Determination of Deuterium Diffusion Coefficient in Metals by Ion Driven Permeation Technique*

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In order to determine the deuterium diffusion coefficient in metals, we have developed a new technique, ion driven permeation in which the implantation of energetic ions is utilized instead of gaseous charging or electrochemical charging for deuterium permeation.

The time sequence of deuterium permeation rate caused by the ion implantation is generally similar to those of the other techniques. The steady state permeation rate and the diffusion coefficient, however, tend to decrease with increasing duration of implantation (or with increasing implanted fluence) because of modifications of the surface or subsurface region, or both, by the bombardment. Therefore, the diffusion coefficients determined from the initial rise of the permeation rate for a fully annealed specimen are reproducible and reliable.

The diffusion coefficient thus determined are

\[
D_{\text{Cu}} = 8.2 \times 10^{-8} \exp \left(-\frac{23.3 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}
\]

and

\[
D_{\text{Ni}} = 3.9 \times 10^{-7} \exp \left(-\frac{38.6 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}
\]

for deuterium in Cu and Ni at 500–1000 K, respectively. Both are in agreement with the literature values.

Applying this technique to Al and Mo, the deuterium diffusion coefficients are determined to be

\[
D_{\text{Al}} = 1.4 \times 10^{-6} \exp \left(-\frac{35.7 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}
\]

and

\[
D_{\text{Mo}} = 3.2 \times 10^{-6} \exp \left(-\frac{54.6 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}
\]

Since energetic deuterium is implanted directly into the bulk, the experimental value for Al seems not to be influenced by the surface oxide, whereas that for Mo is possibly influenced by defects produced by the bombardment.

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I. Introduction

Most data on hydrogen diffusion coefficients of metals at high temperatures have been determined by either the desorption or the gaseous permeation technique\(^{1(2)}\). In both techniques, hydrogen behavior in metals is often influenced by surface oxide so that the diffusion data for easily oxidized metals such as Al\(^{3(12)}\), Nb\(^{13}\), V\(^{14}\) and Mo\(^{15(21)}\) are largely scattered.

Recently, ion driven permeation\(^{22(28)}\), in which energetic hydrogen ions or atoms are directly injected into metals and permeated hydrogen from the back surface is monitored, has been applied for the understanding of hydrogen behavior in the first wall of nuclear fusion reactor. We have already reported that the ion driven permeation is basically controlled by diffusion but is also influenced by modifications of the surface or subsurface
layers, or both, due to the energetic ion bombardment\(^{(24)(25)}\).

In the present work, we have established a method to determine the diffusion coefficient by means of ion driven permeation. The experimental values for the deuterium diffusion coefficient in Cu and Ni are in very good agreement with the corresponding literature values which are less scattered than any other metals. Applying this technique, the deuterium diffusion coefficients in Al and Mo are also determined.

II. Theory

Figure 1 shows a simplified model for the concentration profile of hydrogen implanted into metal. After various collision processes, the implanted hydrogen ions are thermalized with profile of \( G(E, x) \) and then diffuse according to their concentration gradient. Then hydrogen concentration \( C(x, t) \) is given by

\[
\frac{\partial C(x, t)}{\partial t} = D \cdot \frac{\partial^2 C(x, t)}{\partial x^2} + \phi_o \cdot G(E, x),
\]

(1)

where \( D \), \( \phi_o \) and \( G(E, x) \) are the diffusion coefficient, the incident flux and the implanted profile of hydrogen with energy \( E \), respectively.

Suppose range straggling in the implanted profile is much less than specimen thickness \( d \), then, the implanted profile \( G(E, x) \) can be replaced by delta function

\[
G(E, x) = \delta(x-r)
\]

(2)

where \( r \) is the mean projected range of the implanted hydrogen.

Using the surface boundary condition given by Sievert’ law,

\[
C(0, t) = S \cdot P_1^{1/2} \approx 0
\]

(3)

and

\[
C(d, t) = S \cdot P_2^{1/2} \approx 0
\]

(4)

where \( S \) is the hydrogen solubility constant in metal and \( P_1 \) and \( P_2 \) are the residual hydrogen pressures in the front and the back side, respectively. (In the present experimental condition \( P_1 \) and \( P_2 \) are nearly equal to 0.)

Since the implanted fluence \( \phi_0 \) is balanced with the reemission rate \( J_1 \) and the permeation rate \( J_2 \) at the steady state:

\[
\phi_o = J_1 + J_2
\]

(5)

where

\[
J_1 = D \cdot \frac{\partial C(x, t=\infty)}{\partial x} \bigg|_{x=0}
\]

(6)

and

\[
J_2 = -D \cdot \frac{\partial C(x, t=\infty)}{\partial x} \bigg|_{x=d}.
\]

(7)

Then the maximum concentration \( C_0 \), and the reemission and permeation rates at the steady state are respectively given by

\[
C_0 = \phi_0 \cdot r \cdot (d-r)/D \cdot d
\]

(8)

and

\[
J_1 = \phi_0 \cdot (1-r/d),
\]

(9)

\[
J_2 = \phi_0 \cdot r/d.
\]

(10)

Following the Fourier transformation technique under the boundary conditions of eqs. (3) and (4), eq. (1) is analytically solved for the two cases:

\[
C(x, t) = \frac{2\phi_o \cdot d}{D\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \sin \frac{n \cdot \pi \cdot r}{d} \left[ 1 - \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{d^2} \right) \right] \sin \frac{n \cdot \pi \cdot x}{d}
\]

(11)

when bombardment is started at \( t=0 \) (called ‘‘injection’’ hereafter), and
after the bombardment stopped at \( t=0 \) (evolution). According to eq. (7) the hydrogen permeation rate is given by

\[
C(x, t) = \frac{2\phi_o \cdot d}{D \cdot \pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \sin \frac{n \cdot \pi \cdot r}{d} \cdot \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{d^2} \right) \cdot \sin \frac{n \cdot \pi \cdot x}{d}
\]  

(12)

for the injection and

\[
J_2(t) = \frac{2\phi_o}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \cdot \sin \frac{n \cdot \pi \cdot r}{d} \cdot \left[ 1 - \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{d^2} \right) \right]
\]  

(13)

for the evolution.

When \( r/d \) is nearly equals to 0, the \( J_2 \) is simplified as

\[
J_2(t) = \frac{D \cdot C_0}{d} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{d^2} \right) \right]
\]  

(15)

for the injection and

\[
J_2(t) = \frac{D \cdot C_0}{d} \left[ -2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{d^2} \right) \right]
\]  

(16)

for the evolution.

These two equations are the same in the time dependence as those given by hydrogen permeation in gaseous charging\(^{(29)}\).

In the present work, we have determined the diffusion coefficient using the least squares fitting to eqs. (15) and (16), instead of eqs. (13) and (14), for the observed ion driven permeation rate, since the projected range of 30 keV D\(^+\) used here is much less than the specimen thickness \( r/d \approx 10^{-3} \). In Fig. 2 are compared eqs. (13) and (14) for \( r/d = 10^{-3} \) with eqs. (15) and (16), where no significant differences are seen.

II. Experimental

Figure 3 shows the apparatus for measurements schematically. The system is divided into two parts, the ion injection side and the deuterium analyzing side, by the specimen disk. D\(^+\) ions produced in an RF ion source were accelerated up to 30 keV and injected to the specimen disk after passing through a mass analyzing magnet and an aperture (8 mm\(\phi\)).

The background pressure during bombardment in the injection side was kept less than 10\(^{-5}\) Pa. The amount of deuterium permeated through the specimen was analyzed by a quadrupole mass spectrometer in the analyzing chamber, which was evacuated and kept at a pressure less than 10\(^{-7}\) Pa by a turbo-molecular pump with an effective pumping speed of about 80 l/s for D\(_2\). Since the vacuum time constant was about 0.1 s, deuterium piling up in the analyzing chamber was neglected.
The specimen was heated using a Mo heater and the temperature, monitored by Pt-Pt13%Rh thermocouple, was controlled within ±5 K. Pure Cu, Ni, Al and Mo sheets, of which physical parameters are given in Table 1, were mechanically polished and loaded on the specimen holder without any leakage between the injection side and analyzing side. Prior to the measurements, the specimen was fully annealed at about 0.7 Tm (Tm: melting temperature) for more than 1 h in order to avoid the irradiation effect given by the prior run. When the total integrated flux exceeds 1×10²³ ions m⁻², the specimen was replaced with the new one. These procedures assured the reproducibility of the permeation data.

| Specimen | Purity (%) | Thickness (µm) | Annealing temperature (K) | Annealing time (ks) |
|----------|------------|----------------|---------------------------|-------------------|
| Cu       | 99.999     | 40, 100, 300   | 1173                      | 3.6               |
| Ni       | 99.999     | 10, 20, 50, 100| 1173                      | 3.6               |
| Al       | 99.999     | 100            | 823                       | 3.6               |
| Mo       | 99.99      | 100            | 1273                      | 7.2               |

Figure 4 shows the time sequences of the ion driven permeation rate through Cu under the D⁺ (30 keV) bombardment starting at time t=0. The permeation rate increases with time and attains the steady state, where the maximum permeation rate is inversely proportional to the specimen thickness as seen in Fig. 5. By the least squares fitting of the initial permeation increase to eq. (15) we can evaluate the diffusion coefficient. One can see a fair agreement of the experimental data with eq. (15) in Fig. 6. The diffusion coefficients thus calculated are plotted against inverse temperature with open circles in Fig. 7, which show a very good Arrhenius relationship giving

\[
D_{Cu} = 8.2 \times 10^{-8} \times \exp\left(-\frac{23.3 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1}. \quad (17)
\]

The absolute values presently determined are consistent with those given by Katz (30) and Eichenauer (31), although the activation energy is somewhat different.

As shown in the previous work (22)-(25), the permeation rate shows the "spike", that is, the permeation rate, after once attaining the maximum, decreases with the time for prolonged bombardment as seen in Fig. 8. In the course of the spike the apparent diffusion coefficient also decreases with time. In Fig. 8 are compared three diffusion coefficients determined from the injection at t=0, the evolution at
t=150 and the injection at t=180 s, respectively. One can also note that the closed circles in Fig. 7, which are corresponding to the diffusion coefficients determined from the evolution just after attainment of the maximum permeation rate, show the smaller value than the diffusion coefficient determined from the initial injection (open circles).

The cause for the reduction of the permeation rate and of the diffusion coefficient have been attributed to the modification of the surface and/or bulk by energetic ion bombardment and will be discussed in the following section. Therefore, hereafter mention will be made of the diffusion coefficients determined from the initial increase for the fully annealed specimen.

The diffusion coefficient of Ni determined by a similar procedure to the case of Cu are
in excellent agreement with the literature values\(^{(30)-(32)}\) as seen in Fig. 9. It should be noted that the present results show a very good Arrhenius relationship represented by

\[
D_{Ni} = 3.9 \times 10^{-7} \times \exp\left(-38.6 \text{ kJ mol}^{-1}/RT\right) \text{m}^2\cdot\text{s}^{-1} \quad (18)
\]
in a very wide temperature region.

Figure 10 shows the time sequence of the ion

![Figure 10](image1)

**Fig. 10** Time sequences of ion driven permeation for Al.

Driven permeation for Al, which is quite similar to those for Cu and Ni. The permeation rates show the spike and the diffusion coefficient becomes smaller with increasing fluence. The diffusion coefficient calculated from the initial increase of the permeation rate are given in Fig. 11, where the literature values

![Figure 11](image2)

**Fig. 11** Temperature dependence of diffusion coefficient of deuterium in Al determined by ion driven permeation.
are also compared. The present result shows the highest values among those determined by the permeation technique (3)-(8) and is well represented by the following Arrhenius relation:

\[ D_{Al} = 1.4 \times 10^{-6} \times \exp\left(-35.7 \text{ kJ mol}^{-1}/RT\right) \text{m}^2\cdot\text{s}^{-1}. \]  

(19)

The permeation measurements have also been carried out for Mo and the results are given in Fig. 12. The diffusion coefficient is represented by

\[ D_{Mo} = 3.2 \times 10^{-6} \times \exp\left(-54.6 \text{ kJ mol}^{-1}/RT\right) \text{m}^2\cdot\text{s}^{-1}, \]  

(20)

although the determined values are a little scattered as compared with the former three metals. Nevertheless, the present diffusion coefficients are in fair agreement with those given by Hill(16) and Caskey et al.(17).

V. Discussions

In the present work we have developed a new technique, ion driven permeation, for determination of hydrogen diffusion coefficient in metals. The diffusion coefficients of deuterium in Cu and Ni are in agreement with the literature values.

Applying this technique to Al of which the diffusion data are quite scattered, we get the highest values of diffusion coefficient among those determined by the permeation technique (3)-(8). The data scattering for Al in the earlier work has been considered to be due to the surface oxide which works as a permeation barrier. Even under the deuterium bombardment the surface oxide of Al was hardly reduced(33), so the present results could still be influenced by the surface oxide.

Suppose the existence of the surface oxide where the diffusion coefficient is one order smaller than that in the bulk, i.e., \( D_1/D_2 = 0.1 \) in Fig. 1. Equation (1) is numerically solved and compared with the solution for \( D_1 = D_2 \) in Fig. 13. One should note that the difference in time sequences of normalized permeation rate between the two cases is rather small. This means that the diffusion coefficient determined by the ion driven permeation is scarcely influenced by the surface oxide on the injection side, because the energetic hydrogen is directly implanted below the surface oxide.

Although the ion driven permeation technique is proved to give very highly reliable results, the specimen is limited to be fully annealed or to have a virgin surface to the bombardment. With increasing fluence, the ion driven permeation shows the spike which is accompanied by the reduction both in permeation rate and in apparent diffusion coefficient as seen in Figs. 8 and 10. The spike originates from modifications either the surface or the bulk, or both, due to the energetic ion bombardment, so it could be attributed to either
or all of the following three causes\(^{(24)-(28)}\): (1) enhancement of the surface release rate due to surface cleaning by chemical and/or physical sputtering, (2) enhancement of diffusion in the subsurface layers due to the radiation damage which acts as a short diffusion path, and (3) hydrogen trapping in the bulk by radiation damage.

There are differing views as to the main cause of the spike. Nevertheless, the present result that the ion driven permeation through Al whose surface is not reduced shows the spike, suggests the importance of the radiation damage in the subsurface layer and/or bulk.

Recently, Katsuta et al.\(^{(15)}\) have maintained that the literature values of activation energy for hydrogen diffusion in Mo are too large compared with those for the hydrogen diffusion in other bcc metals, and reported very large diffusion coefficients with a small activation energy as seen in Fig. 12. Yamanishi\(^{(3)}\) also gave the activation energy similar to that Katsuta but their diffusion coefficients are a little smaller than the latter. In consideration of the fact that all the diffusion coefficients determined except for Mo show the same or smaller activation energy than the earlier work, it is likely that the present data for Mo is influenced by defect trapping. This argument is also supported by the following discussions. In bcc metals, especially Fe, it is well known that hydrogen trapping reduces the apparent diffusivity drastically at low temperatures\(^{(1)(2)(29)}\). From thermal desorption measurements of implanted deuterium in Mo, Erents and McCracker\(^{(34)}\) reported a significant trapping effect for damaged Mo compared with the fully annealed one. In addition, the present annealing temperature for Mo may not be high enough as viewed from its very high melting temperature. This defect trapping might be the cause of a rather large scattering of the data in the Arrhenius relationship of the diffusion coefficients as compared with the other three metals.

VI. Conclusions

The initial increase in the ion driven permeation rate is similar to that of the gaseous permeation. The steady state permeation rate and the diffusion coefficient, however, tend to decrease with increasing implanted fluence because of modifications of the surface or subsurface region, or both, by the bombardment. Therefore, the diffusion coefficients are determined from the initial permeation rise for a fully annealed specimen.

The diffusion coefficient thus determined are

\[
D_{\text{Cu}} = 8.2 \times 10^{-8} \times \exp (-23.3 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{m}^2 \cdot \text{s}^{-1}
\]

and

\[
D_{\text{Ni}} = 3.9 \times 10^{-7} \times \exp (-38.6 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{m}^2 \cdot \text{s}^{-1}
\]

for deuterium in Cu and Ni at 500-1000 K, respectively. Both are in agreement with the literature values, and the ion driven permeation is proved to be useful for the determination of the diffusion coefficients.

Applying this technique to Al and Mo, we have obtained the deuterium diffusion coefficients as

\[
D_{\text{Al}} = 1.4 \times 10^{-6} \times \exp (-35.7 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{m}^2 \cdot \text{s}^{-1}
\]

and

\[
D_{\text{Mo}} = 3.2 \times 10^{-6} \times \exp (-54.6 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{m}^2 \cdot \text{s}^{-1}
\]

Since energetic deuterium is directly injected into the bulk, the determined value for Al seems not to be influenced by the surface oxide, whereas that for Mo is influenced by defects produced by the bombardment.

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