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Deuterium retention in beryllium, molybdenum and tungsten at high fluences

A.A. Haasz *, J.W. Davis

Fusion Research Group, University of Toronto Institute for Aerospace Studies, 4925 Dufferin Street, North York, Ont., Canada M3H 5T6

Abstract

The retention of 1 keV D in room-temperature beryllium, molybdenum and tungsten has been measured as a function of fluence, for incident D_3^+ fluences ranging from 10^{21} to 10^{25} D/m^2. The amount of D retained in Be tends to saturation ($\sim 2.7 \times 10^{21}$ D/m^2) for incident fluences $> 10^{22}$ D/m^2, with an estimated saturation concentration (based on TRIM vectorized for multicomponent targets, TRVMC, range calculations) of ~ 0.39 D/Be within the implantation zone; this retention level is similar to what has been observed for single-crystal graphite, viz, $\sim 2.2 \times 10^{21}$ D/m^2 or ~ 0.4 D/C. For fluences greater than about 10^{22} D/m^2, the amount of D retained in tungsten also tends to saturation at $\sim 6 \times 10^{20}$ D/m^2. Assuming a maximum ion implantation depth of ~ 40 nm (as calculated by TRVMC), this amounts to a concentration of ~ 0.24 D/W. The amount of D retained in Mo does not appear to reach saturation over the fluence range studied. D retention in Mo is lower than that in W for incident D fluences $\lesssim 10^{25}$ D/m^2, at which point the two retention curves cross.

Keywords: High Z wall material; Low Z wall material; Desorption; Wall particle retention; Tritium inventory

1. Introduction

The latest designs for plasma-facing materials in ITER indicate that the machine will likely contain a mixture of high- and low-Z materials. Beryllium is a leading candidate for first wall cladding, and tungsten is usually considered the primary choice for any high-Z components. Interest in molybdenum is due to its use in a number of current machines, e.g. C-Mod at MIT. Tritium inventory will naturally be a major concern in ITER, and efforts are underway to predict this inventory. Measurements of D retention, especially at very high fluences are essential for such predictions.

The present experiments were undertaken with the objective to measure the amount of 1 keV D retained in polycrystalline Be (9 mm diameter by 0.13 mm thick from Brush Wellman), Mo (8×9 mm^2 by 0.1 mm thick from Johnson Matthey) and W (10×11 mm^2 by 0.025 mm thick from Rembar) foils, implanted at room temperature, for incident fluences in the range 10^{21} to 10^{25} D/m^2. Previous D-retention measurements for graphite [1] and doped graphites [2] showed the implantation zone to be saturated at a level of ~ 0.4 D/C. Depending on the nature of the graphite, any further implanted D was either completely reemitted (in the case of the single-crystal graphite [1,2]), or partially retained in polycrystalline and porous graphite due to the transport of D atoms, and subsequent trapping beyond the implantation zone [3].

The implantation energy of 1 keV was selected to simulate the depth of the implantation zone in plasma-facing materials, which will be associated with the highest energy of the incident particles, as will be the energy available for trap creation through radiation damage.

2. Experiment

The procedure for these experiments follows exactly that of our previous study on doped graphites [2]. In brief, all experiments were performed in our ultrahigh vacuum (UHV) accelerator facility, using a 3 keV D_3^+ ion beam (i.e., 1 keV/D), at normal incidence to the test specimen.

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* Corresponding author.

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In order to reduce the spatial beam flux variations, only the center part of the beam was allowed to impact on the specimen. This was achieved by clamping a pyrolytic graphite mask, with a 2 mm diameter aperture, in front of the specimen. A 0.025 mm thick strip of mica with a 3 mm aperture was inserted between the specimen and mask to allow the implanted ion current to be measured directly. In this configuration, the specimen, kept at 300 K temperature, was loaded with 3 keV D_3^+ ions to the desired fluence. The implantation flux density was $\sim 10^{20}$ D/m^2s, and thus implantation times varied from 10 s to > 20 h. For the highest fluences, the implantations were carried out over 2 or 3 days. All implantations were done on the same spot on each specimen, and surfaces were first 'prepared' by a high fluence ($> 10^{24}$ D/m^2) implantation. Thus a similar surface structure would be studied in each measurement. The implantation times were selected in random order to eliminate the possibility of a changing surface structure progressively affecting the results.

Scanning electron microscopy, SEM, was performed on the implanted surfaces; see Fig. 1. There is a clear enhancement of the grain boundaries on all three metals, but the complex surface structure usually associated with high fluence bombardment is only observed on one of the two Be specimens (Fig. 1a), and on part of the Mo specimen (Fig. 1b). As shown on Fig. 1b, adjacent regions of the D-irradiated Mo specimen had very different surface structure. Different crystal orientation is thought to be the reason for the observed differences.

For the Be specimens, the emission of secondary electrons during implantation, for fluences $\lesssim 10^{22}$ D/m^2, led to significantly higher ion current readings on the specimens, while the total current reading (mask + specimen) remained constant. This is thought to be due to a coverage of BeO, which was gradually sputtered off, but had a much higher secondary electron emission coefficient than either clean Be or carbon. This effect resulted in an estimated uncertainty of $\pm 30\%$ on the fluence measurements for fluences $< 10^{22}$ D/m^2. Ion current (i.e., D_3^+ flux) measurements were quite stable for fluences $> 10^{23}$ D/m^2.

To ensure that the mask did not interfere in the desorption stage of the experiments, the vacuum system was opened, and only the specimen was moved to a heating stage for desorption. During thermal desorption spectroscopy, TDS, the D-loaded Mo or W specimens were heated by placing them on a strip of HPG99 pyrolytic graphite (from Union Carbide) which was resistively heated to > 2100 K. Depending on the contact between the specimen and the heater, the specimens generally reached temperatures > 1900 K. The specimens were prevented from falling off the HPG99 strip during heating by a Mo clip. The temperature of the specimens could be directly measured by an optical pyrometer. Temperature ramping rates during TDS were on the order of 10 to 20 K/s. The ramping rate tended to be somewhat nonuniform and varied from run to run. This has made the evaluation of the thermal desorption spectra subject to some error, especially in the temperature range where peaks are located; however, the integrated amounts of D released are not affected. The amount of deuterium retained in the specimens was calculated by integrating the QMS signals for D_2 and HD during thermal desorption. The QMS was calibrated in situ using H_2 and D_2 calibrated leak bottles; the sensitivity to HD was assumed to be the average of the H_2 and D_2

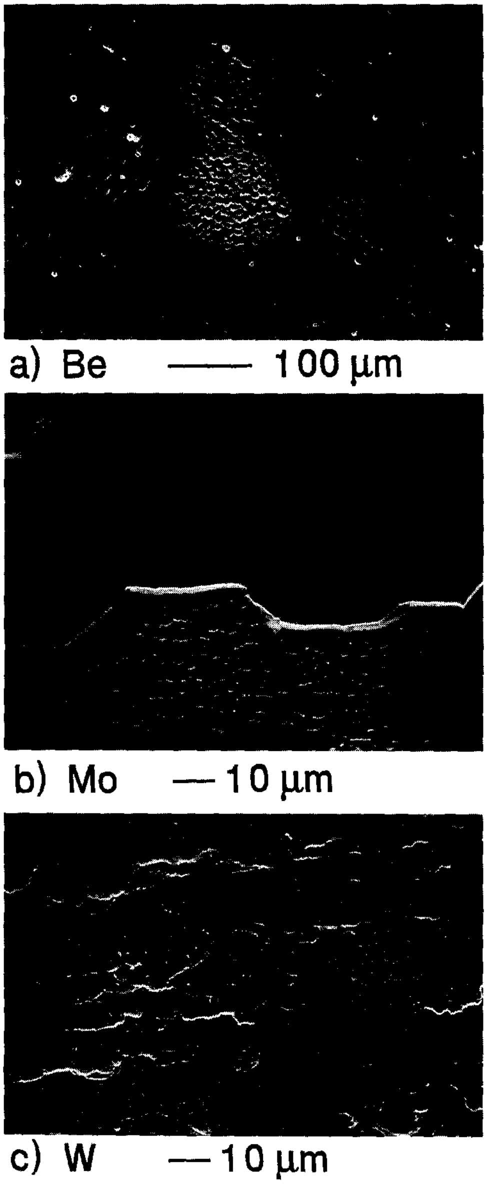

Fig. 1. SEM photographs of the D-implanted regions of the Be, Mo and W specimens. (a) Be, exposed to a cumulative fluence of $\sim 10^{25}$ D/m^2; (b) Mo, exposed to a cumulative fluence of $\sim 3 \times 10^{25}$ D/m^2; (c) W, exposed to a cumulative fluence of $\sim 3 \times 10^{25}$ D/m^2.

sensitivities. As it was sometimes difficult to be certain of the source of the HD molecules, errors are associated with inclusion of the HD signal in the amount retained. (Error bars shown on Fig. 3 are primarily based on this uncertainty.)

To avoid melting the Be specimens during TDS, the temperature of the graphite heater was kept below ~ 1400 K, and the specimens were heated to 1100–1200 K. Because of the sharp release of D from the Be specimens at ~ 500 K, it was necessary to ramp the specimen temperature more slowly; ramp rates of ~ 7 K/s were used.

3. Results and discussion

3.1. Thermal desorption spectra

The thermal desorption spectra for the three metals are shown in Fig. 2. The spectrum for Be is characterized by a sharp release of D at ~ 500 K, followed by two or more much lower level broad peaks; see Fig. 2a. Similar behavior was also reported by Wampler [4] and Möller et al. [5]. At high fluences, the relative amount of D retained in the 500 K trap is larger than at low fluences, a feature also

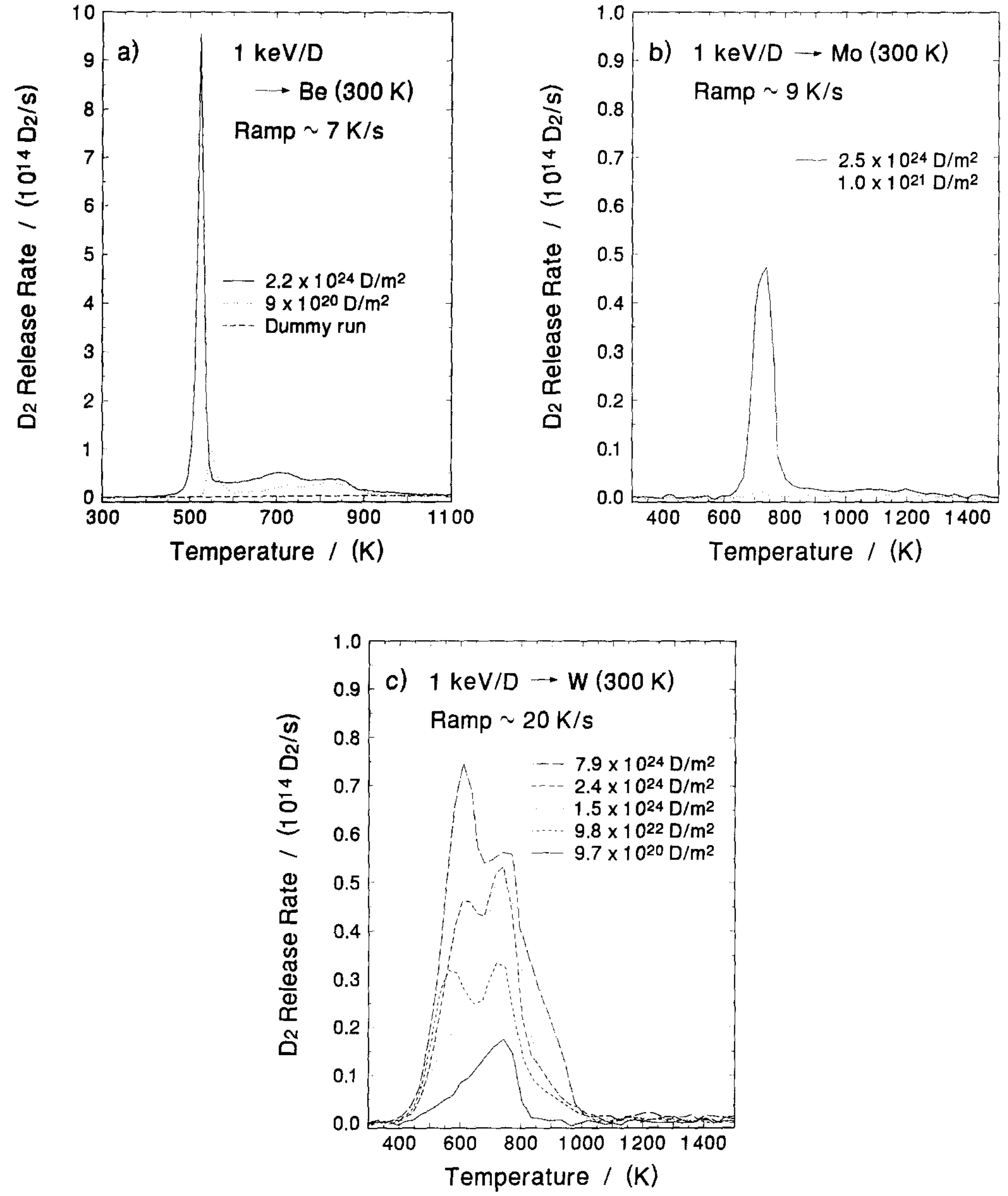

Fig. 2. Thermal desorption spectra for D_2 release following implantation with 3 keV D_3^+ (i.e., 1 keV/D) at 300 K. (a) Be; (b) Mo; (c) W. The estimated error in the temperature measurement is ~ 50 K.

observed previously [4,5]. The fact that the first desorption peak (at 500 K) is not observed for D_2 gas-loaded specimens [6] is evidence that it is the result of radiation damage traps or bubbles, while the remaining D is either in solution, or bound at preexisting trapping sites. This is consistent with high fluences being required to build up the 500 K trap concentration. It is noted that in the gas-loaded case [6], specimens were loaded at 773 K, which may be too high a temperature for the 500 K traps to operate.

For Mo, generally no structure was observed in the spectrum (Fig. 2b), somewhat similar to the measurements of McCracken and Erents [7], although our temperature is shifted by about 100 K higher. Tanabe et al. [8] observed more complex thermal desorption spectra, possibly due to their desorbing of specimens immediately upon beam-off, in order to avoid diffusive loss of retained D. Braganza et al. [9] bombarded their Mo specimen at 250 K, and found the primary desorption peak to be at ~ 300 K; an interstitial trapping mechanism was proposed. Such a peak is not observable in the present experiments due to the higher implantation temperature.

For tungsten, either one or two peaks were observed in the spectrum (Fig. 2c). In general, the second peak was found to dominate except at the highest fluences, although there were some exceptions. Franzen et al. [10] have also observed two desorption peaks at approximately the same temperatures as in the present study. In their case, the low temperature peak was associated with natural defects occurring throughout the material, while the higher temperature peak was associated with ion-induced traps created in the implantation zone.

3.2. *Deuterium retention*

The amount of deuterium retained in the metal specimens is shown in Fig. 3 as a function of incident fluence. The Be retention curve for fluences $> 10^{22}$ D/m^2 tends to saturation, with an increase of ~ 30% in retained fluence over two orders of magnitude change in incident fluence. The retained level for Be at high incident fluences ($\sim 10^{24}$ D/m^2) is $\sim 2.7 \times 10^{21}$ D/m^2; this is very similar to that obtained for single-crystal graphite, $\sim 2.2 \times 10^{21}$ D/m^2 [1,2]. This level is also similar to that obtained by Wampler [4] for 1.5 keV D^+ on Be; however, his fluence was limited to $< 10^{22}$ D/m^2, and thus, according to the present data, was below saturation. Using 'TRIM vectorized for multicomponent targets', TRVMC, the maximum penetration of 1 keV D in Be is ~ 55 nm. This leads to a saturated concentration of ~ 0.39 D/Be, somewhat higher than but in good agreement with the 0.31 ± 0.05 D/Be reported by Wampler [4]. Other recent concentration measurements, 0.3 H, D/Be at room temperature by Tsuchiya and Morita [11] and 0.35 D, T/Be at 373 K by Causey et al. [12] are also in good agreement.

As with Be, for incident fluences $> 10^{22}$ D/m^2, the W retention curve tends to saturate (~ 20% increase over 2 orders of magnitude incident fluences). The retained amount at $\sim 10^{25}$ D/m^2 is $\sim 6 \times 10^{20}$ D/m^2. We note that this level is about 4 times lower than that seen for Be and single-crystal graphite.

The retention behavior of the Mo specimen was found to differ from the Be and W cases, with the amount retained showing no signs of saturation. At an incident fluence of 10^{21} D/m^2 the relative retention levels for the

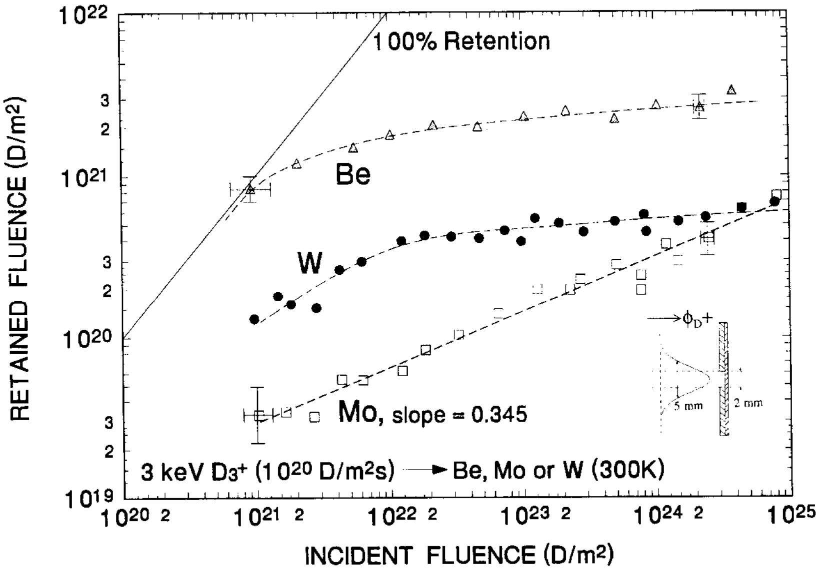

Fig. 3. TDS measurements of D retention in Be, Mo and W implanted with 3 keV D_3^+ (i.e., 1 keV/D) at 300 K, as a function of D^+ fluence. For these experiments, the beam spot size was defined by a 2 mm aperture directly in front of the specimen, resulting in a spot size of 3.1 mm^2. The lines are drawn as a guide to the eye, except the line through the Mo data which is a least squares fit.

three metals are: Mo ~ 3×10^{19} D/m^2; W ~ 1×10^{20} D/m^2; Be ~ 8×10^{20} D/m^2. While the D-retention level for Mo at 10^{21} D/m^2 is considerably lower than the corresponding level for W and Be, at a fluence of ~ 10^{25} D/m^2 the W and Mo retention levels are about equal, with the Mo curve showing an increasing trend. Using TRVMC, the maximum penetration of D in Mo and W was estimated to be about 45 nm and 40 nm, respectively. Using these values, the saturated concentration of deuterium in W and the highest measured concentration in molybdenum is estimated to be about 0.24 D/(Mo or W). Tokunaga et al. [13] compared the measured trapped D profiles in W with TRIM calculations of damage and penetration profiles and found that the trapped profiles more closely followed the calculated damage profile. Since the damage depth profile is shallower than the penetration depth profile, concentrations > 0.24 D/(Mo or W) may be indicated by the present experiments. On the other hand, Franzen et al. [10] observed a diffusion zone of up to 5 μm into W specimens under similar implantation conditions, and D atoms may be trapped at inherent (non-ion damage) traps within this zone. If this were the case in our experiments, then D-concentration values (D/metal atom) would be down by two orders of magnitude.

While the D/atom ratio of deuterium is similar in the three metals studied here and carbon (assuming all D is trapped in the implantation zone), the total amount retained in carbon and beryllium is much higher than in Mo and W due to the larger number of C or Be atoms in the implantation zone. The temperature required for the complete release of deuterium from the metal specimens was 800–900 K. This value is in excellent agreement with previous results for Be [4,5], and recent measurements on Mo [8] and W [10]. In all cases, the release temperature is significantly lower than that seen for carbon, ~ 1500 K [2].

The particle reflection coefficient of normal incident 1 keV D on Mo and W is expected to be in the range of 40–50% [14,15]. If all non-reflected D were retained in the specimens, the amounts retained at low fluences would be much higher than observed. Thus a large fraction of the incident D flux is reemitted before saturation is reached. In contrast, almost all nonreflected D is trapped in carbon [1,16] and beryllium (Ref. [4] and present results) until near-saturation conditions are reached. This may be a further indication that the generation of lattice defects/trapping sites is controlling the rate at which D is being retained in Mo and W. The reproducibility of the retention data below saturation demonstrates that the annealing which occurs during TDS is sufficient to eliminate > 95% of the traps from the Mo specimen and > 80% of the traps from the W specimen. It remains a possibility that some trapping sites in the W specimen are not annealed during TDS, leading to some of the difference observed between the retention behavior of D in Mo and W. In the Mo specimen, the rate of trap generation (as evidenced from the retained amount of D in Fig. 3) is a factor of 3–4 smaller than in W, but with a similar fluence dependence (slope). Both metals have bcc lattice structures, and the dislocation energy in Mo is smaller than in W (~ 33 eV for Mo compared to ~ 38 eV for W [17]). Also, Sakamoto et al. [18,19] found that hydrogen clusters were formed for ion energies below the threshold energy in Mo [18], but not in W [19]. These features have led Sakamoto et al. [19] to predict higher levels of retention in Mo than in W. Such behavior was observed in our present experiments, but not until fluences ~ 10^{25} D/m^2 were reached. If the rate of trap generation via lattice dislocations governs the rate of D retention, it is not clear why this rate should be lower in Mo than in W.

A diffusion-limited transport of D atoms beyond the implantation zone, followed by trapping at pre-existing (non-annealed) trapping sites as observed by Longhurst et al. [20] and Franzen et al. [10], may also be a satisfactory explanation for the observed retention behavior in Mo and W. In this case, the difference in retention behavior between Mo and W might be more closely related to the diffusion coefficients than to trapping site creation. However, the above-mentioned results by Tokunaga et al. [13] and also results by Schulz et al. [21] indicate that the trapped hydrogen is primarily in the implantation zone, at least for Mo.

The general conditions for the formation of hydrogen bubbles [22] (viz., low solubility for hydrogen, low temperature and high D fluence) are all met in these experiments. Therefore, much of the retained deuterium may be contained in bubbles, and it may be the rate of bubble formation which differs for Mo and W. The vacancy clustering mechanism for cavity growth leading to bubble formation [22] is the same in both Mo and W. This does not immediately lead to an explanation for the different retention properties of the two metals.

Future experiments varying the implantation ion energy and the specimen temperature during implantation may be very helpful in determining the mechanism for hydrogen retention in Mo and W.

4. Summary

The retention of 1 keV D in Be, Mo and W has been measured for the fluence range 10^{21} to 10^{25} D/m^2. Contrary to expectations, the amount of D retained in Mo was less than that in W until fluences ~ 10^{25} D/m^2 were reached. The amount of D retained in W tends toward saturation at ~ 6×10^{20} D/m^2, corresponding to ~ 0.24 D/W (assuming all of the D to be trapped in the implantation zone), while no such trend to saturation was observed for Mo. The amount of D retained in Be also tends to saturate at ~ 2.7×10^{21} D/m^2 (or 0.39 D/Be, again based on trapping in the implantation zone only), very similar to that retained in single-crystal graphite.

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