

Deuterium Trapping in Rolled Polycrystalline Tungsten Exposed to Low Energy Plasma

Aleksandr RUSINOV, Mizuki SAKAMOTO¹⁾, Hideki ZUSHI²⁾, Ryohei OHYAMA, Koichiro HONDA, Ikuji TAKAGI³⁾, Tetsuo TANABE and Naoaki YOSHIDA²⁾
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-0811, Japan

¹⁾*Plasma Research Center, University of Tsukuba, Tsukuba 305-8577, Japan*

²⁾*Research Institute for Applied Mechanics, Kyushu University, Kasuga 816-8580, Japan*

³⁾*DNE, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*

(Received 11 November 2011 / Accepted 13 April 2012)

Deuterium retention after low energy plasma exposure was investigated using the polycrystalline tungsten samples of which grain elongation directions are parallel and perpendicular with respect to the surface. The deuterium retention calculated from TDS spectra is 2 - 10 times larger in the sample with perpendicular grain elongation direction than in the parallel one for the irradiation temperatures of 450 - 750 K. Removing of the grain elongation anisotropy by the recrystallization resulted in disappearance of the difference in the deuterium retention of the both kinds of samples. No bubbles and no blisters have been observed in the near surface layer of the samples. Plasma irradiation should produce high energy defects that are responsible for the deuterium retention. The difference in the retention of the both kinds of samples seems to be attributed to the different effective diffusion coefficients depending on the grain elongation direction.

© 2012 The Japan Society of Plasma Science and Nuclear Fusion Research

Keywords: plasma facing material, deuterium, retention, thermal desorption

DOI: 10.1585/pfr.7.1405105

1. Introduction

Bulk tungsten will be used in the future experimental thermonuclear reactor ITER [1]. Inside the tokamak, namely in the divertor region, tungsten will be exposed to intense fluxes of hydrogen isotopes. Nowadays, the interaction between tungsten materials and low energy hydrogen isotope plasma has actively been investigated, e.g. [2–4]. However, it is still necessary to investigate the trapping mechanisms of the isotopes as well as the retention in different kinds of tungsten materials, such as polycrystalline materials, various tungsten deposited layers and others. The database of hydrogen isotope retention in tungsten has wide scattering in data [5]. The reasons could be using of different implantation sources as well as different material structure in the laboratories. Tungsten polycrystalline material with enhanced thermal conductivity along a certain direction is proposed to be used in the divertor of ITER, so called ITER-grade tungsten [6]. During manufacturing process tungsten material is rolled either in the form of a rod or in the form of a plane. Rolling process results in grain elongation anisotropy because the grains are elongated along the rolling direction. The elongated grain orientation of ITER-grade W should be parallel to the heat transfer direction [7]. The thermal conductivity is supposed to be higher for the material with perpendicular grain elongation (later, it will be refer as *perpendicular grains* or

perpendicular sample) with respect to the surface than for the material with parallel grain elongation (later, it will be refer as *parallel grains* or *perpendicular sample*). That is the reason why W material with perpendicular grains is favorable as a plasma facing material in the divertor region. In the laboratory studies W foils or rolled plates with parallel grains are mainly used. From the point of view of hydrogen isotope retention, it is important to know whether the materials with parallel and perpendicular grains have different ability of hydrogen isotopes retention or not. In this study, deuterium retention in tungsten samples with perpendicular and parallel grain elongation directions with respect to the surface is investigated by means of thermal desorption spectroscopy (TDS) and nuclear reaction analysis (NRA).

2. Experimental

The samples with the dimensions of $\text{Ø}10 \text{ mm} \times t1 \text{ mm}$ used in this study were produced by A.L.M.T. corp., Japan. The samples were of two types: one was cut from the rolled rod (*perpendicular sample*), the other one was cut from the rolled plate (*parallel sample*). The density of the perpendicular and the parallel samples was measured to be 19.4 and 19.1 g/cm^3 , respectively, which is similar within the error of 5%. The manufacturing process of the materials involved: 1) sintering of pressed tungsten powder; 2) hot rolling; 3) annealing at the temperature of 1473 K for

author's e-mail: rusinov.aleksandr@gmail.com

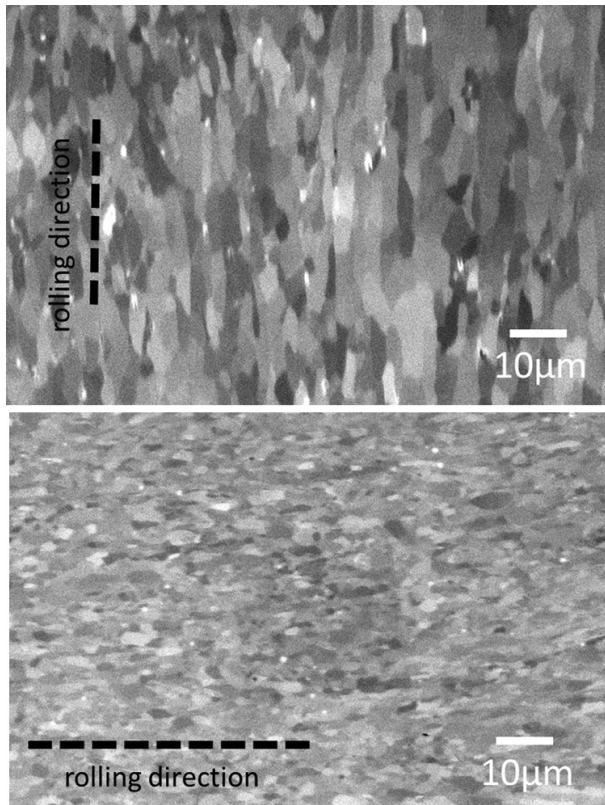


Fig. 1 Cross section of perpendicular (top) and parallel (bottom) as received tungsten samples. The surface direction of the samples is horizontal.

the rod and 1173 K for the plate; 4) polishing. The cross-sections of these samples obtained by secondary electron microscope (SEM) are shown in Fig. 1. The direction of the grain elongation of the perpendicular and parallel samples is perpendicular and parallel to the surface, respectively. The grain sizes are about $10 \times 2 \mu\text{m}$ for the perpendicular sample and about $5 \times 2 \mu\text{m}$ for the parallel one. The purity of the both kinds of materials is 99.99%. The samples were polished mechanically up to a mirror-like surface, washed in an ultrasonic bath in acetone and ethanol and annealed prior to the first irradiation in vacuum (about 1×10^{-6} torr) at 1173 K for 1 hour. Besides, other two samples were prepared. Those were the samples with parallel and perpendicular grains polished to a mirror-like surface and then recrystallized by an electron beam from the rear side in a separate stand in vacuum (at the pressure about 4×10^{-6} torr) at the temperature of 2073 K during 1 hour. SEM observations showed that the average grain size in the recrystallized samples is about $50 \mu\text{m}$.

Irradiation was performed by RF deuterium plasma in the Advanced PWI Simulation Experimental Device and Analysis System (APSEDAS), where a plasma column was sustained by 13.56 MHz RF field within a magnetic field created by the external coils. The scheme of APSEDAS is shown in Fig. 2. The sample is put directly

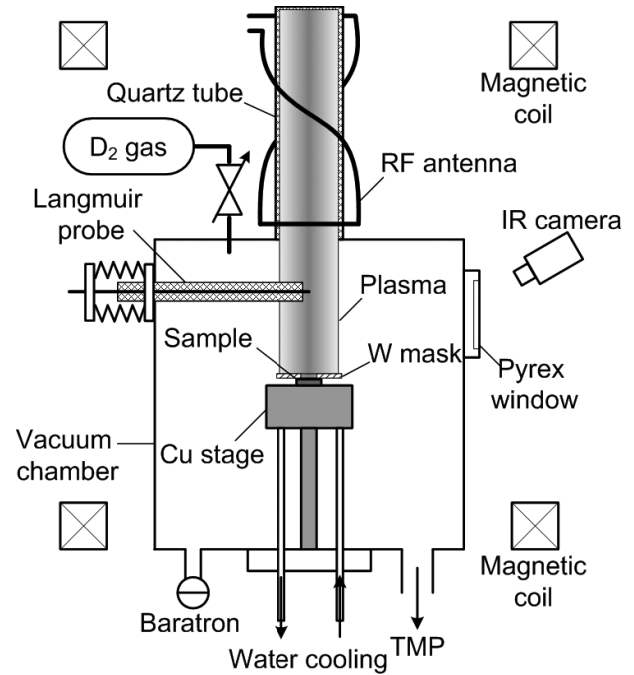


Fig. 2 APSEDAS PWI simulator scheme.

onto grounded and water cooled copper stage which is covered by a stainless steel mask with a hole of $\text{Ø}20 \text{ mm}$ and covered by W mask with a $\text{Ø}8 \text{ mm}$ hole. As the diameter of the plasma column is about 50 mm, the central irradiation area with the diameter of 8 mm is supposed to have relatively uniform ion flux distribution. The energy of ions coming to the surface was estimated to be about 20–30 eV from Langmuir probe measurements at the center of a plasma column. The surface temperature (T_{irr}) during plasma exposure was measured by infrared pyrometers assuming W emissivity of 0.3. It was varied from 450 to 750 K keeping the same ion flux by changing thermal contact with the copper stage with the help of substrates made of stainless steel or tungsten foil. The sample was exposed to the deuterium plasma up to the fluence of $2 \times 10^{25} \text{ D/m}^2$ under the flux of about $3 \times 10^{21} \text{ D/m}^2\text{sec}$ at various T_{irr} . After the irradiation it was moved to a TDS stand where it was put into a Ta bed with a thermocouple attached. After the evacuation the sample was heated by an infrared oven with the ramp of 1 K/sec from 300 K up to 1470 K. TDS signals were calibrated by He leak and the D retention was calculated from TDS spectra integration taking into account D_2 and HD signals with assumption that HD calibration factor is the same as that of D_2 .

Several days after plasma irradiation NRA measurements of deuterium concentration depth profiles had been performed in Kyoto University. The samples were exposed to ^3He ions at the energy of 1.7 MeV, the proton yield was measured and deconvoluted into D profiles up to the depth of $1.5 \mu\text{m}$.

3. Results and Discussion

TDS spectra of $D_2 + 0.5 HD$ desorption rate from the parallel and perpendicular samples irradiated at various T_{irr} are shown in Fig. 3. TDS spectra of both types of samples irradiated at the similar T_{irr} are located in the same temperature regions and have similar structure, though with a little differences. Deuterium desorption in the region of 450 - 650 K is commonly observed for the samples which were exposed at low $T_{irr} = 450$ K (Fig. 3a). This part is similar for both kinds of samples. Substantial part of the retained D is released in the region of 700 - 800 K for the perpendicular sample contrary to the parallel sample. At the T_{irr} higher than 500 K (Fig. 3b,c) low temperature part of the TDS spectra (below 700 K) vanishes, and the TDS spectra have a main peak at 800 - 900 K. This peak shifts to higher temperatures when T_{irr} increases (compare Fig. 3b and Fig. 3c). In fact, the spectra consist of at least two overlapped peaks located close to each other. Note that these peaks are quite narrow with the width at the half maximum less than 100 K. In the case of T_{irr} 730 - 750 K (Fig. 3d) the deuterium desorption from the parallel sample is negligible compared to the perpendicular sample for the desorption temperatures less than 1000 K. There is a high temperature part of the D desorption in the region of 1100 - 1300 K for all T_{irr} . This part is mainly due to HD molecules release, D_2 molecules release wasn't observed within this region. HD desorption here always correlates with H_2 desorption which showed a large peak at the same position with 200 - 400 times larger amplitude. Desorption at such high temperatures is not typical for polycrystalline W materials exposed to hydrogen isotope ions. Most likely, this is background effects related to the desorption from the quartz tube wall. This desorption could be attributed to D atoms adsorbed on the cold regions of the quartz tube wall. As these regions are heated quite enough (that corresponds to the high temperatures of a sample in TDS) the adsorbed D atoms desorb preferentially in the form of HD molecules through the recombination processes with H atoms. Blank TDS runs (without sample) showed similar HD and H_2 peak positions and signal amplitudes. Therefore, this part of desorption wasn't taken into account in the total deuterium retention calculations and discussions.

A lot of studies of D trapping in W materials from the energetic ion beams (\sim keV) by means of TDS show that trapped D atoms can release within 350 - 900 K temperature region [8-11]. The desorption near 600 K region can be attributed to detrapping of D atoms from vacancies [11], while high temperature release near 800 K can be attributed to the release of D adsorbed on the walls of voids and large vacancy clusters [10].

Studies related to deuterium retention in plasma exposed polycrystalline W materials show that at low plasma ions energies (\sim 100 eV) voids, cracks and blisters can be formed and can retain substantial amount of D atoms, especially at T_{irr} near 500 K [6, 12, 13]. At the low $T_{irr} \sim$ 300 - 400 K TDS peaks with the temperatures 650 - 700 K were

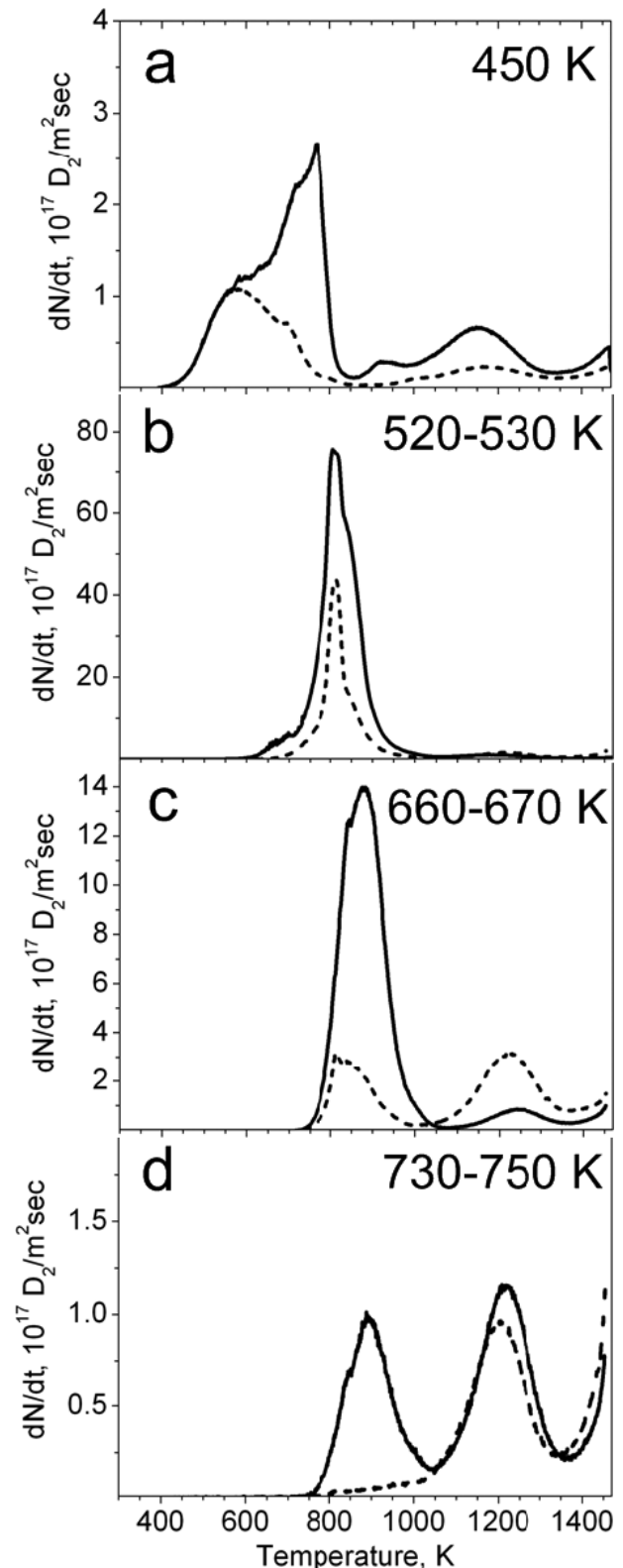


Fig. 3 TDS of $D_2 + 0.5 HD$ for the perpendicular sample (solid lines) and parallel sample (dash lines). The fluence is $2 \times 10^{25} D/m^2$, the irradiation temperatures are shown in the figures.

observed in [6] after 200 eV/D plasma exposure of ITER-grade W. This part of TDS was attributed to detrapping from vacancies with the trapping energy of 1.45 eV. In-

crease in T_{irr} up to 500 K resulted in the substantial increase in the D retention and shift of a TDS peak position to 760 K. It was stated that for $T_{\text{irr}} = 500$ K the concentration of the D atoms trapped in the vacancies increases and the mechanism is not clear yet. In [12] TDS spectra of plasma exposed recrystallized W also have low (~ 600 K) and high temperature (~ 790 K) parts. These two peaks were attributed to the release from vacancies and their complexes, where D was trapped in the form of atoms, and from cracks and large cavities, where D was trapped in the form of molecules. High temperature peak shifted with T_{irr} that was explained by deeper voids and cracks formation. Multiple splashes on TDS spectra of D_2 of recrystallized W exposed to D plasma have been observed. It was explained by the blisters bursting during TDS heating [14].

Peak positions in Fig. 3a-d for the two kinds of samples are located in the same regions for every T_{irr} range. This means that the detrapping energies are the same for both kinds of samples. It is reasonable for the W polycrystalline materials with the same purity and preparation procedure. Taking into account previous literature results, low temperature part of TDS in Fig. 3a can be attributed to D release from vacancies. At higher T_{irr} all D atoms release near 800 K as it is seen in the Fig. 3b. It can be explained by the formation of defects with high detrapping energy such as voids, large vacancy clusters or cracks. Blisters also can be responsible for high energetic trapping sites for deuterium. But this is not the case because we have never observed large blisters by SEM on the surface and splashes in TDS spectra of D_2 . The shift of the peak position near 800 K (compare Fig. 3b and Fig. 3c) could be caused by delaying of the D desorption due to the diffusion from deeper regions and also by the redistribution of the trapped atoms between two (or more) trapping sites. As pointed out above, the peak near 800 K consists of at least two independent peaks which correspond to different detrapping energy. The redistribution could be caused by change of the detrapping probability of each trapping site, which depends on T_{irr} . Increase in T_{irr} results in increase of the detrapping probability of lower energy trapping site and then the amplitude of lower temperature peak decreases. Therefore the “peak” (which consists of overlapped peaks) position appears to shift to higher temperature with increase in T_{irr} .

Temperature dependence of deuterium retention in both kinds of samples obtained from TDS data, is presented in Fig. 4. The D retention was estimated from the integral of the desorption rate shown in Fig. 3. Two main points are seen from this figure: the dependence has a maximum at T_{irr} around 550 K and the retention in the perpendicular sample is larger than that in the parallel one for all irradiation temperatures. The minimal difference in the retention is about 2 times for lowest T_{irr} and about 10 times for highest T_{irr} . NRA measurements of depth profiles of the deuterium concentration (Fig. 5) after deuterium plasma irradiation at $T_{\text{irr}} = 510$ K showed that deu-

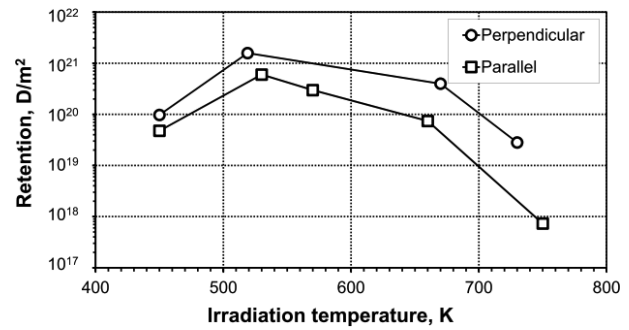


Fig. 4 Irradiation temperature dependence of the D retention in the perpendicular and parallel W samples (the fluence is 2×10^{25} D/m²)

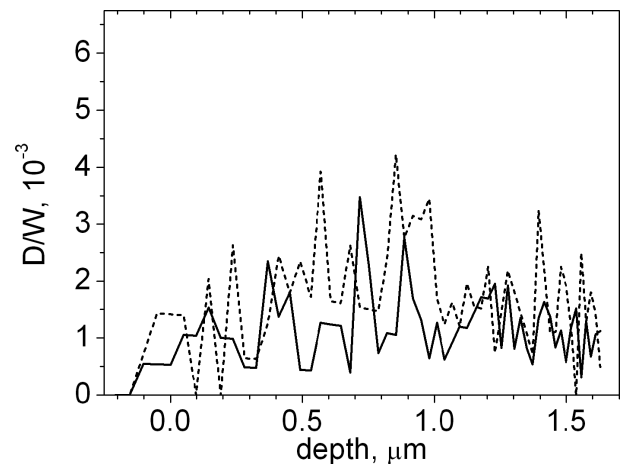


Fig. 5 Deuterium concentration depth profiles for perpendicular sample (dash line) and for parallel sample (solid line)

terium concentration at the depth of 1 μm is an order of $D/W \sim 10^{-3}$ at. fr. The depth profiles are similar for the perpendicular and the parallel samples and the total integral is about 2×10^{20} D/m². This value is about one order of magnitude smaller than TDS results showed.

The retention near $T_{\text{irr}} \sim 500$ K is an order of $10^{20} - 10^{21}$ D/m² (Fig. 4) that is consistent with other investigations of the deuterium retention in polycrystalline tungsten materials exposed to plasma, e.g. [2,3,6]. The maximum in the temperature dependence of the retention has been observed in [2, 3, 15]. The maximum was explained in [15] by enhanced diffusion coefficient in the implantation zone at low temperatures using TMAP modeling. The modeling showed that the retention should increase at low irradiation temperatures because the diffusion coefficient decreases and less implanted particles can leave the material. In order to explain reduction of the retention for T_{irr} less than 600 K, it was proposed that the surface is “agitated” by an incoming flux (ion induced desorption). This effect was successfully simulated by enhanced diffusion coefficient in the implantation zone. Another explanation is possible. It is suggested that at high plasma fluxes even at extremely low ion

energies (several tens of eV) the defects can be generated far beyond the subsurface layer [3, 13]. The mechanism of the defects generation is based on the large stresses inside the material due to extremely high incoming flux of hydrogen. As these stresses exceed the plastic deformation limit (supersaturation within the surface layer) the vacancies, vacancy complexes and microscopic cavities are generated and dislocations movement is activated in order to alleviate these tensions. These defects agglomerate at the grain boundaries which serve as the nucleation centres for large cavities and blisters formation. Formation of blisters leads to higher retention at higher irradiation temperatures as the mobility of the vacancies increases. But, at high temperatures the blisters agglomerate and open porosity starts to develop which lead to decrease in the retention [16]. Accumulation in non-recrystallized W has different features compare to recrystallized material. In [13] experiments with ITER-grade W also didn't show large cavities formation, only blister-associated cracks elongated parallel to the surface and localized at the depths of several hundred nm have been observed. In [6] deuterium retention in the ITER-grade W, which was exposed at $T_{\text{irr}} = 500$ K to the plasma with the energy of 200 eV up to 10^{25} D/m², was also larger than that in high-purity W polycrystalline samples.

As it was suggested above, high energy defects such as vacancy clusters, cracks and/or pores should be responsible for the retention in our samples exposed to D plasma ions at $T_{\text{irr}} > 500$ K. Therefore, we can suggest following explanation of the irradiation temperature dependence of the retention in Fig. 4. At low $T_{\text{irr}} (< 500$ K) the retention is determined by rather low energy defects, probably vacancies. The voids/cracks are not formed due to low vacancy mobility. At higher $T_{\text{irr}} \sim 500$ -600 K new trapping sites are created. The mechanism should be similar to that proposed in [3, 13]. Cracks and voids are formed due higher vacancy mobility and generation of high stress field exceeding plastic deformation limit. The pores and/or cracks grow or are created to relieve the stress. D atoms are accumulated inside these defects. The defects have high detrapping energy and high concentration that results in an increase of the retention and high temperature TDS release. At $T_{\text{irr}} > 700$ K some deuterium is still retained inside those high energy traps. But the probability to stay inside the traps becomes too small to keep high D retention.

The cross-section of a subsurface layer (~ 1 μm) in the parallel sample exposed to D plasma at $T_{\text{irr}} = 500$ K up to the fluence of 2×10^{25} D/m² was examined by means of focused ion beam (FIB) sputtering and subsequent transmission electron microscopy (TEM) analyzing. No bubbles or voids have been observed within the layer. Nevertheless, taking into account TEM resolution (about 10 nm) very fine bubbles with the size of less than 10 nm still might exist in the material. These very fine bubbles or voids might serve as high energy trapping sites for deuterium atoms and

might be an explanation of nature of TDS peak near 800 K. The only unusual thing was quite large distance (an order of nm) between the W grains. This could be attributed to the accumulation of D atoms along the grain boundaries.

The fact that the D retention calculated by means of TDS is much higher than that calculated by NRA means that the main part of deuterium atoms is trapped in the bulk beyond 1.5 μm depth. Therefore, a subsurface layer (several hundreds nm) doesn't play critical role in the total D retention, the main part is trapped inside the bulk. The trapping sites density is supposed to be similar for the perpendicular and the parallel samples within 1.5 μm as it is seen from Fig. 5. Because of same samples preparation procedure the surface state (mainly, chemical composition) is supposed to be similar for all samples, i.e. surface barrier should be similar. Bulk impurities level is also supposed to be similar, i.e. the number of trapping sites related to the impurities is more or less same for all samples. Therefore, neither different trapping sites concentration nor bulk impurities level nor different surface conditions can explain the difference in the retention between the parallel and perpendicular samples. One possible explanation is that larger D retention in the perpendicular sample is caused by more intense migration of D inside the bulk compare to parallel sample. This difference can take place in the case when the presence of deuterium inside the bulk is mainly determined by the migration along the grain boundaries, which is more effective for the perpendicular samples. TEM observations support the idea of deuterium preferential accumulation at grain boundaries. In other words, the effective diffusion coefficient is larger along the grain elongation direction, than perpendicular to this direction that is similar to the thermal conductivity anisotropy in ITER-grade W. Because the intrinsic defects, taking part in the trapping, are same for both kinds of samples, TDS showed same peak positions at the same irradiation temperature. Enhanced D migration inside the bulk of the material causes larger D retention that could be negative from the point of view of the tritium inventory.

TDS spectra of deuterium desorption from the recrystallized parallel and perpendicular samples exposed to D plasma at $T_{\text{irr}} = 500$ K are shown in Fig. 6. The peak positions did not change compare to the non-recrystallized samples (see Fig. 3b), i.e. the detrapping energies did not change after the recrystallization process. The retention in the recrystallized materials is about 6×10^{20} D/m² for both kinds of samples which is similar to that in the parallel sample for $T_{\text{irr}} = 520$ -530 K (Fig. 4). Ion beam experiments show that the recrystallization results in reduction of the retention because the defects level decreases [8, 9]. But here the retention didn't change much. Same detrapping energies for the recrystallized and non-recrystallized samples mean that the nature of the defects is similar. This supports our idea that these are the plasma created defects that determine the retention in our samples, not intrinsic defects beyond the ion stopping range. Moreover, the re-

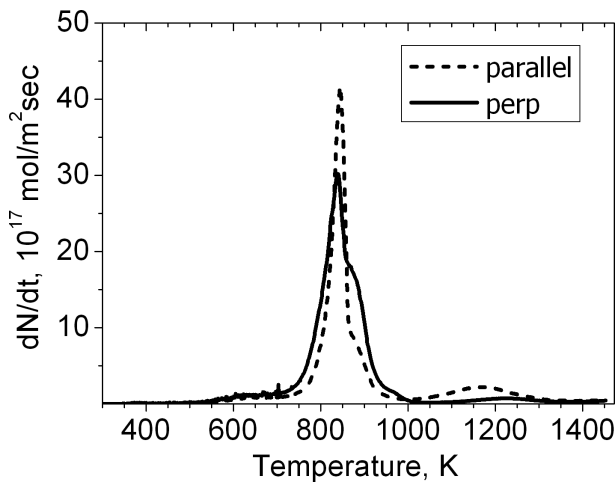


Fig. 6 TDS spectra of $D_2 + 0.5 HD$ from parallel (dash line) and perpendicular (solid line) recrystallized W samples irradiated at $T_{irr} = 500 K$ up to the fluence of $2 \times 10^{25} D/m^2$

tention became similar for the parallel and the perpendicular samples as it is seen from Fig. 6. This supports the idea that the difference in the retention between the perpendicular and parallel samples is caused by the different grain elongation orientation with respect to the surface. The retention became similar in the samples after disappearance of the grain elongation anisotropy due to the recrystallization.

4. Conclusion

Deuterium retention in plasma exposed rolled polycrystalline tungsten samples of which different grain elongations are parallel and perpendicular with respect to the surface was measured. TDS spectra after plasma irradiation at the temperatures of 500-600 K showed that deuterium atoms desorb at high temperatures for the both samples. This indicates that high energy defects are created at these conditions in the material. SEM and TEM observations showed no blisters on the surface and no bubbles or voids inside the subsurface layer. Comparison of depth profiles of deuterium concentration measured by NRA and the deuterium retention calculated by means of TDS data showed that at the irradiation temperature of 500 K the main part of deuterium is located beyond $1.5 \mu m$ depth. The deuterium retention calculated from TDS spectra is 2-10 times larger in the perpendicular sample than that in

the parallel one for the irradiation temperatures 450-750 K though the mechanisms of trapping are supposed to be similar. It was suggested that the difference in the retention can be caused by different migration ability or effective diffusion coefficient of deuterium atoms along and across to the grain elongation. Recrystallization of the samples resulted in the disappearance of the difference in the deuterium retention between the two kinds of samples that was attributed to the grain elongation anisotropy disappearance. The effect of different enhanced migration ability for perpendicularly elongated grains could be negative for tritium permeation and accumulation in fusion applications.

Acknowledgments

This work was partially supported by the Japan Society for the Promotion of Science (JSPS) under Grant-in-Aid for Scientific Research, and NIFS Collaborative Research Program.

- [1] R.A. Causey, *J. Nucl. Mater.* **300**, 91 (2002).
- [2] O.V. Ogorodnikova, T. Schwarz-Selinger, K. Sugiyama *et al.*, *J. Appl. Phys.* **109**, 013309 (2011).
- [3] V.Kh. Alimov, J. Roth, R.A. Causey *et al.*, *J. Nucl. Mater.* **375**, 192 (2008).
- [4] K. Tokunaga, M.J. Baldwin, R.P. Doerner *et al.*, *J. Nucl. Mater.* **337-339**, 887 (2005).
- [5] O.V. Ogorodnikova, J. Roth and M. Mayer, *J. Nucl. Mater.* **313-316**, 469 (2003).
- [6] O.V. Ogorodnikova, T. Schwarz-Selinger, K. Sugiyama *et al.*, *Physica Scripta* **T138**, 014053 (2009).
- [7] T. Hirai, G. Pintsuk, J. Linke *et al.*, *J. Nucl. Mater.* **390-391**, 751 (2009).
- [8] A. Rusinov, Yu. Gasparyan, N. Trifonov *et al.*, *J. Nucl. Mater.* **415**, S645 (2011).
- [9] O.V. Ogorodnikova, J. Roth and M. Mayer, *J. Nucl. Mater.* **373**, 254 (2008).
- [10] M. Poon, A.A. Haasz and J.W. Davis, *J. Nucl. Mater.* **374**, 390 (2008).
- [11] H. Eleveld and A. van Veen, *J. Nucl. Mater.* **212-215**, 1421 (1994).
- [12] V.Kh. Alimov, H. Nakamura, B. Tyburska-Puschel *et al.*, *J. Nucl. Mater.* **414**, 479 (2011).
- [13] V.Kh. Alimov, B. Tyburska-Puschel, S. Lindig *et al.*, *J. Nucl. Mater.* **420**, 519 (2012).
- [14] W.M. Shu, M. Nakamichi and V.Kh. Alimov, *J. Nucl. Mater.* **390-391**, 1017 (2009).
- [15] T. Venhaus, R. Causey, R. Doerner *et al.*, *J. Nucl. Mater.* **290-293**, 505 (2001).
- [16] V.Kh. Alimov, J. Roth and M. Mayer, *J. Nucl. Mater.* **337-339**, 619 (2005).