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Permeation flux of hydrogen through plasma facing materials

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A general formula for simultaneous gas- and plasma-driven permeation of hydrogen (tritium) has been developed by an electrical circuit analog, in which the permeation potential and resistance are defined for both diffusion in the bulk and recombination on the surface and the gradient of permeation potential against permeation resistance is considered to be the general driving force for permeation through a laminate. This formula is applied to calculate the permeation flux of hydrogen through 316 stainless steel. [S0163-1829(97)06416-3]

A complete understanding of hydrogen (tritium) transport is important for characterizing materials used in the components that are directly exposed to the plasma confined in a tokamak. The analysis of hydrogen transport through plasma facing materials, therefore, has been carried out so far by many research groups. Waelbroeck *et al.* have developed a single transport parameter to describe the hydrogen permeation flux (Φ_p) focusing on gas-driven permeation (GDP).[1,2] Doyle and Brice have introduced a similar transport parameter to describe steady-state hydrogen transport in materials exposed to hydrogen plasma.[3–5] Nagasaki *et al.* have modified the formalism of Doyle and Brice.[6,7] Shu *et al.* have developed coupled parameters to distinguish the regimes of plasma-driven permeation (PDP).[8,9] Those models have mostly focused on distinguishing the specific regimes for one layer membrane.[1–9] However, it is crucial to determine Φ_p from bulk properties and surface characteristics of materials as well as the experimental conditions.

Hydrogen permeation consists of both surface process and bulk process. The driving force for diffusion in the bulk has usually been considered to be the hydrogen concentration gradient. This idea, however, will encounter two difficulties when it is extended to permeation through a laminate. First, hydrogen concentration in a laminate is not a continuous function of membrane depth because the concentration at the interface is discontinuous. Second, the surface recombination cannot be described by a concentration gradient alone because the recombination rate is generally proportional to the square of hydrogen concentration.

Therefore, alternative parameters, namely the permeation potential and permeation resistance, have been developed to resolve the two problems mentioned above. The gradient of the permeation potential against permeation resistance is considered to be the general driving force of permeation. Details of the analog approach have been described elsewhere.[10] There, the following quantities are defined and related: permeation resistances per unit area to diffusion on the front and back sides δ_f and δ_b and to recombination on both sides ρ_f and ρ_b and permeation potentials at the front and back boundaries of the jth ($j=1,2,\ldots,n$) lamina μ_{jf} and μ_{jb} and those at the vacuum-membrane (upstream) and membrane-vacuum (downstream) interfaces $\mu_{V\text{-}M}$ and $\mu_{M\text{-}V}$ as

$$\delta_f \equiv \frac{r}{D_f S_f}, \quad \delta_b \equiv \sum_{j=1}^{n} \frac{L_j}{D_j S_j}, \quad \rho_f \equiv \frac{1}{S_f\sqrt{k_f \Phi_f}},$$

$$\rho_b \equiv \frac{1}{S_b\sqrt{k_b \Phi_b}}, \tag{1}$$

$$\mu_{jf} = \frac{C_{jf}}{S_j}, \quad \mu_{jb} = \frac{C_{jb}}{S_j}, \quad \mu_{V\text{-}M} = \sqrt{P}, \quad \mu_{M\text{-}V} = 0, \tag{2}$$

where r is the implanted range; L_j, D_j, and S_j are the thickness, diffusion coefficient, and solubility coefficient for the jth lamina, respectively; k_f and k_b are recombination coefficients on the front and back sides; S_f and S_b are solubility coefficients in the implanted layer and final lamina; D_f is diffusion coefficient in the implanted layer; Φ_f and Φ_b are fluxes through the front and back surfaces; C_{jf} and C_{jb} are concentrations of hydrogen at the front and back boundaries in the jth lamina; and P is the hydrogen pressure at the upstream chamber. The hydrogen pressure at the downstream chamber has been supposed to be zero.

It has also been assumed in Eqs. (1) and (2) that hydrogen dissolves in materials as atoms and the solubility of hydrogen at constant temperature is proportional to the square root of the hydrogen pressure. As shown in Eq. (1), the permeation resistances for recombination decrease with an increase

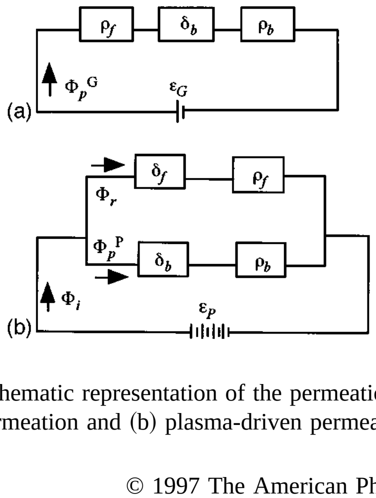

FIG. 1. Schematic representation of the permeation circuits: (a) gas-driven permeation and (b) plasma-driven permeation.

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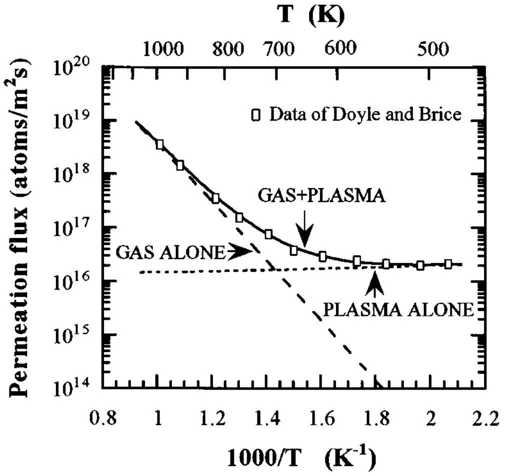

FIG. 2. Comparison between calculated and experimental results of permeation flux for 316 stainless steel.

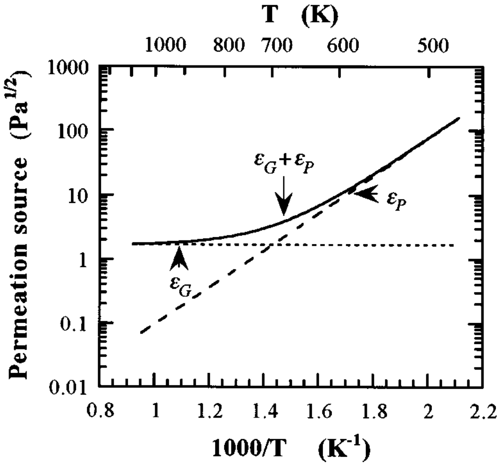

FIG. 3. Temperature dependences of permeation sources for 316 stainless steel.

in fluxes through them, while the permeation resistances for diffusion are independent of the fluxes.

With these definitions and relations, the permeation potential can be seen to be a continuous function of the permeation resistance from upstream vacuum-membrane interface to membrane-downstream vacuum interface of a laminate (for instance, $\mu_{2f}=\mu_{1b}$). This approach, therefore, allows a derivation of the general expression of permeation flux in simultaneous gas- and plasma-driven permeation. It leads to a quantitative analysis of the contributions of GDP and PDP in simultaneous gas- and plasma-driven permeation and a further examination of the dependencies of permeation flux on various parameters.

The permeation circuits of gas- and plasma-driven permeations in steady states are schematically shown in Figs. 1(a) and 1(b), respectively. The circuit of GDP is considered to be a series connection of ρ_f, δ_b, and ρ_b. In the series circuit, Φ_p^G (the permeation flux of gas-driven permeation), starting at the front surface, goes through ρ_f, δ_b, and ρ_b into the downstream chamber. The permeation source in GDP, ϵ_G, is given by

$$\epsilon_G=\mu_{V\text{-}M}-\mu_{M\text{-}V}=\sqrt{P}. \tag{3}$$

In PDP, the incident flux Φ_i, diverges at the implanted range into Φ_r (recycling flux) and Φ_p^P (permeation flux of plasma-driven permeation). Φ_r, starting at the implanted range (corresponding to μ_r), flows through δ_f and ρ_f to the upstream vacuum (corresponding to $\mu_{V\text{-}M}$). On the other hand, Φ_p^P, starting at the implanted range (corresponding to μ_r), goes through δ_b and ρ_b into the downstream vacuum (corresponding to $\mu_{M\text{-}V}$). Therefore, the PDP circuit can be considered to be a parallel connection of the resistors on the front side $(\delta_f+\rho_f)$ and those on the back side $(\delta_b+\rho_b)$ on the basis of the same permeation potential at the implanted range (μ_r) for both branches and those at the front and back surfaces $(\mu_{V\text{-}M}=\mu_{M\text{-}V}=0$, neglecting the hydrogen pressure in the upstream chamber).

On the assumption that $\delta_f+\rho_f\ll\delta_b+\rho_b$ (this is valid for almost all cases because the implanted range is much smaller than the membrane thickness and because the recombination coefficient on the front side is much larger than that on the back side), the permeation source in PDP, ϵ_P, is given as

$$\epsilon_P=(\delta_f+\rho_f)\Phi_j=r\Phi_i/(D_fS_f)+\sqrt{\Phi_i}/(S_f\sqrt{k_f}). \tag{4}$$

It should be observed that the permeation source in PDP is a function of material properties and material-plasma parameters on the front side besides the incident flux, whereas the permeation source in GDP is dependent only on gas pressure.

According to the principle of superposition, the permeation flux in simultaneous gas- and plasma-driven permeation Φ_p is given by

$$\Phi_p=\Phi_p^G+\Phi_p^P. \tag{5}$$

Considering that $\delta_f+\rho_f\ll\delta_b+\rho_b$, Φ_p is given as

$$\Phi_p=\frac{\epsilon_G+\epsilon_P}{\delta_b+\rho_p}=\frac{\sqrt{P}+\delta_f\Phi_i+\sqrt{\Phi_i}/(S_f\sqrt{k_f})}{\delta_b+1/(S_b\sqrt{k_b\Phi_p})}. \tag{6}$$

Therefore, the permeation flux in simultaneous plasma- and gas-driven permeation is obtained as

$$\Phi_p=\frac{4[\sqrt{P}+r\Phi_i/(D_fS_f)+\sqrt{\Phi_i}/(S_f\sqrt{k_f})]^2}{[1/(S_b\sqrt{k_b})+\sqrt{1/(S_b^2k_b)+4[\sqrt{P}+r\Phi_i/(D_fS_f)+\sqrt{\Phi_i}/(S_f\sqrt{k_f})]\Sigma_{j=1}^{n}L_j/(D_jS_j)}]^2}. \tag{7}$$

Thus, the permeation in simultaneous GDP and PDP through a laminate is easily calculable for given material properties such as diffusion coefficients and solubility coefficients and the experimental conditions such as pressure, incident flux, and the thickness of each lamina, as well as material-plasma parameters such as implanted range and the recombination coefficient on the front side. This equation also can be used to examine the dependences of permeation flux upon the material properties and the experimental parameters. Waelbroeck *et al.*[1] and Brice and Doyle[5] have also modeled the simultaneous GDP and PDP. In the model of Waelbroeck *et al.*,[1] however, the implanted range and multiple layers have not been taken into account and the permeation flux has been given by an implicit function of a dimensionless permeation number. On the other hand, in the model of Brice and Doyle,[5] the permeation flux has been given by an explicit expression, but the multiple layers and the effects of solubility coefficients on the permeation flux have not been considered.

From Eq. (7), the relative contribution of GDP and PDP in simultaneous gas- and plasma-driven permeation is examined as follows. (i) When the permeation source in GDP is much larger than that in PDP, i.e., $\sqrt{P} \gg r\Phi_i/(D_f S_f) + \sqrt{\Phi_i}/(S_f \sqrt{k_f})$, the permeation is simplified to GDP and Φ_p in Eq. (7) becomes

$$\Phi_p = \frac{4P}{\left(1/(S_b\sqrt{k_b}) + \sqrt{1/(S_b^2 k_b) + 4\sqrt{P}\sum_{j=1}^{n} L_j/(D_j S_j)}\right)^2}. \tag{8}$$

(ii) When the permeation source in GDP is much smaller than that in PDP, i.e., $\sqrt{P} \ll r\Phi_i/(D_f S_f) + \sqrt{\Phi_i}/(S_f\sqrt{k_f})$, the permeation is controlled by PDP; Eq. (7) is simplified to

$$\Phi_p = \frac{4[r\Phi_i/(D_f S_f) + \sqrt{\Phi_i}/(S_f\sqrt{k_f})]^2}{\left(1/(S_b\sqrt{k_b}) + \sqrt{1/(S_b^2 k_b) + 4[r\Phi_i/(D_f S_f) + \sqrt{\Phi_i}/(S_f\sqrt{k_f})]\sum_{j=1}^{n} L_j/(D_j S_j)}\right)^2}. \tag{9}$$

Figure 2 shows an application of the general formula to the permeation flux of hydrogen through 316 stainless steel. The open squares in this figure are the experimental results of Doyle and Brice under the conditions of $P = 2.8$ Pa, $L = 4\times 10^{-6}$ m, $r = 4\times 10^{-8}$ m, and $\Phi_i = 3.1\times 10^{19}$ atoms/m^2 s.[11] The curves for ''GAS+PLASMA,'' ''GAS ALONE,'' and ''PLASMA ALONE'' are calculated with Eqs. (7), (8), and (9), respectively. In the calculations, the diffusion and solubility coefficients are taken from Louthan and Derrick[12] and the recombination coefficients on both sides are cited from Doyle and Brice.[11]

It can be seen in Fig. 2 that the formula for simultaneous plasma- and gas-driven permeation [Eq. (7)] agrees very well with the experimental results. Both the results calculated for ''GAS ALONE'' [Eq. (8)] and ''PLASMA ALONE'' [Eq. (9)] approximately follow two straight lines on this Arrhenius plot. As temperature increases, the former increases rapidly, whereas the latter decreases gradually. Below 500 K, plasma-driven permeation dominates the permeation flux. In other words, Eq. (9) is the asymptotic solution of Eq. (7) for low temperatures. Above 1000 K, on the other hand, plasma-driven permeation can be neglected, and Eq. (8) is the asymptotic solution of Eq. (7) for high temperatures.

The asymptotes can be explained by the temperature dependences of permeation sources shown in Fig. 3. The permeation source in GDP, ϵ_G, is independent of temperature [Eq. (3)]. On the other hand, the permeation source in PDP, ϵ_P, decreases with the increasing temperature [Eq. (4)]. The total permeation source in simultaneous gas- and plasma-driven permeation, $\epsilon_G + \epsilon_P$, approaches ϵ_P at the temperatures lower than 500 K and ϵ_G at the temperatures higher than 1000 K.

In conclusion, the gradient of permeation potential against permeation resistance is considered to be a general driving force for permeation through a laminate. The general expression of Φ_p for simultaneous gas- and plasma-driven permeation in a steady state gives a simple way to examine the dependences of permeation flux upon hydrogen pressure, incident flux, sample size, implanted range, recombination coefficients, diffusion, and solubility coefficients on both sides. GDP and PDP are distinguished by comparing the permeation sources ϵ_G and ϵ_P. When $\epsilon_G \gg \epsilon_P$, gas-driven permeation dominates the permeation. On the other hand, if $\epsilon_G \ll \epsilon_P$, plasma-driven permeation predominates over gas-driven permeation.

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