Tritium retention in tungsten

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1. Introduction

The retention of hydrogen isotopes (H, D and T) in the first, plasma exposed wall is one of the key concerns for the operation of future long pulse fusion devices. A large level of retention would result in a high radioactive inventory in the wall after shutdown. Also T is a precious resource and thus high retention in the first wall would degrade the fueling efficiency of a burning fusion plasma. Therefore, a candidate material for the first wall should, among other properties like a low erosion yield, retain as little hydrogen as possible. Therefore, tungsten (W) is currently the favored first wall material: It features a low sputtering yield and has a very low solubility for hydrogen [1]. However, solubility only governs the amount of interstitially dissolved solute hydrogen as function of external hydrogen gas pressure and temperature and does not include the contribution of hydrogen stored at lattice imperfections (defects or impurity atoms). For typical polycrystalline W material the amount of hydrogen retained at lattice imperfections is larger than the solute hydrogen by several orders of magnitude [2]. Therefore, while a high endothermic heat of solution is a necessary requirement for a first wall material, it alone does not determine the retained amount of hydrogen, which is really governed by the lattice imperfections that are intrinsic to the material or are generated as a result of the interaction with the fusion plasma. During plasma operation the first wall is exposed to a high flux ($\sim 10^{22}$ to $10^{24}$ (m$^{-2}$ s$^{-1}$)) of energetic (eV to keV) ions and neutrals. For burning fusion plasmas also MeV neutrons impinge on the surface at fluxes of $\sim 10^{18}$ (m$^{-2}$ s$^{-1}$). This particle bombardment leads to formation of defects: For particles with energies above the damage threshold energy [3, 4], kinetic displacement damage occurs. For particle below the damage threshold, defects are created by the oversaturation of the surface with hydrogen by the intense ion influx [5]. The defects generated by ions or fast neutrals are usually limited to the near surface region (\~\mu m) and, therefore, their amount is usually small compared to the intrinsic defects distributed throughout the entire bulk of the material. But they can influence the diffusive transport of hydrogen into the bulk thus affecting the uptake and therefore retention of hydrogen (see section 4.2). This is different for the neutron bombardment from burning fusion plasmas: The neutrons lead to displacement damage throughout the entire bulk and can thus increase the total amount of traps by orders of magnitude (see section 4.1). The number of lattice imperfections just defines potential trapping sites, but their contribution to retention depends on whether or not they are filled with hydrogen during plasma operation and whether or not they remain filled after plasma off. The traps in the material are filled by the solute diffusion front that propagates from the plasma wetted surface into the bulk. The filling is therefore limited by the depth
reached by the diffusing hydrogen and the retained fraction in the traps after plasma off depends on the temperature history of the material and the de-trapping energies of hydrogen from the traps.

In summary, the tritium retention depends on a large number of effects and can only be predicted by dedicated modeling (see section 2) taking into account the trap density evolution (see section 3 and 4), temperature history and ion flux/fluence exposure of the material.

2. Modeling tritium retention in W

In a thermodynamic picture [6], the retention of hydrogen in a metal is given by the equilibrium between the chemical potential of hydrogen in the surrounding atmosphere and that in the metal. This results in the well-known Sieverts law, which predicts a square root dependence of the solute hydrogen concentration with the pressure of hydrogen in the surrounding atmosphere. Based on the experimental data in [1], the solute concentration in a perfect W crystal as function of temperature $T$ (K) and ambient pressure $P$ (Pa) can be written as in Eq. (1)

$$
C_{Sol} = S(T)\sqrt{P} \\
S(T) = S_0 e^{-E_S/\kappa_B T} \\
S_0 = 0.001332 \left( \frac{\text{at. frac.}}{\sqrt{\text{Pa}}} \right), E_S = 1.04064 \text{ (eV)}
$$

For typical pressures ($10^{-4}$ Pa) and temperatures (1000 K) at the first wall of a fusion experiment, this results in values of $C_{Sol}$ of $\sim10^{-12}$ (at. frac.) in thermodynamic equilibrium. If one compares this to the typical trap densities in polycrystalline W which are in the order of $10^{-4}$ to $10^{-3}$ (see e.g. [7,8]), it is obvious that the retention is determined by the lattice imperfections which can trap orders of magnitude more hydrogen than what is dissolved in thermodynamic equilibrium. It is possible to include trapping effects in the chemical potentials [6] and thus treat retention using a thermodynamic equilibrium approach. But since the first wall of a fusion device is usually not in thermodynamic equilibrium, it is also desirable to model the time evolution of retention. To that end diffusion trapping codes have been the work horse for modeling retention on realistic time (days) and length (mm) scales. The majority of these diffusion trapping codes [9, 10, 7] describe the transport of hydrogen through the material as a combination of solute diffusion hindered by trapping at single occupancy traps with a fixed de-trapping energy. This approach has been very successful in interpreting laboratory experiments (e.g. [7]). However, first principle calculations, e.g. [11], predict that multiple hydrogen atoms may populate a trap and that the de-trapping energy is fill level dependent. The difference between the single occupancy and
fill-level dependent trapping was investigated in [12]. There it was shown that the two models could only be discerned in low temperature isotope exchange experiments and that for all other cases the simple single occupancy model does suffice. Therefore, despite the fact that the fill level dependent model is the more accurate description, this discussion on modeling is restricted to the single occupancy mode approximation.

Diffusion trapping codes distinguish two hydrogen populations:Interstitial solute hydrogen that can migrate through the material via diffusion and immobile, trapped hydrogen bound in a particular trap. The exchange between the two populations (via trapping & de-trapping) is governed by processes with an Arrhenius type temperature dependence. The main equation for the diffusive transport and exchange with trapped population is given in Eq. (2)

\[
\frac{\partial C_{\text{Sol}}(x,t)}{\partial t} = D(T) \frac{\partial^2 C_{\text{Sol}}(x,t)}{\partial x^2} + S(x,t) + \sum_{i=0}^{N^{\text{Trap}}-1} \frac{\partial C_{i}^{\text{Trap}}(x,t)}{\partial t}
\]

\[
C_{\text{Sol}} = \text{Conc. of solute H (at. frac.)}
\]

\[
D = \text{Diffusion coefficient (m}^2/\text{s)}
\]

\[
S = \text{Implantation source (s}^{-1})
\]

\[
C_{i}^{\text{Trap}} = \text{Concentration of H trapped in i-th trap type (at. frac.)}
\]

The main equation for the evolution of the local trapped population is given in Eq. (3)

\[
\frac{\partial C_{i}^{\text{Trap}}(x,t)}{\partial t} = \alpha_i(T)C_{\text{Sol}}(x,t)(\eta_i(x,t) - C_{i}^{\text{Trap}}(x,t)) - C_{i}^{\text{Trap}}(x,t)\beta_i(T)
\]

\[
\eta_i(x,t) = \text{Concentration profiles of trap type i (at. frac.)}
\]

\[
\alpha_i(T) = \text{Arrhenius factor for trapping into trap type i (s}^{-1})
\]

\[
\beta_i(T) = \text{Arrhenius factor for de-trapping from trap type i (s}^{-1})
\]

The derivation of the above equations can be found e.g. in [13]. Equations (2) and (3) form a coupled partial differential equation system which has to be solved numerically. To that end boundary conditions have to be implemented which describe the surface processes involved in hydrogen entering and leaving the surface [14]. Thermal hydrogen enters the W surface by first dissociating and chemisorbing at surface sites. Then it either recombines with another chemisorbed hydrogen atom and leaves the surface again or enters the surface into a solute site in the bulk by thermally activated hopping over a surface barrier. For energetic particles the surface barrier is of no consequence and the particles implanted directly into the
bulk. The reverse process of hydrogen leaving the surface first involves a transition out of the bulk onto a
surface site where again it can either recombine and leave the surface or re-enter the bulk. The release of
hydrogen from the surface can either be limited by the recombination process or by the diffusive transport
towards the surface. Typically for plasma wetted W-surfaces, the release is diffusion limited, which can
be included in the model as a simple Dirichlet type boundary condition ($C_{sat} = 0$). At low temperatures
or due to surface impurities, the release can also be recombination limited. In this case a more complex
flux balance model [14] between the chemisorbed concentration and the subsurface solute concentration
has to be setup and coupled to the diffusive flux to/from the bulk via a Neumann boundary condition.

Despite the fact that Equations (2) and (3) can only be solved numerically, a few qualitative concepts on
how retention evolves with temperature and time can be derived:

In the absence of traps the solute transport is very fast. The commonly accepted value for the solute
diffusion coefficient of hydrogen in W from [1] suggests that at ambient temperatures (~300K), once the
source of hydrogen (e.g. plasma, ion beam, external gas pressure) is turned off, the solute diffuses out of
the surface quickly and that only the trapped amount remains and determines the long term retention in
W.

The contribution of a trap at depth $x$ to the retention depends on whether or not the solute diffusion front
has reached depth $x$ while the source of hydrogen was present. Therefore, the buildup of retention is
diffusion limited and increases roughly proportional to the square root of time (if the trap density is
constant in time and depth!). Even if the solute diffusion front has reached the trap at depth $x$, it may not
be filled because the temperature is too high and de-trapping (governed by $\beta_i$ in Eq. (3)) wins over
trapping (governed by $\alpha_i$ in Eq. (3)).

Apart from the temperature during hydrogen loading of the surface, also the temperature evolution after
the source of hydrogen is turned off is important. Since hydrogen has to transported from depth $x$ by
diffusion to the surface where it can be released, a fast cool down can tip the balance between $\beta_i$ and $\alpha_i$
and lead to a strong increase of trapping by freezing in the hydrogen which did not have time to diffuse
out of the surface.

This means that retention in W will only saturate when all traps (intrinsic and generated by the impinging
particle flux) throughout the entire bulk are filled to their equilibrium level $C_{i, Trap,EQ}^{Trap,EQ} (C_{Sol, T, \eta_i})$
where $\frac{\partial C_{i, Trap,EQ}}{\partial t} = 0$ in Eq. (3). From $C_{i, Trap,EQ}$ the total retained amount $\Theta (m^{-2})$ in a W first wall
component of thickness $\Delta X (m)$ is given by $\Theta = \varrho_W \int_0^{\Delta X} C_{i, Trap,EQ}^{Trap,EQ} (x) dx$ ($\varrho_W$ density of W (m$^{-3}$)).
The time $\tau^{EQ}$ to reach this saturation during plasma exposure at the first wall depends on the fraction of the implanted (not kinetically reflected) hydrogen flux $\Gamma_{impl}(m^{-2}s^{-1})$ that enters the bulk, compared to the flux of hydrogen that effuses out of the bulk at the same time by diffusion and recombination. The ratio between these two fluxes is the recycling coefficient $R$. So under constant conditions $(T, \Gamma_{impl})$ $\tau^{EQ}$ becomes $\tau^{EQ} \sim \Theta^{EQ} / \left(1 - R\right) \times \Gamma_{impl}$. In [15] it was shown that $R$ is generally almost equal to one, i.e., only a tiny fraction ($O(10^{-4})$) of the incident flux is actually retained. This means that at low temperatures and fluxes ($C_i^{Trap, EQ}_{high} \Gamma_{impl}^{low} \Rightarrow \tau^{EQ}_{long}$), where most laboratory experiments are performed, the retention will not saturate since only the trap sites very near to the surface are loaded with hydrogen. This means that these experiments are heavily affected by the defect evolution near to the surface taking place during implantation. In contrast in a future fusion reactor, where the wall is at high temperature and the ion fluxes are high ($C_i^{Trap, EQ}_{low} \Gamma_{impl}^{high} \Rightarrow \tau^{EQ}_{short}$), the retention will be determined by trapping all through the bulk and modifications near to the surface will play no role unless they permanently affect the transport of solute to the bulk (e.g. via a diffusion barrier). So for retention in future long pulse fusion devices saturable near surface defects are of little importance, whereas processes like neutron damage that increase the trap density throughout the bulk will dominate retention.

The diffusion trapping approach generally achieves a qualitative match with the experimental findings on the fluence and temperature dependence of hydrogen retention in W: In Fig. 1 based on data taken from [16] and [17], the temperature dependence of D retention in W is depicted for thick (2 mm) samples and thin (500 um) layers for total exposure fluences of $10^{27}$ and $3\times10^{26}$ D/m², respectively. As expected from the model at high temperatures the retention decreases because de-trapping then wins over trapping and the reduction in $C_i^{Trap, EQ}$ wins. At low temperature where de-trapping is low, the model predicts only a weak dependence on temperature, since the increase of diffusivity $D(T)$ with temperature is compensated by a reduction of the solute concentration gradient $\nabla C_{SOL}$ due to enhanced out diffusion at the surface. Therefore, the net diffusion flux $(D(T) \times \nabla C_{SOL})$ of hydrogen into depth, where it can decorate defects and contribute to retention, is almost independent on temperature as can be seen in the data in Fig. 1 for the thin layers. The increase in retention at low temperatures for the thick samples is due to creation of additional trapping sites in the recrystallized material due to the high solute concentrations during the high flux ($O(10^{23})$ (m² s⁻¹)) bombardment. (see also section 4.2)

In Fig 2 taken from [18] the retention in W taken from different experiments with different W grades and ion fluxes are summarized and plotted versus the incident ion fluence. As expected from the model, the retention increases roughly proportionally to the square root of fluence which, for a given flux,
corresponds to a time. This square root dependence on time is typical for a diffusion limited process such as the filling of trap sites by the solute diffusion front propagating through the material. The large scatter in the data is due to different W grades and fluxes.

The diffusion trapping approach can also achieve a quantitative match but usually this requires fitting the trapping $\alpha_i$ and de-trapping $\beta_i$ parameters (see e.g. [7]). The trap type, the trap density depth profile and the evolution of the trap density are generally the major unknowns in interpreting a retention experiment (see also Section 4).

While many authors assign certain de-trapping activation energies to particular defects (see e.g. [19]), this assignment is arbitrary since generally all types of defects are present in an experiment and thus which defect corresponds to which de-trapping energy cannot be disentangled. Recent experimental evidence with samples that dominantly contained a single defect type suggests that dislocations are a major source of trap sites for hydrogen in W [20,21]. In Fig 3 taken from [20] the evolution of retention as function of annealing temperature (3 b.) is compared to the evolution of the dislocation and grain boundary density (3 a.). From this comparison it seems that the retention is only linked to the dislocation density since a further decrease of the grain boundary density at the highest annealing temperatures had no effect on the retained amount of hydrogen. But dislocations alone cannot explain all the observed binding energies. As suggested by first principles calculations [11,22] also vacancy like defect (single vacancies, vacancy clusters and gas filled pores) [21,23] act as strong traps for hydrogen.

3. **Influence of impurities**

Impurities influence the retention in and the release of hydrogen from W: If located at the surface, they can affect the recombination rate, whereas if they are located in the bulk, they can act as additional trap sites but can also affect the solute diffusion by forming diffusion barriers. As pointed out above, modifications of the solute diffusion rate can affect retention in the W bulk which makes it an important factor in predicting the retention in future fusion devices.

For He pre-implanted or D+He co-bombarded W, a clear decrease in bulk retention and permeation flux has been reported in literature [24, 25, 26]. This suggests that the He nano-bubbles that form [27] in the He implantation range reduce the solute diffusion coefficient by forming a near surface diffusion barrier. A similar effect also exists for impurities like N or C that occupy interstitial sites thus potentially blocking the interstitial solute diffusion pathways of hydrogen. In [28] it was shown that hydrogen does not diffuse in W/N layers up to 600 K; similarly in [29], it was shown that W implanted with C showed a reduced bulk diffusion of D.
However, not all impurities introduce diffusion barriers; in [26] the co-bombardment with D and Ar has shown no reduction in retention compared to pure D bombardment but a slight increase which can be attributed to the generation of additional trap sites by Ar. This difference between N, C and Ar could be speculated to be due to the fact that Ar in W is not an interstitial but a substitutional species, i.e., it is not expected to block the interstitial path ways. This speculative picture however, still needs a thorough theoretical investigation by DFT and MD methods.

4. Defect production and evolution

4.1. Defects production by n-damage

As pointed out above in future fusion devices retention will be dominated not be near surface but by bulk defects. The trap level in the bulk will be heavily increased by n-damage which homogenously creates trap sites throughout millimeters of W material. Investigating damage by MeV fusion neutrons in W is difficult because the energy spectrum of current n-sources (different types of fission reactors) is quite different from that of a burning fusion plasma and the handling of the highly activated W samples after n-irradiation makes retention experiments challenging. Therefore, W self-implantation has been established as a viable proxy for n-irradiation [30, 24] and most experimental data is based on W self-implantation experiments. There exists also data from n-damaged W material [31] and the principal trends are comparable: Both find the appearance of a new deep trap site that manifests itself in a TDS spectrum at 800 to 1000K corresponding to 1.8 to 2 eV binding energy. Depth profiling suggests that the maximum trapped concentration of hydrogen in this type of defect at 300 K is in the order of ~10^{-2} (at. frac.), which is at least two orders of magnitude larger than the density of the intrinsic defects. This maximum trapped concentration saturates as function of displacements per atom (DPA). From self-implantation experiments the saturation occurs around 0.2 to 0.5 DPA [30, 32]. Since DPA is a purely calculated number which depends on the code and displacement threshold energy used in the calculations, not all studies can be directly compared which explains the variation in the saturation DPA levels reported. In [4] the issue of DPA calculation is discussed and a list of best practices for DPA calculation is given.

The maximum trapped concentration is decreased if the sample is annealed or damaged at higher temperature. The level of this trap annealing as function of annealing / irradiation temperature is summarized in Fig. 4 based on data taken from [33] for self-implanted and [31] for n-damaged W.

The maximum D-concentration for self-implanted and n-damaged W-material decays with temperature at a similar rate. The offset between the two curves could be attributed to the different initial DPA values.
but could also simply be due to the uncertainty in the determination of the D concentration from nuclear reaction analysis (NRA) depth profiling.

From positron annihilation (PAS) [34] and transmission electron microscopy (TEM) [35] the dominant defects produced by self-implantation are dislocation and vacancy clusters but also small pores have been reported. PAS and TEM analysis of n-damaged W is ongoing and preliminary results suggests similar defect structures as in self-implanted W with the addition of transmutation products like Re.

The available data suggests that n-irradiation will be pose an issue for T retention for future fusion reactors since it produces a large number of deep traps throughout the bulk that can retain large amounts of hydrogen even at high temperatures.

4.2. Defect production by low energy high flux ions

Exposure of W surfaces to high flux plasmas also leads to a modification of the near surface defect structure even if the incident particle energy is below the damage threshold [5]. The driving force behind this damage production channel is the high solute hydrogen concentration. From a simple flux balance picture [15] the solute concentration near the surface can be estimated from Eq. (4).

\[
C_{\text{Sol}} \sim \frac{R_p \Gamma_{\text{ImpI}}}{\varepsilon W \times D(T)}
\]  

(4)

For the exposure parameters in [5] with fluxes of \( \Gamma_{\text{ImpI}} \sim 10^{23} \text{ m}^{-2} \text{ sec}^{-1} \), temperatures of 500 K, typical implantation range of hydrogen in W of the order of \( R_p \sim 1 \text{ nm} \) and diffusion coefficient \( D(T) \) from [1], Eq. (4) yields solute concentrations in the order of \( C_{\text{Sol}} \sim 10^{-5} \) (at. frac.). Using Eq. (1) this concentration can be converted to a required external pressure of \( 10^{18} \text{ Pa} \) to achieve the same solute concentration in thermodynamic equilibrium with an ambient hydrogen gas. Of course this high pressure is beyond the validity range of ideal gas law used in the derivation of Eq. (1) but it still suggests that \( C_{\text{Sol}} \sim 10^{-5} \) is a rather high solute concentration at 500 K.

Such a high solute concentration reduces the activation energy for the formation of vacancies [11, 22] leading, probably in combination with low energy bombardment, to a large number of vacancies near the surface which act as trap sites for the hydrogen. These so called super abundant vacancies [36] can also migrate to form other defect types like dislocations or vacancy clusters.

In addition, any pre-existing pores or cavities beneath the surface will be filled with hydrogen from the solute until the gas pressure in the cavity equilibrates with the surrounding solute concentration level or the cavity grows and eventually ruptures by opening a channel to surface. These growing cavities may
become visible at the surface as blisters, holes, cracks or protrusions [38, 42 and references therein]. The variety of observed surface morphological modifications is generally referred to as “blistering”.

Unfortunately, the appearance of “blistering” depends on various parameters (e.g., particle energy, flux and fluence, surface temperature and initial crystal and surface structure), and the underlaying formation mechanisms could be quite different and are still under discussion. An example for the interdependence of parameters is the disappearance of the blistering at elevated temperatures in dependence of flux: [20] ~500 K for ~10^{20} m^{-2} sec^{-1}, [37] ~600 K for ~10^{22} m^{-2} sec^{-1} and, and >1200 K for ~10^{24} m^{-2} sec^{-1} [38]. Another example is the disappearance or at least the reduction of blistering if the intrinsic defect density is increased, e.g., by self-implantation [39].

The early description of the phenomena “blistering” [40] is the precipitation of gas in bubbles within the ion range. The formation of these bubbles is attributed to stress fields originating from the presence of the implanted (solute and trapped) atoms [40,41]. However, this picture cannot explain the appearance of cavities far beyond the penetration depth of the impinging particles [42, 43,44], i.e., when diffusion processes are involved. A further obvious indication for the variation of the driving mechanism for “blistering” with cavity formation is the shape of the cavities (Fig. 5): They range from cracks inside a crystallite i) parallel to the surface independent of crystallite orientation and ii) aligned to selected crystallite orientation over iii) delamination along gain boundaries roughly parallel to the surface to iv) extrusions of material along the gliding system of W [42, 45]. Overall, the surface morphology modifications can be classified based on i) depth (implantation versus diffusion range), ii) position (inside crystallite or along grain boundaries) and iii) surface topography and cavity shape.

All these defects mentioned in this section only affect the very near surface up to a couple of µm which means they make the interpretation of current lab experiments difficult or even impossible. As long as they only form saturable defects they are of little importance for future fusion devices which will be dominated by bulk retention. But if they affect the diffusive transport into the bulk they may become import also for future devices. For instance the cavities are sinks for solute hydrogen with the potential to be non-saturable and if they rupture, they open up additional loss channels of hydrogen towards the surface thus limiting the amount of hydrogen that can diffuse into the bulk.

**Conclusions**

The retention of hydrogen isotopes in tungsten is a key process for the operation of future long pulse fusion devices. While the principal physical picture of diffusion trapping driven retention is well understood and is capable of interpreting and predicting retention, the evolution of the underlying defect
density is still generally unknown and usually is introduced as an ad-hock fit parameter. In particular the formation of defects by low (below damage threshold) energy particles is not well understood. It plays an important role in current laboratory experiments which are usually dominated by these defects near to the surface. In contrast in future fusion devices, the high fluxes and temperatures will result in retention being dominated by hydrogen trapped at defects deep in the bulk of the first wall material. However, also the near surface defects may affect bulk retention by modifying the solute transport into the bulk by forming diffusion barriers or fast release channels towards the surface. The bulk defect density is determined by intrinsic defects and defect evolution by neutron damage. Neutron damage is currently investigated by using W self-implantation as a proxy and current results suggest that the defects produced are similar to those generated by the currently available fission neutron sources. Neutron damage produces a large number of deep traps which can potentially retain a large amount of hydrogen and only release it at high (> 800 K) temperatures. This is an unfortunate combination which will be a challenge for future burning fusion devices.
Figure captions

**Fig. 1:**
Temperature dependence of retention in thick recrystallized W and thin W layers exposed to low energy D plasmas (38 eV/D, \( \sim 10^{22} \text{ m}^{-2} \text{ sec}^{-1} \)) based on data from [16].

**Fig. 2:**
Fluence dependence of retention in polycrystalline W from various experiments based on data from [18].

**Fig. 3:**
Correlation between D retention (in b.) in W and the evolution of dislocation \( \phi \) and grain boundary density \( S_V \) (in a.) from [20].

**Fig. 4:**
Annealing of n- or self-implantation damage in W characterized by the maximum D concentration in the near surface damage zone obtained from NRA depth profiling of the trapped D decorating the defects. Data was taken from [31, 33].

**Fig. 5:**
Different cavity shapes on cross-sectional views under 38° with SEM: a) inside crystallites parallel to the surface [46], b) inside crystallites aligned to selected orientations [45], c) delamination along gain boundaries [42], and d) extrusions of material along gliding system [45].
Fig. 1

Fig. 2
Fig. 3

Fig. 4
Fig. 5
References

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