Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 337–339 (2005) 600–603
journal of nuclear materials
www.elsevier.com/locate/jnucmat

# Deuterium retention and release from molybdenum exposed to a Penning discharge

R.A. Causey *, C.L. Kunz, D.F. Cowgill

*Sandia National Laboratories, P.O. Box 969, Livermore, CA 94550, USA*

**Abstract**

Both molybdenum and tungsten are candidate materials for plasma-facing applications in fusion reactors. While tungsten has a higher melting point and a higher threshold for sputtering, it is a brittle material that is difficult to machine into shapes required for fusion applications. For this reason, molybdenum is now receiving serious consideration as an alternative for tungsten. If molybdenum is to be used as a plasma-facing material, the hydrogen retention and recycling characteristics must be known. In this report, we present experimental results on deuterium retention in molybdenum after exposure to a Penning discharge at temperatures from 573 to 773 K. $D_2^+$ ions with energies of 1.2 keV were implanted into the 50 mm diameter molybdenum samples at fluxes of $10^{20}$ D/m$^2$ s. Thermal desorption spectroscopy was used to determine both the amount of retained deuterium and the release kinetics. Low retention values similar to those measured previously for tungsten were observed.


*PACS:* 52.40.−w; 52.65.−v
*Keywords:* Molybdenum; Deuterium retention; Wall materials

## 1. Introduction

Molybdenum is one of several refractory metals being considered for use in fusion reactors. With its low erosion yield and very good thermo-physical properties, molybdenum is a candidate for divertor applications in next-step fusion devices. As a plasma facing material, molybdenum will be subject to intense fluxes of energetic deuterium and tritium ions and neutrals. This implantation process leads to concerns about tritium inventories in the molybdenum after long-term exposure to the DT plasma. The purpose of the experiments reported here was to determine the fractional retention of deuterium implanted into molybdenum at moderate temperatures. Additionally, we sought evidence of high energy trapping of deuterium in microbubbles as seen in TEM experiments by Sakamoto et al. [1].

In this paper, we report on experiments performed on the retention of deuterium in molybdenum at temperatures from 573 K to 773 K using a Penning discharge. High purity molybdenum samples were exposed to 600 eV deuterons at a flux of $1.5 \times 10^{20}$ D/m$^2$ s during 1-h exposures. The experimental results were modeled using the DIFFUSE [2] finite element computer code using accepted values for the hydrogen diffusivity and recombination rate coefficient.

* Corresponding author. Tel.: +1 925 294 3326; fax: +1 925 294 3231.
*E-mail address:* causey@ca.sandia.gov (R.A. Causey).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.10.005

## 2. Experimental procedures

The plasma used in these experiments was generated by a Penning discharge. The configuration consists of two parallel plates at equipotential that serve as cathodes. Along the rims of the plates are electrically isolated concentric shields that serve as anodes. There is a solenoidal magnetic field perpendicular to the set of electrodes (see reference [3] for a more detailed description of the system). A 25.4 mm diameter button heater electrically isolated from the biased sample by a 1 mm thick sapphire disk was used to heat the sample.

For all experiments, a discharge current density of 12.5 A/m$^2$ was used. With the ions being primarily $D_2^+$, the particle flux to the cathodes was $1.5 \times 10^{20}$ D/m$^2$ s (not including neutrals, if present). A bias voltage of 1200 V was required to maintain the Penning discharge. Again assuming primarily $D_2^+$ ions, the energy of the individual bombarding deuterons was 600 eV. The deuterium gas pressure in the system was held at 2.25 Pa and the magnetic field strength at 250 G. Each plasma exposure was conducted for 1 h. After removal from the implantation chamber, the samples were allowed to sit in room temperature air for approximately 10 days before placing them in a thermal desorption system. The samples were then elevated from room temperature up to 1373 K on a linear ramp of 1.67 K/s. A mass spectrometer was used to monitor the mass 3 (HD) and mass 4 ($D_2$) peaks.

The samples used in this study were 99.95% molybdenum from EagleAlloys. These sample were left in the "as received" condition after cutting, but were annealed in vacuum at a temperature of 1273 K for 1 h prior to plasma exposure. The disk samples were 50 mm in diameter and 2 mm thick.

## 3. Results and discussion

Before beginning a discussion of the experimental results and their interpretation, it is important to note that the retention results include only trapped deuterium. Hydrogen isotopes are mobile in molybdenum at room temperature [4], and the small amount of non-trapped deuterium remaining in the samples at the end of the plasma exposure was either released from the surface or migrated to traps by the time the thermal desorption was performed. The fractional retention of the deuterium fluence retained in the sample as a function of temperature is shown in Fig. 1, where they are compared to the lower temperature results of Wilson and Pontau [5]. In their study, Wilson and Pontau performed their experiments with TZM, an alloy of molybdenum containing 0.5% titanium and 0.1% zirconium. Their deuterium was implanted with an energy of 3.3 keV/D and a flux of $1 \times 10^{19}$ D/m$^2$ s for $10^3$ s. The new data, while having a stronger temperature dependence than the earlier results, follow the general trend of rapidly decreasing fractional retention with increasing temperature. As will be shown later, the change for the slope in the two data sets is due to an apparent change in trapping energies.

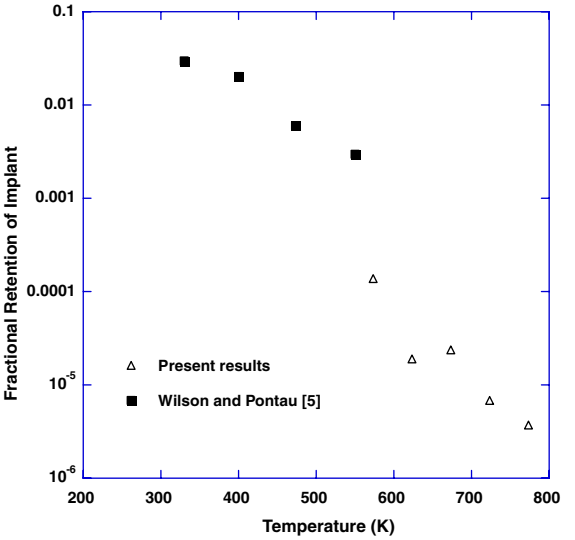


Fig. 1. Deuterium fractional retention of implanted fluence in molybdenum compared to that in TZM at lower fluxes (Wilson and Pontau [5]).

Figs. 2 and 3 show the thermal desorption spectra for the two samples implanted at 573 K and 673 K, respectively, as well as the fits to the data using the DIFFUSE code [2]. The code was used to model the plasma exposure, the waiting time in air, and the thermal desorption. The diffusivity given by Perkins [4] ($D = 4.8 \times 10^{-7}$ exp($-0.39$ eV/$kT$) m$^2$ s) was assumed for both samples. Additionally, it was assumed that the recombination rate coefficient was infinite (like that of tungsten [6]). Many researchers have examined the trapping of hydrogen isotopes in implanted molybdenum [7–10], and an energy of 1.4 eV most accurately represents a consensus of those studies. Using this set of parameters, it was not possible to duplicate either the retention or release data. The assumption of an additional trap of 2.1 eV for the 573 K sample and a 2.9 eV trap for the 673 K sample improved the fit considerably. These traps were assumed to exist only over the first 50 nm of the samples (about 2.5 times the implant range of the deuterons). Assuming both traps to extend beyond the implant zone was based on the belief that mobile vacancies would extend outside of that area. Overall, the fitting results were not strongly affected by assumptions on the density or location of the 1.4 eV traps. The trap energy of 2.1 eV and trap density of $1.5 \times 10^{-2}$ atomic fraction for the 573 K sample were fitting parameters necessary to generate even reasonable agreement between experimental results and computer

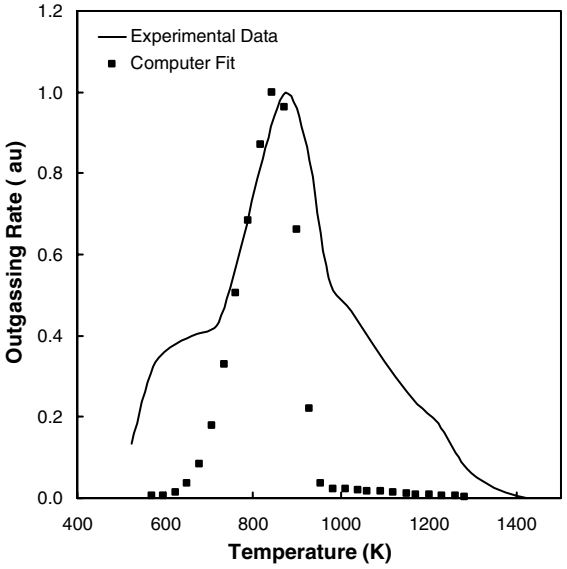


Fig. 2. Thermal desorption spectra of deuterium from molybdenum implanted at 573 K. DIFFUSE [2] results obtained used trap energies of 1.4 eV and 2.1 eV with trap densities of $3 \times 10^{-4}$ and $1.5 \times 10^{-2}$, respectively.

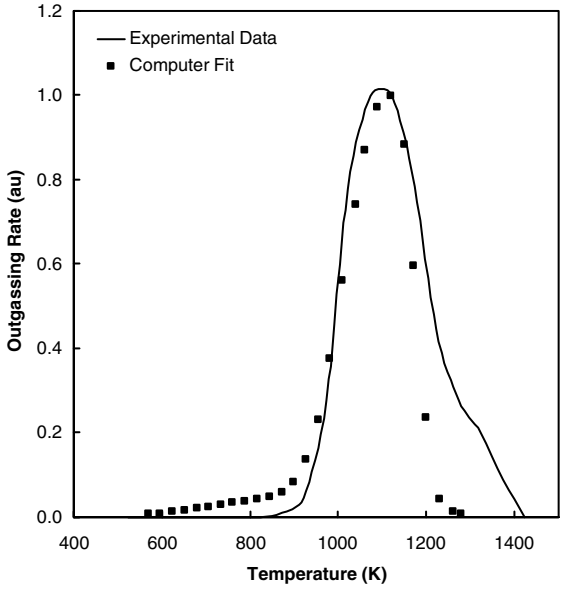


Fig. 3. Thermal desorption spectra of deuterium from molybdenum implanted at 673 K. DIFFUSE [2] results obtained using trap energies of 1.4 eV and 2.9 eV with trap densities of $3 \times 10^{-4}$ and $3.5 \times 10^{-3}$, respectively.

results. A trap energy of 2.9 eV with a trap density of $3.5 \times 10^{-3}$ were the parameters necessary for the 673 K sample. It is interesting to note that the 573 K sample released deuterium both at temperatures below and above that of the main peak. It is hypothesized that perhaps the release at temperatures below the peak is the transition away from the release controlled by the 1.4 eV trap, and the release at temperatures above the peak is the transition to the higher 2.9 eV trap seen for the 673 K sample. The samples implanted at 723 K and 773 K showed only the 2.9 eV desorption peak.

When the thermal desorption spectra of these samples are compared to earlier results [5,11–15], it is apparent that the relatively intense deuterium implantation of the samples at temperatures of 573 K and above changed the retention characteristics of the molybdenum. In materials such as molybdenum, where all of the hydrogen isotopes remaining in the samples are trapped, the temperature of release is a direct measurement of the trapping energy. Other researchers examining the release of implanted hydrogen isotopes from molybdenum have reported the isotopes being re-emitted at temperatures of 300 K up to 700 K. The differences between those studies and that reported here is either the implantation temperature or fluence. Haasz and Davis [11] performed their implantations at room temperature and reported low temperature release. Several other researchers performed their implantation at temperatures from room temperature to as high as 873 K [12–15], but in every case the flux and/or fluence were too small to permit a sufficient amount of trapped hydrogen to be seen at elevated temperatures during thermal desorption. In the experiments reported here, the retention levels were of the order of $10^{19}$ D/m$^2$, an amount that is difficult but not impossible to measure on most thermal desorption systems. A sample implanted with only 1% of this amount of deuterium would not contain a measureable amount of deuterium for laboratory-sized samples.

We are left with the task of describing what physical phenomenon could result in such high temperature trapping as well as what could shift the apparent trap energy by 0.8 eV when increasing the implant temperature by only 100 K. The first task is easier than the second. Sakamoto et al. [1] observed microbubbles in samples implanted with 4 and 8 keV protons at temperatures of 573 K and above, but no such microbubbles at lower temperatures. Based on the similarities of the implant conditions for their experiments and ours, we conclude that our samples also developed microbubbles during the implantation. We have evidence from the work of Van Veen et al. [15] that atomic hydrogen can be chemisorbed on the surfaces of voids in proton irradiated tungsten. In that case, the release of the hydrogen was effectively controlled by a 1.8–2.1 eV trap. The 0.8 eV shift in the activation energy is simply not understood. Possibilities include changes in the void size or the movement of impurities to the void wall surfaces.

While interesting effects were seen in these experiments, it is important not to overlook the primary result. The primary result is the very low retention fraction noted for all of the samples. Retention fractions of

$10^{-4}$–$10^{-6}$ as reported here will strongly limit the tritium inventory of molybdenum in next-step devices. Molybdenum used in next-step devices such as ITER would almost certainly be operated at temperatures above the 773 K maximum temperature used in these experiments. The elevated temperatures would lead to tritium retention fractions in those applications being even lower than the values measured in these experiments.

## References

[1] R. Sakamoto, T. Muroga, N. Yoshida, J. Nucl. Mater. 212–215 (1994) 1426.
[2] M.I. Baskes, SAND83-8231, 1983.
[3] W.L. Hsu, R.A. Causey, J. Vac. Sci. Technol. A 5 (1987) 2768.
[4] W.G. Perkins, J. Vac. Sci. Technol. 10 (1973) 543.
[5] K.L. Wilson, A.E. Pontau, J. Nucl. Mater. 85&86 (1979) 989.
[6] R.A. Causey, T.J. Venhaus, Phys. Scr. T 94 (2001) 9.
[7] M.S. Keriem, D.P. van der Werf, F. Pleiter, J. Phys: Condens. Matter 5 (1993) 1801.
[8] P. Nordlander, J.K. Norskov, et al., Phys. Rev. B 40 (1989) 1990.
[9] I. Takagi, S. Watanabe, et al., Fusion Sci. Technol. 41 (2002) 897.
[10] A.L. Hanson, D.H. Vincent, C.N. Davids, J. Nucl. Mater. 98 (1981) 259.
[11] A.A. Haasz, J.W. Davis, J. Nucl. Mater. 241–243 (1997) 1076.
[12] G.M. McCracken, S.K. Erents, in: S.T. Picraux (Ed.), Applications of Ion Beams to Metal, Plenum, New York, 1974, p. 585.
[13] T. Tanabe, H. Hachino, M. Takeo, J. Nucl. Mater. 176&177 (1990) 666.
[14] R. Sakamoto, T. Muroga, N. Yoshida, J. Nucl. Mater. 233–237 (1996) 776.
[15] A. Van Veen, H.A. Filius, et al., J. Nucl. Mater. 155–157 (1988) 1113.