Effect of Carbon and Boron Additions on Deuterium Diffusion in Molybdenum

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The desorption behavior of deuterium from molybdenum, Mo-0.009-0.092%C, and Mo-0.006-0.092%B which were prepared by arc-melting in Ar+10%D2 was studied using a vacuum desorption method in the temperature range from 533 to 953 K. The diffusivity of deuterium in molybdenum was given as \( D = 1.65 \times 10^{-5} \exp \left( -\frac{60 \text{ kJ mol}^{-1}}{RT} \right) \text{ m}^2\text{s}^{-1} \). The additions of carbon and boron to molybdenum decreased the diffusivity. This decrease was considered due to the trap effect of carbide and boride. The trapping energy obtained was 54 kJ mol\(^{-1}\) for both Mo-C and Mo-B alloys.

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I. Introduction

The mechanical properties of molybdenum is known to be degraded by interstitial impurities such as oxygen and nitrogen. A lot of efforts to purify molybdenum have been made\(^{(1)-(3)}\). The arc-melting in a hydrogen atmosphere is one of the methods to obtain the purified molybdenum\(^{(1)}\). However, excessive hydrogen dissolved in molybdenum gives rise to the grain boundary embrittlement\(^{(1)}\). The addition of carbon or boron to molybdenum reduces such brittleness\(^{(4)}\). These elements are considered to act as hydrogen trapping sites in a form of solute atoms or chemical compounds and to improve the strength of grain boundaries.

The examination of hydrogen migration behavior in molybdenum is one of methods to obtain the information on the interaction between interstitial impurities and hydrogen. This paper describes the effect of carbon and boron on the deuterium diffusivity in molybdenum using a vacuum desorption technique. Since hydrogen gas coming out from the wall of the reaction chamber during the vacuum heating causes large errors in measurements of the desorption rate of the specimens, deuterium is adopted for the examination in place of hydrogen.

II. Experimental

Molybdenum powder was electron-beam(EB) melted to obtain molybdenum ingots of which the purity was higher than 99.99%. Mo-0.009-0.092%C and Mo-0.006-0.092%B alloys were prepared by arc-melting from the EB melted molybdenum and Mo\(_2\)C or MoB\(_2\) powders. The button shape ingots of 30 g were then arc-melted in a mixed gas of Ar and 10 vol\%D\(_2\) for about 30 s. The melting was conducted using a non-consumable tungsten electrode at 50 V and 300 A. The 99.99% Mo contains carbon less than 8 mass ppm, oxygen of 12 mass ppm, nitrogen of 2 mass ppm, silicon of 10 mass ppm, iron of 40 mass ppm and Al of 15 mass ppm.

The deuterium concentration in the alloys was about 4 mass ppm. The specimens for the deuterium experiment were prepared by slicing the ingots in a thickness of 0.5-3.0 mm. Figure 1 shows a schematic feature of the apparatus for measuring the deuterium desorption rates. The specimens were placed in a quartz tube which was connected with a vacuum chamber where a quadrupole mass spectrometer was installed. The chamber was evacuated through an orifice of 20 mm
diameter down to $4 \times 10^{-6}$ Pa. The pumping speed is kept constant at 100 l.s$^{-1}$. The response time for the pressure change in the vacuum range from $1 \times 10^{-7}$ to $1 \times 10^{-2}$ Pa was within 0.1 s. The signal of the mass spectrometer was periodically calibrated with a hydrogen standard leak having a flow rate of $6 \times 10^{-12}$ mol·s$^{-1}$. The sensitivity of D$_2$ signal was assumed to be proportional to that of H$_2$. The specimen holder was moved into an electric furnace which was heated up in the temperature range from 533 to 953 K beforehand. The measurement was started within 60 sec after a test temperature of the specimen was attained. The microstructure of the specimens was examined by means of optical microscopy, transmission microscopy and X-ray diffraction.

III. Results and Discussion

1. Deuterium desorption behavior of pure Mo, Mo–C and Mo–B alloys

In order to obtain the information on the deuterium diffusivity in molybdenum, it is necessary to examine precisely the desorption behaviors of deuterium from the specimens.

Figure 2 shows the deuterium desorption rate, $J$, for pure molybdenum as a function of time, $t$, at 684 K. The specimen thickness, $L$, was changed from 0.5 to 2.74 mm. The desorption rate exponentially decreased with time except at the initial stage of the desorption. It is found that the slope of the desorption rate increases with increasing thinness of the specimen.

Figure 3 represents the relation between the slope of the desorption rate, $\partial(\ln J)/\partial t$, and the thickness of specimens. As is seen in this figure, the slope is linearly increased with the inverse of the squared thickness.

On the assumption that the deuterium is uniformly distributed in the specimen at the initial stage and the concentration at the specimen surface can be ignored during the desorption, the
concentration profile in the specimen resulting from the bulk diffusion is mathematically given using Fick’s law. The concentration change with time, \( \partial C/\partial t \), in the plate during the desorption is expressed as

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},
\]

where \( D \) is a diffusion constant and \( x \) is the distance from the desorption surface. The boundary conditions are

\[
C = C_0 \quad -L/2 \leq x \leq L/2 \quad t = 0
\]

and

\[
C = 0 \quad x = \pm L/2 \quad t > 0.
\]

\( C_0 \) is an initial concentration. The solution of eq. (1) is generally given as

\[
C = \frac{4C_0}{\pi} \sum (-1)^n/(2n+1)^2 \exp \left\{ -D(2n+1)^2 \pi^2 t/L^2 \right\} \cos \left\{ (2n+1) \pi x/L \right\}.
\]

The desorption rate at the surface is then represented as

\[
J = -D \frac{\partial C}{\partial x}{x=\pm L/2}
\]

\[
= 4DC_0/L \sum (-1)^n \exp \left\{ -D(2n+1)^2 \pi^2 t/L^2 \right\}.
\]

That is,

\[
\ln J = K_d - D \pi^2 t/L^2 \quad \text{for large } t,
\]

where \( K_d \) is a constant and \( t \) the desorption time. Equation (6) gives a linear relation between \( \partial \ln J/\partial t \) and \( L^{-2} \). The data in Fig. 3 indicates that the above equation holds. The desorption rate in the present study, therefore, can be considered to be controlled by the diffusion process in the specimen and to correspond to the diffusion rate of deuterium in the molybdenum.

Figures 4 and 5 show the desorption rate of deuterium as a function of time at 740 K for Mo-0.031%C and Mo-0.006%B, respectively. The desorption rate exponentially decreases with time except at the initial stage. These desorption rates were plotted against the inverse of the squared thickness of the specimens as shown in Fig. 6. It is clearly seen that the relation of eq. (6) is satisfied also for Mo-C and Mo-B alloys. Therefore, under the present experimental condition, the diffusivity of deuterium in Mo, Mo-C and Mo-B alloys can be obtained by measuring the desorption rate.
2. Diffusivity of deuterium in pure Mo, Mo-C and Mo-B alloys

The diffusivity of deuterium in pure molybdenum ingots obtained through the above procedures were plotted as a function of the reciprocal temperature in Fig. 7. The diffusivity, $D$, is given by this Arrhenius plot as

$$D = 1.65 \times 10^{-5} \cdot \exp\left(-60 \text{ kJ} \cdot \text{mol}^{-1}/RT\right) \text{m}^2\text{s}^{-1}. \quad (7)$$

In Fig. 7, various reference data$^{(5)-(8)}$ for hydrogen isotopes are also plotted. The activation energy of the present result agrees with those by Hill$^{(5)}$ and Caskey$^{(6)}$ et al. This figure also indicates the difficulty in discussing the isotope effect on the diffusivity because of the rather scattered data.

Figures 8 and 9 represent the Arrhenius plots of the diffusivity of deuterium in Mo–C and Mo–B alloys, respectively. The dashed line in these figures is the diffusivity in the pure molybdenum. The clear dependence of the diffusivity on the carbon or boron concentration is observed. It decreases with increasing concentration. In the case of boron, the diffusivity takes a minimum at around 0.029% boron and increases again at 0.092%. The temperature dependence of the diffusivity for Mo–C and Mo–B alloys is somewhat different from that of the pure molybdenum. The deviation from the line for pure Mo is considered as due to the change in the lattice parameter caused by the alloying or the trapping effect of C and B. However, the lattice constant of the specimens measured by X-ray diffraction was $0.3147 \pm 0.00005 \text{nm}$ and no significant differences were observed between the pure molybdenum and the alloys. Therefore, the lowering of the diffusivity of deuterium is considered to be caused by the trapping.

The contribution of traps to the diffusivity is essentially expressed by Oriani model$^{(9)}$.

$$D_{\text{eff}} = D / \left[1 + K \cdot \exp\left(E_B/RT\right)\right], \quad (8)$$

where $D_{\text{eff}}$ is the effective diffusivity, $D$ the lattice diffusivity of deuterium, $K$ the ratio of the number of trapping sites to that of lattice sites, $E_B$ the binding energy. By fitting the curves in Figs. 8 and 9 to eq. (8), $K$ and $E_B$ values for
Mo-C and Mo-B alloys can be obtained. In eq. (8), \( D \) is replaced by eq. (7) for pure molybdenum. In these figures, the fitted lines with the most proper \( K \) and \( E_B \) are indicated. The trap energy and the trap number ratio for molybdenum alloys which are summarized in Table 1 are around 54 kJ·mol\(^{-1}\) and 1\(-10\)\(^{-4}\) – 1\(-10\)\(^{-3}\), respectively. The trap energy was not different between Mo-C and Mo-B alloys. The trap number ratio increased with carbon concentration, while it took a maximum at 0.029\% of boron.

Figure 10 shows optical micrographs of as-cast Mo-C and Mo-B alloys. Fine precipitates are observed in the matrix and at grain boundaries. In the case of Mo-0.092\%B, the precipitates coalesced and fine needle-like precipitates almost diminished in the matrix. Such difference in the precipitate distribution depending on the boron concentration seems to be related to the balance between the cooling time from the melting and the precipitating rate. These precipitates were identified with Mo\(_2\)C and Mo\(_2\)B by electron diffraction, respectively, for Mo-C and Mo-B alloys. The solubility of boron in molybdenum is assumed to be 0.5–15 mass ppm in the present test temperature range\(^{(10)}\). In the case of carbon, the solubility is about 0.01 mass ppm even at 1000 K\(^{(11)}\). In consideration of the large amount of boron and carbon in the present alloys, the distribution of boride and carbide in the specimens can
Fig. 10 Micrographs of Mo-C and Mo-B specimens which were arc-melted in Ar+10%D$_2$.
be regarded to hardly change during the desorption experiment. The deuterium trapping effect, therefore, appears to be related to the size and the distribution of the precipitates, as is shown in Fig. 10.

The hydrogen trapping is generally caused by the chemical affinity with the solute interstitial atoms, the elastic field of dislocation or the interfaces between the precipitates and the matrix. As for solute atoms, no data on the C–H or B–H interaction energy have been reported. In consideration of 8.7 kJ⋅mol⁻¹ (0.09 eV) of the binding energy for interstitial pairs of H–N or H–O in Nb(12) and a low solubility of C or B in molybdenum, it seems to be difficult to explain the present result by the chemical affinity of solute interstitial atoms. The interaction energy between dislocations and hydrogen is approximately 27 kJ⋅mol⁻¹ (9)(13)(14). The present value is twice as large as this value. As for the trap energy of precipitates, the reported value is only 77–96 kJ⋅mol⁻¹ for TiC(15). It is a strong interaction energy and seems difficult to be compared with the present result. As was seen in Table 1 and Fig. 10, the trap density appears to be related to the density of the fine precipitates in the matrix of Mo–C and Mo–B alloys. That is, $K$ values increase with increasing precipitate density. These results indicate that the decrease in diffusivity of deuterium for Mo–C and Mo–B alloys is considered as due to the trapping of the precipitates of Mo₂C or Mo₂B.

IV. Conclusion

The diffusivity of deuterium in molybdenum was evaluated by the desorption behavior in vacuum, and the effect of carbon and boron on the deuterium diffusion was examined. The main results are as follows:

1. Deuterium diffusivity in molybdenum in the temperature range from 533 to 953 K is given as

$$D = 1.65 \times 10^{-5} \cdot \exp (-60 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{m}^2\text{s}^{-1}.$$

2. The diffusivity of deuterium decreased with addition of carbon or boron to molybdenum. This decrease was considered as due to the trapping effect of molybdenum carbide or boride.

3. The trapping energy of both carbide and boride was obtained as 54 kJ⋅mol⁻¹ from the curve fitting.

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