Measurements of Permeation of Hydrogen Isotopes through \( \alpha \)-Iron by Pressure Modulation and Ion Bombarding*

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Permeation response of hydrogen and deuterium through \( \alpha \)-iron under the condition of pressure modulation was measured to determine the diffusion coefficient which contained no surface effects. The diffusion coefficients of hydrogen isotopes are obtained between 500 and 1000 K.

Permeation under hydrogen ion bombardment was also studied to extend the temperature range of diffusion coefficient measurements.

The ratio of the diffusion coefficients of hydrogen isotopes (\( D_H/D_D \)) depends on the temperature; the value of the ratio approaches unity with increasing temperature. This behavior differs from that of common fcc metals in which the value of the ratio approaches \( \sqrt{2} \) with increasing temperature. The isotope effect of hydrogen diffusivity in \( \alpha \)-iron cannot be explained by the classical rate theory, and the quantum-mechanical correction is needed.

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1. Introduction

Many studies have been done for the measurement of diffusion coefficient of hydrogen in iron. The isotope effect of hydrogen diffusion has also been studied in the vicinity of room temperature\(^{(1)-(3)}\) and at higher temperatures\(^{(4)-(5)}\). However, any consistent result has not been obtained. For bcc metals such as Nb, V and Ta, the study\(^{(6)-(10)}\) of the isotope effect of hydrogen diffusion is performed only at lower temperatures from 140 to 600 K. On the other hand, for fcc metals such as Ni, Pd and Cu\(^{(11)-(14)}\), the isotope effect is measured up to nearly 1000 K. In order to reasonably explain the isotope effect of diffusion, data in a broad temperature range are needed. To obtain the diffusion coefficients of hydrogen in metals by a permeation method, a sufficient consideration should be paid for the elimination of the influence of surface impedance on entering and releasing of hydrogen. The authors have already shown the method to obtain the diffusion coefficients without the influence of surface effect by the analysis of hydrogen permeation response under the oscillating pressure conditions\(^{(15)}\).

The method has also been applied to the measurement of diffusivity of hydrogen in nickel\(^{(16)}\).

The purpose of this paper is to obtain the diffusion coefficients of hydrogen and deuterium in \( \alpha \)-iron at high temperatures by two kinds of hydrogen gas permeation, a pressure modulation method and an ion bombardment method, and to consider the isotope effect of diffusion.

II. Experimental Apparatus and Procedure

1. Specimen

Iron specimens used were prepared from three times zone-refined Johnson-Matthey iron. They were rolled to 0.3–0.6 mm in thickness, and formed into thin discs 28 mm in diameter.

After the mechanical and chemical polishing, the specimens were annealed for 28.8 ks at 973 K in pure hydrogen atmosphere.
2. Experimental apparatus and procedures

The specimen was mounted on a permeation apparatus shown in Fig. 1. In order to remove the strain, which was introduced on mounting, the specimen was annealed for 21.6 ks at 973 K in the permeation apparatus in vacuum. Hydrogen gas used was purified by permeation through a Pd film. The diffusion coefficients of hydrogen were measured by the pressure modulation permeation method and the permeation method under hydrogen ion bombardment.

(1) Permeation by the pressure modulation

The hydrogen pressure on the entry side was controlled oscillatingly with 2.0 to 8.0 kPa in mean pressure and 133 Pa in amplitude. The response of the permeation in the output chamber was measured at various frequencies of the oscillating pressure. The pressures of hydrogen in the input chamber (the entry side) and the output chamber (the release side) were measured by a semiconductor pressure transducer and a quadrupole mass spectrometer, respectively. From the pressure change in the input and the output chamber, the phase lag \( \phi \) of the pressure oscillations was measured. The frequency dependence of the phase lag was analyzed to determine the diffusion coefficient of hydrogen.

Fick's diffusion equation is solved under the boundary conditions that hydrogen concentration is nearly zero at the output surface, and that the hydrogen concentration oscillates periodically at the inlet surface. The oscillating part of the diffusion flow, \( J \), on the outlet side is derived as:\(^{16}\):

\[
J = \frac{\sqrt{2} C_0 D}{L} \frac{\alpha}{\sqrt{\sin^2 \alpha + \sinh^2 \alpha}} \sin(\omega t - \phi_d),
\]

where

\[
\phi_d = \tan^{-1} \left( \frac{\tan \alpha - \tanh \alpha}{\tan \alpha + \tanh \alpha} \right)
\]

\[
\alpha = \sqrt{\frac{\omega}{2D \cdot L}} = \sqrt{\frac{\pi f}{D \cdot L}}
\]

and \( \omega \) is the angular frequency; \( \omega = 2\pi f \).

If the measured phase lag \( \phi \) of hydrogen pressure modulation is approximated as \( \phi_d \), the value of \( \alpha \) is calculated from eq. (2). If the diffusion process is rate-determining, the linear relationship holds between \( \alpha^2 \) and \( f \): \( \alpha^2 = (\pi L^2 / D) f \). The diffusion coefficient \( D \) is determined from the slope of this linear relation. The permeabilities of hydrogen and deuterium in \( \beta \)-iron can be calculated from the stationary partial pressures of \( \text{H}_2 \) and \( \text{D}_2 \) gas measured by the mass filter.

(2) Hydrogen permeation by ion bombardment

In the measurement of hydrogen permeation under the periodic pressure modulation, at higher frequencies the amplitude of the pressure modulation in the output chamber becomes too small to enable the analysis to be made. The lower the temperature of the experiment is, the narrower in the analyzable frequency range is. The limiting temperature of the analysis of the modulation method differs depending on the metal and the specimen thickness. For the \( \beta \)-iron specimen 0.5 mm thick, the lower limit is nearly at 500 K. In order to extend the temperature range of diffusion coefficient measurement another method is required.

As an alternative of the pressure modulation permeation, a transient change in permeation rate caused by bombardment of the input chamber side of the specimen with hydrogen ions is used to analyze the diffusivity of
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hydrogen. If the hydrogen pressure in the input chamber is held constant, e.g. at $1.33 \times 10^{-2}$ Pa, hydrogen permeates through the specimen at a constant rate. On bombarding the input side of the specimen with hydrogen ions, the partial pressure of hydrogen in the output chamber increases and soon reaches a new steady state. When the ion bombardment is turned off, the additional permeation rate of hydrogen decreases gradually and comes back to the previous level. The permeation rate changes reversibly by turning-on and off of the ion bombardment, and the effect can be observed even at low temperatures. The diffusivity at lower temperatures, which can not be obtained by the pressure modulation method, can possibly be obtained from the analysis of this transient curve of permeation rate.

III. Results and Discussion

1. Permeability of hydrogen and deuterium in $\alpha$-iron

The permeation rate is measured with a mass filter as a partial pressure of mass number 2 or 4 in the output chamber. As the ionization efficiency of the mass filter is not a unity, the partial pressure is not derived directly from the ion current. So the permeation rate of hydrogen is not directly measured; a calibration is necessary for determining the permeability from the reading of ion current of the mass filter. Since the permeability of hydrogen through nickel is well established, the calibration curve is prepared from the permeation experiment with a nickel specimen. Arrhenius plots of the permeability of hydrogen and deuterium through Johnson-Matthey iron 0.49 mm thick are shown in Fig. 2. The permeability of hydrogen is higher than that of deuterium, and the logarithm of the permeability is proportional to the reciprocal temperature over all the range of temperatures examined. The permeabilities of hydrogen and deuterium in $\alpha$-iron are expressed, respectively, as:

$$P_H = 1.77 \times 10^{-5} \exp (-31.6(kJ/mol)/RT) \ mol \ H_2 \cdot m^{-1} \cdot s^{-1} \cdot MPa^{-0.5}.$$  (4)

$$P_D = 1.05 \times 10^{-5} \ exp (-32.4(kJ/mol)/RT) \ mol \ D_2 \cdot m^{-1} \cdot s^{-1} \cdot MPa^{-0.5}.$$  (5)

The temperature dependence of this result is nearly equal to the previous results$^{(9)(17)}$, but the values of the present results are nearly two thirds of the previous data. This difference will be caused from the ambiguities of the calibration curve; purity and surface cleanliness of the nickel specimen, and the accuracy of permeability data of nickel by Eichenauer and coworkers$^{(11)}$, which were used in the calibration of the mass filter.

2. Diffusivity of hydrogen and deuterium in $\alpha$-iron

The diffusion coefficients of hydrogen isotopes are measured by two permeation methods.

(1) Hydrogen permeation by pressure modulation

The experimental results of hydrogen gas permeation through Johnson-Matthey iron are shown in Fig. 3. The frequency dependence and the pressure dependence of $\alpha^2$ are examined at various temperatures. In this experiment the plot of $\alpha^2$ vs $FL^2$ shows a straight line pass-
ing through the origin. Therefore, the permeation process can be considered as diffusion controlled, and the diffusion coefficient $D$ is obtained from the slope of the straight line in $\alpha^2$ vs $fL^2$ diagram. Any change in the mean pressure has no effect on $\alpha^2$ vs $fL^2$ plots.

For the permeation of deuterium gas similar results are obtained, as shown in Fig. 4. The specimen used for deuterium permeation is the same one as used for hydrogen. The temperatures examined range from 973 to 573 K, and the mean pressure in the input chamber is 2 kPa. A linear relationship exists between $\alpha^2$ and $fL^2$. The slope for deuterium is larger than that of hydrogen; i.e., the diffusivity of deuterium is smaller than that of hydrogen.

(2) Hydrogen permeation by ion charging

When hydrogen gas in the input chamber holds a constant pressure ($=1 \times 10^{-2}$ Pa), hydrogen is released from the output side with a steady permeation rate. If hydrogen ions bombard the specimen, the permeation rate of hydrogen changes, and consequently a transient curve is obtained, as shown in Fig. 5. It is supposed that the cause of this transient change is either (a) a cleaning effect of the specimen surface by ion bombardment, or (b) the increase in absorption rate of hydrogen at the entrance surface. Though the cause of the permeation change is not clear, the phenomenon can be considered to be due to the change in the subsurface condition at the inlet side by the ion bombardment.

The permeation curve is built up on bombarding ions, and it decays on stopping the ion bombardment. From these transient curves the diffusion coefficient of hydrogen can be obtained by the same analysis as used in the ordinary hydrogen permeation. In order to obtain the diffusion coefficient from the permeation transient, a theoretical permeation rate, which is solved under certain boundary conditions, is compared with the experimental curve. The
boundary conditions considered are: (1) Hydrogen concentration at the inlet surface changes stepwise by the ion bombardment; this condition is referred to as "c=const.". (2) Hydrogen flux from the surface to the bulk changes stepwise by ion charging; this condition is referred to as "J=const.". For the decay curves, the boundary conditions are: (3) Excess hydrogen escapes only from the exit surface ("one-side decay"), and (4) the release of hydrogen takes place from both surfaces ("two-side decay"). For all cases the boundary conditions at the outlet surface are so kept that the hydrogen concentration is effectively zero.

The agreement of the experimental curve with the theoretical equation can be examined by the relationship between the parameter \( \tau (=D/L^2t) \), which is obtained from the theoretical equation, and time \( t \), which is obtained from the experimental curves. The linear dependence of \( \tau \) on \( t \) shows an agreement of the experiment with the theory. The diffusion coefficient can be obtained from the slope of this linear dependence. The analysis under the conditions, "J=const." and "one-side decay", shows a better linear relationship between \( \tau \) and \( t \). Figure 6 shows the apparent diffusion coefficients of hydrogen obtained by the four analyzing conditions of ion bombardment method. The dependence of the apparent diffusion coefficients on the ion beam energy is also shown. The values derived under the condition of "one-side decay" are the largest, and in sequence of "J=const.", "two-side decay" and "c=const.", the values of diffusion coefficient become smaller. The apparent values of diffusion coefficients depend on the beam energy, but they tend to constant values at ion energies above 2 keV. The apparent values under the conditions of "J=const." and "one-side decay" were chosen as the diffusion coefficient and are shown in Fig. 7 together with the results obtained by the pressure modulation method. The diffusion coefficients of hydrogen obtained by the two methods agree well and are expressed by a single Arrhenius equation within the experimental errors. But for deuterium the values by the ion bombardment method are smaller than the extrapolation of the results obtained by the pressure modulation method. The transient response of hydrogen permeation rate by ion charging may include some surface impedance, and the apparent diffusivity
becomes smaller. This effect may be larger for deuterium. The smallness of the change in transient response of permeation rate, which is the case with deuterium at low temperatures, will also cause a large analytical error to be included.

There is a possibility of measuring the diffusion coefficients at lower temperatures, where the pressure modulation method does not work, by the ion bombardment method. But, in order to obtain more accurate values of diffusion coefficients, detailed investigations into the surface effect are needed. Therefore, the temperature dependence of the diffusion coefficient was determined by attaching importance to the results by the pressure modulation method.

The diffusion coefficients obtained by the pressure modulation method is presented by a single Arrhenius equation even at temperatures, where Nagano(3) observed the decline of the data obtained by the time lag method of gas permeation. The delay of the response of the hydrogen concentration at the subsurface layer to the change in the hydrogen pressure in the input chamber will be negligible in the pressure oscillation response at low frequencies and for small amplitude of the modulation.

The diffusion coefficients determined in the present work are

\[
D_H = 4.43 \times 10^{-8} \exp\left( -5.31(kJ/mol)/RT \right) \quad m^2/s \quad (6)
\]

and

\[
D_D = 4.28 \times 10^{-8} \exp\left( -6.47(kJ/mol)/RT \right) \quad m^2/s. \quad (7)
\]

This result for hydrogen is very close to the diffusion coefficient represented as \(D_1\) (= \(4.0 \times 10^{-8} \exp\left( -4.53(kJ/mol)/RT \right) \) \(m^2/s\)) in a review article by Volkl and Alefeld(18).

3. **Isotope effect of diffusion**

The pre-exponential factors of the diffusion coefficients of hydrogen and deuterium show an isotope effect that \(D_{0,H}\) is slightly larger than \(D_{0,D}\) and the ratio \((D_{0,H}/D_{0,D})\) is nearly 1.04. The isotope effect in the activation energy is that \(Q_H > Q_D\) and the difference is 1.16 kJ/mol.

The ratio of the diffusion coefficients of hydrogen isotopes \((D_H/D_D)\) is obtained and the temperature dependence of the ratio is shown in Fig. 8. The data by Quick and Johnson(5) show that the ratio \(D_H/D_D\) is nearly 2 in the vicinity of room temperature and decreases with increasing temperature to reach nearly \(\sqrt{2}\) at 473 K. Kumnick and Johnson(1), and Nagano and coworkers(2)(3) also showed that the ratio decreases with increasing temperature. In the temperature range of the present experiment, the values of \(D_H/D_D\) are smaller than \(\sqrt{2}\), and the ratio also decreases with increasing temperature. This characteristic differs from the isotope effect in common fcc metals: In nickel and copper \(D_H/D_D\) approaches \(\sqrt{2}\) at high temperatures(11)-(13). On the other hand, in many cases of bcc metals it approaches a unity with increasing temperature: Many of bcc metals have a tendency to show no isotope effect in the pre-exponential factor. This can not be explained by the classical rate theory(18)-(20), which considers the motion of a particle in the periodic potential energy field. These isotope effects in the pre-exponential factors of fcc and bcc metals at high temperatures can be predicted by the quantum mechanical modification of the classical rate theory(12)(21), which assumes quantized vibrational states of diffusing atom and calculates a quantum mechanical partition function. Theories(22)(23) explaining the isotope

![Fig. 8 Ratio of diffusion coefficient of hydrogen to that of deuterium in \(\alpha\)-iron.](image)
effect at low temperatures are also proposed based on the quantum mechanics. The present experimental results are obtained at high temperatures, and the diffusion behavior of hydrogen isotopes in α-iron can be explained by the quantum mechanical modification of classical diffusion theory.

IV. Conclusion

From the measurements of permeation of hydrogen and deuterium through α-iron by the pressure modulation method, the temperature dependence of the diffusion coefficients without the influence of the surface effects is obtained;

\[ D_H = 4.43 \times 10^{-8} \exp\left(-5.31\frac{\text{kJ/mol}}{RT}\right) \text{ m}^2/\text{s} \]

and

\[ D_D = 4.28 \times 10^{-8} \exp\left(-6.47\frac{\text{kJ/mol}}{RT}\right) \text{ m}^2/\text{s} \]

The isotope effect is explained by the classical rate theory with quantum mechanical modification.

For the permeabilities of hydrogen and deuterium in α-iron the results are as follows;

\[ P_H = 1.77 \times 10^{-5} \exp\left(-31.6\frac{\text{kJ/mol}}{RT}\right) \text{ mol H}_2/\text{m}^2\cdot\text{s}^{-1}\cdot\text{MPa}^{-0.5} \]

and

\[ P_D = 1.05 \times 10^{-5} \exp\left(-32.4\frac{\text{kJ/mol}}{RT}\right) \text{ mol D}_2/\text{m}^2\cdot\text{s}^{-1}\cdot\text{MPa}^{-0.5} \]

From the build-up and decay curves of hydrogen permeation rate by ion bombardment, the diffusion coefficients can possibly be obtained at low temperatures, where the pressure modulation permeation method does not work. But, careful examination of the surface conditions is needed to derive a reliable value for the diffusion coefficient.

REFERENCES