

論文

照射損傷を受けたタングステン中の重水素滞留挙動に及ぼす Pd 表面被覆の影響

Vladimir Kh. Alimov¹, 波多野雄治¹, 杉山一慶², 高木郁二³, 松山政夫¹

¹富山大学水素同位体科学研究センター
〒930-8555 富山市五福 3190

²Max-Planck-Institut für Plasmaphysik, EURATOM Association,
D-85748 Garching, Germany

³京都大学大学院工学研究科原子核工学専攻
〒606-8501 京都市左京区吉田本町

Deuterium Retention in Self-Damaged Tungsten with and without Deposited Pd Layer

Vladimir Kh. Alimov¹, Yuji Hatano¹, Kazuyoshi Sugiyama², Ikuji Takagi³,
Masao Matsuyama¹

¹Hydrogen Isotope Research Center, University of Toyama,
Toyama 930-8555, Japan

²Max-Planck-Institut für Plasmaphysik, EURATOM Association,
D-85748 Garching, Germany

³Department of Nuclear Engineering, Kyoto University
Kyoto 606-8501, Japan

(Received January 31, 2013; accepted May 7, 2013)

Abstract

Influence of Pd deposition on deuterium (D) retention in W samples irradiated with W self-ions was examined to understand the correlation between the probability of occupation of radiation-induced traps by D and the concentration of D in a solid solution state under plasma exposure. W samples were irradiated with 4.8 MeV W ions

to 0.65 and 12 dpa, and a thin Pd layer was deposited on the sample with the higher damage level by a technique of sputter-deposition. Then, the samples were exposed to DC glow-discharge D plasma at 403 K. In spite of the higher damage level, the concentration of trapped D in the damaged zone of the Pd-covered sample was far smaller than that in the non-covered one. The small D retention in the Pd-covered sample was explained by a decrease in the D concentration in the solution state owing to the enhanced recombinative release by Pd and the consequent reduction in the occupation probability of radiation-induced traps. These observations indicated that tritium inventory in neutron-irradiated W materials can be significantly reduced by enhancement of tritium reemission by surface modifications.

1. Introduction

Tungsten (W) and its alloys are recognized as candidates of plasma-facing materials of future fusion reactors. Because defects such as vacancies and voids act as strong traps for hydrogen isotopes, tritium (T) inventory in neutron-irradiated W materials is an important problem in safety assessment of fusion reactors. Indeed, significant increase in deuterium (D) retention in W after neutron irradiation in a fission reactor was reported in Refs. [1–6]. It is also known that irradiation effects by neutrons can be simulated by irradiation with high energy ions [7].

Under exposure to hydrogen isotope plasma, a majority of hydrogen particles impinging on the W surface are emitted back to the plasma through recombination into molecules on the surface and subsequent desorption. A minor portion of impinging hydrogen isotopes settles in interstitial sites in the bcc lattice, diffuses in the lattice, and then gets trapped when they encounter unoccupied defects. Under exposure to high flux

plasma, formation of bubbles and blisters takes place in the near-surface regions by precipitation of molecular hydrogen isotopes in cavities. The hydrogen isotope retention in blisters and bubbles increases practically infinitely with increase in internal pressure, and these defects can be called as unsaturable traps. On the other hand, in the bulk of materials where chemical potential is far lower, hydrogen isotopes are trapped in atomic form in defects such as dislocations, vacancies, and vacancies clusters with finite capacity. These defects are often referred as saturable traps. In this study, the attention is focused on the trapping effects in the bulk of materials, and hence only saturable traps are considered below. Inventory of hydrogen isotopes increases with increase in the fraction of occupied traps. Based on the model proposed by Beshers [8], the fraction of occupied traps θ_t at temperature T is expressed as

$$\theta_{t,i}/(1 - \theta_{t,i}) = \theta_L \exp(E_{\text{bin},i}/kT), \quad (1)$$

where θ_L is the fraction of occupied interstitial sites, $E_{\text{bin},i}$ is the binding energy between hydrogen isotope and defect, i is the type of defect and k is the Boltzmann constant. This equation suggests that the fraction of occupied trap sites and consequently inventory of hydrogen isotopes increases with an increase in the concentration of hydrogen isotopes in the solid solution state C_{SS} because C_{SS} is proportional to θ_L . Even under the conditions where $E_{\text{bin},i}/kT \gg 1$ (i.e. $\theta_t \approx 1$), the inventory of hydrogen isotopes depends on C_{SS} if a discharge pulses are short enough to keep the penetration depth of hydrogen isotopes smaller than the thickness of W materials [9]. If $E_{\text{bin},i}/kT \gg 1$, clear interface between filled zone ($\theta_t \approx 1$) and empty zone ($\theta_t \approx 0$) can be observed, and the velocity of the interface is

$$dx/dt = D_L C_{\text{SS},s}/xN_t, \quad (2)$$

where x is the depth from the surface, t is time, D_L is the diffusion coefficient of hydrogen isotopes in the lattice of W, and N_t is the trap density [10]. Here, C_{SS-S} is the concentration of hydrogen isotopes in the solution state just beneath the plasma-facing surface. Although C_{SS} including C_{SS-S} is far smaller than the concentration of trapped hydrogen isotopes, the variation in C_{SS} has strong influence on total inventory of hydrogen isotopes. Indeed, such correlation between C_{SS} and inventory of D was demonstrated by a gas absorption technique under equilibrium conditions in our previous papers [5,11]; C_{SS} was determined as a function of pressure of D_2 gas and temperature. However, the correlation under non-equilibrium conditions, such as under plasma exposure, has not been proven.

The objective of the present study is to demonstrate the effects of surface modification of W on D inventory in MeV-range W-ion-irradiated W. A thin Pd layer was prepared on the surface of the W-ion-irradiated W sample, and then the samples with and without Pd layers were exposed to weakly-ionized D plasma created by DC glow discharge. Weakly-ionized plasma is suitable to examine the interaction between hydrogen isotopes and saturable traps because such low-flux plasma does not form blisters. As previously reported [11], the W-ion-induced defects in the sample without Pd layer become fully occupied during plasma exposure of surface to a depth depending on implantation fluence (or time) and are empty at greater depths; the D depth profiles are consistent with saturable traps being filled by D atoms diffusing from the surface. The mass balance at the plasma-facing surface can be expressed as $\alpha\phi_{in} = k_r C_{SS-S}^2$ where α is the sticking coefficient of impinging particles, ϕ_{in} is incident flux and k_r is the surface recombination rate constant. Hence, $C_{SS-S} = (\alpha\phi_{in}/k_r)^{1/2}$. Although k_r for a clean W surface is very high ($k_r \geq 10^{-11} \text{ m}^4 \text{ s}^{-1}$ at $\leq 1000 \text{ K}$ [7]), such surface state is available

only in an ultra-high vacuum. The values of k_r reported for W with ion-implantation [12] and linear plasma machines [5] are just $k_r \geq 10^{-20} \text{ m}^4\text{s}^{-1}$ owing to contamination by impurities such as oxygen and carbon. On the other hand, Pd is a noble metal and its surface is less sensitive to contamination by impurities. In addition, solubility of hydrogen isotopes in Pd is significantly larger than that in W, and Pd overlayers would provide high $C_{\text{SS-S}}$ together with low C_{SS} in the W substrate.

2. Experimental

Polycrystalline mechanically-deformed W from A.L.M.T. Co., Japan, with a purity of 99.99 mass%, was used in this work. Two W disc-type samples, 6 mm in diameter and 0.2 mm in thickness, were prepared by cutting a polycrystalline tungsten rod annealed at 1173 K for 3.6 ks in a hydrogen atmosphere to relieve internal stresses occurred in the manufacturing process. The samples were mechanically polished to a mirror finish with diamond powders (9- and 3- μm -sized grains) and colloidal silica suspension (40-nm-sized grains). After cleaning in an ultra-sonic bath with acetone, surfactant and de-ionized water for 5 min each, the samples were annealed at 1173 K for 1.8 ks in vacuum ($\sim 10^{-6}$ Pa). The grains are elongated along the direction normal to the surface, which is similar to ITER-grade W.

The first W sample (sample #1) was irradiated with 4.8 MeV W ions at temperature of 573 K to damage levels of 0.65 displacements per atom (dpa) at the damage peak, whereas the second sample (sample #2) was irradiated with 4.8 MeV W ions at 300 K to 12 dpa. The damage profiles were calculated using the program SRIM 2008.03 [13], “full cascade option”, with the displacement energy of $E_d = 90 \text{ eV}$ as the more reliable value for the W lattice [14,15]. Note that for irradiation with 4.8 MeV W

ions, the damage peak situated at a depth of 0.23 μm .

The damaged sides of sample #1 were exposed to D plasma formed by DC glow discharge at temperature of 403 K [11]. The sample was set on a holder equipped with an ohmic heater and a thermocouple served as anode, whereas W disc located at a distance of about 10 cm from the sample holder was used as a cathode. Deuterium pressure in the chamber was maintained at 1 Pa, DC discharge voltage was 400 V, and discharge current averaged about 0.18 A. Because the sample was set on an anode, the main impinging particles are D atoms and molecules (D neutrals) in addition to electrons. The energies of atoms were in the range from few eV (atoms originated in the glow discharge) to ~ 150 eV (atoms reflected from the W cathode). The flux of implanted deuterium was estimated to be about 2×10^{18} D/m²s with the use of Ti probe exposed in the DC glow discharge at 300 K for 10 and 60 min, while the D retention in the Ti probe was determined by thermal desorption spectroscopy [11]. The implantation fluence was about 6×10^{22} D m⁻².

Sample #2 was exposed to the D plasma in a similar manner at 403 K to the implantation fluence of about 6×10^{22} D/m², but with Pd cathode instead of W one. Owing to far larger sputtering yield for Pd than W by 400 eV D ions, the surface of sample #2 was covered by sputtered Pd particles. Here, the sputtering yield for W is 3×10^{-3} [16]. The sputtering yield for Pd is not available, but that for Ag locating next to Pd in the periodic table is 0.1 [16]. Thickness of the deposited Pd layer on the sample was determined by means of Rutherford backscattering spectroscopy (RBS) at ³He ion energies of 2.8 MeV and evaluated with SIMNRA program [17]. The backscattered ³He was energy-analyzed at a scattering angle of 165° by a small-angle surface barrier detector. It was found that after D plasma exposure for 30 ks (that corresponded to the

implantation fluence of about 6×10^{22} D/m²), a thickness of Pd layer was around 270 nm. After the RBS measurement, the Pd layer on sample #2 was thinned by sputtering with Ar ions in a commercial glow-discharge optical emission spectroscopy (GDOES) device (Horiba Jobin Yvon, GD-Profilier 2). Repeated RBS measurement performed after that showed that a thickness of the Pd layer was reduced to 58 nm (Fig. 1). Sample #2 with 58 nm Pd layer was exposed to the D plasma with the use of the W cathode at 403 K to the implantation fluence of about 6×10^{22} D/m². Namely, sample #2 was sequentially exposed to D plasma 2 times with the in-situ Pd deposition up to 270 nm

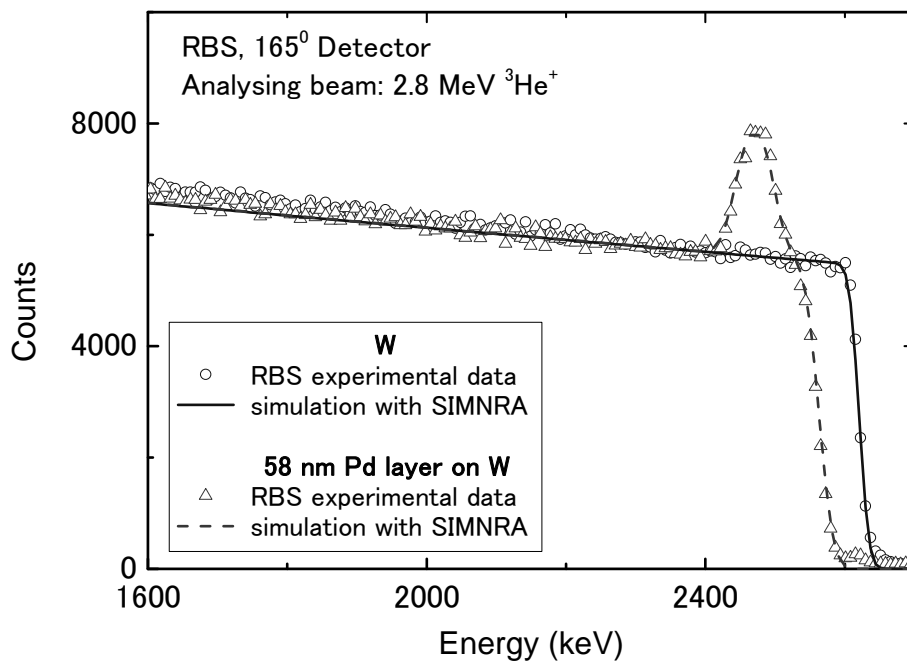


Fig. 1 Rutherford backscattering (RBS) spectra for 2.8 MeV ³He ions incident on tungsten with and without 58 nm thick Pd layer deposited on the W surface. The symbols and solid lines represent respectively experimentally measured and calculated RBS spectra. The RBS spectra were calculated by the SIMNRA program [17].

and with the pre-prepared thin Pd layer (58 nm).

The deuterium profiles in samples #1 and #2 after exposure to the D plasma were determined by nuclear reaction analysis (NRA) at IPP, Garching. The $D(^3\text{He},p)^4\text{He}$ reaction was utilized, and both the α particles and protons were analyzed. To determine the D concentration at larger depths, an analyzing beam of ^3He ions with energies varied from 0.69 to 4.0 MeV was used. The proton yields measured at different ^3He ion energies allow measuring the D depth profile at depths of up to 6 μm .

3. Results and discussion

Generation of displacement damage in the sample #1 at 573 K and subsequent exposure to D plasma at temperature of 403 K leads to accumulation of deuterium at depths up to 2 μm (i.e., in the damage zone) to concentrations of about 0.6 at.% as shown in Fig. 2. Note that after exposure to D_2 gas at pressure of 1 Pa (the same deuterium pressure was maintained under DC glow discharge) and temperature of 403 K for 30 ks (i.e., for time period of the D fluence), the D concentration in the damage zone does not exceed 10^{-3} at.%. It should be noted that, in undamaged W exposed to the D plasma, the D concentration at depths $\geq 0.1 \mu\text{m}$ is below the NRA detection limit of 5×10^{-4} at.%.

In the sample #2 exposed to the D plasma with the Pd cathode, deuterium is accumulated mainly in the 270 nm thick Pd layer (Fig. 2). However, after thinning of the Pd layer to 58 nm and second D plasma exposure with the W cathode, the D concentration in the W damage zone is significantly lower than that for the W sample #1 without Pd film (Fig. 2), in spite of higher defect concentration. Note that in the sample #2 irradiated with 4.8 MeV W ions at 300 K to the damage level of 12 dpa, a

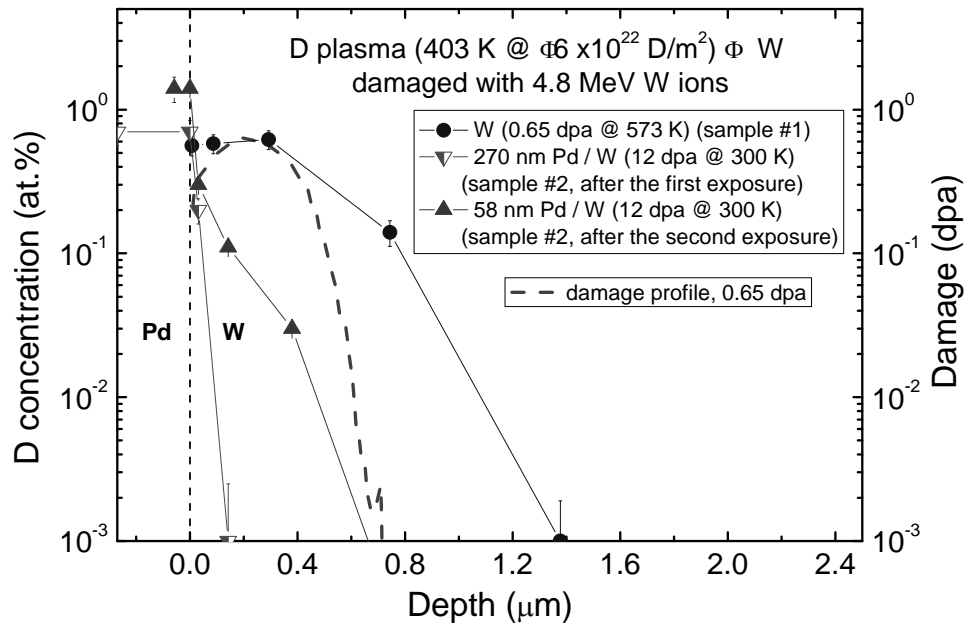


Fig. 2 Depth profiles of D retained in the sample #1 and sample #2 after the first and second D plasma exposures. Thickness of the Pd layer on the sample #2 after the first and second D plasma exposures is indicated in the legend. A boundary between the Pd layer and the W substrate corresponds to a depth of 0 μm . Damage profile is plotted in a logarithmic scale on the right ordinate axis.

concentration of defects responsible for trapping of diffusing D atoms is slightly higher than that for W-ion irradiation at 573 K to 0.65 dpa [5].

Obviously, the deposited Pd film on the W surface serves as a storage for implanted D and reduces flux of diffusing D atoms penetrating into the damage zone by increasing $k_r C_{SS} s^2$. Note that the diffusivity of D in Pd is $4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 403 K [18]. Hence, the mean diffusion length of D during the exposure to D plasma for 30 ks is evaluated to be 5 μm . This value of mean diffusion length is far larger than the thickness of Pd layer (58 nm). It means that the low concentration of trapped D in W damage zone in sample #2 was not owing to slow diffusion in the Pd layer. The D

concentration in sample #2 beneath the surface (Pd region) was ca. 1 at.% (6.9×10^{26} D m^{-3}). Since $\alpha\phi_{\text{in}}$ under exposure to D plasma was about 2×10^{18} D $\text{m}^{-2}\text{s}^{-1}$, the k_{r} was evaluated to be 4×10^{-36} m^4s^{-1} . This value is in reasonable agreement with that reported by Pick and Sonnenberg [19]. The entropy and enthalpy of H solution in Pd are -60 J $\text{mol}^{-1}\text{K}^{-1}$ and -10 kJ mol^{-1} , respectively [18]. Hence, the above-mentioned D concentration (1 at.% at 403 K) corresponds to equilibrium pressure of 31 kPa. On the other hand, the concentration of D in a solid solution state in W at this pressure (31 kPa) and temperature (403 K) can be evaluated from the solubility data reported by Frauenfelder [20] to be 2.5×10^{13} D m^{-3} (3.9×10^{-16} in $[\text{D}]/[\text{W}]$). According to Eq. (1), at this fraction of occupied interstitial sites, θ_{L} , the fraction of occupied traps, θ_{t} , becomes equal to or below 0.1 if $E_{\text{bin}} \leq 1.2$ eV. Since the activation energy for diffusion of H in W is 0.39 eV, this E_{bin} corresponds to the activation energy for desorption of ca. 1.6 eV. This means that occupation probability of mono-vacancies [21] and dislocations [22] by D is negligibly small. Namely, low concentration of trapped D in sample #2 can be explained by low occupation probability of defects with small E_{bin} owing to low D concentration in the solid solution state. In other words, under plasma exposure, the retention of hydrogen isotopes in irradiated W can be reduced by reduction in the D concentration in the solid solution state by enhancement of recombinative release.

4. Summary

Preparation of a Pd layer on an MeV-range W-ion-irradiated W sample resulted in significant reduction in D retention after exposure to DC glow-discharge D plasma at 403 K. The reduced D retention was explained by decrease in D concentration in a solid solution state caused by enhancement of recombinative D release by the Pd layer and

consequent reduction in occupation probability of radiation-induced traps. These observations indicated that tritium inventory in neutron-irradiated W materials can be significantly reduced by enhancement of tritium reemission by surface modifications.

References

- [1] M. Shimada et al., *J. Nucl. Mater.* **415** (2011) S667.
- [4][2] M. Shimada et al., *Phys. Scr.* **T145** (2011) 0014051.
- [6][3] Y. Oya et al., *Phys. Scr.* **T145** (2011) 0014050.
- [7][4] M. Shimada et al., *Fusion Eng. Des.* **87** (2012) 1166.
- [8][5] Y. Hatano et al., Trapping of hydrogen isotopes in radiation defects formed in W by neutron and ion irradiations, *J. Nucl. Mater.* (2013),
<http://dx.doi.org/10.1016/j.jnucmat.2013.01.018>.
- [6] Y. Hatano et al., Retention of hydrogen isotopes in neutron irradiated tungsten, *Mater. Trans.* **54** (2013) 437.
- [7] J. Roth and K. Schmid, *Phys. Scr.* **T145** (2011) 0014031 and references therein.
- [8] D. N. Beshers, *Acta Metall.* **6** (1958) 521.
- [9] D. G. Whyte, *J. Nucl. Mater.* **390-391** (2009) 911.
- [10] W. R. Wampler, R. P. Doerner, *Nucl. Fusion* **49** (2009) 115023.
- [11] V. Kh. Alimov, Y. Hatano, K. Sugiyama, J. Roth, B. Tyburska-Püschel, J. Dörner, J. Shi, M. Matsuyama, *J. Nucl. Mater.* (2013),
<http://dx.doi.org/10.1016/j.jnucmat.2013.01.208>.
- [12] R.A. Anderl, D.F. Holland, G.R. Longhurst, R.J. Pawelko, C.L. Trybus, C.H. Sellers, *Fusion Technol.* **21** (1992) 745.

- [13] J.F. Ziegler, SRIM - The Stopping and Range of Ions in Matter, ver. SRIM-2008.3, available on <http://srim.org>.
- [14] Standard Practice for Neutron Radiation Damage Simulation by Charge-Particle Irradiation, E521-96, Annual Book of ASTM Standards, Vol. 12.02, American Society for Testing and Materials, Philadelphia, 1996, p. 1.
- [15] Q. Xu, T. Yoshiie, H.C. Huang, Nucl. Instr. Meth. B **206** (2003) 123.
- [16] H.H. Andersen and H.L. Bay, Chapter 4 Sputtering Yield Measurements, in *Sputtering by Particle Bombardment I*, Ed. by R. Behrisch, Springer-Verlag Berlin Heidelberg, 1981.
- [17] M. Mayer, SIMNRA User's Guide, Tech. Rep. IPP 9/113, Garching, 1997.
- [18] Y. Fukai, *The Metal-Hydrogen System Basic Bulk Properties*, Springer-Verlag Berlin Heidelberg, Germany, 2005, pp. 14–27.
- [19] M. A. Pick and K. Sonnenberg, J. Nucl. Mater. **131** (1985) 208.
- [20] R. Frauenfelder, J. Vac. Sci. Technol. **6** (1969) 388.
- [21] H. Eleveld and A. van Veen, J. Nucl. Mater. **212-215** (1994) 1421.
- [22] O.V. Ogorodnikova, B. Tyburska, V. Kh. Alimov and K. Ertl, J. Nucl. Mater. **415** (2011) S661.