EUROfusion

EUROFUSION CP(15)04/02

A. Založnik et al.

The Influence of the Annealing Temperature on Deuterium Retention in Self-Damaged Tungsten

(18th May 2015 – 22nd May 2015)
Aix-en-Provence, France

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The influence of the annealing temperature on deuterium retention in self-damaged tungsten

Anže Založnik[1], **Sabina Markelj**[1], **Thomas Schwarz-Selinger**[2], **Lukasz Ciupinski**[3], **Justyna Grzonka**[3], **Primož Vavpetič**[1], **Primož Pelicon**[1]

[1]Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[2]Max-Planck-Institut für Plasmaphysik, Boltzmannstrasse 2, D-85748 Garching, Germany
[3]Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland

E-mail: `anze.zaloznik@ijs.si`

May 2015

Abstract. The influence of the annealing temperature on deuterium retention was studied for self-ion damaged tungsten in the range from 600 K - 1200 K. Samples were damaged by 20 MeV W ions at room temperature to the peak damage level of 0.5 dpa. Samples were then annealed at the desired temperature for 1 hour and exposed to deuterium atom beam with the flux of 2.6×10^{19} D/m^{2}s for 144 hours. Unannealed sample was also used as a reference. Nuclear reaction analysis technique was used for deuterium depth profile analysis and thermal desorption was performed on the same samples to measure the amount of total retained D. Scanning transmission electron microscopy was used for the calculation of dislocation densities in the samples. After annealing at 1200 K approximately 65 % of those initial defects which retain deuterium were annealed.

1. Introduction

Because of its favorable properties, such as low sputtering yield, low hydrogen retention, high thermal conductivity and high melting temperature, tungsten is considered to be the most suitable material for plasma facing components in future fusion devices (such as ITER, DEMO) [1, 2]. During the fusion reactor operation plasma facing components will be subjected to high fluxes of high energy ions, atoms and neutrons [3]. This will induce defects (such as interstitials, vacancies, dislocations...) in the material degrading its favorable properties.

Deuterium behaviour in neutron-irradiated tungsten is a subject of active research [4, 5]. However, in order to avoid the activation of the material and due to easier and faster way of damage creation tungsten self-implantation is often used for material damaging instead of neutrons [6, 7, 8]. High energy W ion bombardment is expected to produce similar defects in the material as neutron bombardment does, however one should take notice that there are some differences [9].

To study the influence of neutron-like damage on hydrogen retention we have exposed self-damaged samples to low energy neutral deuterium atoms. Defects in the bulk of the material act as strong binding sites for deuterium atoms causing the atoms to fill the defects without creating any additional damage. The effect of tempering on damage annealing have been studied by the analysis of D concentration depth profile, by thermal desorption (TDS) of deuterium and by scanning transmission electron microscopy (STEM).

2. Experiment

For this experiment five self-ion damaged recrystallized polycrystalline W samples were used. Samples were first chemo-mechanically polished to a mirror finish according to the procedure proposed by Manhard et al. [10]. After polishing the samples were heated in ultra high vacuum to 2000K for 2 min for recrystallization. Self-ion damaging was performed with 20 MeV W^{6+} ions at room temperature with the fluence of 7.8×10^{17} at/m^2. The resulting damaged layer was calculated by SRIM 2013 software [11] to be 2.4 μm thick. With a displacement energy E_d = 90 eV, lattice binding energy E_L = 3 eV and the "full cascade option" the number of atoms receiving an energy transfer larger than E_d convert to 0.5 dpa in the damage peak (see Fig. 1).

The sample annealing and deuterium atom exposure were both performed in the same vacuum chamber. Samples were mounted on the temperature controlled sample holder, capable of heating the samples up to 1200 K. Four samples were heated to desired annealing temperature (600 K, 800 K, 1000 K and 1200 K) and held at constant temperature for 1 h. According to [8] this time is long enough in sense that longer times would have no influence on further damage annealing. One sample was not annealed and was used as a reference. After annealing all samples were exposed to the deuterium atom beam with thermal energy of 0.2 eV and flux of 2.6×10^{19} D/m^{2}s for 144 h with corresponding fluence of 1.3×10^{25} D/m^2. The deuterium atom beam was created by thermal dissociation of deuterium gas flowing through a hot W capillary of a commercial hydrogen atom beam source (HABS) [12]. During the exposure the sample temperature was held constant at 500 K. Such exposure conditions are adequate to saturate damaged layer with deuterium atoms.

Deuterium concentration depth profile analysis was performed at separate experimental chamber, using Nuclear Reaction Analysis (NRA) technique. The ^3He ion beam with different energies (4300, 3400, 2580, 1550 and 770 keV) was used for determination of deuterium depth profile by analysing the energy of protons produced by the nuclear reaction $D(^3He, p)\alpha$ [13]. Experimental setup is described in detail in [14]. In order to obtain absolute deuterium concentrations, measured NRA spectra were analysed by SIMNRA [15] and NRADC software [16].

Thermal desorption was used to measure the total amount of D retained in the samples. Samples were installed in the glass tube of the TESS device with a background pressure of $10^{-7} - 10^{-8}$ mbar during the heating ramp. A movable oven with maximal temperature of 1323 K and heating rate of 15 K/min was used for sample heating. Desorbed gas species were monitored by a quadrupole mass spectrometer. Details about the setup and the calibration procedure can be found in [17] and references therein.

STEM analysis was performed in order to observe the dislocation densities in the samples. STEM Hitachi HD2700 with an accelerating voltage of 200 kV was used on lamellae, cut perpendicularly to the sample surface by a Focused Ion Beam (FIB) system. The final thinning was carried out with low energy argon ions polishing for the reduction of damage introduced during FIB processing.

3. Results

3.1. Deuterium depth profile analysis

After the annealing and D atom exposure, samples were transported to the ion beam analysis vacuum chamber for D depth profile measurement. Corresponding depth profiles obtained for different annealing temperatures are shown in Fig. 1. Deuterium concentration for all samples was found to be noticeable to the depth of approximately 2.5 μm what coincides with the calculated damage profile and dropped significantly under 0.01 atomic % for larger depths. Deuterium concentration was decreasing more or less homogeneously in the damaged layer with increasing annealing temperature.

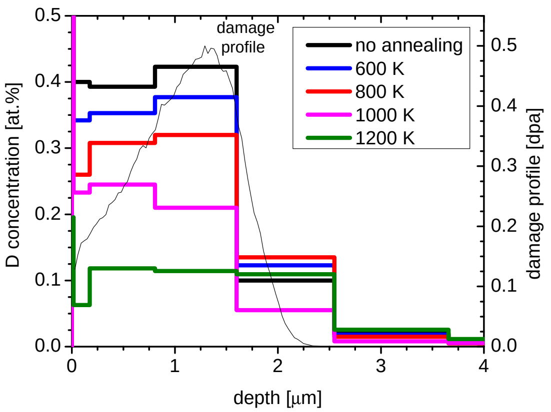


Figure 1: D concentration depth profiles for samples, annealed at different temperatures. The initial damage profile, calculated by SRIM, is also included.

By summing the deuterium concentration in the analyzed layer obtained by NRA we calculated the total amount of retained D in the sample. This is shown for different annealing temperatures in Fig. 2, together with the maximal concentration also obtained by NRA as well as the total D amount obtained by TDS. Annealing temperature was found to have strong influence on the retained D concentration in the damaged layer. The maximal concentration and the total retained D amount in the unannealed reference sample were 0.42 atomic % and 52×10^{19} D/m^2, respectively. On the other hand, for the sample annealed at 1200 K, the maximal concentration was 0.12 atomic % and total D amount was 21×10^{19} D/m^2, what is 71 % and 60 % lower than in unannealed case, respectively. This reduction is in good agreement with the results, obtained by plasma exposure with ion energy of 15 eV [7, 8], where also 70 % D concentration decrease was observed for annealing temperature of 1150 K.

3.2. Thermodesorption analysis

After D depth profile analysis, thermal desorption analysis was performed. Samples were linearly heated to around 1270 K with a heating rate of 15 K/min. For different annealing temperatures different shapes of thermal desorption spectra were observed in mass channel 4, corresponding to D_2 molecules, as shown in Fig. 3. Deuterium desorption in the form HD was 7 % for all samples except for the one annealed at 1200 K where it was twice as much. Here, only D_2 desorption is shown for simplicity. For unannealed sample and sample annealed at 600 K, two peaks are visible in the spectrum, one significantly more pronounced than the other. Only one symmetrical peak was observed in case of annealing temperatures of 800 K and 1000 K, and one asymmetrical peak is visible in case of annealing at 1200 K. These differences may be explained with different stages of damage annealing, occurring at different temperatures. According to [18, 19], at temperatures in the range between 400 K - 720 K single vacancies become mobile and can form larger defects or annihilate at sinks such as grain boundaries (stage III). Between 720 K and 920 K a recovery region of uncertain origin is observed and in temperature range 920 K - 1220 K a large vacancy recovery is taking place (stage IV). Since the temperature regions are only approximate, the results of unannealed sample and the sample, annealed at 600 K, may be assigned to stage III recovery, annealing temperature of 800 K and 1000 K to intermediate recovery region and the results for annealing at 1200 K to stage IV recovery.

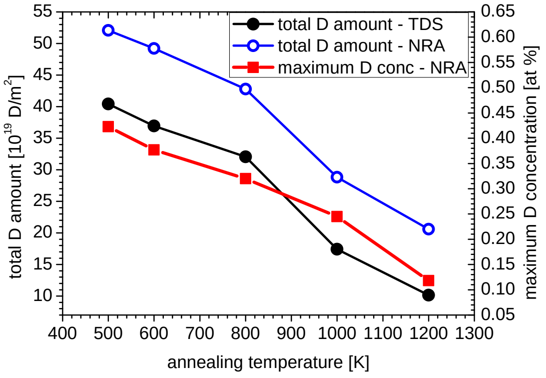


Figure 2: Maximal D concentration and total retained D amount obtained by NRA and TDS measurement for different annealing temperatures. The unannealed sample is marked at 500 K, which is the exposure temperature.

Total D concentration, obtained by integrating the thermal desorption spectra over time and dividing by the damaged area of the sample (1.13 cm^2) is shown in Fig. 2. Comparing to the total D concentration, obtained by NRA depth profile analysis, one can notice a difference in total concentration values corresponding to TDS and NRA analysis. A possible reason for the difference is that the profile of D atoms, effusing from the HABS during D atom exposure, is not homogeneous. The depth profile analysis was performed with an ion beam of dimension 2 mm in diameter in the center of the sample, where maximal deuterium flux density was obtained. Therefore,

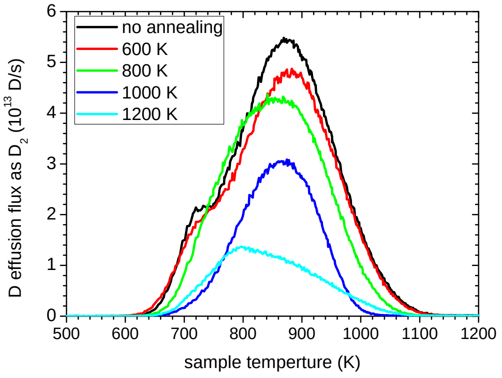


Figure 3: D_2 thermal desorption spectra for damaged samples, annealed at different temperatures. Heating rate was 15 K/min.

the total amount obtained by NRA is only local. On the other hand, since D_2 molecules in TDS are effusing from the entire sample surface, the total amount of D obtained by TDS is averaged over the exposed sample area. However, both methods give the same dependency of total concentration on annealing temperature.

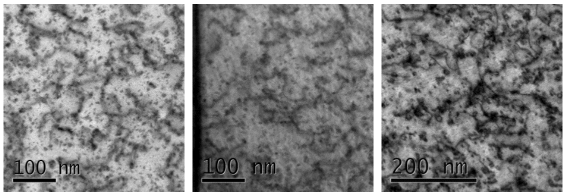
3.3. STEM analysis

STEM analysis was used to determine the dislocation densities in the samples. It was not performed on the identical five samples, however the samples have undergone the same treatment as the samples used for D depth profiling and thermal desorption. The only difference was at the highest annealing temperature, namely, the sample used for STEM was annealed at 1130 K instead of 1200 K and that the deuterium exposure was performed at 450 K. STEM analysis confirmed the thickness of the damaged layer to be approximately 2.3 μm for all samples, which is in good agreement with the SRIM calculation. In Fig. 4 STEM images of damaged regions are shown, where a decrease of the dislocation densities can be observed.

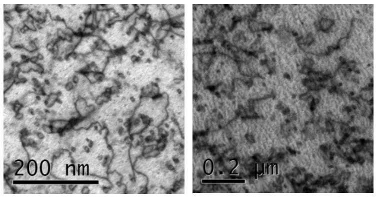
The dislocation density ρ is calculated using the line-intercept method. Five lines of different angular orientation are randomly drawn over the STEM image. The dislocation density is:

$$\rho = Nt/L, \tag{1}$$

where N is the number of defect intersections with the lines, L is the total length of lines and t is the lamella thickness, which was estimated to be approximately 80 nm. The dislocation densities with the estimated contributions of dislocation lines and loops for two regions are shown in the Fig. 5. It should be taken into account that calculated values also include the defects induced by the FIB processing. Dislocation density drops by 66 % for the highest annealing temperature compared to the unannealed sample. This is in good agreement with the total D concentration results obtained by NRA and TDS, where also 60 % decrease was observed.



(a) no annealing (b) 600 K (c) 800 K



(d) 1000 K (e) 1200 K

Figure 4: STEM images of the damaged region of W samples, annealed at different temperatures.

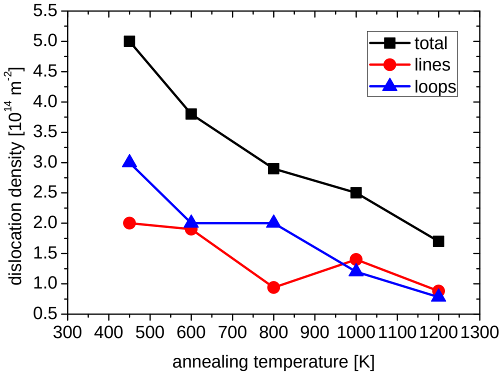


Figure 5: Total dislocation densities together with dislocation line and dislocation loop densities for samples, annealed at different temperatures. The unannealed sample is marked at 450 K, which is the exposure temperature.

4. Discussion and conclusions

The influence of annealing temperature on deuterium retention has been studied on self-ion damaged tungsten samples. Samples were annealed for 1 h at four different temperatures in the range from 600 K to 1200 K and afterwards exposed to D atom beam at 500 K with flux of 2.6×10^{19} D/m^{2}s for 144 hours. Unannealed sample was also used as a reference. Deuterium concentration depth profiles were measured by NRA technique with ^3He ion beam at different impact energies. Thermal desorption was also performed on the same samples after NRA analysis, measuring the total amount of retained deuterium. Scanning transmission electron microscopy was used to calculate the dislocation densities in the samples.

The annealing temperature was found to have strong influence on D retention as confirmed by both, depth profile analysis and TDS. Different shapes of TDS spectra were observed for annealing at different temperatures, what may be associated with different recovery stages at different temperatures. The annealing of the sample up to 1200 K decreased the total amount of retained D by 60 %, meaning that such high temperature is still not enough to completely anneal the damage. STEM analysis has also shown the decrease of dislocation densities with increasing annealing temperature, obtaining similar decrease trend as in the case of NRA and TDS analysis. One could infer from this that dislocations may be the dominant defect type responsible for D retention in self-damaged tungsten.

These results are in good agreement with the results, obtained by D plasma exposure [7, 8]. However, in the plasma exposure case the total and maximal deuterium concentration are for a factor of three higher as compared to the case of atom exposure. The explanation for this discrepancy could be due to the 100 K lower exposure temperature and higher ion flux (5×10^{19} D/m^{2}s) together with the neutral flux in the background. Namely, in the case of ion implantation two desorption peaks can be observed, with the low temperature one being more pronounced. In our case the high temperature peak is larger whereas the low temperature peak is hardly visible. The low temperature trap seems to be active at our exposure temperature of 500 K, meaning that atoms are actively trapping and de-trapping from this trap during the exposure. The steady state of trap saturation is flux dependent, the higher the flux the higher is the deuterium concentration in the individual trap. In the case of plasma exposure the flux is higher and the temperature is lower, meaning that the new arriving atoms fill any available empty trap faster. On the other hand for atom exposure the atom flux is lower meaning that the arrival rate of atoms into the bulk is slower compared to the de-trapping from the low temperature trap, hence the factor of three discrepancy.

It is worth mentioning that the observed reduction in trap density is rather small compared to the D retention observed for exposure at sample temperatures in this temperature range. While D retention at 1200 K is negligible (see also the TDS spectra) the trap density in these materials is still significant.

Acknowledgment

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. This work was done within the EUROfusion work project PFC. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The author would also like to thank Dr I. Čadež for constructive and valuable discussions.

References

[1] V. Philipps, J. Nucl. Mater. 415 (2011) S2-S9
[2] R. A. Pitts et al., J. Nucl. Mater. 438 (2013) S48-S56
[3] M. R. Gilbert et al., J. Nucl. Mater. 442 (2013) S755-S760
[4] Y. Hatano et al., Nucl. Fusion 53 (2013) 073006
[5] M. Shimada et al., Nucl. Fusion 55 (2015) 013008
[6] O. V. Ogorodnikova, K. Sugiyama, J. Nucl. Mater. 442 (2013) 518-527
[7] O. V. Ogorodnikova et al., J. Nucl. Mater. 451 (2014) 379-386
[8] E. Markina et al., J. Nucl. Mater. (2014), http://dx.doi.org/10.1016/j.jnucmat.2014.12.005
[9] O. V. Ogorodnikova, V. Gann, J. Nucl. Mater. 460 (2015) 60-71
[10] A. Manhard et al., Prakt. Metallogr-PR M 50 (2013) 5-16
[11] http://www.srim.org
[12] K.G. Tschersich et al., J. Appl. Phys. 104 (2008) 034908 (http://www.mbe-komponenten.de/products/mbe-components/gas-sources/habs.php)
[13] M. Mayer et al., Nucl. Instrum. Meth. B 267 (2009) 506-512
[14] S. Markelj et al., Phys. Scr. T159 (2014) 014047
[15] M. Mayer, SIMNRA User's Guide, Report IPP 9/113, Max-Planck-Institut für Plasmaphysik, Garching, 1997 (http://home.rzg.mpg.de/%7Emam/)
[16] K. Schmid, U. von Toussaint, Nucl. Instrum. Meth. B 281 (2012) 64-71
[17] P. Wang et al., Nucl. Instrum. Meth. B 300 (2013) 54-61
[18] L. K. Keys, J. Moteff, J. Nucl. Mater. 34 (1970) 260-280
[19] H. Schultz, Mater. Sci. Eng. A141 (1991) 149-167