

Task 2-1(3) COMPARISON OF DEUTERIUM RETENTION FOR ION-IRRADIATED AND NEUTRON-IRRADIATED TUNGSTEN

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The behavior of D retentions for Fe²⁺ irradiated tungsten with the damage of 0.025-3 dpa was compared with that for neutron irradiated tungsten with 0.025 dpa. The D₂ TDS spectra for Fe²⁺ irradiated tungsten consisted of two desorption stages at 450 K and 550 K although that for neutron irradiated tungsten was composed of three stages and addition desorption stage was found around 750 K. The desorption rate of major desorption stage at 550 K increased as the number of dpa by Fe²⁺ irradiation increased. In addition, the first desorption stage at 450 K was only found for the damaged samples, indicating that the second stage would be based on intrinsic defects or vacancy produced by Fe²⁺ irradiation and the first stage should be the accumulation of D in mono vacancy leading to the lower activation energy, where the dislocation loop and vacancy was produced. The third one was only found for the neutron irradiation, showing the D trapping by void or vacancy cluster and the diffusion effect is also contributed due to high FWHM of TDS spectrum. It can be said that the D₂ TDS spectra for Fe²⁺-irradiated tungsten could not represent that for neutron-irradiated one, showing that the deuterium trapping and desorption mechanism for neutron-irradiated tungsten has a difference from that for ion-irradiated one.

I. INTRODUCTION

Plasma facing components research for fusion applications has recently focused on tungsten materials due to low sputtering yield and low tritium retention [1-4]. One of the key issues under performance evaluation of plasma facing materials is tritium retention and recycling under fusion relevant conditions. To predict hydrogen isotope recycling, including tritium, it is important to

elucidate the effects of radiation damages especially the impact of neutron irradiation for tungsten. It is thought that the neutron irradiation would produce additional trapping sites and tritium retention would dramatically enhance. Recently, energetic ion irradiation experiment was performed on tungsten to demonstrate neutron irradiation effect on tritium retention [5-9]. However, the neutron irradiation may introduce some other effects and comparison of D retentions for ion-irradiated tungsten and neutron-irradiated tungsten with the same plasma device and TDS system is quite meaningful.

In our previous research, it was found by TDS (Thermal Desorption Spectroscopy) that the deuterium retention for the 0.025 dpa neutron-irradiated tungsten was about three times as large as that for un-irradiated one [10]. The TDS spectrum was extended toward higher temperature side, indicating that deuterium was stably trapped in radiation damages. The behavior of hydrogen isotopes implanted into tungsten with vacancies was simulated by Monte Carlo technique and correlation between hydrogen isotope distribution and trap density and distribution were evaluated [11]. In order to elucidate hydrogen isotope trapping mechanisms for damaged tungsten, comparison of deuterium retention for ion-irradiated and neutron-irradiated tungsten is quite important.

II. EXPERIMENTAL

The disk-type samples with 6 mm diameter and ~ 0.2 mm thickness were prepared from a rod of tungsten under stress-relieved conditions supplied by Allied Tungsten Co. Ltd, whose grains were normal to the surface. The samples were polished mechanically to mirror finish

surfaces and cleaned by an ultra-sonic bath with, acetone, ethanol and de-ionized water for 5 minutes each.

2.8 MeV Fe^{2+} was implanted into all the surface area of W specimens at room temperature by Tandatron Accelerator System, RAPID (Rutherford Backscattering Spectroscopic Analyzer with Particle Induced X-ray Emission and Ion Implantation Devices), at The University of Tokyo. The implantation depth of Fe^{2+} was 0.5 μm by TRIM estimation. Three different damaged samples were prepared by changing the ion fluences of 2.7×10^{17} , 3.3×10^{18} and 3.3×10^{19} $\text{Fe}^{2+} \text{m}^{-2}$, corresponding to the damages of 0.025 dpa, 0.3 dpa and 3 dpa, respectively.

Thereafter, the samples were transferred to Idaho National Laboratory and exposed to the deuterium plasma by TPE [12,13]. The tungsten mask was used to mount the tungsten sample with the clearance hole of ϕ 8 mm. The sample temperature was monitored by the thermocouple touched on the backside of the sample. The plasma diagnostics, namely electron temperature and density profiles, were evaluated by a pneumatically actuated Langmuir probe. The un-irradiated tungsten sample was also used to compare the D retention in tungsten with the same deuterium plasma exposure condition. The primarily species was D^+ [10]. The ion flux and energy were $\sim 1.0 \times 10^{22}$ $\text{D}^+ \text{m}^{-2} \text{s}^{-1}$ and 100 eV. The sample temperature was set to be almost constant to be 473 K and the deuterium plasma fluence was within the order of $\sim 6 \times 10^{25}$ $\text{D}^+ \text{m}^{-2}$. After the ion implantation, the sample was cooled down to room temperature within 30 minutes by contacting the Cu plate with cooling water. The oxidized sample without ion irradiation was also prepared to evaluate the surface effect for the D retention. The sample was oxidized at 673 K for 2 hours in air atmosphere after the sample pretreatment including polishing and rinsing. Thereafter, the D plasma exposure was performed at 473 K with the same experimental condition.

The deuterium retention and desorption behaviors were analyzed by TDS which was located near the TPE device. So, the sample was quickly replaced to the TDS chamber with several minutes' air exposure. TDS was applied with heating rate of 10 K min^{-1} from room temperature to 1273 K. The sample heating was continued to keep 1273 K for 30 minutes to confirm the total deuterium desorption from the sample. Only the peaks associated with D_2^+ and HD^+ were considered for the estimation of D retention because no other desorption species like water form or hydrocarbon form was observed. The TDS calibration was done by three standard leaks [10]. The surface morphology was observed by SEM (Scanning Electron Microscope, VE-9800, KEYENCE Inc.). For the observation of ion implantation effect on the surface morphology, 2.4 MeV Cu^{2+} was irradiated into tungsten samples with 0.03, 0.3 and 3 dpa at the Institute of Applied Mechanics, Kyushu

University and the TEM (Transmission Electron Microscope, JEM 2000EX, JASCO Inc.) observation was performed. The thickness of the sample was less than 0.1 μm and electrical polishing was performed before the irradiation.

III. RESULTS AND DISCUSSION

Figure 1 shows the D_2 TDS spectra for tungsten with the damage of 0.025 – 3 dpa by Fe^{2+} irradiation. The major desorption stage was located at the temperature of 550 K. Some reports for plasma exposure showed the D desorption was initiated at the lower desorption temperature than plasma exposure temperature [13]. Most of deuterium would be desorbed just after the plasma exposure and some of deuterium would be stabilized during the desorption process by the trapping site with lower activation energy. For the Fe^{2+} irradiated tungsten, an additional desorption stage was found at lower temperature side. Both of these peak intensities were increased as the number of dpa increased. Comparing the TDS spectra with that for the neutron-irradiated tungsten, it was clear the shape of TDS spectra was quite different and another large desorption peak was found at around 750 K for the neutron-irradiated tungsten. The D_2 desorption spectra were extended toward lower temperature side and the D_2 desorption rate was increased as the amount of irradiation damages increased for ion irradiated tungsten. However, it was found that the D_2 TDS spectra for Fe^{2+} -irradiated tungsten could not represent that for neutron-irradiated one, indicating that the deuterium trapping mechanism for neutron-irradiated tungsten has a difference from that for ion-irradiated one. Total D retention for 0.025 dpa Fe^{2+} irradiated tungsten was 1.5 times as large as that for un-irradiated tungsten, which was almost a half compared to that for 0.025 dpa neutron irradiated tungsten. For the dpa dependence by Fe^{2+} irradiation, the D retention increased almost twice as the dpa increased one order between 0.025 dpa and 3 dpa ranges. The D desorption stages were assumed to consist of three stages at around 450 K, 550 K and 750 K, namely Peaks 1, 2 and 3, and peak separation was performed.

Fig. 2 shows the result of D retentions for Peaks 1, 2 and 3, and total D retention as a function of dpa by Fe^{2+} irradiation. Large D desorption was found for second stage for 3 dpa Fe^{2+} irradiated tungsten. The D desorption stage of Peak 3 was observed only for 0.025 dpa neutron irradiated tungsten as mentioned above. Fig. 3 shows SEM images for (a) 0.025 dpa Fe^{2+} irradiated tungsten and (b) 0.3 dpa Fe^{2+} irradiated one after D plasma exposure and TDS. The surface morphology for the sample before experiment is rather smooth (not shown in this paper) and only the grain boundary was found. Some impurities with white color in the picture were adsorbed on the surface especially for the 0.025 dpa sample and small pores (black dots) were introduced which would be

formed on the surface by Fe^{2+} irradiation or D plasma exposure. In the case of 0.3 dpa Fe^{2+} irradiation, the morphology was quite different as shown in Fig. 3 (b). The fracture around the grain boundary was found for the D plasma exposure area. Many cavities and fractures existed in grains, which would induce the peel. To reveal microstructure change by ion irradiation, TEM observation for 2.4 MeV Cu^{2+} irradiated tungsten was performed and shown in Fig. 4. In the un-irradiated sample, almost all the dislocations which would be introduced during the fabrication process for rod type sample were removed, but all the defects should not be completely removed from the sample due to stress-relieved condition. A large number of dislocation loops with the size less than 10 nm was dispersedly observed for 0.03 dpa sample. The density of dislocation loops was enhanced as the number of dpa (irradiation fluence) was increased and the nucleation of dislocation loop was found.

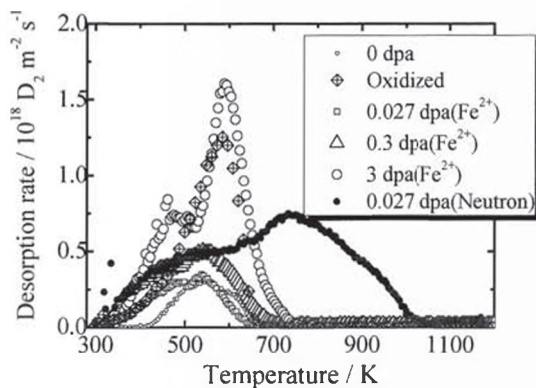


Fig. 1 D_2 TDS spectra for Fe^{2+} irradiated tungsten samples after plasma exposure at TPE. The TDS spectra for neutron irradiated tungsten and oxidized tungsten were also shown.

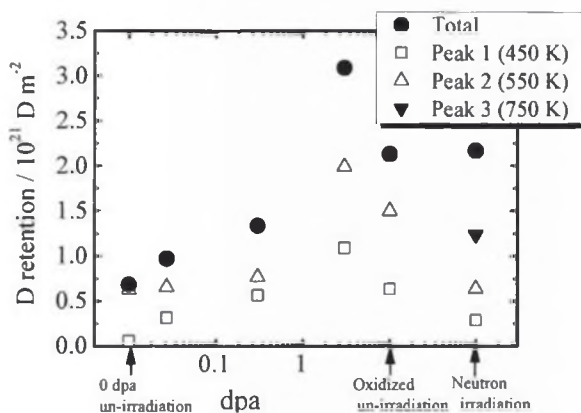


Fig. 2 The D retentions for tungsten as a function of damage density [dpa]. The D retentions for oxidized sample with un-irradiation and neutron irradiated sample were also shown.

Based on these experimental results, D retention behaviors for ion-irradiated tungsten and neutron-irradiated tungsten are discussed. The D retention was clearly changed by the number of damages introduced in tungsten. By the introduction of damages, D desorption stage in lower temperature side namely 450 K was emerged, which was not observed for un-irradiated sample, indicating that accumulation of damages in ion-irradiated area would enhance D trapping with different activation energy. The activation energy for D desorption at Peak 1 should be less than 1.48 eV, which corresponded to that at Peak 2 estimated by low energy (1.5 keV) ion implantation experiment and was almost consistent with the reported value of 1.45 eV [8]. Recently, hydrogen-vacancy binding energies have been reported and multiple hydrogen trapping in a vacancy reduces the binding energy [14,15], which would produce additional desorption stage at lower temperature side. However, most of D was retained in a vacancy with one atom or two atoms due to H atoms also stabilize vacancies as reported in [15]. However, the TDS spectrum for neutron-irradiated one had one more additional desorption stage, which was not observed for ion-irradiated sample and the desorption temperature extended to higher temperature side more than 900 K. This difference should be caused by D trapping in deeper regions, because the neutron irradiation produces the irradiation damages throughout the sample, although the ion irradiation limits within the depth less than one micro meter. The D depth profiling by NRA as reported in Ref. [16] indicate the enhancement of D retention within the depth of 3 μm compared to that for un-irradiation case. At this time, the D depth profile for the 2.8 MeV Fe^{2+} irradiated sample was not evaluated but the TRIM estimation showed the damage was introduced within the depth of 0.5 μm , indicating that the effect of D diffusion toward the depth by neutron irradiation would make a large contribution on high activation energy for D desorption although the D accumulation for ion-irradiated sample would be limited within the shallow surface region. The FWHM for Peak 3 was large of about 250 K compared to that for Peaks 1 and 2 of 130 K 115 K, which is also support the different desorption and / or trapping mechanism. In the present study, the oxidized sample was also prepared and performed with the same D plasma exposure condition to observe the surface effect on D trapping and desorption. As seen in Fig. 1, only the one desorption stage located at 660 K was found, indicating that the surface trapping effect does not largely impact on the desorption temperature and only the D retention enhancement with the same trapping state as the un-irradiated sample was contributed, which would interfere the diffusion toward the surface. The retention enhancement factor, namely the ratio of D retention for neutron or ion irradiated sample to that for un-irradiated sample, was also evaluated to be 1.5 to 5 in the present study, which was almost consistent with

that reported by G. M. Wright [5,6] and W. R. Wampler [9] as shown in Fig.5.

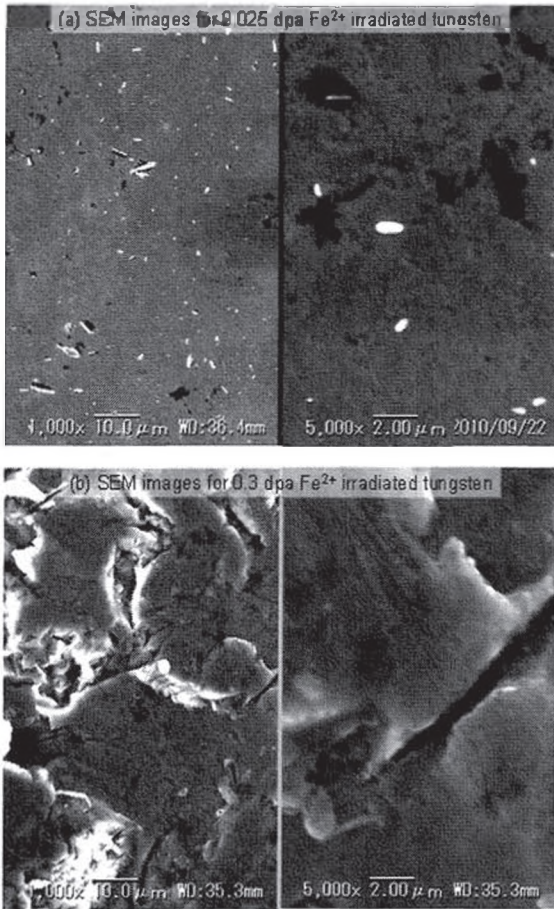


Fig. 3 SEM micrographs for Fe²⁺ irradiated tungsten with 0.025 dpa and 0.3 dpa after D plasma exposure and TDS.

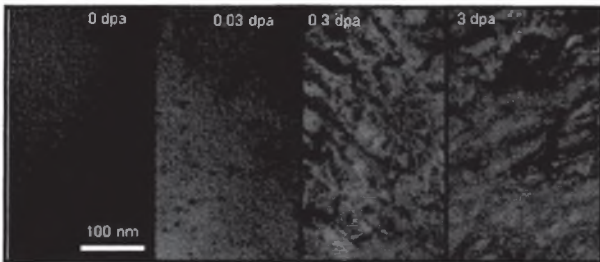


Fig. 4 TEM micrographs for Cu²⁺ irradiated tungsten with 0-3 dpa without D plasma exposure.

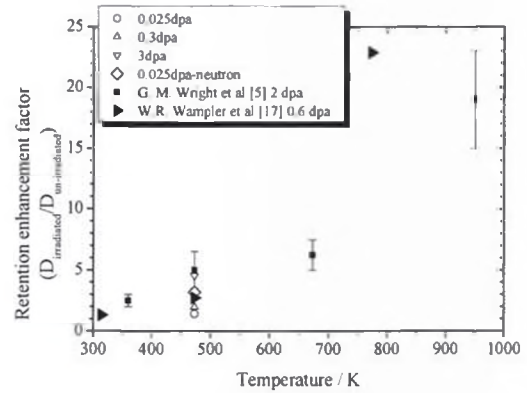


Fig. 5 Deuterium retention enhancement factor as a function of irradiation temperature.

IV. CONCLUSIONS

The behavior of D retentions for Fe²⁺ irradiated tungsten with the damage of 0.025-3 dpa was compared with that for neutron irradiated tungsten with 0.025 dpa. The D₂ TDS spectra for Fe²⁺ irradiated tungsten consisted of two desorption stages at 450 K and 550 K although that for neutron irradiated tungsten was composed of three stages, showing that an additional desorption stage was found around 750 K. The desorption rate of major desorption stage at 550 K increased as the number of dpa. The first desorption stage at 450 K was only found for the damaged samples. The second stage would be based on existence of intrinsic defects or vacancy produced by Fe²⁺ irradiation and the first stage should be the accumulation of D in mono vacancy leading to the lower activation energy, where the dislocation loop and vacancy were produced. The third one was only found for the neutron irradiation, showing the D trapping by void or vacancy cluster and the diffusion effect is also contributed due to high FWHM. Therefore, D₂ TDS spectra for Fe²⁺-irradiated tungsten could not represent that for neutron-irradiated one, indicating that the deuterium trapping and desorption mechanism for neutron-irradiated tungsten has a difference from that for ion-irradiated one.

ACKNOWLEDGMENTS

This study was supported by JSPS Kakenhi No. 22360389 and 19055002 from MEXT, Japan, and Japan-US collaboration program (TITAN). The TEM observation was performed under the collaboration program at the Institute of Applied Mechanics, Kyushu University.

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