

Correlation of surface chemical states with hydrogen isotope retention in divertor tiles of JET with ITER-Like Wall

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To understand the fuel retention mechanism, correlation of surface chemical states and hydrogen isotope retention behavior determined by XPS (X-ray photoelectron spectroscopy) and TDS (Thermal desorption spectroscopy), respectively, for JET ITER-Like Wall samples from operational period 2011-2012 were investigated. It was found that the deposition layer was formed on the upper part of the inner vertical divertor area. At the inner plasma strike point region, the original surface materials, W or Mo, were found, indicating to an erosion-dominated region, but deposition of impurities was also found. Higher heat load would induce the formation of metal carbide. At the outer horizontal divertor tile, mixed material layer was formed with iron as an impurity. TDS showed the H and D desorption behavior and the major D desorption temperature for the upper part of the inner vertical tile was located at 370 °C and 530 °C. At the strike point region, the D desorption temperature was clearly shifted toward higher release temperatures, indicating the stabilization of D trapping by higher heat load-

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1. Introduction

Evaluation of hydrogen isotope retention in the plasma-facing components is one of important issues to understand fuel distribution during the fusion reactor operation. In our previous studies, the tungsten (W) samples placed in the Large Helical Device (LHD) at National Institute for Fusion Science (NIFS), were exposed to plasma discharges and retention enhancement of hydrogen isotopes were evaluated [1-3]. It was found that the accumulation of low-Z mixed-material layer on the surface of the first wall is one of key issues for the determination of hydrogen isotope retention in first wall. These results are useful for the prediction of fuel retention during fusion reactor operation. In ITER, W bulk material will be placed in the divertor region and beryllium (Be) will be used on the first wall. Therefore, the fuel retention behavior for these wall materials will give the important information for reactor safety. The JET tokamak has been operated since year 2011 with the ITER-Like Wall (JET-

ILW), which means that Be is used for the first wall and

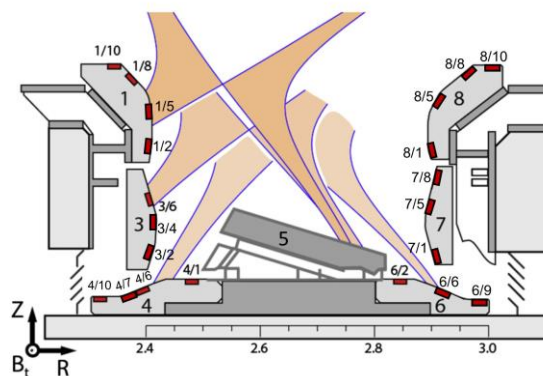


Fig. 1 Cross-section of the JET divertor area with three typical plasma configurations and the tile and sample positions.

W coating on graphite for the divertor. The fuel retention distribution has been reported in several papers [4-12]. However, the interaction behavior of hydrogen isotope with materials is not sufficiently revealed. Therefore, this study has been focused on the correlation between surface chemical states and hydrogen isotope retention using X-ray Photoelectron Spectroscopy (XPS) and Thermal

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Desorption Spectrometry (TDS) under the framework of Broader Approach (BA) activities performed at International Fusion Energy Research Centre (IFERC), National Institutes for Quantum and Radiological Science and Technology (QST), Rokkasho site, Japan.

2. Experimental

The samples were cored from the inboard and outboard vertical divertor tiles and the horizontal divertor tiles as shown in Fig. 1. S-coordinate to specify the tile position can be found in Ref. [7]. We believe that the temperature did not increase during coring. Because the coring was conducted by using the drill with relatively low speed (less than ~ 300 rpm). The sampled tiles have $25 \mu\text{m}$ W coating on carbon-fibre composite (CFC) tiles. It should be noted that the surface coating material of tile 3 is Mo. The cored tile samples were cut into four pieces

and two of them were used for TDS and XPS analyses. For TDS, the heating rate was set to be $0.5 \text{ }^\circ\text{C s}^{-1}$ from $200 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$. Some temperature deviation was found at the temperature less than $200 \text{ }^\circ\text{C}$ due to heater control issue, but this deviation did not give a large impact on retention evaluation. The sample temperature was measured by a K-type thermocouple placed on the sample holder. Most of desorbed species were analyzed by a quadrupole mass spectrometer. The D_2 desorption rate was calibrated by the standard leak of $1.08 \times 10^{14} \text{ D s}^{-1}$ (calibrated in November 27, 2012) with the depletion rate of $3.6\% \text{ year}^{-1}$. The ionization probability table for H_2 of 0.44 and D_2 of 0.35, which can be found in the manual of QMS (Spectra Inc.) and that of HD was used an average value of 0.395. In the case of XPS measurement using (PHI 5000 Versa Pro II, Ulvac-Phi Inc.), Al-K_α was used as an X-ray source. The analyzed area was approximately

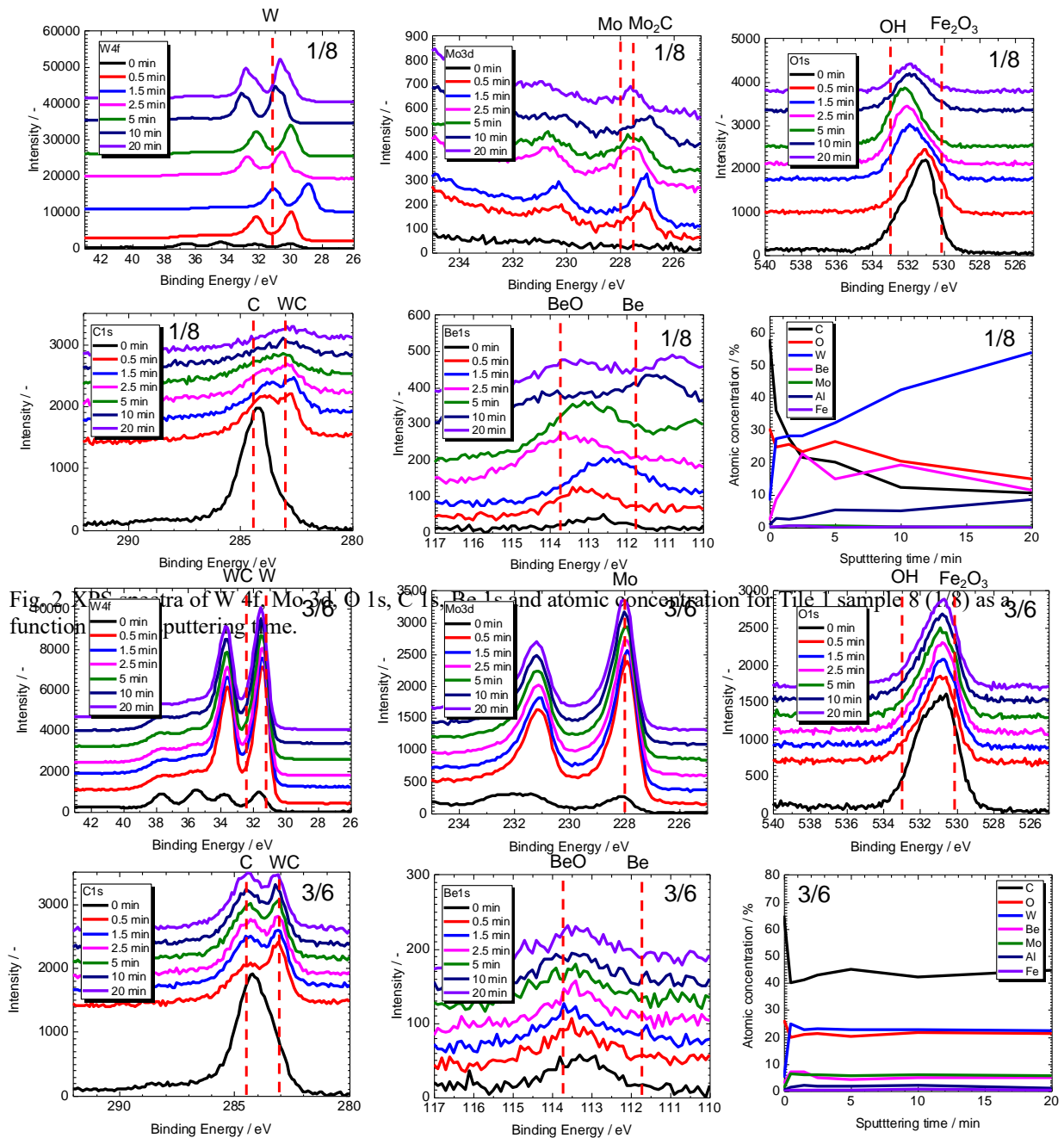


Fig. 3 XPS spectra of W 4f, Mo 3d, O 1s, C 1s, Be 1s and atomic concentration for Tile 3 sample 6 (3/6) as a function of Ar^+ sputtering time.

100 μm of diameter. The 3 keV Ar^+ sputtering etching was applied to obtain the depth profile of chemical states for constituent atoms. The maximum 20 minutes sputtering corresponds to the depth of 100 nm by rough estimation with assuming as W bulk target.

3. Results and discussion

Table 1 Summary of Typical XPS peak positions [13, 14]

W 4f	W:31.2 eV, WO_3 : 36.1 eV, WO_2 : 33.47 eV, WC: 32.5 eV
Fe 2p	Fe:706.95 eV, FeOOH : 711.25 eV, Fe_2O_3 :710.9eV, Fe_3O_4 :710.8 eV
O 1s	H_2O : 533.1 eV, Fe_2O_3 530.1 eV, FeO :529.8 eV
C 1s	Graphite:284.5 eV, WC: 283.0 eV, CO_2 :291.9 eV, Carbonate: 289.4 eV
Be 1s	Be:111.8 eV, BeO :113.7eV, BeF_2 115.3 eV
Mo 3d	Mo:228.0eV, Mo_2C 227.8eV, MoO_2 : 228.9 eV, MoO_3 :232.5 eV

Fig. 2 shows typical XPS spectra for sample 1/8 (Tile 1, inboard upper part, see Fig. 1). The typical chemical states for each element were summarized in Table 1 [13,14]. At the top surface, large C 1s peak was located at 284.1 eV, corresponding to the chemical state of graphite. Under the Ar^+ sputtering, the C 1s spectrum was split into two states, namely 284.1 eV and 282.8 eV. This indicates the formation of metal carbide (WC, Mo_2C or Be_2C). In addition, the existence of oxygen made complex chemical shift. The peak position of Be 1s spectra were located at the binding energy of 113.3 eV, 112.4 eV, 111.2-110.7 eV, corresponding to the chemical state of BeO , Be_2C and Be, respectively. At the deeper region (sputtering time of 10-20 min), negative peak shift of Be

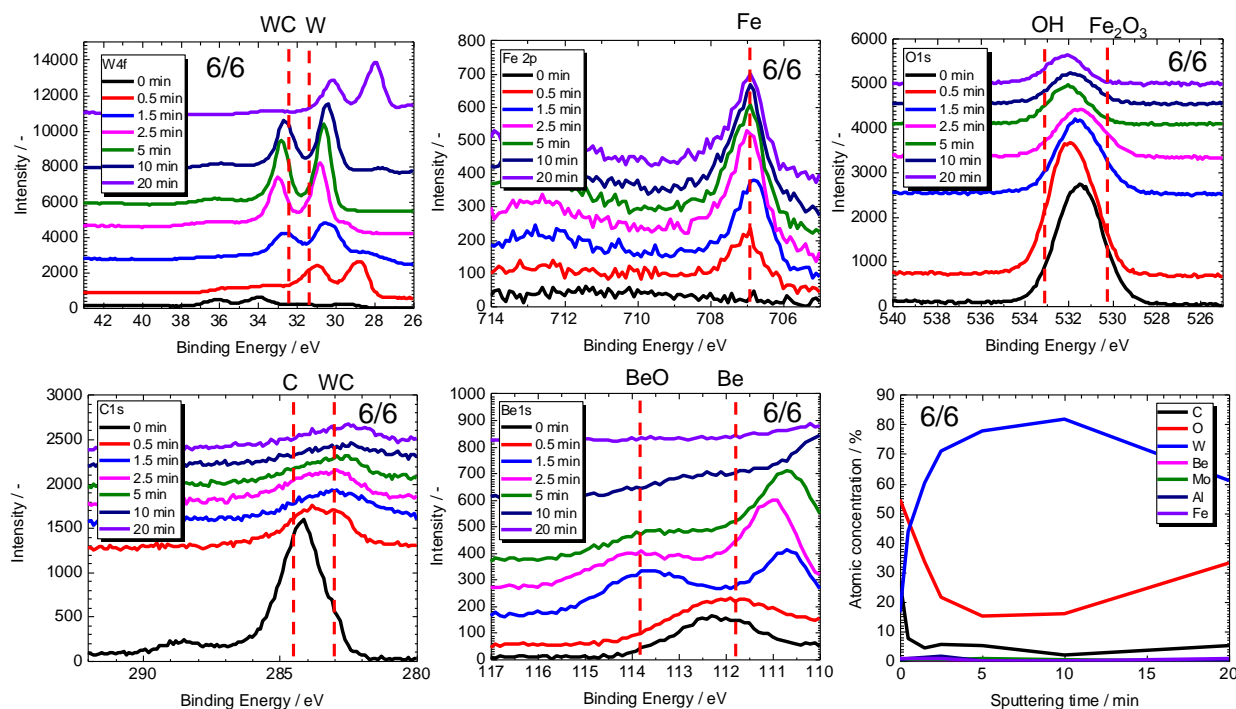


Fig. 4 XPS spectra of W 4f, Fe 2p, O 1s, C 1s, Be 1s and atomic concentration for Tile 6 sample 6 (6/6) as a function of Ar^+ sputtering time.

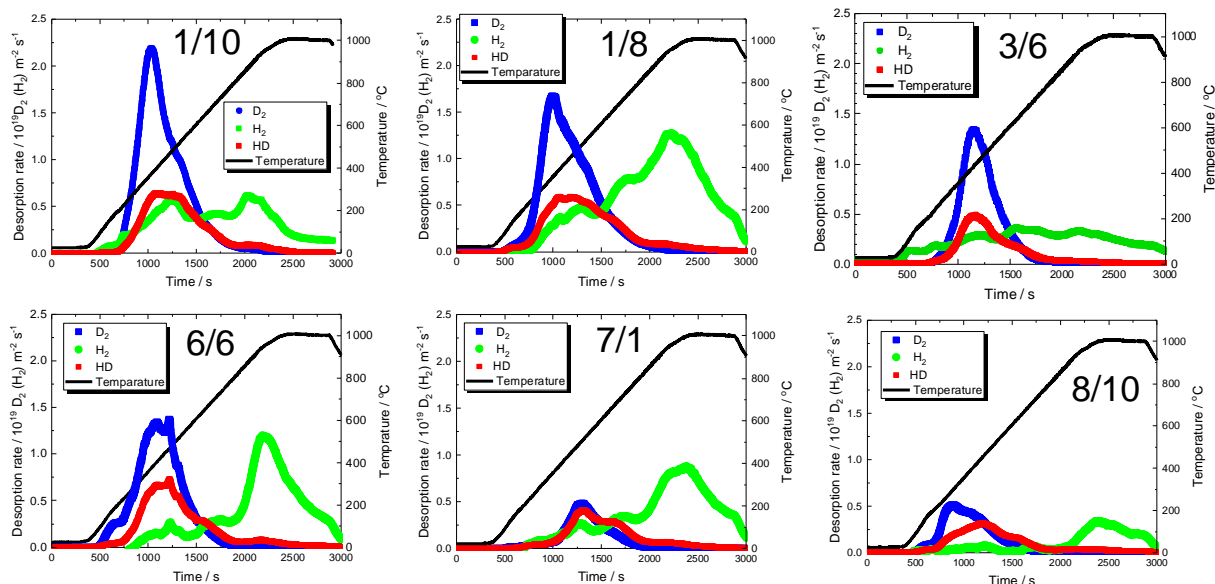


Fig. 5 D_2 , HD and H_2 TDS spectra for Tiles 1/10, 1/8, 3/6, 6/6, 7/1 and 8/10.

1s and split of W 4f_{3/2} were observed, indicating that the formation of Be-W compounds could occur [7, 13]. At this time, there are only a few reports about the chemical shift by interaction between Be and W. So, it may require more detail analysis using standard samples.

In case of sample 3/6 (Tile 3, inner strike point, see Fig. 1) as shown in Fig. 3, co-existence of W and Mo indicated to an erosion-dominant region. It is noted that Tile 3 is Mo-coated tile that initially had no W. In addition, large amount of C was also observed to form metal carbide (283.1 eV). In previous papers, it has been reported that this area should be both affected by sputter erosion and by impurity deposition, which would lead the existence of carbon [8-11]. Most of strike point was located at this tile, which enhanced the formation of metal carbides due to higher heat loads in this region. Two chemical states of O 1s at top surface were found at the binding energies of 531.8 eV and 530.7 eV, indicating the formation of hydroxide and oxide, but beneath the surface, most of the chemical state was oxide.

The experimental results for sample 6/6 (slope part of Tile 6, see Fig. 1) are shown in Fig. 4. According to Tokitani et al., the mixed-material deposition layer, which mainly included Be and Ni with the thickness of ~2 μm, was formed on the surface [12], which enhanced large chemical shift of the W 4f core level. No existence of Mo was found, but clear observation of Fe was confirmed at the binding energy of 706.9 eV, corresponding to the Fe metal state. Two chemical states of oxygen also existed beneath the surface. The formation of mixed material layer may induce negative peak shifts for W 4f and Be 1s due to the surface core level shift, where the coordination number was reduced by the formation of mixed material layer with weak bonding or pile up of the deposits due to the formation of W-Be alloy [15]. But, to confirm the mechanism of negative peak shifts in detail, more experimental data should be accumulated.

TDS experiment was applied to evaluate total H and D retentions for the tiles. Typical TDS spectra for the samples 1/10, 1/8, 3/6, 6/6, 7/1 and 8/10 are shown in Fig. 5. It was found that major D desorption temperatures were located at 370 °C and 530 °C. Large D desorption was found for Tile 1, namely for samples 1/10 (apron part) and 1/8 (upper part), where major D desorption was located at 370 °C. For the sample 3/6 located at inner strike point on

Tile 3, large D desorption temperature was shifted to 430 °C, which would be caused by the stabilization of trapped D by higher heat load. In addition, no large H retention was seen supporting this hypothesis. For sample 6/6 (slope part on Tile 6), the shape of TDS spectra was quite different from the above. The D desorption was initiated at lower temperature of 120 °C and two large D desorption was located at 400 °C and 460 °C, which may be caused by the exposure of gaseous D and energetic D direct implantation. For outer divertor tiles, Tile 7 sample 7/1 and Tile 8 sample 8/10 (apron part), the D desorption was quite small compared with that for inner samples. Earlier results have shown the Tiles 7 and 8 being low-deposition areas [9], hence there are no major fuel co-deposition processes taking place. Both samples had two D desorption temperatures at 500 °C and 650 °C for sample 7/1 and 300 °C and 380 °C for sample 8/10. The fuel accumulation may be due to implantation-induced retention.

Based on previous reports [16,17], the desorption temperature of hydrogen isotope for graphite should be above 600 °C due to stable C-D bond formation. The D desorption for W is clearly controlled by the damage concentration and impurities, and its desorption temperatures were extended from 150 - 500 °C [18-20]. For Be, Fujii et al showed the TDS spectra in Ref. [21], where major desorption temperature was located at 430 °C using the heating rate of 1 °C s⁻¹. Based on these information and atomic concentration evaluated by XPS, major D trapping would be caused by the interaction with W near surface region [7,9] due to no large D desorption at higher temperature above 600 °C. It is also noted that there was observed large H desorption located at above 800 °C. The origin for this H release at high temperatures is still unknown, and further analyses are required.

Finally, the D and H retentions for JET ITER-Like Wall samples are summarized as a function of divertor S-coordinate in Fig. 6. Higher D and H retentions were found for inner upper divertor region (Tile 1). As moving to outer divertor region, their retention was clearly reduced. For the strike point region (Tile 3), slightly higher retention was found compared with erosion-dominated areas like the outer divertor. Therefore, it can be said that the deposition and formation of mixed material layer would work as hydrogen isotope trapping sites in the divertor of JET ITER-like wall.

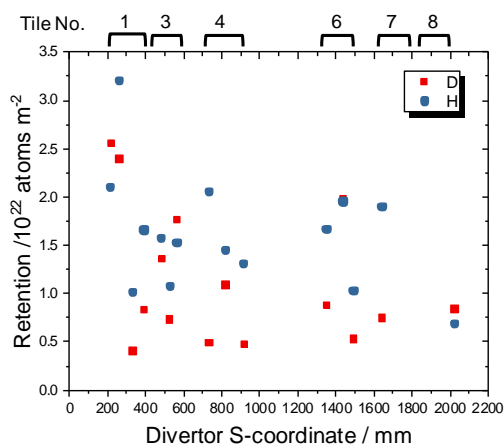


Fig. 6 H and D retentions as a function of divertor S-coordinate.

4. Conclusions

Hydrogen isotope retention and chemical state of the divertor tiles for JET ITER-Like Wall were evaluated by TDS and XPS at QST IFERC Rokkasho site under the framework of BA activities. A deposition layer was found in the upper divertor area (Tile 1). At the inner strike point region (Tile 3), the existence of W and Mo was found, indicating for erosion-dominated region, but the impurity deposition was also found. Higher heat load would induce the formation of metal carbide. In the case of outer horizontal tile (Tile 6), mixed material layer was formed and iron impurity was seen clearly being deposited. TDS showed the H and D desorption behavior and major D desorption temperature for Tile 1 was located at 370 °C and 530 °C. At the strike point region, the D desorption temperature was clearly shifted toward higher temperature

side, indicating of emptying the low-energy traps by higher heat load. It can be concluded that the D retention behavior was clearly changed by the surface chemical states and the formation of mixed material layer at the divertor of JET ITER-Like Wall.

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