Journal of Nuclear Materials 390–391 (2009) 651–654

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Ion-driven deuterium retention in high-Z metals

O.V. Ogorodnikova *

Max-Planck-Institut für Plasmaphysik, EURATOM-Association, Boltzmannstraße 2, 85748 Garching, Germany

ARTICLE INFO

PACS:
61.80.Jh

ABSTRACT

The candidate armour material must provide high temperature resistance and accommodate the operation conditions with minimal erosion and acceptable tritium retention. Refractory metals such as tungsten and molybdenum can provide these capabilities and accommodate the high energy deposition. However, a major concern is the possible tritium and helium inventories from ion implantation. The deuterium retention in polycrystalline tungsten (W) and molybdenum (Mo) has been investigated for various irradiation temperatures, incident ion energies and fluences at Garching ion beam facility by means of thermal desorption spectroscopy. Lower deuterium retention in Mo compared to W was observed at moderated temperatures. Model including the deuterium implantation, diffusion, trapping and second order of desorption was used to understand deuterium inventory and release kinetics. The mechanism of the deuterium retention in W and Mo is discussed.

1. Introduction

One of the most critical issues in the field of plasma–wall interaction is the tritium (T) retention in the plasma-facing materials. Although the main mechanism of hydrogen isotope retention in the present tokamaks is hydrogen isotope co-deposition with carbon to form the hydrocarbon films, the bulk deuterium inventory can be not negligible. If the T retention remains unacceptable high with the carbon targets, a full tungsten device could be considered in a second phase of ITER construction [1]. From this point of view, it is important to estimate the hydrogen isotope inventory in the bulk of high-Z metals, such as tungsten (W) and molybdenum (Mo) and their composites.

Molybdenum is currently used as the plasma-facing material in the Alcator C-Mod device and several limiter tokamaks such as the Frascati Tokamak Upgrade (FTU) and the Tokamak Research Institute for Applied Mechanics (TRIAM) [2]. ASDEX-Upgrade is a full-tungsten machine since 2007 [3]. Both W and Mo are candidate materials for plasma-facing applications. Both materials W and Mo are refractory metals. Both metals have high melting points, good mechanical strength, excellent sputtering resistance and low solubility for hydrogen. Tungsten has a higher melting point and higher threshold for sputtering, that makes it more resistant to transient events with high heat loads but it is brittle material that is difficult to machine into shapes required for fusion application. Mo is much more ductile and, considerably, more easily machined. One of the most important issues of Mo and W for fusion application is the tritium retention. Despite of the many studies on this topic [4–9], there are uncertainties in the interpretation of experimental data and there is still a lack in our understanding of the mechanisms of deuterium trapping in high-Z metals. In this paper, the retention of ion-implanted deuterium in W and Mo in the temperature range from 323 to 500 K is investigated. The previously developed model [8,9] is validated against experimental data for various ion energies, irradiation temperatures and fluences at Garching ion beam facility. The initial effort focuses on simulation of experimental data and on trying to better understand the behavious of implanted D in metals in order to extrapolate in ITER operation conditions.

2. Experimental procedures

High purity (99.96%) polycrystalline tungsten (PCW) and polycrystalline molybdenum (PCMo) samples produced by Plansee AG (Reutte, Austria) have dimensions of $12 \times 15 \times 0.5\ \mathrm{mm}^3$ and $12 \times 15 \times 1\ \mathrm{mm}^3$, respectively. The mean grain size observed by SEM was 20 and 40 μm in the virgin samples of Mo and W, respectively. All specimens were mechanically polished and outgased at 1273 K for 30 min in the implantation chamber with a background pressure of 10^{-6} Pa [8].

Mass-analyzed deuterium implantations were performed in the Garching high current source using D_3^+ ions with energy of $E_0 = 600$ eV, corresponding to 200 eV per deuteron, and with energy of $E_0 = 3$ keV, corresponding to 1 keV per deuteron, at normal incidence at a pressure of about 10^{-6} Pa. Irradiation by 2 keV D^+ has been done using D_2^+ ions with energy of 4 keV. The flux at the sample surface was about $2.5–5 \times 10^{19}\ \mathrm{D/m^2s}$. The retention of implanted deuterium was investigated by thermal desorption spectroscopy (TDS). The TDS experiments were performed in the

---

* Tel.: +49 89 3299 1919.
E-mail address: olga.ogorodnikova@ipp.mpg.de

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.01.181

same chamber as the implantations just about 10 min after the ion beam was switch off. The samples were annealed from room temperature up to 1273 K on a linear ramp of 7 K/s. A mass spectrometer was used to monitor the mass 2(H_2), mass 3 (HD) and mass 4 (D_2) peaks. Details can be found in Ref. [8].

3. Results and discussion

Fig. 1 shows TDS from Mo irradiated by 200 eV D^+ at room temperature as well as the fits to the data using the calculations. The model of deuterium behavior in metals includes the implantation profile, deuterium diffusion, trapping and thermal release of deuterium by recombination on the surface [10]. Diffusion of deuterium is described by the diffusion equation with ion source:

$$\partial u(x,t)/\partial t = \partial/\partial x(D\partial u/\partial x) + (1-r)I_0\varphi(x) - \partial Y/\partial t, \quad 0 < x < L, \tag{1}$$

where u is the mobile deuterium concentration, $D = D_0 \exp(-E_m/kT)$ is the diffusion coefficient and $\varphi(x)$ is the deuterium implantation profile which is taken from TRIDYN calculations [11]. Trapping of deuterium in bcc metals is described by the trapping equation:

$$\partial Y(x,t)/\partial t = (2Da/3)(u(W-Y) - (12Y/a^3)\exp(-E_b/kT)), \tag{2}$$

where a is the lattice constant, Y is the trapping concentration; W is the density of traps, and E_b is the binding energy of deuterium with a trap defined as the difference of the deuterium energy to be in a trap site and in a solution site. The trapping energy is defined as the energy to release the deuterium atom from a defect: $E_t = E_b + E_m$. The boundary conditions on the inlet ($x = 0$) and the outlet ($x = L$) sides consider deuterium desorption in molecular form and are given by the balances of fluxes [10]. The code was used to model the ion implantation, the waiting time in vacuum, and the thermal desorption. The diffusivity, D, and solubility, K_s, of hydrogen in Mo and W are given in Table 1. The recombination coefficient of hydrogen on a metal surface is defined by a sticking coefficient $s = s_0 \exp(-2E_c/kT)$ which is a function of the surface barrier E_c

$$K_r = s\mu/K_s^2, \tag{3}$$

where $\mu = 1/\sqrt{2\pi mkT}$ (m is the mass of hydrogen isotope molecule and k is Boltzmann's coefficient) and $K_s = K_{s0}\exp(-Q_s/kT)$ is solubility (Q_s is the heat of solution). The sticking coefficient for a clean surface ($E_c = 0$) can be approximately estimated as $s_0^{clean} \approx D_0 K_{s0}^2 \lambda^2/\mu$, where λ is the lattice parameter. This results in a sticking factor of about 0.7 and 0.2 for W and Mo, respectively [12]. Thus, the recombination coefficient on clean Mo and W surfaces is quite high (Fig. 2). This means that the recombination on Mo and W surfaces is fast. A presence of impurities on a metal surface increases the surface barrier E_c, and, consequently, decreases the recombination coefficient. As calculations show, an increase of E_c up to 1 eV does not change the deuterium retention in W and an increase of the surface barrier up to 0.5 eV does not significantly influence deuterium retention in Mo. It seems that the surface barrier does not significantly change the deuterium retention in the present experiments if the activation energy of chemisorption is less than the heat of solution, $E_c < Q_s$. But, certainly, an increase of Ec influences the permeation.

Table 1

Diffusivity, $D = D_0 \exp(-E_m/kT)$, and solubility, $K_s = K_{s0}\exp(-Q_s/kT)$, of hydrogen isotopes for W and Mo.

Materials	Diffusivity		Solubility	
	D_0 (m^2/s)	E_m (eV)	K_{s0} (at./m^3($\sqrt{Pa}$)$\times 10^{23}$)	Q_s (eV)
H_2/W [18]	4.1×10^{-7}	0.39	17.7	1.03
H_2/Mo [19,20]	4.8×10^{-7}	0.39	8.66	0.54

The trap energies of 1.4 ± 0.05 eV and 0.8 ± 0.05 eV were fitting parameters to give good agreement between experimental data and computer results using the solubility and diffusivity of hydrogen from literature (Table 1). The similar trapping energies, 1.45 and 0.85 eV were obtained for W [8,9]. Small amount of these traps are intrinsic and uniformly distributed over all entire thickness of Mo and W. High amount of these traps are distributed near the implantation side and grows up to saturation concentration, W_m, during implantation. The mechanism of the defect creation during low-energy implantation was proposed in [9]. The saturation density of low-energy traps of 0.85 eV is higher for Mo compared to W. The saturation density of high-energy traps of 1.45 eV is similar for both W and Mo at room temperature. The low-energy traps, 0.85 eV, were identified as dislocation sites and grain boundaries. The high-energy traps, 1.45 eV, can be D agglomeration in clusters in the form of D_2 molecules and D trapping by vacancies [8,9].

The perturbed angular correlation measurements (PAC) show that a vacancy in W can trap one or two hydrogen atoms at RT with detrapping energies of 1.55 and 1.38 eV, respectively [13] while the trap energies of 1.42 and 0.79 eV were obtained for one and two hydrogen in a vacancy in Mo [14]. These values are in a good agreement with the present trap energy of 1.4 eV (Table 2). The binding energy of hydrogen with vacancy can be roughly estimated by the following equation [15]:

$$E_b^{\text{calc}} = (Q_c + Q_s)/2, \tag{4}$$

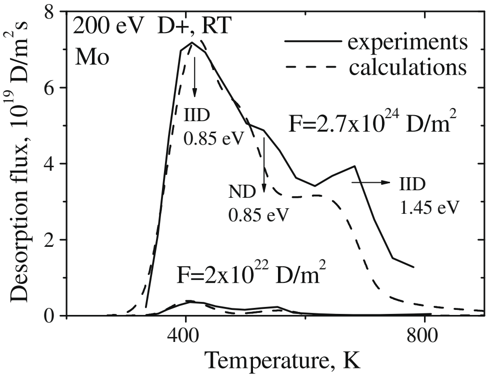

Fig. 1. Experimental thermodesorption spectra of deuterium from polycrystalline Mo irradiated with 200 eV D^+ ions at room temperature for fluence of $F = 2 \times 10^{22}$ D/m^2 and $F = 2.7 \times 10^{24}$ D/m^2. Calculations (dashed lines) are in a good agreement with experiments. IID: ion-induced defects, ND: natural defects.

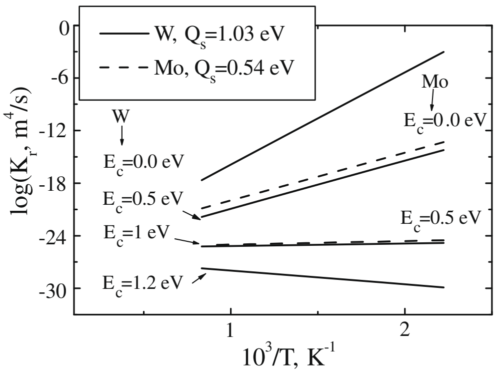

Fig. 2. Recombination coefficient on clean, E_c = 0.0 eV, and contaminated, E_c > 0 eV, W and Mo surfaces.

Table 2
Deuterium dissociation energy from vacancy. DV: deuterium atom in vacancy, D_2V: molecular deuterium in vacancy.

Material	E_t^{TDS} [present work]	E_t^{PAC} [perturbed angular correlation]	E_t^{calc}	Effective-medium theory
W	DV: 1.45 eV	DV:1.55 eV [13] D_2V: 1.38 eV [13]	1.27–1.39 eV	DV: 1.54 eV [21]
Mo	DV: 1.4 eV	DV: 1.42 eV [14] D_2V: 0.79 eV [15]	1.09 eV	DV: 1.35 eV [22] D_2V: 1.34 eV [22]

where Q_c and Q_s are the heats of chemisorption and solution, respectively. Taking $Q_c = 0.73–0.97$ eV for W [16,17] and $Q_c = 0.86$ eV for Mo [16], the detrapping energies of hydrogen from a vacancy $E_t^{cacl} = E_b^{calc} + E_m$ are presented in Table 2. One can conclude that the dissociation energy of 1.4 eV corresponds to deuterium atom or molecule trapped by a vacancy. Due to a small difference between trap energies of atom and molecule with a vacancy in W, it is not possible to distinguish these energies in the present experiment.

The first TDS peak for Mo on Fig. 1 corresponds to *D* retention in near surface ion-induced defects (IID) of 0.8 eV, the second peak corresponds to *D* retention in natural traps of 0.8 eV and the third peak is due to trapping of deuterium by near surface IID of 1.4 eV. Calculations using only natural or only ion-induced defects do not describe well fluence and energy dependences of *D* retention.

The fluence dependences of retained deuterium in W and Mo irradiated at 323 and 500 K are shown in Fig. 3. The fluence dependences of the *D* retention in polycrystalline W and Mo are practically similar at room temperature implantation within uncertainties of measurements. The *D* retention in Mo decreases with increasing of the irradiation temperature from 323 to 500 K. In contrast to recrystallized W using in previous studies [8,9], the retention of *D* in W 'as-received' does not decrease at irradiation temperature of 500 K compared to implantation at room temperature. Introduction of higher trap concentration of 1.45 eV results in a good agreement with experiments.

A comparison of the *D* retention in Mo and W irradiated by 1 keV deuterium ions at 400 K is shown in Fig. 4. The *D* retention in W by 1 keV deuterium ions irradiation at 400 K is higher compared to Mo. This confirms the mechanism of the formation of additional high-energy traps in W at moderated temperatures. Thermal desorption spectra of deuterium from Mo (Fig. 5) for 1 keV D^+ ions irradiation are perfectly described by the same fitting parameters as for 200 eV D^+ implantation in Mo (Fig. 1). The deuterium retention decreases in the first peak compared to 200 eV D^+ implantation (RT) due to increasing of irradiation temperature (400 K), but the *D* retention increases in the high-temperature peak of 1.45 eV because of deeper penetration into material and trapping by ion-induced vacancies generated within the implantation range by sufficiently energetic ions.

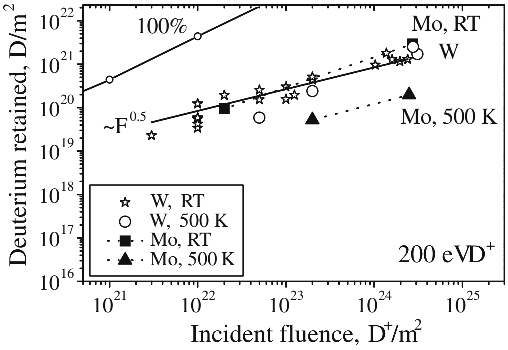

Fig. 3. Fluence dependence of retained deuterium in W and Mo irradiated with 200 eV D^+ ions at room temperature and 500 K. Lines are only to guide the eye. The reflection coefficient of 200 eV D^+ from tungsten is $r = 0.6$ and from Mo is $r = 0.53$ [11].

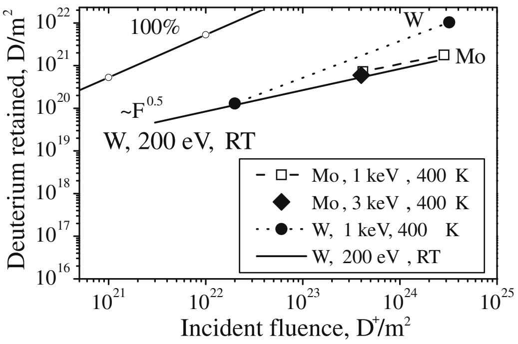

Fig. 4. Fluence dependence of retained deuterium in W and Mo irradiated with 1 keV D^+ ions at 400 K. The deuterium retention in W irradiated by 200 eV D^+ ions at RT and in Mo irradiated by 3 keV D^+ ions at 400 K is shown for comparison. Lines are only to guide the eye. The reflection coefficient of 1 keV D^+ from tungsten is $r = 0.52$ and from Mo is $r = 0.42$ [11].

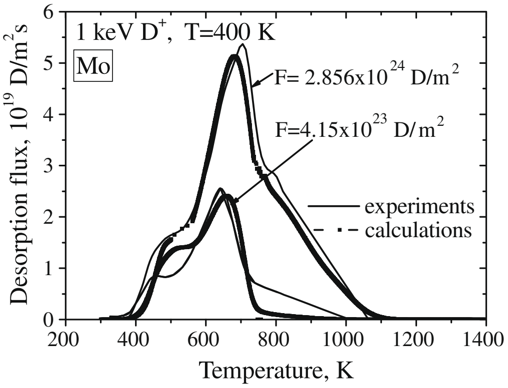

Fig. 5. Experimental thermodesorption spectra of deuterium from polycrystalline Mo irradiated with 1 keV deuterium ions at 400 K. Calculations are in a good agreement with experiments.

An increase of both temperature and ion energy significantly enhances the *D* inventory in W. However, it is necessary to note that the temperature effect is stronger than the energy effect. An increase of the *D* retention with ion energy is not linear but has a maximum or saturates at high fluences. The *D* retention in W is increased with ion energy up to 2 keV D^+ ions but decreases with 3 keV D^+ (Fig. 6). There is some ion energy threshold (probably about 2 keV for our conditions) after which the deuterium retention does not further increase. The threshold depends on fluence and irradiation temperature. To explain the lower *D* inventory in recrystallized W by energetic ions implantation compared to low-energy deuterium ions irradiation at high fluences, a stress-induced change of the diffusion coefficient near the implantation side was suggested in [9]. This model yields a good agreement with experimental data and it can describe simultaneously TDS spectra, the energy, fluence and temperature dependences of the retained *D* amount, and the deuterium depth profiles with the same set of parameters. In principal, the similar tendency is observed for polycrystalline Mo: the *D* inventory by 3 keV D^+ irradiation is similar to that one by 1 keV D^+ irradiation as shown in Fig. 4. Further experimental investigations are needed to fully understand the influence

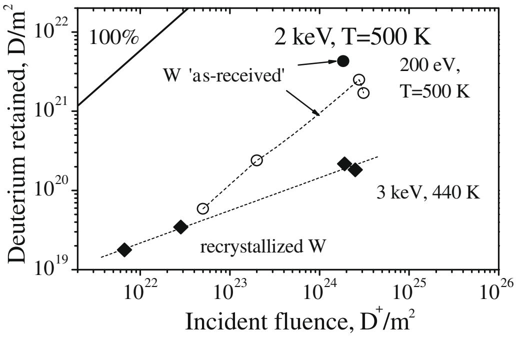

Fig. 6. Fluence dependence of retained deuterium in polycrystalline W irradiated with deuterium ions with different energies at 440–500 K. Lines are only to guide the eye.

of the stress field on the diffusion mechanism of deuterium and agglomeration in clusters in various high-Z materials for different incident ion energies and irradiation temperatures.

4. Conclusions

Ion-driven retention of deuterium in tungsten and molybdenum has been studied by means of thermal desorption spectroscopy (TDS). The fluence dependences of the *D* retention in Mo and W at RT are practically similar, whereas the irradiation temperature dependencies of the *D* inventory indicate additional high-energy trap formation in W.

Calculations based on the model including trap production, diffusion and recombination, show the presence of ion-induced and natural defects in polycrystalline W and Mo which act as trap sites for deuterium. The trap sites are similar for W and Mo because of the similarities in the structure and properties between Mo and W. Trap energies were found to be 0.85 ± 0.05 eV and 1.45 ± 0.05 eV. Both trapping sites can exist in W and Mo as intrinsic defects and as ion-induced traps. Ion-induced traps are produced in W and Mo during implantation by the stress field induced by the incident ion flux for low-energy ions and by both stress and atomic displacement damage for high-energy ions. The rate of ion-induced defect production depends on the energy of the incident ions, ion flux, target temperature and exposure time. Formation of additional high-energy traps in W at moderated temperatures is, probably, connected with vacancies movement and agglomeration. Although the vacancies are immobile at implantation temperatures of 400–500 K, the stress-induced field can initiate their movement and growth.

The increase of the *D* retention with ion energy due to deeper implantation depth and ion-induced defect production is not linear but has a maximum. The energy threshold after which the deuterium retention does not further increase depends on fluence and irradiation temperature. Further experimental and theoretical investigations are needed to create general model of *D* retention in high-Z metals to make reliable predictions for ITER and DEMO.

Acknowledgements

I would like to thank A. Weghorn for the technical assistance. This work was partly financed from the Impuls- und Vernetzungsfond der Hemholtz-Gemeinschaft e.V.

References

[1] J. Roth, E. Tsitrone, A. Loarte, Nucl. Instrum. and Meth. B 258 (2007) 253.
[2] B. Lipschultz, Y. Lin, M.L. Reinke, D. Whyte, A. Hubbard, I.H. Hutchinson, J. Irby, B. LaBombard, E.S. Marmar, K. Marr, J.L. Terry, S.M. Wolfe, the Alcator C-Mod group, Phys. Plasma 4 (2006).
[3] R. Neu, V. Bobkov, R. Dux, A. Kallenbach, Th. Pütterich, H. Greuner, O. Gruber, A. Herrmann, Ch. Hopf, K. Krieger, C.F. Maggi, H. Maier, M. Mayer, V. Rohde, K. Schmid, W. Suttrop, ASDEX Upgrade Team, J. Nucl. Mater. 363–365 (2007) 52.
[4] S. Nagata, K. Takahiro, J. Nucl. Mater. 283–287 (2000) 1038.
[5] R.A. Causey, C.L. Kunz, D.F. Cowgill, J. Nucl. Mater. 337–339 (2005) 600.
[6] G.M. Wright, D.G. Whyte, B. Lipschultz, R.P. Doerner, J.G. Kulpin, J. Nucl. Mater. (2007).
[7] M. Poon, A.A. Haasz, J.W. Davis, J. Nucl. Mater. 374 (2008) 390.
[8] O.V. Ogorodnikova, J. Roth, M. Mayer, J. Nucl. Mater. 313 (2003) 469.
[9] O.V. Ogorodnikova, J. Roth, M. Mayer, J. Appl. Phys. 103 (2008) 1.
[10] O.V. Ogorodnikova, M.A. Fuetterer, E. Serra, G. Benamati, J.-F. Salavy, G. Aiello, J. Nucl. Mater. 273 (1999) 66.
[11] W. Eckstein, Computer Simulation of Ion–solid Interaction, Springer, Berlin, 1991.
[12] O.V. Ogorodnikova, J. Nucl. Mater. 290–293 (2001) 459.
[13] J.R. Fransens, M.S. Abd El Keriem, F. Pleiter, J. Phys.: Condens. Matter 3 (1991) 9871.
[14] M.S. Abd El Keriem, D.P. van Werf, F. Pleiter, J. Phys.: Condens. Matter 5 (1993) 1801.
[15] A.E. Gorodetsky, A.P. Zakharov, V.M. Sharapov, V.Kh. Alimov, J. Nucl. Mater. 93&94 (1980) 588.
[16] I. Toyoshima, G.A. Somorjai, Catal. Rev. Sci. Eng. 19 (1) (1979) 105.
[17] T.U. Nahm, R. Gomer, Surf. Sci. 380 (1997) 434.
[18] R. Frauenfelder, J. Vac. Sci. Technol. 6 (1968) 388.
[19] W.G. Perkins, J. Vac. Sci. Technol. 10 (1973) 543.
[20] E. Fromm, E. Gebhardt (Eds.), Gase und Kohlenstoff in Metallen, Springer-Verlag, Berlin, 1976.
[21] P. Nordlander, J.K. Norskov, F. Besenbacher, J. Phys. F: Met. Phys. 16 (1986) 1161.
[22] P. Nordlander, J.K. Norskov, F. Besenbacher, S.M. Myers, Phys. Rev. B 40 (1989) 1990.