

Hydrogen isotope exchange in tungsten during annealing in hydrogen atmosphere

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Abstract.

The radiological safety of the future thermonuclear fusion devices depends critically on the total tritium inventory in the plasma-facing components. The planned method to remove tritium from the ITER reactor tungsten divertor is to perform vacuum baking. We show that tritium removal from tungsten can be enhanced by the isotope exchange mechanism by doing the baking in H₂ atmosphere. The results show that the retained deuterium from 30 keV implantation can be expected to drop almost to zero after 24h annealing at 250°C in H₂ atmosphere. Annealing in vacuum requires temperatures above 400°C for close to zero retention.

Keywords: isotope exchange, tritium, retention, fusion, tungsten

1. Introduction

The safety of the future thermonuclear fusion devices and experimental and demonstrative reactors like ITER and DEMO depends largely on the total tritium (T) inventory in the plasma-facing components (PFCs). Methods to reduce this inventory includes the choice of the plasma-facing material and using different tritium removal techniques. The usual T removal method is to perform thermal treatments to detrap and remove trapped tritium from intrinsic and plasma-induced traps [1]. Another method to reduce T inventory is to locally heat the surface using high-power pulsed flashlamp irradiation [2] or the pulsed laser-induced desorption [3, 4]. A method that does not need high temperatures is the use of hydrogen isotope exchange, where another hydrogen isotope is introduced in the material by low energy implantation to replace the unwanted isotope in the material [5, 6, 7]. The above-mentioned methods all have some shortcomings or disadvantages. The thermal treatment requires relatively high temperatures to remove the major fraction of the trapped T, which in ITER and other

large tokamaks is difficult due to the large component masses involved. In fact, the ITER strategy to remove and recover the trapped tritium from the plasma-facing components is to perform vacuum baking, at 240°C for the first wall and at 350°C for the tungsten (W) divertor [8]. The relatively low temperature of 350°C is shown to only remove about 40 % of the retained deuterium (D) from the JET ITER-Like W divertor during annealing for 15h [1]. Usually in the experiments the T is replaced by deuterium (D) for safety reasons. Significant laser-induced hydrogen desorption has been observed only when the sample surface temperature during the laser pulse is close to the melting point [9]. Also the removal efficiency from deeper in the component is unclear. Further, it has been shown that low energy (below displacement threshold energy) high flux hydrogen implantation creates hydrogen trapping defects in the near surface region [10, 11, 12]. Therefore, T isotope removal by isotope exchange mechanism by H irradiation might not be a viable method due to the subsequent increase of T trapping in the H induced traps [6].

In this study, we show that hydrogen isotope exchange in W also takes place during low temperature annealing in hydrogen atmosphere. Thus, T removal from W could be done at moderately low temperatures and without the need of H irradiation. At the least, the T retention after vacuum annealing in W could be further reduced by continuing the annealing in hydrogen atmosphere.

2. Experimental

2.1. Material and D implantation

The sample material is high purity (99.99%) polycrystalline W sheet (thickness of 1 mm) produced by Plansee AG (Reutte, Austria). The main impurities, excluding Mo, in the W samples are carbon $\sim 10 \mu\text{g/g}$ and oxygen $\sim 5 \mu\text{g/g}$, corresponding to about 10^{25} and 5×10^{24} atoms/ m^3 , respectively. The sheet was cut into pieces ($10 \times 10 \text{ mm}^2$) which were mirror-polished with colloidal silica (grain size of $\sim 0.05 \mu\text{m}$), giving a surface roughness of less than about 10 nm root mean square [13]. The samples were then pre-annealed in a vacuum of $\sim 10^{-5}$ Pa at 1270 K for 2h a priori implantation.

Deuterium implantation was done at room temperature using the 500 kV accelerator at the university of Helsinki. Low flux 60 keV D_2^+ ions (30 keV per D atom) were implanted perpendicular to the surface in a vacuum of $\sim 10^{-6}$ Pa. The implantation flux and dose was 3×10^{17} D/ (m^2s) and 5.8×10^{20} D/ m^2 , respectively. The beam was swept for homogeneous exposure over a 6 cm diameter implantation area, and the whole sample surface area was implanted. The sample was mounted on a large aluminium backing, which together with the very low implantation flux should not heat

the sample noticeably over room temperature.

2.2. Annealing

The D implanted samples were annealed in a quartz tube furnace in close proximity (~ 1 mm) of a K-type thermocouple. The tube was pumped to a vacuum better than 10^{-2} Pa before heating. When annealing in H_2 atmosphere was applied, the gas was let into the pre-pumped tube up to 1 atm pressure and then pumped down to 100 Pa with a membrane pump. After the H flushing procedure the pressure was slowly increased by adjusting the pumping speed to the H leak until ~ 1 atm H_2 gas pressure was attained. Continuous H gas flushing was then maintained during the whole annealing.

Prior to inserting the quartz tube into the furnace, it was preheated 10-15 K over the target temperature. The tube was then inserted into the ceramic furnace and the desired temperature was achieved in about 1000-1500 seconds. A PID controller kept the temperature at the thermocouple within ± 3 K range with respect to the target temperature. The measurement time started as the temperature reached about 3 K from the desired value. The cooling was done rapidly by extruding the tube from the oven.

2.3. Elastic recoil detection analysis

ERDA was performed using 32 MeV ^{35}Cl ions from a 5 MV tandem accelerator at University of Helsinki. Medium heavy ions were chosen to maximize yield, separation of D and H signals, and depth resolution at the surface, and to minimize irradiation-induced damage of the sample. An incident angle of $\alpha = 60^\circ$ with respect to the sample surface normal was used and recoiled H and D atoms were detected in horizontal geometry under a scattering angle of $\Theta = 50^\circ$. The ERDA detector has a nominal energy resolution of 15 keV and was located at a distance of 45 mm from the target. Detector solid angle was limited with collimator aperture of 2 mm in width and 14 mm in height. Havar stopper foil of 4 μm thickness was used for filtering of scattered ions and recoils other than H and D. The depth resolution at the surface is about 50 nm and about 150 nm at the implantation depth calculated by WDepth code [14]. Maximum probing depth for D is 450 nm with the used beam and measurement geometry. Measurement data was collected in list mode to monitor H and D desorption during measurement.

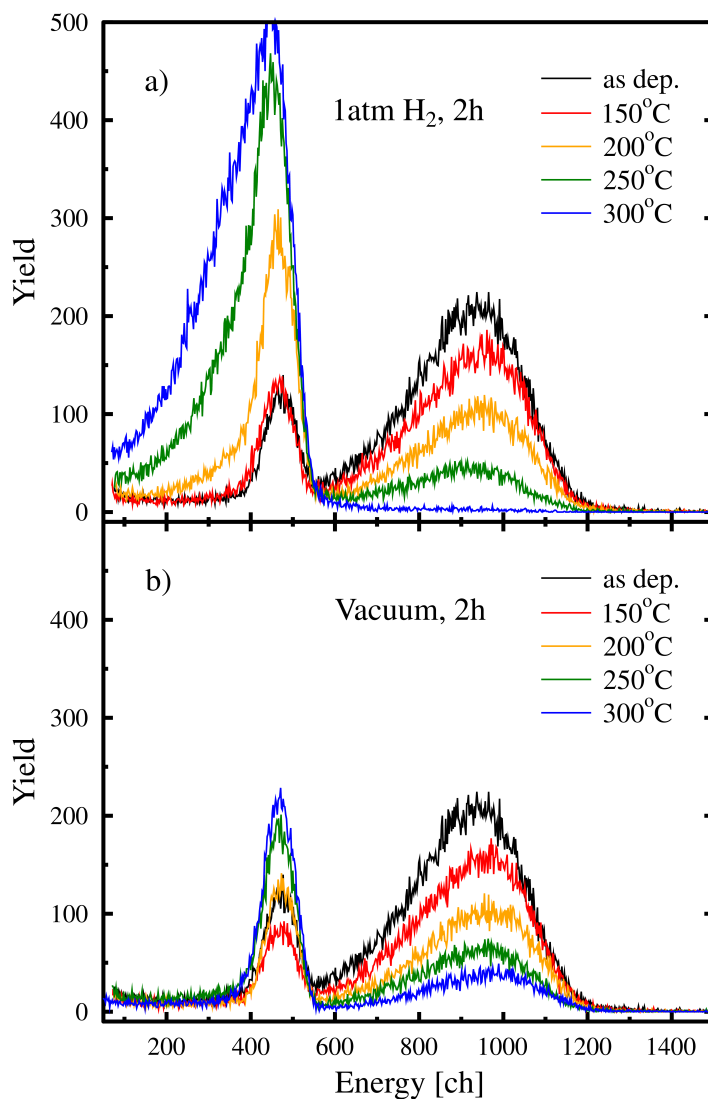


Figure 1. The ERDA spectra of the D implanted W annealed for 2h at different temperatures in either vacuum or H₂ atmosphere. The D signal is approximately between channels 500 (corresponding to a depth of ~400 nm) and 1200. The H signal is below channel ~550, with the surface H approximately between channels 400 and 550. a) annealing done in hydrogen atmosphere. b) annealing done in vacuum.

3. Results and discussion

The experimental ERDA spectra are shown in Figure 1. Figure 1 a) shows the D and H signal after 2h annealing in hydrogen atmosphere, and b) the corresponding signals

after annealing in vacuum. Each experiment was done on a different sample. We can see a decrease in the D signal for increasing annealing temperatures. Moreover, in the H_2 gas annealing we can observe an increase in the H signal in the near surface region above temperatures of 200°C . Even if the ERDA depth resolution is not good enough to resolve the surface H from the H in the bulk, the broadening and the increase of the H signal clearly indicates H diffusion into the bulk.

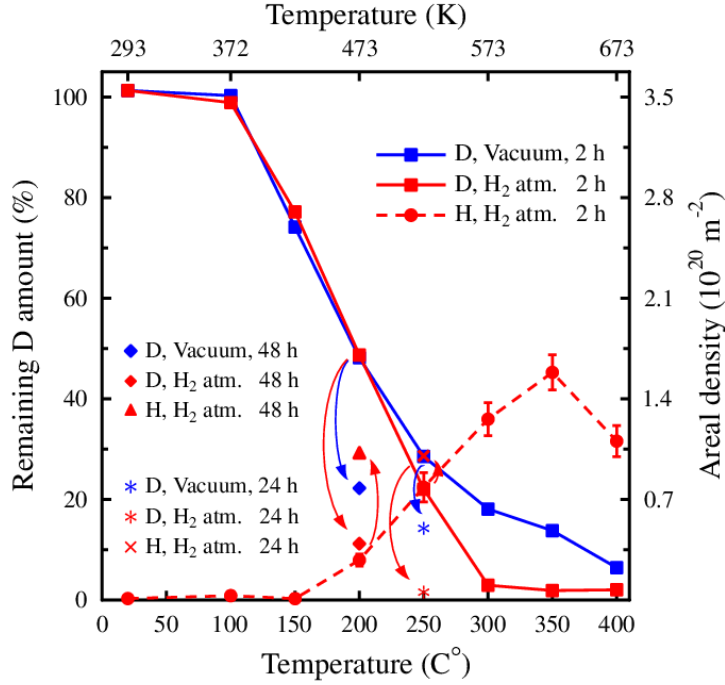


Figure 2. Remaining D and H amounts in the D-implanted depth region after annealing at different temperatures in either vacuum (blue) or H_2 atmosphere (red). The amounts are integrated from the experimental ERDA spectra between depth region from zero to about 400 nm. The surface H peak of about $0.2 \times 10^{20}/\text{m}^2$ is excluded.

Figure 2 shows the remaining integrated D amount in the samples after annealing at different temperatures in either vacuum or H_2 atmosphere. The amounts refer to the integrated signal obtained from the ERDA measurements. The approximate surface H amount, $(0.19 \pm 0.09) \times 10^{20} \text{ H}/\text{m}^2$, not included in Fig. 2, for all temperatures is due to H atoms accumulated at the W surface during the room temperature normal atmosphere storage of the samples between the annealing and the ERDA measurements. This measured surface areal concentration is surprisingly close to both the theoretical and experimental value of $\sim 0.2 \times 10^{20} \text{ H}/\text{m}^2$ for a full monolayer on the W (100) surface

[15, 16]. The errors for the D amounts are about of the size of the squares in the figure and comes from the square root of the signal areas and the small overlap of the D and H signals, see Figure 1. The errors for H amounts are considerably larger due to the overlap of the sub-surface H and H in the surface peak signals.

From the initial D fluence of 5.8×10^{20} D/m² about 10% (0.6×10^{20} D/m²) is directly reflected (backscattered) during the implantation according to SRIM-2013 simulations [17]. Hydrogen atoms are very mobile in W at room temperature with a migration barrier ~ 0.25 eV [18]. Thus, all the measured hydrogen amounts seen in Fig. 2 are hydrogen being trapped in intrinsic or implantation-induced traps. We can see that about 1.7×10^{20} D/m² (additional to reflection) is missing from the implanted D amount. The major part of this missing D corresponds to out-diffusion from the sample surface and a minor part diffusion deeper into the sample during and directly after implantation. The remaining trapped (retained) D amount (3.5×10^{20} D/m²) starts to decrease during annealing above temperature of about 100°C due to detrapping processes starting to take place as follows. D implantation in the keV/D energy range has been shown to produce mostly mono-vacancies to which D atoms trap [19]. Each mono-vacancy can trap at most five to six D atoms at room temperature, with decreasing binding energy for each additional D atom in the mono-vacancy [20, 21]. When the mono-vacancy traps five D atoms, the zero point energy corrected binding energy is about 1.0 eV which leads to D detrapping above 100°C as shown in thermal desorption spectrometry experiments [13, 22]. D detrapping will also occur from other defects with low detrapping energies, e.g., dislocations. At higher temperatures more and more D atoms detrapp from the vacancies and at 400°C only a minor fraction of the initial amount is left in the implanted region. This remaining amount includes D trapped in larger vacancy clusters mainly produced during the implantation and grain boundaries. Previous study with identical D implantation in W showed that the implantation produced mostly mono-vacancies, while the production of larger vacancy clusters was seen to decrease fast with the increasing cluster size [19].

Figure 2 shows the remaining D amounts for annealings done in either vacuum or in H₂ atmosphere. The D amounts are found to be identical for 2h annealings at low temperatures. However, at 250°C the D amount in the samples annealed in H₂ atmosphere drops rapidly below the vacuum annealing amount. In parallel, there is an increase in the trapped H amount in the implanted region. This behaviour is typical for hydrogen isotope exchange and has been observed previously during low energy plasma irradiation of W [6, 7]. Annealing at 200°C for 48h further decreases the trapped D in samples annealed in both vacuum and H₂ atmosphere. For H₂ atmosphere annealing the remaining D amount is only 10% compared to the initially retained amount. Annealing

at 250°C for 24h in H₂ atmosphere is sufficient to remove effectively all retained D. At this temperature it may be that even a shorter annealing time would be enough.

Hence, the isotope exchange and T removal can be achieved by annealing in H₂ atmosphere only, and no H irradiation is required. However, the effectiveness of the hydrogen exchange process in H₂ gas annealing compared to H irradiation procedure is very low. The reason for this can be found by looking at the H-W system. The solution energy for H atoms in the W bulk compared to H the gas phase is about 1 eV [23, 24], which is among the highest ones for H in metals. Consequently, the equilibrium solute H concentration is very low for temperatures under 1000°C. At 400°C the equilibrium H concentration in W is about 6×10^{15} H/cm³ (H/W $\sim 1 \times 10^{-7}$) [25].

The potential energy barrier from the sample surface to the bulk is about 1.6 eV [15]. Assuming this energy barrier, 10^{15} /cm² surface H coverage with a jump frequency of 10^{13} /s we get a surface to bulk atomic H flux of $\sim 10^{11}$ /(cm²s) at 200°C and $\sim 10^{14}$ /(cm²s) at 300°C. This substantial increase of the H flux at 300°C coincides with the clear drop in the D amount for 2h annealing done in H₂ atmosphere compared to vacuum annealing in Fig. 2. It is further observed that the 2h H₂ atmosphere annealing at 200°C is not long enough for any isotope exchange to take place. However, the longer 24h annealing at this temperature shows clear isotope exchange.

The isotope exchange has been simulated by Doyle *et al* [5], Barton *et al* [26] and Hodile *et al* [27]. These simulations give insight into the isotope exchange mechanism. Each isotope has a similar detrapping rate from traps which are mostly vacancies. The empty traps are then again most probably filled with the isotope with largest solute concentration around the traps. The annealing in H₂ atmosphere keeps the concentration of H in the sample constant, while the detrapped D most probably diffuses out from the sample.

Even though the isotope exchange efficiency by H₂ gas annealing is rather low, the 250°C 24h annealing removed within the experimental accuracy all the retained D. The JET ITER-Like W divertor 15h vacuum annealing [1] at 350°C removed about 40 % of the retained D. However, no comparison can be done between the present and the ITER-Like W divertor annealing due to the very different D loading conditions, and hydride and deposit formation. However, the present results show that the H₂ atmosphere gas annealing can be quite effective compared to vacuum annealing, and more research with the actual divertor material is needed.

4. Conclusions

It is shown that annealing done in hydrogen atmosphere can be a promising method to remove tritium from the plasma-facing components in the present and future thermonuclear fusion devices. The hydrogen atmosphere annealing can also be used after vacuum annealing to further reduce the wanted isotope in the material. The low H solubility can partly be compensated with a longer annealing time to increase the isotopic exchange.

The H atmosphere annealing compared to vacuum annealing clearly lowers the temperature needed to remove a substantial amount of the trapped hydrogen isotopes.

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