Deuterium trapping at defects created with neutron and ion irradiations in tungsten

Y. Hatano¹, M. Shimada², T. Otsuka³, Y. Oya⁴, V.Kh. Alimov¹, M. Hara¹, J. Shi¹, M. Kobayashi⁴, T. Oda⁵, G. Cao⁶, K. Okuno⁴, T. Tanaka⁷, K. Sugiyama⁸, J. Roth⁸, B. Tyburska-Püschel⁸, J. Dorner⁸, N. Yoshida⁹, N. Futagami⁹, H. Watanabe⁹, M. Hatakeyama¹⁰, H. Kurishita¹⁰, M. Sokolov¹¹ and Y. Katoh¹¹

Contact of main author

Tel.: +81-76-445-6928 Fax.: +81-76-445-6931

E-mail: hatano@ctg.u-toyama.ac.jp

PACS 28.52.Fa, 61.80.Hg, 61.82.Bg, 67.63.-r

Abstract

The effects of neutron and ion irradiations on deuterium (D) retention in tungsten (W) were investigated. Specimens of pure W were irradiated with neutrons to 0.3 dpa at around 323 K and then exposed to high-flux D plasma at 473 and 773 K. The concentration of D significantly increased by neutron irradiation and reached 0.8 at% at 473K and 0.4 at% at 773 K. Annealing tests for the specimens irradiated with 20 MeV W ions showed that the defects which play a dominant role in the trapping at high temperature were stable at least up to 973 K, while the density decreased at temperatures equal to or above 1123 K. These observations of the thermal stability of traps and the activation energy for D detrapping examined in a previous study (≈1.8 eV) indicated that the defects which contribute predominantly to trapping at 773 K were small voids. The higher concentration of trapped D at 473 K was explained by additional contributions of weaker traps. The release of trapped D was clearly enhanced by the exposure to atomic hydrogen at 473 K, though higher temperatures are more effective for using this effect for tritium removal in fusion reactors.

¹ Hydrogen Isotope Research Center, University of Toyama, Toyama, Japan

² Fusion Safety Program, Idaho National Laboratory, Idaho Falls, ID, USA

³ Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Japan

⁴ Faculty of Science, Shizuoka University, Shizuoka, Japan

⁵ Department of Nuclear Engineering and Management, The University of Tokyo, Japan

⁶ Department of Engineering Physics, The University of Wisconsin, Madison, WI, USA

⁷ National Institute for Fusion Science, Toki, Japan

⁸ Max-Planck-Institut für Plasmaphysik, EURATOM Association, Garching, Germany

⁹ Research Institute for Applied Mechanics, Kyushu University, Kasuga, Japan

¹⁰ Institute for Materials Research, Tohoku University, Oarai, Japan

¹¹Oak Ridge National Laboratory, Oak Ridge, TN, USA

1. Introduction

Tritium inventory in plasma-facing materials (PFMs) is an important issue to assess the safety margins of fusion reactors. As reviewed in [1], ion-irradiation experiments have clearly shown that the formation of radiation defects increases the retention of hydrogen isotopes in tungsten (W), a potential PFM candidate, owing to the strong trapping effects of those defects. To understand the effects of neutron (n) irradiation, the authors irradiated W to 0.025 dpa (displacement per atom) with neutrons in a fission reactor at the coolant temperature of the reactor (around 323 K) and measured deuterium (D) retention after exposure to high-flux D plasma at 373, 473 and 773K under the framework of the Japan-US joint research project TITAN[2–7]. A significant increase in D retention with neutron irradiation was observed even at a damage level as low as 0.025 dpa, and the D concentration in n-irradiated W reached values of 0.1-0.2 at% at all temperatures examined [3,7]. The desorption of D from nirradiated specimens continued up to temperatures above 1173 K, while that from nonirradiated specimen was completed at ≈700K after plasma exposure at 473K [2] and at ≈970K after exposure at 773K [6]. The activation energy for D detrapping, E_{det} , from defects that contribute to dominant trapping at 773K was evaluated to be ≈1.8 eV [6, 7]. However, the retention of hydrogen isotopes at a higher damage level has not been examined. A simulation of tritium release performed in a previous study [6] showed that a trap density of 0.1–0.2 at% and E_{det} of 1.8 eV are sufficiently high to retard the tritium release at moderate temperatures (e.g. ≤ 673 K), and hence tritium removal by baking in vacuum could be difficult. Nevertheless, it was also found that release of trapped D was strongly enhanced under exposure to H₂ gas at 673K [6]. This observation suggests that tritium removal may be possible by exposure to H and/or D. However, the mechanisms underlying this enhanced release of D have not been clarified in detail.

In this study, W specimens were irradiated with neutrons at around 323 K to 0.3 dpa, and the concentration of retained D after exposure to D plasma at 473 and 773 K were examined by nuclear reaction analysis (NRA). Radioactivity in n-irradiated W was also measured, because this information would be helpful for detailed planning of specimen handling in future programs on plasma–surface interaction studies with n-irradiated specimens (e.g. [8]). The D concentration in the n-irradiated W specimen was relatively high even after plasma exposure at a high temperature (0.4 at% at 773 K). To understand the mechanisms underlying such significant trapping at high temperature, the thermal stability of defects was examined using specimens irradiated with 20MeV W ions. The effects of coexistence of H on D release from an ion-irradiated specimen was investigated at a relatively low temperature (473 K) for a better understanding of the mechanism underlying the enhancement of D release by H.

2. Experimental procedures

2.1. Neutron irradiation and post-irradiation examinations

Disc-type specimens (\emptyset 6×0.2 mm) were prepared by slicing rods of pure W (99.99 mass%) supplied by A. L. M. T. Co., Japan under stress-relieved conditions (1173 K, 1 h). The impurity content is summarized in table 1. The total concentration of impurities in at% was calculated to be 0.05. The surfaces of the specimens were polished with abrasive papers and diamond powders (9 and 3 μ m), and were given a mirror-like finish with a colloidal silica suspension (40 nm). Then, the specimens were annealed at 1173K for 30 min in vacuum (10–6 Pa) to remove H contained as an impurity and relieve stress induced by polishing.

The specimens were sealed in Mo envelopes and irradiated with neutrons in the high-flux isotope reactor (HFIR) at Oak Ridge National Laboratory (ORNL) for 33 and 391 h at the coolant temperatures of the reactor (around 323 K). The damage level reached 0.025 and 0.3 dpa. Radioactivity induced in the specimens was evaluated using the FISPACT-2001 computer code. These specimens were shipped to Idaho National Laboratory (INL) after storage in a water pool and hot cell for around 300 days and 800 days, respectively.

At INL, the radioactivity of the specimens was examined by γ -ray spectroscopy. The surfaces of the specimens were covered by thin oxide layers formed during neutron irradiation and/or storage in a water pool. Therefore, they were gently polished with a lapping film (3M, aluminium oxide, $0.3\mu m$). The specimens were then exposed to D plasma in a linear plasma machine called the tritium plasma experiment (TPE) at 473 ± 10 and 773 ± 10 K. The temperature of each specimen was measured with a thermocouple pressed against the back of the specimen with a linear motion feedthrough. The depth profiles of D were measured by NRA with 3.5MeV 3 He ions at the University of Wisconsin. The retention of D was measured by thermal desorption spectroscopy (TDS); the temperature ramp rate was adjusted to 0.167 K s $^{-1}$ (10 K min $^{-1}$). Details of the analyses are described elsewhere [2, 3].

2.2. Ion irradiation, annealing and D measurements

Owing to a limited number of n-irradiated specimens, the thermal stability of the traps was examined using plates of recrystallized W (99.99 mass%, $10 \times 10 \times 2$ mm) treated at 2073K for 1 h in vacuum ($\leq 10-3$ Pa) [9]. Those plates were supplied by the same manufacturer as the n-irradiated specimens and the impurity content was similar to that shown in table 1 except that the content of Na and Mo was 1 and < 1 mass ppm, respectively. The specimens were damaged at room temperature by irradiation with 20 MeV W ions to 0.5 dpa at the damage peak. The damage profile was evaluated by the SRIM2008 program¹ by setting the displacement energy to 90 eV [9]. The thickness of the damaged zone created by 20MeV W ions was evaluated to be $\approx 2\mu m$ as shown later. These specimens were annealed in vacuum (10-5 Pa) at 973, 1123, 1273 and 1573 K for 6 h. Then, the specimens were exposed to D₂ gas instead of D plasma at 673 K and 100 kPa in the manner described in [6, 10] in order to examine D trapping at a constant concentration of D in the solid solution state. Next, the

1

¹ Ziegler J.F., www.srim.org/.

concentration of trapped D was measured by NRA with 0.69–4.0 MeV 3 He ions at the Max-Planck-Institut für Plasmaphysik [10]. As reported in previous papers [6, 7], the probability of trap occupancy by D sensitively depends on the concentration of D in the solid solution state if the temperature is sufficiently high to attain trapping–detrapping equilibrium. Under plasma exposure, the concentration of solute D can vary even at a constant incident flux of D with variation in the rate of recombinative release caused by modifications in surface states [11]. In contrast, the concentration of solute D is precisely determined by solubility, temperature and pressure under gas exposure. Hence, the annealing effects on trap density can be clearly observed under exposure to D_2 gas. Prior to the annealing experiments, the TDS spectrum of D after exposure to D_2 gas at 773 K was examined at a ramp rate of 0.5 K s⁻¹ to understand whether the desorption temperature of D from the ion-irradiated specimens is similar to that from n-irradiated specimens.

The release of D and effects of coexisting H were examined by heating D-loaded specimens in vacuum or under exposure to H neutrals (atoms and molecules) at 473 K. First, the ion-irradiated specimens were exposed to D_2 gas at 673 K and 100 kPa or D neutrals at 473 K in a dc glow-discharge device in a manner described elsewhere [10] in order to introduce D into the traps. In the case of exposure to neutrals, each specimen was put on a holder which served as an anode. The cathode was a tungsten disc located at a distance of about 100 mm. The discharge voltage, current and deuterium pressure were 400V, 0.18A and 1 Pa, respectively. In addition to D_2 molecules, the specimen was exposed to D atoms, whose energy ranged from a few eV (atoms formed in the glow-discharge plasma) to 400 eV (those reflected from the W cathode). The implantation flux of D was measured to be 2×10^{18} D m⁻² s⁻¹ by exposure of the Ti probe at room temperature for 10 and 60 min and D retention measurement by TDS [10]. The fluence of D to W specimens was 6×10^{22} D m⁻². Then, D-loaded specimens were heated in the same device in vacuum (10^{-3} Pa) or under exposure to H neutrals at 473 K for 10 h. The discharge conditions for exposure to H neutrals were similar to those for D neutrals. Finally, the profiles of D were analysed by NRA.

3. Result and discussion

3.1. Radioactivity in neutron-irradiated specimens

Measurements of γ -ray spectra carried out for the n-irradiated specimens showed the presence of ^{188}W and ^{188}Re . The latter is the daughter of the former, and the half-life of the latter (17 h) is far shorter than that of the former (69.4 days). Hence, the radioactivity of these two nuclides was almost equal (secular equilibrium). The values of radioactivity of ^{188}W and ^{188}Re in the specimens irradiated to 0.025 and 0.3 dpa were 50 and 4 MBq g $^{-1}$ at 353 days and 926 days after completion of irradiation, respectively. The lower radioactivity for the higher neutron dose was due to the longer period of time between completion of irradiation and measurement. Figure 1 shows the radioactivity of major radionuclides evaluated with the

FISPACT-2001 code as a function of elapsed time after completion of irradiation. In this evaluation, the duration of neutron irradiation was set to 30 days (720 h). The half-filled circles in this figure indicate the values of radioactivity of ^{188}W and 188Re calculated from the measured values for the specimens irradiated to 0.025 and 0.3 dpa by assuming that the radioactivity immediately after the completion of irradiation is proportional to the irradiation duration. The values evaluated with the FISPACT-2001 code and those calculated from the measured values agreed with each other within a factor of 2. Both ^{188}W and ^{188}Re emit high-energy β -rays, while the probabilities of γ -ray emission are relatively low. The maximum energies of β -rays from ^{188}W and ^{188}Re are 0.349 MeV and 2.12 MeV, respectively [12]. Hence, β -rays from ^{188}Re were the most important radiation from the viewpoint of safe handling of the n-irradiated specimens.

Although the FISPACT-2001 code predicted the presence of 181 W and 185 W, these nuclides were not detected by γ –ray spectroscopy. The absence of a γ -ray peak from 185 W can be explained by low probability of γ -ray emission of 185 W (0.019%) [12]. No detection of 181 W was attributed to the fact that the cut-off energy in the measurement (50 keV) was comparable to the energy of the most intense x-rays from 181 W (57.5 keV) [12].

3.2. Depth profiles of D in neutron-irradiated specimens

The depth profiles of D in the n-irradiated specimens measured by NRA after exposure to plasma at 473 and 773K to $(5-7) \times 10^{25}$ D m⁻² are shown in figures 2(a) and (b) together with those in the non-irradiated specimens. After exposure to D plasma at 473 K, D penetrated to a depth of around 3 µm, and the D concentration in the penetration zone increased with increase in neutron dose. The concentration of D reached 0.8 at% at 0.3 dpa, while it was 0.3–0.4 at% at 0.025 dpa and 0.1 at% in the non-irradiated specimen. After exposure to plasma at 773 K, the D concentration in the non-irradiated specimen was significantly low (~0.01 at%). The results of TDS measurements showed that the D retention in the non-irradiated specimen exposed at 773K was lower than that in the specimen exposed at 473K by an order of magnitude. Hence, the lower D concentration at 773K was ascribed to the enhanced recombinative release of D and not to deeper penetration by enhanced diffusion. On the other hand, the concentrations of D in the n-irradiated specimens reached 0.2 at% at 0.025 dpa and 0.4 at% at 0.3 dpa even at 773 K. In addition, D penetrated beyond the detection range of NRA (~5 µm) owing to enhanced diffusion of D. These observations clearly indicated that strong traps for D were formed by neutron irradiation, and the concentration of those traps increased with increase in neutron dose.

Although the damage level increased by an order of magnitude, the concentrations of D after n-irradiation to 0.3 dpa were only higher by a factor of 2 than those at 0.025 dpa at 473 and 773 K. According to Roth and Schmid [1] who summarized the correlation between damage level and trap density in W irradiated with high-energy heavy ions at room temperature, the density of traps sharply rises at dpa values < 0.1 and ceases to increase at

around 0.3–0.4 dpa and a D concentration of 1.0–1.4 at%. It is plausible that saturation with traps also takes place with neutron irradiation, and the trap density after irradiation to 0.3 dpa was close to the saturation level. However, measurements of D retention after neutron irradiation to higher damage levels are necessary to draw a final conclusion.

In the specimen irradiated with neutrons to 0.3 dpa, the D concentration after plasma exposure at 773K was lower than that at 473 K, but only by a factor of 2. This observation is not trivial because vacancies in tungsten can migrate over long distances at 773K as described in the review papers by Balluffi [13] and Schultz [14]. The mechanisms underlying such weak temperature dependence will be discussed later.

3.3. Thermal desorption of D from neutron- and ion-irradiated specimens

In figure 3, the TDS spectra of D for the n-irradiated specimens (0.025 dpa) are compared with those for the non-irradiated and ion-irradiated (0.5 dpa) specimens. The spectra for nirradiated and non-irradiated specimens, except for the one for the n-irradiated specimen exposed to plasma at 473 K, are similar to those reported in previous papers [2, 6, 7]. In a previous study [2], the oxide films formed during neutron irradiation and/or storage in a water pool remained on the edge and back of the specimen even after plasma exposure, and spikes were observed in the TDS spectrum at temperatures below 400 K. Spikes were also observed at similar temperatures in the TDS spectrum of a non-irradiated specimen intentionally oxidized in air at 673K for 2 h and then exposed to plasma at 473 K. Hence, these spikes were ascribed to desorption of D from oxide films. As described in section 2.1, the oxide films were removed by gentle polishing in this study, and hence no spike was observed. The desorption of D from the non-irradiated specimen was completed at around 700 K, as described previously. On the other hand, the D release from the n-irradiated specimens continued to high temperatures above 1173 K. These observations suggest the formation of traps by neutron irradiation. The broad desorption peak after plasma exposure at 473K indicates the presence of various types of traps with different activation energies for detapping E_{det} [2, 3, 15]. At 773 K, only strong traps with large E_{det} contribute to D retention. The value of $E_{\rm det}$ for such strong traps was evaluated to be ≈ 1.8 eV by simulation using the TMAP program in previous studies [6, 7]. The retention of D in the n-irradiated specimen after exposure to plasma at 773K was 6.4×10^{21} D m⁻² and significantly greater than that at 473 K. This difference can be explained by the deeper penetration of D (figure 2). As described in a previous paper [6], the penetration depth of D was calculated to be 50-100 µm as the quotient of the amount of retained D $(6.4 \times 10^{21} \text{ D m}^{-2})$ and D concentration (0.1-0.2 at% = (6.3-12.6))× 10²⁵ D m⁻³) by assuming uniform D concentration throughout the penetration depth. The measurements of TDS spectra for the specimens irradiated to 0.3 dpa will be carried out in the near future, and the results will be reported in a separate paper.

The ion-irradiated specimen also showed D desorption in the high-temperature region, i.e. 930–1150 K. This temperature range of D desorption agreed with that for the n-irradiated specimen exposed to plasma at 773 K, although the desorption peak observed for the ion-irradiated specimen was much narrower and smaller than that for the n-irradiated specimen. Therefore, it is reasonable to consider that the types of defects which play a dominant role in the trapping effects in these two different specimens were similar. Ion irradiation creates defects only in a shallow region behind the surface, while neutron irradiation forms defects uniformly throughout the bulk of the material. The thickness of the damaged zone formed by irradiation of 20 MeV W ions was $\approx 2\mu m$, as described above [6]. Hence, the number of traps in the ion-damaged specimen was significantly smaller than that in the n-irradiated specimen. This is the cause of the smaller D retention in the ion-irradiated specimen than in the n-irradiated one. The narrower desorption peak observed for the former can also be attributed, at least in part, to the shallow depth of D penetration in comparison with the latter (50–100 μm , as described above).

3.4. Thermal stability of defects formed by ion irradiation

Figure 4 shows the correlation between the annealing temperature and concentration of trapped D examined after exposure to D_2 gas at a constant temperature (673 K). The D concentration at the damage peak was 0.38% before annealing; the data point was plotted at 673K because exposure to D_2 gas was performed at this temperature. The trap density showed no significant reduction after annealing at 973 K, whereas it clearly decreased after annealing at 1123 K. A further drop in the concentration of trapped D was observed after annealing at 1573 K.

These observations can be interpreted on the basis of literature data on the recovery of defects in n-irradiated W. According to Keys and Moteff [16] and Anand et al [17] who examined damage annealing over a wide range of temperature after fast neutron irradiation, a large extent of defect recovery in W takes place in two temperature regions: 473–773K (stage III) and 1073–1273K (stage V). Both Keys and Moteff [16] and Anand et al [17] reported that the recovery of defects in stage III was a second-order reaction with an activation energy of ≈1.7 eV. None of the researchers attributed this recovery stage to vacancy migration because the activation energy of vacancy migration is believed to be larger [16, 17]. However, as shown in later review papers by Balluffi [13] and Schultz [14], experiments with high-purity W showed that the activation energy of vacancy migration is 1.7 eV, and Balluffi [13] and Schultz [14] attributed the stage III recovery to vacancy migration. In addition, Eleveld and van Veen [18] examined positron annihilation in ion-damaged W and observed vacancy migration and clustering at 600–750 K. Therefore, it is plausible that formation of small voids by vacancy clustering takes place at stage III. Anand et al [16] ascribed the recovery in stage V to the annealing of defect clusters, and this is consistent with the observation of void

growth by Eleveld and van Veen [18]. It should be noted that a part of vacancies can be present in the form of clusters even immediately after the irradiation of neutrons and heavy ions below the stage III temperature (without any subsequent annealing) owing to cascade collisions [19]. Indeed, the irradiation of W thin films prepared for transmission electron microscope observation with 2.4MeV Cu ions resulted in the formation of nanosized voids, and subsequent annealing led to the visible growth of voids only at/above 1073 K. Details will be reported in a separate paper.

As described above, the activation energy for detrapping E_{det} for defects which play a dominant role in trapping at 773K was evaluated to be \approx 1.8 eV. This value corresponds to E_{det} for hydrogen chemisorbed on the inner surface of a void, as reported by van Veen et al (1.8-2.1 eV) [20]. In addition, the traps in the ion-irradiated specimen were stable up to 973 K, and then their density started to decrease with increase in annealing temperature to 1123 K. Such a change in trap density with annealing temperature agrees well with the abovementioned annealing behaviour of small voids. Therefore, it is plausible that D introduced into the irradiated specimens by exposure to D plasma and D₂ gas at 773K was mainly trapped in small voids formed by cascade collisions or the clustering of mono-vacancies during the exposure. The maximum temperature in TDS measurements, 1173 K, corresponds to stage V where the annealing of voids takes place. Hence, the growth of voids and consequently reduction in trap density can take place during the measurements. To understand such annealing effects better, the n-irradiated specimen subjected to the TDS measurement was exposed to D plasma again at 773 K, and a second TDS measurement was carried out. Indeed, a significant reduction in trap density was observed after the first TDS measurement. In the case of plasma exposure at 473 K, long-range migration of vacancies is small and the contributions of mono-vacancies to the trapping should be larger than in the case of exposure at 773 K. The activation energy for D detrapping from a mono-vacancy is smaller than that from a small void and is 1.43-1.55 eV [18]. In addition, Edet decreases with increase in the number of D atoms trapped in a mono-vacancy [21, 22]. This is one of the reasons for the broad desorption peak observed after the exposure at 473 K. Indeed, 't Hoen et al [23] performed positron annihilation Doppler broadening and D retention measurements for W specimen irradiated with 12.3MeV W ions and reported that clustering of vacancies took place at 650 K. They observed reduction in D retention with increase in the exposure temperature and explained this observation by the reduced amount of mono-vacancies and small vacancy clusters in combination with the strong depopulation with D due to thermal trapping and detrapping [23]. In any case, an improvement of modelling such as TMAP is necessary to analyse the desorption spectra acquired under the conditions where annealing of defects is significant.

3.5. Release of D by heating in vacuum and under exposureto H neutrals at 473K

Figure 5 shows the depth profiles of D after the exposure of ion-irradiated W to D neutrals and D_2 gas, and subsequent heat treatments at 473K in vacuum and under exposure to H neutrals. The damage profile calculated with the SRIM2008 program is also given in this figure. The thickness of the damaged zone was $\approx 2~\mu m$, as mentioned in section 2.2. No significant difference was observed between the profiles after exposure to D_2 gas and annealing in vacuum for 10 h. This observation indicates that D trapped in ion-induced defects was immobile at 473K in this time scale. However, the D concentration in the specimen exposed to D neutrals clearly decreased by subsequent exposure to H neutrals. In other words, the release of D from radiation-induced traps was strongly enhanced by the coexistence of H, even at 473 K. Subsequent TDS measurements showed that D retention, which was 9.2×10^{20} D m⁻² after exposure to D neutrals, decreased to 3.8×10^{20} D m⁻² by exposure to H neutrals.

In a previous paper [6], the enhanced release of D by H at 673K was explained by blocking effects. That is, H atoms in an excess amount immediately filled traps which had become vacant by D detrapping and consequently prevented retrapping of D. However, the probability of D detrapping, P_{det} , is rather low at 473 K. P_{det} can be expressed as $P_{\text{det}} = v \exp(-E_{\text{det}}/kT)t$ where v is the vibration frequency, k is the Boltzmann constant and t is the time. With $v = 10^{13} \text{ s}^{-1}$, $E_{\text{det}} = 1.8 \text{ eV}$ and t = 36 ks (10 h), $P_{\text{det}} = 0.02$ under the present conditions. The above-mentioned blocking effects should play a significant role in the enhanced D release when $P_{\text{det}} \geq 1$. Hence, the enhanced D release at 473K cannot be explained solely by the blocking effects by H. It is plausible that the presence of H enhances detrapping of D, for example, by isotope effects in the binding energy between hydrogen isotopes and defects. However, further investigation is necessary to come to a conclusion on this point.

The thickness of the depleted region of D after exposure to H neutrals was $\approx 1.4 \mu m$. Hence, in spite of the strong enhancement by H, the rate of D release at 473K is too low to remove D from materials with macroscopic thickness. In other words, higher temperatures are preferable for tritium removal by D and/or H in future fusion reactors.

4. Conclusion

Neutron- and ion-irradiation of W resulted in a significant increase in D retention owing to the formation of defects that act as traps. The D concentrations in specimens irradiated with neutrons to 0.3 dpa were 0.8 at% at 473K and 0.4 at% at 773 K. The desorption temperature also increased owing to the trapping effects with traps of higher activation energy for detrapping. These traps were stable at temperatures corresponding to stage III in the recovery process (473–773 K), while a significant reduction in trap density was observed by annealing at temperatures corresponding to stage V (\geq 1073 K). The thermal stability of the traps and the value of the activation energy for detrapping evaluated in a previous study (\approx 1.8 eV [6, 7])

showed that the defects which play a dominant role in the trapping effects at 773K are small voids. The broad desorption spectrum observed after exposure to D plasma at 473K indicated additional contributions of weaker traps such as mono-vacancies. Significant enhancement of D release under exposure to H neutrals was observed at 473 K, although the rate of release at this temperature was too low for practical application in tritium removal in future fusion reactors.

Acknowledge

The authors would like to express their sincere gratitude to Professor Y. Ueda, Osaka University, for fruitful discussion. This work was supported by the Japan–US joint research project TITAN, Kakenhi on Priority Areas, 476, Tritium for Fusion, from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Collaboration Research Programs of National Institute for Fusion Science (NIFS10KUMR004 and NIFS11KEMF018) and Research Institute for Applied Mechanics, Kyushu University (24FP-20).

References

- [1] Roth J. and Schmid K. 2011 Phys. Scr. **T145** 014031
- [2] Shimada M. et al 2011 J. Nucl. Mater. 415 S667
- [3] Shimada M. et al 2011 Phys. Scr. **T145** 014051
- [4] Oya Y. et al 2011 Phys. Scr. **T145** 014050
- [5] Shimada M. et al 2012 Fusion Eng. Des. 87 1166
- [6] Hatano Y. *et al* Trapping of hydrogen isotopes in radiation defects formed in W by neutron and ion irradiations *J. Nucl. Mater.* at press
- [7] Hatano Y. et al 2013 Mater. Trans. 54 437
- [8] Unterberg B. et al 2011 Fusion Eng. Des. 86 1797
- [9] American Society for Testing and Materials 1996 Standard practice for neutron radiation damage simulation by charged-particle irradiation, E521-96 Annual Book of ASTM Standards vol 12.02 (Philadelphia: American Society for Testing and Materials) p 8
- [10] Alimov V.Kh. *et al* The effect of displacement damage on deuterium retention in tungsten exposed to D neutrals and D_2 gas *J. Nucl. Mater.* at press
- [11] Livshits A.I. et al 1990 J. Nucl. Mater. 170 79
- [12] Browne E. and Firestone R.B. 1986 Table of Radioactive Isotopes ed V.S. Shirley (New York: Wiley)
- [13] Balluffi R.W. 1978 J. Nucl. Mater. 69&70 240
- [14] Schultz H. 1991 Mater. Sci. Eng. A 141 149
- [15] Merrill B.J. et al 2013 J. Plasma Fusion Res. Ser. 10 71
- [16] Keys L.K. and Moteff J. 1970 J. Nucl. Mater. 34 260
- [17] Anand M.S. et al 1978 Radiat. Eff. 39 149
- [18] Eleveld H. and van Veen A. 1994 J. Nucl. Mater. 212-215 1421
- [19] Buswell J.T. 1970 Phil. Mag. 22 787
- [20] Van Veen A. et al 1988 J. Nucl. Mater. 155–157 1113
- [21] Liu Y.L. et al 2009 Phys. Rev. B 79 172103
- [22] Ohsawa K. et al 2012 Phys. Rev. B 85 094102
- [23] 't Hoen M.H.J. et al 2013 Nucl. Fusion 53 043003

Table 1.Impurity content in W specimen (mass ppm).

Element	С	N	О	Na	Mg	Al	Si	K	Ca	Cr	Mn	Fe	Ni	Cu	Mo	Sn
Content	< 10	< 10	< 10	< 1	< 1	< 2	< 5	< 5	< 1	< 1	< 1	1	< 1	< 1	2	< 2

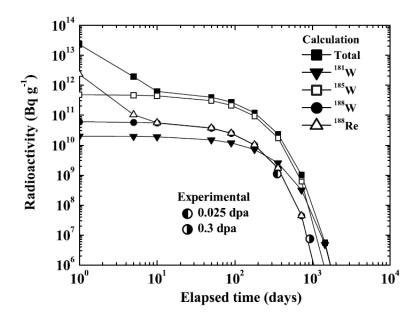


Figure 1. Radioactivity in W irradiated with neutrons in HFIR for 30 full power days evaluated using the FISPACT-2001 code. Half-filled circles indicate the radioactivity of ¹⁸⁸W and ¹⁸⁸Re calculated from the measured values for W specimens irradiated to 0.025 and 0.3 dpa by assuming that the radioactivity immediately after completion of neutron irradiation is proportional to the duration of irradiation.

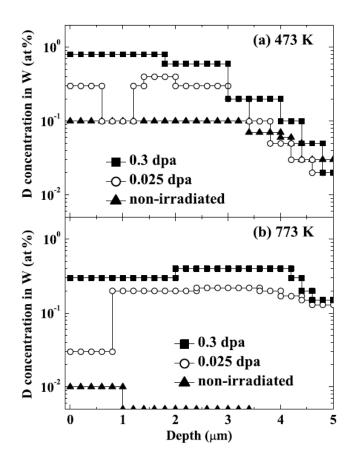


Figure 2.Depth profiles of D in non-irradiated and n-irradiated W specimens (0.025 and 0.3 dpa) after exposure to D plasma at 473 K (a) and 773K (b).

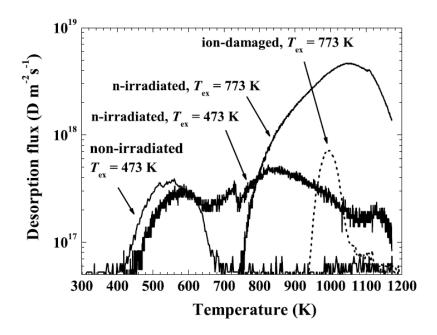


Figure 3. Thermal desorption spectra of D from non-irradiated, n-irradiated (0.025 dpa) and ion-damaged W (0.5 dpa); $T_{\rm ex}$ indicates temperature of exposure to D plasma and D_2 gas.

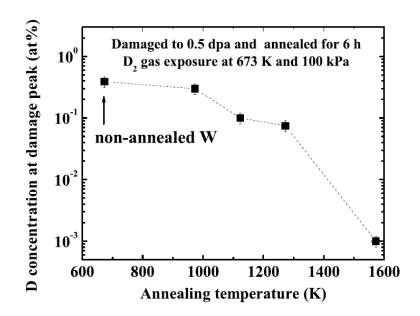


Figure 4.Effects of annealing in vacuum on trap density in ion-irradiated W (0.5 dpa).