Deuterium retention in radiation damaged tungsten exposed to high-flux plasma

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2 Theoretical background

Deuterium retention in pre-damaged tungsten is the result of a complicated interplay between many processes, including implantation, diffusion and deuterium trapping. Figure 2.1 illustrates these plasma-surface interaction (PSI) processes. When the deuterium ions from the plasma strike the tungsten target, they are neutralized and a large part will be reflected directly. The remaining part will penetrate into the tungsten and reach depths of typically a few nm. After thermalization, deuterium atoms diffuse through the material. At the surface they can recombine and leave the material. In the tungsten they can be trapped in pre-existing defects or in deuterium traps created by implantation of high-energy tungsten ions prior to the plasma exposure.

This chapter describes the above processes and the implementation at Pilot-PSI in more detail. The composition of the plasma produced in the Pilot-PSI setup is outlined in section 2.1. The interaction of this plasma with the tungsten surface is discussed in section 2.2. The deuterium retention processes are explained in section 2.3 and defect creation is described in section 2.4. A comparison between high-energy ion and neutrons irradiation is made in section 2.4.1 and the plasma damage processes and the blister formation mechanisms are described in section 2.4.2.

2.1 Plasma composition

The plasma composition, the ion flux and ion impact energy at the tungsten target determine the reflection, penetration and damage creation in tungsten. Deuterium plasmas...
produced in the experiments described in this thesis typically have an electron density \( n_e \) of \( \sim 10^{20} \) m\(^{-3} \) and an electron temperature \( T_e \) of \( \sim 1 \) eV (section 3.3.1). The plasma is quasi-neutral \( (n_i = n_e) \) and the electron-ion collision frequency is high, so that electrons and ions are in thermal equilibrium \( (T_i = T_e) \).

Hydrogen plasmas are dominated by H\(^+\) ions and contain only small fractions of neutral species in the beam centre (see also section 3.3, [25–29]). Note that these experiments are performed using protium instead of deuterium, but the behaviour of deuterium plasmas is assumed to be identical.

### 2.1.1 Ion flux

The ion flux \( (\Gamma_i) \) is estimated according to general plasma sheath theory [30]. Here, it is assumed that the ions are accelerated to the sound velocity at the sheath entrance (Bohm criterion [31]) and that the plasma density at the sheath entrance drops by a factor of two compared to the pre-sheath value. The ion flux is given by

\[
\Gamma_i = \frac{n_e}{2} \sqrt{\frac{k_B(T_e + \gamma T_i)}{m_i}} = \frac{n_e}{2} \sqrt{\frac{4k_B T_e}{3m_p}} \left[ \text{m}^{-2}\text{s}^{-1} \right],
\]

with \( m_i \) as the deuterium ion mass and \( m_p \) as the proton mass. The adiabatic index \( (\gamma) \) was taken to be 5/3 (adiabatic flow with isotropic pressure). The total amount of deuterium ions that arrive at the target can be calculated by integration of the ion flux over the target. This value can also be found using the ion saturation current. The ion saturation current \( (I_{sat}) \) is reached at sufficient negative target bias, when all electrons are repelled and only ions arrive at the target. The amount of ions can then easily be calculated as follows: \( I_{sat}/q \), where \( q \) is the elementary charge. Both methods for calculating the total amount of deuterium ions always agreed within factor two.

### 2.1.2 Ion impact energy

Calculation of the ion impact energy \( (E_{ion}) \) is unfortunately not straightforward, because the plasma potential varies over the radius of the plasma beam. Indeed, Shumack \textit{et al} [32] and Wiegers\textit{et al} [33] showed that a radial electric field formed in the plasma beam and a radial development of the current distribution. This means that the target effectively short-circuits the plasma beam leading to local differences from the floating potential. To estimate the ion energy, we ignore the radial dependence, assume 1D linear geometry, no ionisation and a non-collisional sheath. This allows us to use the formulation derived by Stangeby [30].

The ion impact energy is the sum of the ion energy at the entrance of the plasma sheath \( (E_{se}) \), and the energy gained during acceleration in the sheath \( (eV_{drop}) \). The minimal requirement for ions to enter the sheath is the sound speed [31] with an energy \( (E_{se}) \) of \( \sim 2k_B T_i \) (see chap. 25 in [30]). The voltage drop \( (V_{drop}) \) across the sheath is approximately \( 3k_B T_e/\epsilon \) [30]. Consequently, the ion energy of a floating target is \( \sim 5k_B T_e \).
2.2 Plasma-surface interactions

Given the normal Pilot-PSI operating conditions, $E_{\text{ion}}$ is about 5 eV for a floating tungsten target.

In the case of externally biasing the target, the potential drop in the sheath is equal to the difference between the plasma potential ($V_p$) and the biasing voltage ($V_{\text{bias}}$). The ion impact energy is then given by $E_{\text{ion}} \approx 2k_BT_e + e(V_p - V_{\text{bias}})$. The plasma potential is estimated by adding the voltage drop over the sheath to the floating potential ($V_{\text{float}}$):

$$V_p = V_{\text{float}} + 3k_BT_e/e.$$ Here, it is assumed that the plasma potential does not change when a bias is applied. Under the plasma conditions used in experiments in this thesis, the floating potential was only a few V ($\sim -2$ V). The contribution of $V_{\text{float}}$ and thereby the variation in $V_{\text{float}}$ is only small with respect to a bias of typically 40 V, so that the ion impact energy is $\sim 40$ eV.

2.2 Plasma-surface interactions

A comprehensive and extensive overview of plasma-surface interactions (PSI) and related technological issues is presented in *The plasma boundary of magnetic fusion devices* by P. Stangeby [30] and in review article *Plasma-material interactions in current tokamaks and their implications for next step fusion reactors* by G. Federici et al [34]. Hydrogen recycling on plasma facing materials (PFM) is discussed by Wu [35]. In this section the PSI processes are specified for low temperature, high density deuterium Pilot-PSI plasmas impinging on tungsten.

**Reflection** - The fraction of incoming ions that are directly scattered depends mainly on the incident energy, angle, material and surface structure. During the collision, the incoming deuterium ions pick-up an electron from the surface, thereby recoiling as atomic deuterium. The binary collision approximation [36] used normally is not valid in the low energy range ($< 10$ eV) under which our experiments have been carried out. Molecular dynamic simulations indicated very low sticking coefficients [37]. These agree with experiments of deuterium atoms on tungsten where reflections of $0.96 \pm 0.02$ were found [38]. In this thesis, we assume a reflection of 95%.

**Erosion** - Physical sputtering occurs due to momentum and energy transfer in collisions between incoming particles and target atoms. When the target atom receives an energy in excess of the surface binding energy (in case of tungsten, this is 8.9 eV [39]) the atom will be ejected, i.e. the surface is eroded. The threshold for physical sputtering of deuterium on tungsten is about 200 eV [40]. Since the incoming ion energies of Pilot-PSI plasmas stay below 50 eV (section 2.1.2), we do not have to consider physical sputtering.

Besides physical sputtering, chemical sputtering can occur. The chemical reaction between an incoming particle and the material lowers the surface binding energy, so that the newly formed compound easily can be eroded. This is an important sputtering mechanism for carbon PFMs. Hydrocarbons that are formed are eroded from the surface and contaminate the plasma. Tungsten is a refractory metal, no chemical erosion of deuterium takes place.
2 Theoretical background

**Implantation** - Particles that are not reflected will instantaneously neutralize when they arrive at the target. Depending on their ion impact energy, they either interact with the deuterium covering the surface and form a chemisorbed layer \[41\] or they penetrate into the material. The typical implantation depth of deuterium atoms with an energy of 10 – 40 eV is in the nanometer range as calculated with SRIM \[42\]. The kinetic energy of the incoming atoms (5 – 40 eV) is much higher than the thermal energy of deuterium (0.01 – 0.1 eV). The difference in energy is lost in interatomic collisions with the atoms in the tungsten lattice. Once the deuterium is thermalized it will occupy an interstitial position. The retention processes within the material are further described in section 2.3.

**Surface processes** - Surface reactions are interactions that involve adsorption of one of the reactants. The rate equations of these mechanisms are of importance for an accurate estimation of the D\(_2\) molecules that leave the surface and enter the plasma.

![Figure 2.2: Recombination mechanisms.](image-url)

Two atoms, that are adsorbed on the tungsten, freely diffuse over the material surface and have a probability to recombine once they meet each other. The binding energy of D\(_2\) to the tungsten surface is low. The molecular deuterium desorbs from the surface due to exothermic recombination. This reaction is referred to as the Langmuir-Hinshelwood mechanism (figure 2.2). The molecule release rate is given by

\[
J_r = K_{\text{rec}} C_s^2 \quad \text{[m}^{-2}\text{s}^{-1}],
\]

where \(K_{\text{rec}}\) is the recombination rate coefficient (\(K_{\text{rec}} = K_0 \exp[-E_{\text{rec}}/k_B T]\)) and \(C_s\) the deuterium concentration in the surface monolayer. The recombination rate coefficients reported in literature are very scattered \[43–47\]. The values measured by Anderl et al (\(K_0 = 3.2 \times 10^{-15} \text{ m}^4 \text{s}^{-1}, E_{\text{rec}} = 1.16 \text{ eV}\) \[43\] are most accepted and will be used in this thesis.

A secondary mechanism is the Eley-Rideal recombination \[48\]. Figure 2.2 shows Eley-Rideal recombination, where only one of the two atoms is adsorbed, the other one directly reacts from the gas phase. Eley-Rideal recombination is a non-thermal surface reaction. This process could also include reaction with deuterium ions directly from the incoming plasma.

### 2.2.1 Deuterium back-flux

The released deuterium molecules and the reflected deuterium atoms combined cause a back-flux of particles that interfere with the plasma beam. In this section, we estimate the
interaction of the back-flux with the plasma beam to assess the relative importance.

The rate coefficient (kr) for charge exchange between D_2 and D^+ in the energy range < 10 eV is at maximum 10^{−15} m^3 s^{−1} [49]. The relative velocity (v) of about 10 km s^{−1} [28] and D^+ density (ni) of ~10^{20} m^{−3} can be used to estimate the mean free path,

\[ \lambda_{\text{mfp,D}_2} = \frac{v}{k_r n_i} > 0.1 \text{ m}. \] (2.3)

The full width at half maximum of the plasma beam is typically 1 cm. Thus, the D_2 molecules fly right through.

The interaction of the deuterium atoms with the plasma flux also takes place via charge exchange. The reaction rate coefficient between D and D^+ is an order of magnitude higher: \( k_r \approx 10^{−14} \text{ m}^3 \text{s}^{−1} \) [50], so that

\[ \lambda_{\text{mfp,D}} = \frac{v}{k_r n_i} \approx 0.01 \text{ m}. \] (2.4)

Significant part of the reflected neutrals experience charge exchange with the ions from the plasma beam. The ions created via charge exchange can be accelerated towards the target. The particle flux might therefore be somewhat higher than calculated solely with equation 2.1.

### 2.3 Deuterium retention

Deuterium retention refers to a whole range of processes in which deuterium is lost from the plasma and incorporated in the wall material. The energy diagram of deuterium dissolved in tungsten is schematically depicted in figure 2.3. In the solute state, the deuterium atom is highly mobile; by hopping between interstitial positions it can easily diffuse through the material. In this diffusion process, the atom can either reach a crystallographic defect and get trapped or reach the surface and desorb.

#### 2.3.1 Solubility

Sieverts’ law relates the equilibrium concentration of solute atoms in a metal to the partial pressure above the surface of the metal [57]. The concentration of solute deuterium at the surface (Cs) of a material exposed to a deuterium gas at pressure \( p \) is given by

\[ C_s = K_{\text{sol}} p^{1/2} \quad [\text{m}^{−3}], \quad \text{where} \]

\[ K_{\text{sol}} = S_0 \exp \left( \frac{−E_S}{k_B T} \right) \quad [\text{m}^{−3} \text{Pa}^{−1/2}], \] (2.5)

with the Boltzmann constant \( k_B \) and the sample temperature \( T \). The solubility, \( K_{\text{sol}} \), is determined by the enthalpy of solution (\( E_S \)) and the solubility coefficient (\( S_0 \)). Capture of deuterium in tungsten is an endothermic process, i.e. energy must be added to introduce deuterium into solution. The mostly used values of the solubility are measured by Frauenfelder: \( S_0 = 17.7 \times 10^{23} \text{ m}^{−3} \text{Pa}^{−1/2}, E_S = 1.04 \text{ eV} \) [55] and were used for the work presented in this thesis.
Figure 2.3: Energy diagram of hydrogen in tungsten. The dissociation energy of deuterium from the D$_2$ molecule is $\frac{1}{2}E_{D_2}^D$. The chemisorption energy ($E_C$) at the surface, the enthalpy of solution ($E_S$), the migration barrier ($E_M$) and the trapping energies ($E_t$) of deuterium in crystallographic defects are indicated. Their values are given in Table 2.1.

<table>
<thead>
<tr>
<th>Activation energy</th>
<th>eV</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>dissociation energy</td>
<td>$\frac{1}{2}E_{D_2}^D$</td>
<td>2.3</td>
</tr>
<tr>
<td>chemisorption energy</td>
<td>$E_C$</td>
<td>0.4–0.9</td>
</tr>
<tr>
<td>migration barrier</td>
<td>$E_M$</td>
<td>0.39</td>
</tr>
<tr>
<td>enthalpy of solution</td>
<td>$E_S$</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**trapping energy of deuterium in atomic form (D) in a**

- dislocation
  
  \[ E_{t,D}^{\text{dis}} = E_m + E_{b}^{\text{dis}} \]
  
  0.85 [54]

- grain boundary
  
  \[ E_{t,D}^{\text{gb}} = E_m + E_{b}^{\text{gb}} \]
  
  0.85 [54]

- vacancy
  
  \[ E_{t,D}^{\text{vac}} = E_m + E_{b}^{\text{vac}} \]
  
  1.45 [54], 1.43–1.55 [51], 1.07–1.34 [55], 1.17–1.6 [56]

- vacancy cluster
  
  \[ E_{t,D}^{\text{vc}} = E_c + E_s + E_m \]
  
  1.9–2.3 [51], 1.84–2.34 [52], 2.1 [55]

**trapping energy of molecular deuterium (D$_2$) in a**

- vacancy cluster
  
  \[ E_{t,\frac{1}{2}D_2}^{\text{vc}} = E_s + E_m \]
  
  1.45 [52], 1.4 [51]

Table 2.1: The diffusion parameters and trapping energies ($E_{\text{type of defect,species}}^t$) of deuterium in tungsten.

### 2.3.2 Diffusivity

Deuterium movement through tungsten is determined by atomic diffusion. Diffusion is a jump process of interstitial deuterium via thermal excitation and is defined by

\[
D_{\text{dif}} = D_0 \exp \left[-\frac{E_M}{k_B T}\right], \quad [\text{m}^2 \text{s}^{-1}].
\]  

(2.7)
2.3 Deuterium retention

The pre-exponential factor \((D_0)\) and the migration barrier \((E_M)\) vary over a broad range in literature between \(3.5 \times 10^{-11} \text{ – } 6 \times 10^{-4}\) and \(0.25 \text{ – } 1.80\) eV, respectively [44, 46, 53, 58-61]. The recommended [61] and widely accepted values determined by Frauenfelder were used in the work presented in this thesis: \(D_0 = 4.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}\), \(E_M = 0.39\) eV [53].

Diffusion of deuterium in tungsten is described by the transport equation,

\[
\frac{\partial C_D(x,t)}{\partial t} = D_{\text{dif}} \frac{\partial^2 C_D(x,t)}{\partial x^2} + S(x,t).
\]  

\((2.8)\)

\(C_D(x,t)\) is the deuterium concentration in \(\text{m}^{-3}\) as function of depth \((x)\) and time \((t)\). The diffusion rate \((D_{\text{dif}})\) is assumed constant throughout the sample. \(S(x,t)\) is the particle source/sink term, it is negative in case of trapping and positive for de-trapping. The one-dimensional case can be solved analytically, when neglecting trapping and de-trapping \((S = 0)\) and assuming a constant surface concentration over time \((C_D(0,t) = C_s)\). The solution is then given by

\[
C_D(x,t) = C_s \text{ erfc} \left[ \frac{x}{2 \sqrt{D_{\text{dif}} t}} \right] = C_s \text{ erfc} \left[ \frac{x}{\lambda_D(t)} \right],
\]  

\((2.9)\)

where \(\text{erfc}\) is the complementary error function and \(\lambda_D(t)\) the typical diffusion length (see also figure 2.4a). In figure 2.4b the situation is shown for a case where deuterium is lost by trapping in defects. In this example, we assume a situation with a high trap energy, i.e. the probability for release is negligible. As result of particle trapping, the diffusion slows down. The typical depth up to where the traps are filled \((\lambda_{\text{eff}}(t))\), is proportional to the effective diffusion length \((\propto \sqrt{D_{\text{eff}} t})\).

**Figure 2.4:** a) The solid lines represent the solute concentration of deuterium versus the depth (complementary error function, equation 2.9), the associated diffusion length \((\lambda_D)\) is indicated by the dotted lines. After an exposure time that is four times as long (blue), the deuterium diffuses twice as deep into the material (red). b) The trapped deuterium concentration \((\rho_t)\) in the case of trapping in high energy traps, where the probability for release is negligible, is approximately a moving front. The typical depth \((\lambda_{\text{eff}})\) of the deuterium is related to the effective diffusion coefficient.
2.3.3 Deuterium trapping

In general, ‘trapping’ refers to extra low energy sites for atoms dissolved in the tungsten lattice. Crystallographic defects that trap deuterium are for example vacancies, dislocations, grain boundaries and voids (figure 2.5). These can exist naturally in the material, i.e. pre-existing, or be produced by damage creation. One can distinguish between saturable and unsaturable traps. Saturable traps fit a maximum number of deuterium atoms, while unsaturable traps can accommodate a variable number of deuterium atoms, for example a void with variable deuterium pressure.

![Figure 2.5: Schematic representation of material defects.](image)

Each of the defect types can be characterized by a trap energy \( E_{\text{type of defect}} \) (figure 2.3) and a defect density \( \rho_{\text{trap}}(x,t) \). Table 2.1 gives an overview of trap energies mentioned in the literature. Pre-existing defects are typically homogeneously distributed over the full depth range, their concentration depends on the material and fabrication. Defects created by high energy tungsten ions (section 3.2) extend only over the first 1.5 µm. Damage created during plasma exposure develops over time \( t \).

The deuterium sink as result of trapping \( (S_{\text{trap}}) \) depends on the diffusion coefficient, the concentration of solute deuterium \( (C_D) \) and the concentration of empty traps \( (\rho_{\text{trap}}^e) \):

\[
S_{\text{trap}} = -\alpha_{t} \frac{\rho_{\text{trap}}^e}{N} C_D = -\frac{D_{\text{dif}}}{\lambda^2} \frac{\rho_{\text{trap}}^e}{N} C_D \quad [\text{m}^{-3}\text{s}^{-1}],
\]

(2.10)

where \( N \) is the lattice atom density \( (N_W = 6.3 \cdot 10^{28} \text{ m}^{-3}) \), \( \lambda \) the lattice parameter \( (\lambda_W = 3.15 \text{ Å}) \) and \( \alpha_t \) the trapping rate coefficient, which is determined by \( D_{\text{dif}}/\lambda^2 \). Once trapped, the de-trapping depends on the trap energy and occupation of the trap. The de-trapping particle source is given by

\[
S_{\text{de-trap}} = \alpha_r \rho_{\text{trap}}^D = \nu_0 \exp \left( \frac{-E_{\text{type of defect}}}{k_B T} \right) \rho_{\text{trap}}^D \quad [\text{m}^{-3}\text{s}^{-1}],
\]

(2.11)

in which \( \rho_{\text{trap}}^D \) is the concentration of traps occupied by deuterium. The release rate \( (\alpha_r) \) is calculated by multiplying the attempt frequency by the success rate. The nominal attempt frequency is typically the Debye frequency \( (\nu_0) \), which under our conditions is in the order of \( 10^{13} \text{ s}^{-1} \). The success rate is given by \( \exp \left( \frac{-E_{\text{type of defect}}}{k_B T} \right) \).
2.4 Defect creation

2.4.1 Ion versus neutron irradiation

The 14.1 MeV neutrons, created by DT fusion, are not confined by the magnetic field. When escaping through the wall of the fusion reactor they produce damage. Due to the low interaction cross-section of these neutrons with the wall material, the introduced defects will be distributed homogeneously throughout the entire thickness of the tungsten components. This is expected to have a significant effect on the material properties and hydrogen retention. Unfortunately, neutron irradiation experiments at relevant conditions are time consuming and require costly infrastructure. Alternatively, for the work presented in this thesis high energy tungsten ions were used to simulate neutron damage. In this section we will give a short summary of the damage creation process and focus on the differences and similarities between ion and neutron damage in tungsten. An extensive description of radiation damage mechanisms can be found in [62] by Was.

Radiation damage mechanism

The use of energetic particle irradiation, such as protons, electrons and ions, as surrogate for neutron irradiation benefits from a shorter experiment time, production of little or no radioactivity and lower costs. Deuterium retention in damage created by electrons [64], protons [20, 65–67] and heavy ions [16, 17] have been investigated. Each type of irradiation creates a different damage morphology. Figure 2.6 illustrates the different damage morphologies after 1 MeV particle irradiation of pure nickel [63].

Electrons produce isolated Frenkel pairs, which are vacancy and interstitial pairs, in the depth range of a few micrometers, while protons produce small and widely spaced damage cascades over the whole depth range. Because of the small mass in both cases, the typical damage rate (defined in displacements per atom (dpa) per second) is small.

![Figure 2.6](image-url)

**Figure 2.6:** Schematic representation of the damage morphology after various type of particle irradiation (same energy) on pure nickel. The average PKA energy ($T$) and the displacement efficiency ($\varepsilon$) is specified for each case [63]. The line schematically shows the path of the incident particle. A vacancy is represented by a square, an interstitial by a dot and the size of the formed defect clusters are illustrated by the ovals.
In comparison, heavy ions and neutrons produce damage in large clusters. Heavy ions are very efficient in creating a large damage cascade, reaching a damage level equivalent to a year of neutron irradiation within hours. Although it is well-known that the effects of neutron irradiation cannot fully be simulated, high energy ion irradiation is the most promising approach to neutron irradiation.

Both neutron and high energy ion impact transfer a large amount of kinetic energy to the tungsten material. The energy transfer from an incident particle to a lattice atom, the so-called primary knock-on atom (PKA), takes place on a typical timescale of attoseconds. Afterwards, the PKA can penetrate further within the sample. If its energy is sufficient it can cause further collisions and in such a way form collision cascades. Two elementary types of defects are formed: vacancies and interstitials. Interstitials are highly mobile, and they can disperse away from the main cascade. The result is a depleted zone in the centre of the collision cascade, surrounded by an interstitial mantle. These collision cascades are created within 0.1 ps. During the following tens of picoseconds, the absorbed energy dissipates. Spontaneous recombination and clustering take place, so that stable Frenkel pairs and defect clusters are formed. On longer timescales (>10⁻⁸ s) thermal migration causes defect reactions.

**Neutron irradiation**

Neutrons do not have an electrical charge and therefore easily penetrate into a material, where they produce atomic displacements, embrittlement and nuclear reactions. Nuclear reactions in tungsten can cause transmutation into Rh, Ta and He. Due to the short range interaction of the nuclear potential, collisions with large energy transfer to the lattice atom dominate. The average energy transfer, \( T \), of a neutron to the PKA is given by

\[
T = \frac{\gamma E_i}{2}, \quad \text{where} \quad \gamma = \frac{4mM}{(M+m)^2}.
\]  

(2.12)

For neutron irradiation \((m=1 \text{ } u)\) at \(E_i=14.1 \text{ MeV} \) on tungsten \((M=184 \text{ } u)\), the average energy of the PKA is \(\bar{T} \approx 152 \text{ keV}\).

**High energy ion irradiation**

The average PKA energy of the 12.3 MeV W⁺⁺ ions was estimated using SRIM to be \(~17 \text{ keV}\). Although heavy ions come closest to reproduce the energy distribution of the recoils as obtained under neutron irradiation, the projected range of the heavy ions is short. The high electronic energy loss results in a non-uniform defect depth distribution (see also figure 3.3). The differences in depth distribution between neutron and ion are not necessarily a problem. The time- and length-scale of deuterium diffusion are much smaller than the typical ion damage depth range (\(\mu m\)), thus not affected by the damage distribution. In conclusion, ion irradiation will be able to provide us with useful information for understanding of the physical processes.
2.4 Defect creation

2.4.2 Plasma damage

Depending on the specific plasma conditions, extra damage can be created in the material during deuterium loading. An incoming deuterium particle requires an energy of at least 2 keV to knock a heavy tungsten atom from its lattice position \((E_{\text{displ}} = 90 \text{ eV})\). Such energies are by far not reached in Pilot-PSI. A more relevant process in which damage can be created is when more deuterium is forced into the material than can be contained in a solute state (section 2.3.1). At such high flux, cavity growth might take place and subsequently blister-like features can be formed. Surface blistering is unfavourable for ITER operation and needs to be avoided as it may alter mechanical properties (decrease the heat conduction, create areas with high strain fields or cause embrittlement), store tritium or enhance tungsten erosion when blisters burst. Tungsten erosion will efficiently cool the plasma via Bremsstrahlung, and possibly kill the fusion process.

Blister formation process

Due to its relevance, blistering induced by hydrogen loading has been extensively studied \([69, 70]\) in relation to plasma-surface interactions in nuclear fusion devices \([14]\) as well as for semi-conductor technology \([71, 72]\). Blistering occurs in metals with a low solubility, at low temperatures and for very high fluences \([70]\). Depending on the bombardment conditions, such as the ion-energy \([73, 74]\), particle fluence and surface temperature, and material grade, such as grain structure, impurity content and pre-treatment, various types of blister-like features are formed. The reported surface features vary from smooth spherical blisters \([69, 75]\) to plateau-like \([76]\) and stepped high dome structures \([77, 79]\).

In the blister formation process, two stages can be distinguished. First, deuterium accumulates at a nucleation point, which is then followed by growth of the cavity. Currently, there is no consensus about how the initial nucleation takes place. Of course, any pre-existing defects in the material, such as dislocations, grain boundaries or vacancies can serve as a nucleation site \([80]\). In addition, Fukai \([81]\) argues that the hydrogen in the tungsten lattice can lower the vacancy formation energy and Poon \([82]\) suggests that plasma impurities, such as nitrogen and oxygen, are able to create crystallographic defects that serve as nucleation point. Hydrogen precipitates at these nucleation sites \([70, 83]\). Since the solubility of hydrogen in tungsten is very low, atomic hydrogen in solution can recombine into \(H_2\) gas \([84]\). The next step is cavity growth. Three mechanisms for cavity growth are proposed by Condon \([70]\): plastic deformation, dislocation loop punching and vacancy clustering.

Cavity formation by plastic deformation requires hydrogen supersaturation. First, pressure builds up in a void or between grain boundaries as result of a high solute deuterium concentration (Sieverts’ law). When the pressure exceeds a critical value it creates mechanical deformation in the surrounding material. If this occurs close to the surface, this leads to material bulging outwards.
Theoretical background

Figure 2.7 shows dislocation loop punching. Dislocation loop punching also requires hydrogen supersaturation. Initially, hydrogen is accumulated at a nucleation site (figure 2.7a), the gas pressure increases by absorbing the dissolved hydrogen. When the pressure exceeds $\sim 0.2\mu$ ($\mu$ is the shear modulus, the shear modulus of tungsten is $\sim 160$ GPa) patches of material are forced into the surrounding bulk material to form an interstitial loop (figure 2.7b). The dislocation loop is pushed away from the cavity, moving along the direction of its Burgers vector (figure 2.7c). During this process, the volume of the bubble increases. This leads to a decrease in pressure and the process repeats itself.

Vacancy clustering is independent of the dissolved hydrogen but requires vacancy supersaturation and a temperature above the vacancy mobility temperature ($\sim 550$ K) [85]. When vacancies are mobile, they can encounter each other and form small clusters.

The values mentioned for the gas pressure of $\text{H}_2$ in cavities vary over a wide range: a rough estimate from measurements performed by Shu et al [78] is a few GPa to a few tens of GPa. Shu et al compare this to similar pressures of hydrogen in voids of tungsten mentioned by van Veen et al [64]. Van Veen et al refer to the rough estimate given by Mills et al [86] based on the equation of state for $\text{H}_2$ gas that yields a corresponding pressure of the order of 10 GPa, which is lower than, but close to, the pressures required for loop punching. Evans et al expect volume increase by loop punching for bubbles in tungsten with diameters in the order of 1 nm beyond 10 GPa. Balden et al [87] report of estimated values of $\sim 1$ GPa and You [88] predicts with finite element studies that a few hundred MPa should be enough to start blister formation.