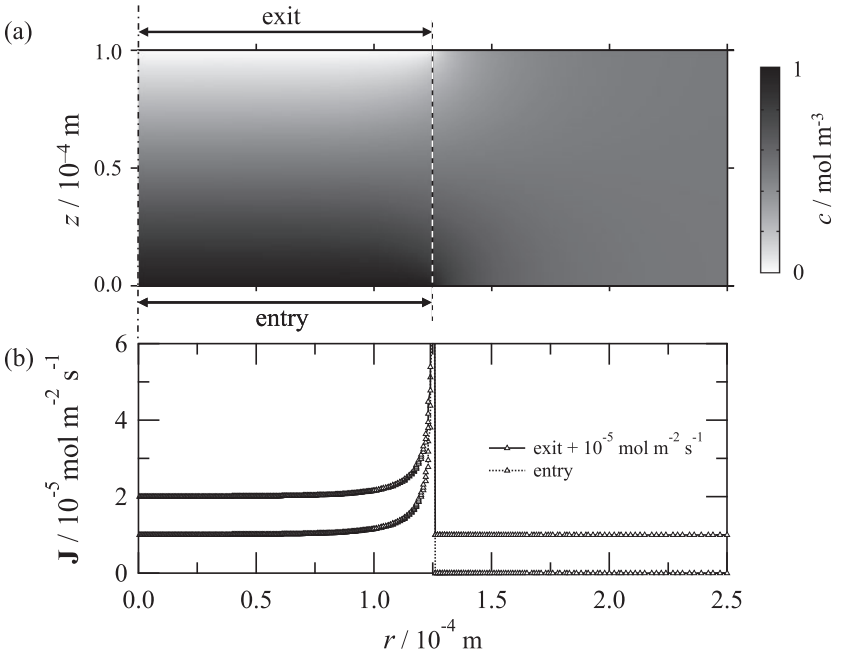


Fig. 5. (a) Cross-sectional distribution of hydrogen in the sheet and (b) local fluxes of the entry and exit sides during permeation measurement when both the entry and exit sides were 2.5×10^{-4} m in diameter. The hydrogen diffusion coefficient of the sheet was 10^{-9} m^2 s^{-1}. In (b), the exit flux was shown with an offset of 10^{-5} mol m^{-2} s^{-1}.

posed of comparable domains. The plots coincide with the calculated results from the reported relation[6] using a mean diffusion coefficient D_{mean} as follows:

$$D_{\mathrm{mean}} = \frac{D_{\mathrm{A}} w_{\mathrm{A}} + D_{\mathrm{B}} w_{\mathrm{B}}}{w_{\mathrm{A}} + w_{\mathrm{B}}}. \quad \text{..... (11)}$$

The grain boundary is a steric mismatch of lattices and the boundary width is considered to be in atomic scale. Assuming that $w_{\mathrm{B}} = 10^{-9}$ m for the grain boundary width, the value of $D_{\mathrm{B}} = 10^{-4}$ m^2 s^{-1} can be estimated for the hydrogen diffusion coefficient of the grain boundary. Though the value is five orders in magnitude larger than that of single grains, it is in good agreement with the value reported previously.[9]

As discussed above, FEM calculation is effective to simulate hydrogen diffusion in both the grain and boundary. In this paper, the diffusion problem in a perpendicularly structured heterogeneous sheet was treated. However, it is applicable to other structured sheets including horizontally structured, obliquely structured, and mix structured heterogeneous sheets. A concave structure of the grain boundary may collect hydrogen flux and play the role of

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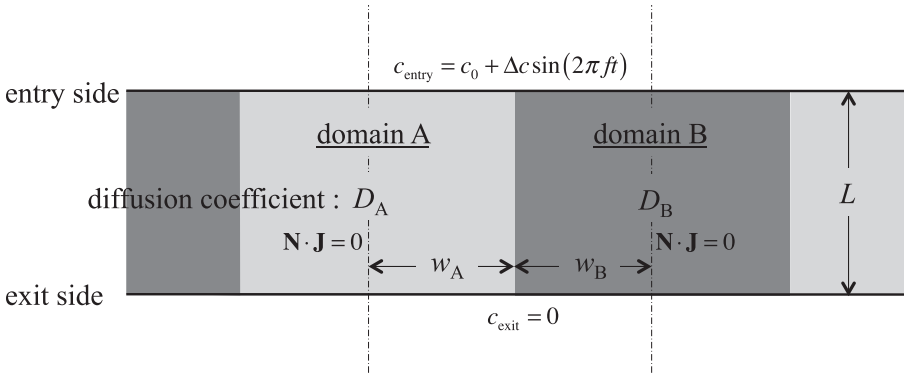


Fig. 6. Schematic diagrams of a heterogeneous sheet composed of domains used for a two-dimensional diffusion problem. Lamella of domains with different diffusivities was located perpendicularly with different width or thickness, respectively. A dotted line indicates the symmetric center of the domain for the periodic boundary condition of FEM calculation used.

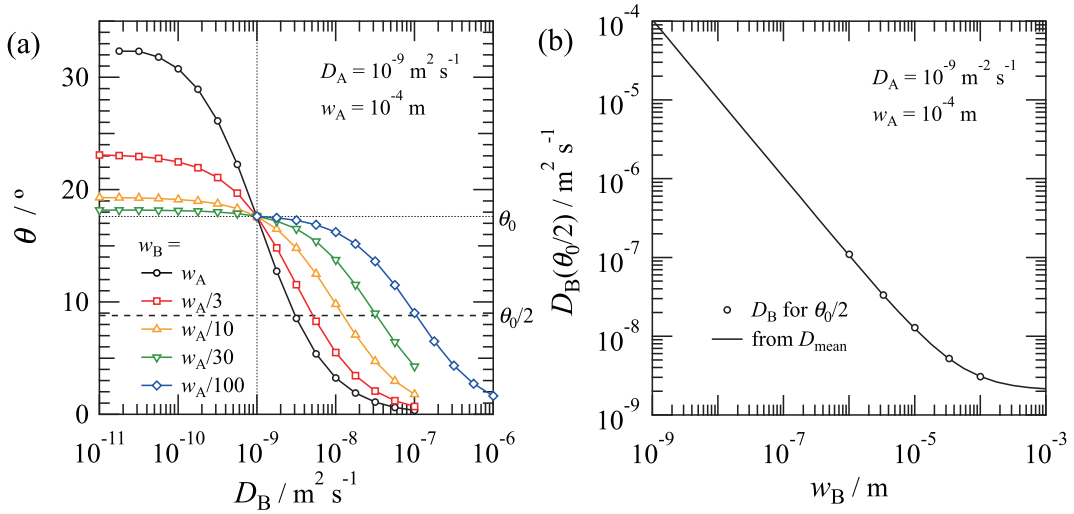


Fig. 7. (a) Relation between θ and diffusion coefficient D_B of domain B in a heterogeneous sheet with $L = w_A = 10^{-4}$ m, $D_A = 10^{-9}$ m^2 s^{-1}, and $f = 0.01$ Hz when the width w_B of domain B was changed. (b) Plot of $D_B(\theta_0/2)$, showing a half of θ_0 obtained in the homogeneous sheet, as a function of w_B. The relation calculated from Sekine[6] was also plotted as a solid line. (Online version in color.)

a so-called hydrogen trap. In order to clarify the effects of these structures in detail, more complicated calculations in three dimensions are necessary. A part of them has already been conducted. In the near future, the authors will present the results.

4. Conclusions

Sinusoidal perturbation of hydrogen permeation in a steel sheet was simulated by FEM calculation. In the case of permeation in a homogeneous sheet, the result coincided with the algebraic result reported by Sekine. Simulation of localized hydrogen permeation using a micro-capillary cell resulted in detecting resolution of 43.3%. In the case of permeation in a heterogeneous sheet with two domains, the permeation behavior was characterized by a mean diffusion coefficient. Assuming a grain boundary width of 10^{-9} m, the diffusion coefficient in the grain boundary was estimated to be 10^{-4} m^2 s^{-1}, which is five orders in magnitude larger than that in the grain.

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