

Trapping of Tritium by Stainless Steel Exposed to Plasmas in Experimental Campaigns of LHD

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Retention behavior of tritium by stainless steel exposed to plasmas in the Large Helical Device (LHD) has been studied by β -ray-induced X-ray spectrometry (BIXS) and an imaging plate (IP) technique. Plasma-exposed stainless steel samples were prepared by exposing the small plates at the location of 6.5L in LHD. X-ray photoelectron spectroscopy (XPS) was also applied to analyze deposition layers on the surface of a sample. XPS analyses showed that the deposition layers contain B, C, O and Ti as well as constituent elements of stainless steel. Chemical form of metallic elements was mainly oxides, but a part was metallic state. The plasma-exposed sample was exposed to tritium gas along with a bare stainless steel plate for comparison. The BIXS and IP measurements showed that the tritium retention largely increased by plasma exposure and it strongly depended on sample temperatures during vacuum heating and tritium exposure. In addition, it was seen from the IP images that non-uniform tritium distribution on the surface was formed even tritium exposure at room temperature.

Keywords: tritium retention, plasma exposure, BIXS, imaging plate, plasma-facing materials

1. Introduction

Reduction of tritium retention in the plasma-facing materials (PFMs) and the structural materials of fusion experimental device such as ITER is one of great important issues from viewpoints of the safety and economy of tritium as well as the fuel particle balance in the reactor core, since a huge amount of tritium is used in the device. These materials are exposed to various energy particles, and surfaces of them are modified. Deposition layers are formed on the surfaces as a result of plasma exposure. They will affect tritium retention. The tritium retention strongly depends on surface states such as chemical state and composition of constituent elements in the deposition layers. Namely, it is important to understand the correlation between tritium retention and surface states of deposition layers.

We have examined so far the trapping and release behavior of tritium in the PFM's of the Large Helical Device (LHD) as an example of the effects of exposure to plasmas for tritium retention [1]. Stainless steel plate is used as a protection plate in LHD. Small stainless steel

samples were fixed at four different locations, which are 1.5U, 5.5U, 6.5L and 9.5L in LHD [2], and those samples were exposed to plasmas for one cycle in the 13th experimental campaign. After plasma exposure, they were applied to tritium exposure at 623 K for 4 hours after heating in vacuum at 673K.

It was seen that all of the stainless steel samples were covered with deposition layers, although their thickness was different from each other. Tritium retention in each sample was strongly dependent on the sample location [1]. In addition, significant non-uniform tritium distribution appeared in the plasma-exposed surface of the 6.5L sample, although other samples showed almost uniform distribution. Therefore, the present study was focused on the trapping behavior of tritium in the 6.5L sample.

2. Experimental

The samples used in this study are stainless steel type 316 (SS316), and size of the sample plates was 10×10 mm and 0.5 mm in thickness. These sample plates were finally electropolished, and they were fixed at four

different walls in LHD before beginning of the 13th plasma campaign, which was conducted for 13 weeks from October 2009. After plasma exposure, only 6.5L sample was provided for surface analyses and tritium exposure experiments in this study.

As a first step, the plasma-exposed surface was observed by a digital microscope. This sample was also used to analyze chemical states of surface elements by X-ray photoelectron spectroscopy (XPS). The XPS analysis was performed on a Thermo Fisher Scientific Model ESCLAB250Xi XPS system using Al(K α) X-rays with an energy of 1486.6 eV.

Tritium exposure tests were conducted by the following procedures. The 6.5L sample and a bare SS316 plate with the same size as a reference sample were set in the tritium exposure device, and it was evacuated below 2×10^{-6} Pa at room temperature. The latter sample was used for comparison. In order to examine the effects of pre-heating in vacuum of the samples, at first, they were exposed to tritium gas at room temperature. After β -ray-induced X-ray spectrometry (BIXS) and imaging plate (IP) measurements of them, as the second examination, those samples were again set in the tritium exposure device and then it was evacuated below 6×10^{-6} Pa at 673 K. After this evacuation, the samples were exposed to tritium gas at room temperature for 4 hours. Subsequently, as the third examination, the samples were repeatedly set in the tritium exposure device, and those were heated at 673 K in vacuum and exposed to tritium gas at 623 K for 4 hours. Total pressure and tritium concentration of tritium gas used in this study were 2.66 kPa and 4.8%, respectively.

After each procedure of the tritium exposure, to estimate the amount and distribution of tritium retained in surface layers, both of 6.5L and bare SS316 sample were contacted with an IP along with a set of standard tritium sources, which were made of a polymer material labeled with tritium. In this procedure, a thin poly-phenylene-sulfide film (PPS: 1.2 μm) was inserted between the samples and IP to avoid contamination of the IP surface. After exposure to IP for a given time, two-dimensional mapping of β -ray dose was obtained by measuring the intensity of photo-stimulated luminescence with the imaging analyzer (Fujifilm FLA-7000). The spatial resolution was 25×25 μm . Some examples of tritium measurements by a similar IP technique have been recently reported by Hatano [3-4]. The BIXS was also employed to evaluate the tritium retention in surface layers and the tritium distribution in depth of a sample. The details of BIXS are described elsewhere [5].

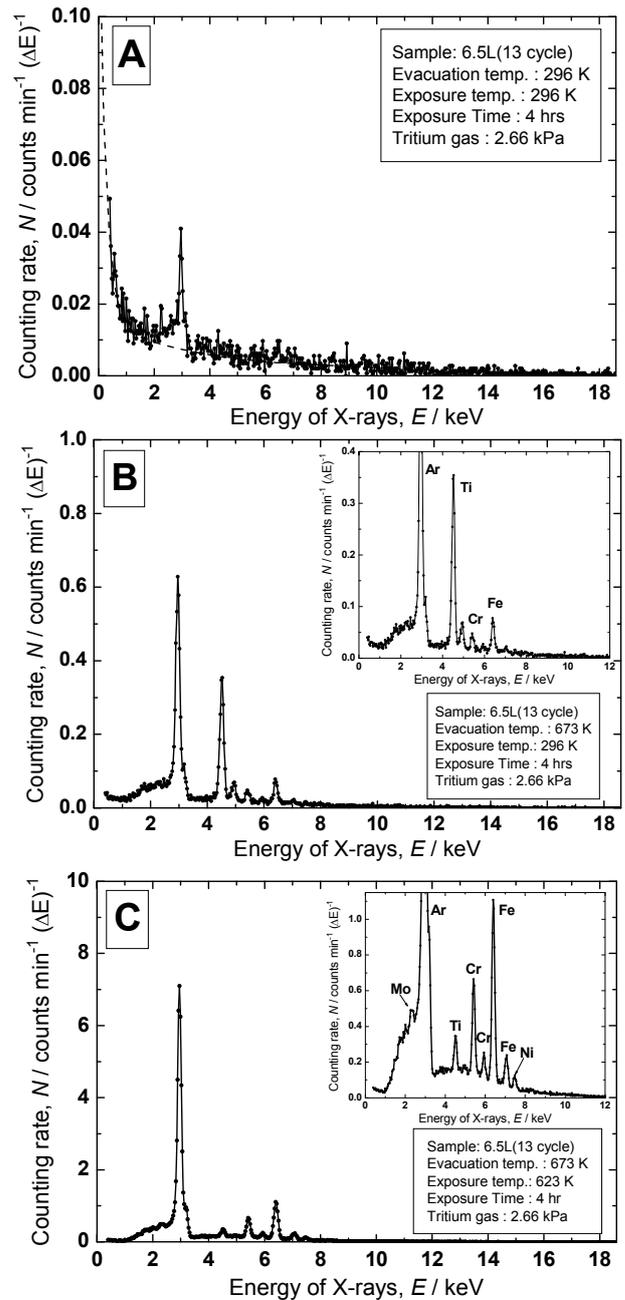


Fig. 1 X-ray spectra observed by BIXS for 6.5L sample. Each of upper, middle and bottom figures was observed after vacuum heating and tritium exposure under the following conditions. (A) ; heated at 296 K and exposed at 296 K, (B); heated at 673 K and exposed at 296 K, and (C); heated at 673 K and exposed at 623 K. The dashed line in the figure (A) shows the background level of the present X-ray detector.

3. Results and discussion

3.1 Tritium measurements by BIXS

Figure 1 shows the X-ray spectra observed by BIXS measurements. All measurements by BIXS were carried out under the argon atmosphere. Each X-ray spectrum consists of characteristic X-ray peaks and a bremsstrahlung X-ray peak. Number of characteristic X-ray peak observed was dependent on conditions of the vacuum heating and exposure temperature. In the case that both temperatures

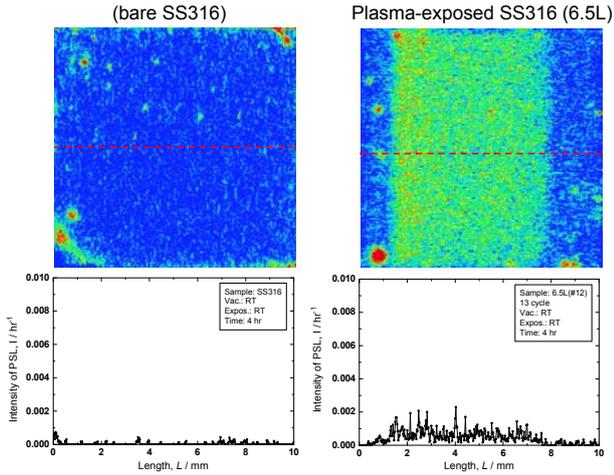


Fig. 2 IP images and line analyses for bare SS316 and 6.5L samples. Both temperatures in vacuum heating and tritium exposure were 296 K.

during vacuum heating and exposure processes were room temperature as shown in Fig. 1 (A), only a single peak of Ar($K\alpha$) X-rays was observed. On the other hand, plural characteristic X-ray peaks appeared as shown in Figs. 1 (B) and (C), when vacuum heating and/or exposure temperature were raised. Those X-ray peaks were assigned to Ti, Cr, Fe, Ni and Mo from energies of X-rays as shown in the inset of Figs. 1 (B) and (C). It is considered that appearance of a rather large titanium peak in Fig. 1 (B) is due to the use of a titanium sublimation pump as one of vacuum pumps in LHD. It should be noted that intensity of the Ti($K\alpha$) peak in Fig. 1 (B) is 5 times larger than that of Fe($K\alpha$) peak. Other characteristic peaks are due to constituent elements deposited on the surface by sputtering of stainless steel walls with plasmas in LHD.

It is known that intensity of an Ar($K\alpha$) peak corresponds to the amount of tritium retained in surface layers of a sample because of a short escape depth of β -rays [6]. Intensity of an Ar($K\alpha$) peaks in Figs. 1 (A), (B) and (C) was 0.13, 3.5 and 39 counts/min, respectively. The amount of tritium retained in surface layers largely increased with increasing temperatures of vacuum heating and tritium exposure: namely, tritium activity increased 27 times by elevating the temperature of vacuum heating, and it increased about 300 times by elevating both temperatures of vacuum heating and tritium exposure. The former increase may be due to removal of impurities adsorbed on the surface and diffusion of metallic species from bulk to the surface since the tritium exposure temperature was the same. On the other hand, it is expected that the latter increase was caused by acceleration of tritium diffusion into the deposited layers since the exposure temperature increased.

In addition, the shape of the bremsstrahlung X-ray peak in Fig. 1 (C) was different from that in Figs. 1 (A) and (B). Namely, the shape in Fig. 1 (C) was convex above 3.5 keV.

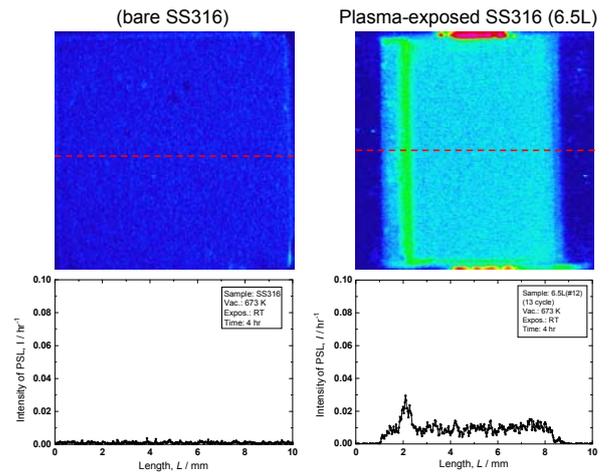


Fig. 3 IP images and line analyses for bare SS316 and 6.5L samples. Vacuum heating was 673 K and exposure temperature was 296 K.

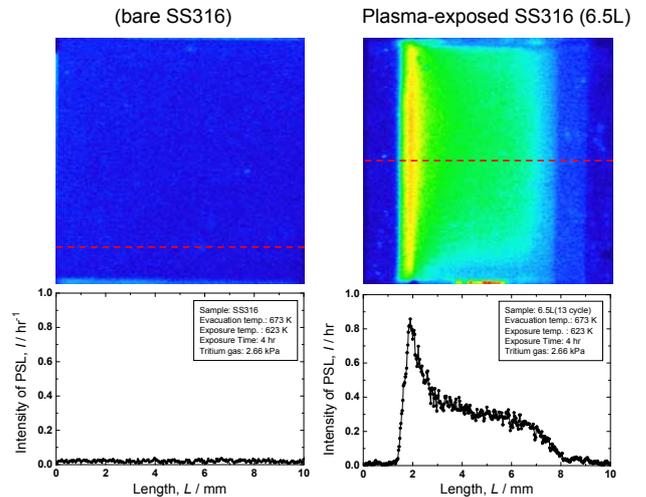


Fig. 4 IP images and line analyses for bare SS316 and 6.5L samples. Vacuum heating was 673 K and exposure temperature was 623 K.

This indicates the diffusion of tritium into the bulk as well as adsorption on the surface. It can be seen, therefore, that the amount of tritium retained in surface layers is strongly affected by both of vacuum heating and exposure conditions even though the surface is covered with the deposited layers.

3.2 Measurements of surface tritium distribution by IP technique

Surface tritium distribution was measured by an IP technique. To determine tritium activity in surface layers, seven standard polymer plates labeled with a given concentration of tritium were used. Main deposition of the surface of plasma-exposed sample was carbon described later and its thickness was thinner than about $1\mu\text{m}$. Therefore, escape depth of β -rays in the sample was assumed to be almost same as the standard samples. Figure 2 shows the observed IP image (upper) and the result of

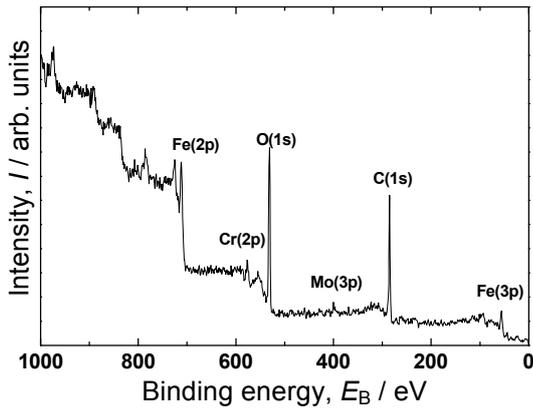


Fig. 5 An example of XPS spectra observed by wide scan.

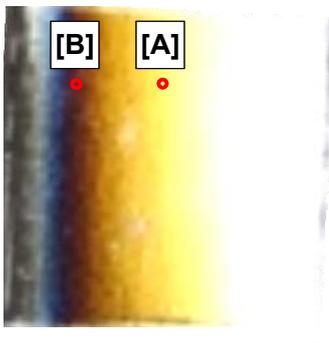


Fig. 6 Photograph of the sample surface and the analyzed spots by XPS.

line analysis (lower) at the red broken line in the image, where both the vacuum heating and exposure temperatures were room temperature. In comparison, similar measurements for a bare stainless steel that is not exposed to any plasma are also shown. Image of tritium distribution measured by IP technique is represented by a color measure. Red color shows the highest activity, while blue color does the lowest activity. Namely, tritium activity decreases relatively with the following color change: red, yellow, green and blue. Surface tritium activity of the 6.5L sample was estimated to be 128 MBq/m^2 , while that of bare SS316 was 16 MBq/m^2 . Difference in tritium activity was as large as 8 times. It is clear that such a large difference in tritium retention is due to the plasma exposure.

To examine the effects of vacuum heating, exposure to tritium gas was carried out at room temperature after vacuum heating at 673 K. After this, surface tritium distribution was similarly measured by IP technique. The results are shown in Fig. 3. Tritium retention in surface layers of the 6.5L sample was estimated to be 1.97 GBq/m^2 as an average, while that of bare SS316 sample was 0.16 GBq/m^2 . The difference in tritium retention of both samples became larger by increasing in temperature of vacuum heating. In addition to this, high retention area appears in the left side of the 6.5L sample as green color.

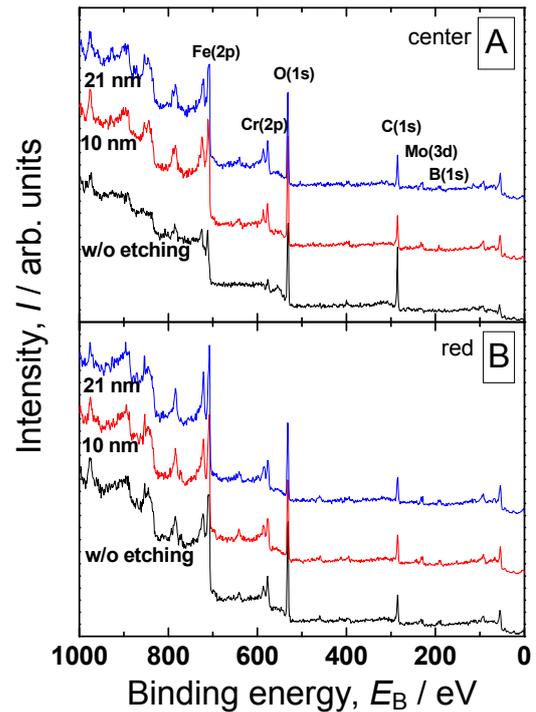


Fig. 7 Changes in XPS spectra for two spots with depth.

This is clearly shown by the result of line analysis. Tritium activity in the green region was 4.06 GBq/m^2 , which is about twice of the average concentration. These indicate that high tritium retention appears even though exposure temperature is low, when the sample was pre-heated in vacuum at high temperature. It is considered, therefore, that the large increase in tritium retention is due to the change in adsorption properties of deposition layers by vacuum heating as mentioned above.

Further examination for the vacuum heating effects was carried out: namely, both samples were simultaneously exposed to tritium gas at 623 K after vacuum heating at 673 K. The results are shown in Fig. 4. Tritium retention in surface layers of the 6.5L sample was estimated to be 56.0 GBq/m^2 as an average. This activity was 437 times larger than that observed in Fig. 2, and it was close to the result observed by BIXS. On the other hand, tritium retention of bare SS316 was 3.23 GBq/m^2 . Tritium retention of the 6.5L sample was about 17 times larger than that of bare SS316 sample. Furthermore, remarkably non-uniform tritium distribution appeared clearly in the left side of 6.5L sample and the tritium activity in the yellow region was as high as 119 GBq/m^2 .

3.3 XPS analyses of the plasma-exposed surface

In order to examine causes of non-uniformity in the tritium distribution on the deposition layers of the 6.5L sample, the plasma-exposed surface and its depth profile was analyzed by XPS without any heating treatment. Figure 5 shows an example of XPS spectra observed by

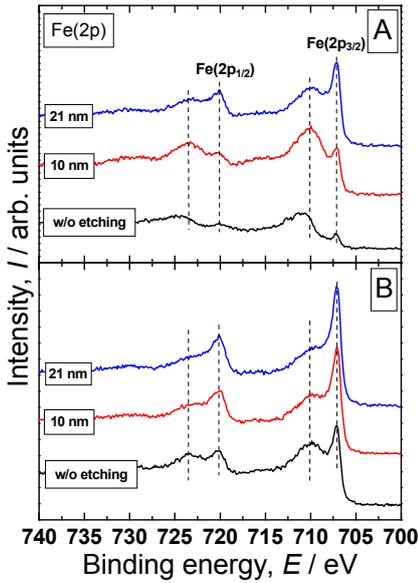


Fig. 8 Changes in Fe(2p) peak with depth.

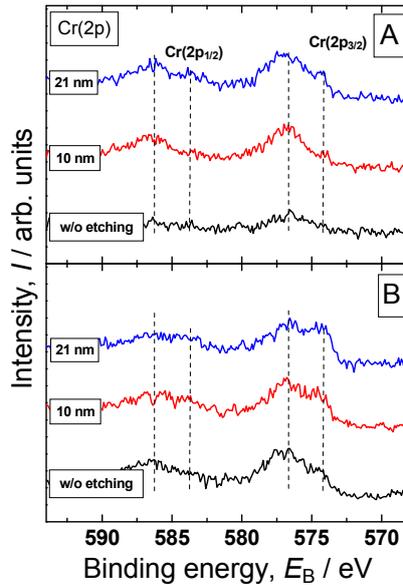


Fig. 9 Changes in Cr(2p) peak with depth.

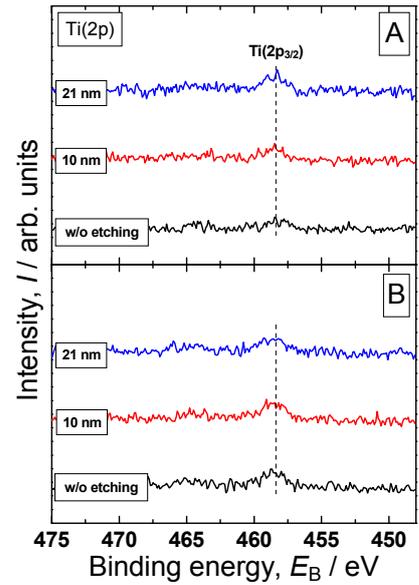


Fig. 10 Changes in Ti(2p) peak with depth.

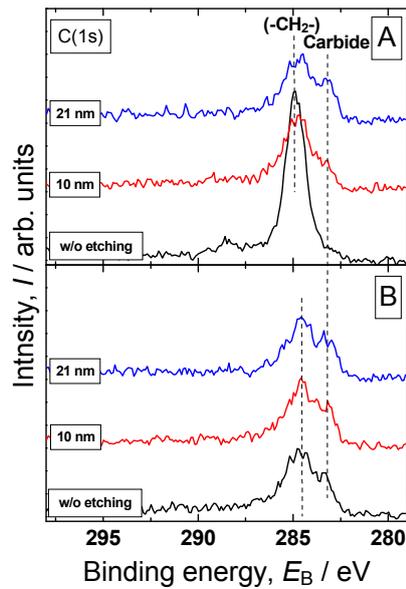


Fig. 11 Changes in C(1s) peak with depth.

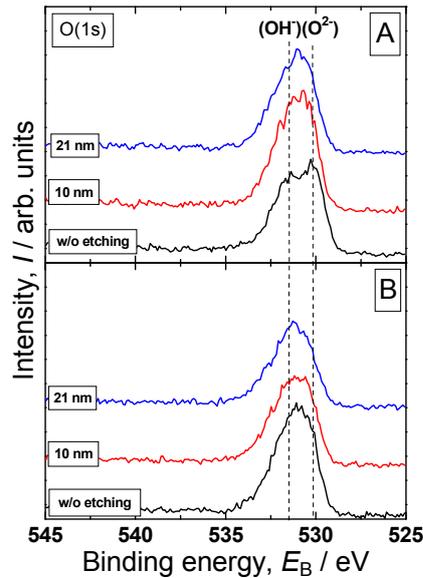


Fig. 12 Changes in O(1s) peak with depth.

wide scan from 0 to 1200 eV. The analyzed spot was almost center of the sample surface. As clearly seen from the spectrum, major elements on the surface are carbon and oxygen. In addition to these elements, small amount of elements such as iron, chromium and molybdenum also deposited on the surface. However, titanium was scarcely deposited in surface layers.

Depth profiles of two spots on the sample surface, [A] and [B], were measured as an example. Location of two spots is shown in Fig. 6. The former spot was the center of the surface, while the latter one is the region of left side, which corresponds to the region in which much tritium was retained as shown in Fig. 4. Changes in XPS spectra for

two analyzed spots of the deposition layers were measured with etching by argon. The results are shown in Fig. 7. Etching rate by argon ions was assumed to be 1.0 nm/s, which was obtained from the sputtering of Ta₂O₅ by argon. Difference in peak intensity was observed between two spots: namely, intensity of a carbon peak in the spot [B] was less than that in the spot [A], while that of oxygen was contrarily larger. It should be noted that intensities of metallic Fe, Cr and Mo peaks in spot [B] is larger than those in spot [A], although oxygen peak in spot [B] is more intense than that in spot [A]. Such a remarkable difference in both measurement spots was observed for the as-received surface only, and it became small with depth.

Figs. 8 to 12 show the spectra observed by narrow scan of each element for two spots of [A] and [B]. The observed spectra for iron are illustrated in Fig. 8. It is seen from binding energy that chemical forms of iron consist of metallic iron (707.1 eV ($2p_{3/2}$) and 720.1 eV ($2p_{1/2}$)) and the mixed oxides of FeO, Fe₂O₃ and FeO(OH) (710.1 eV ($2p_{3/2}$) and 723.2 eV($2p_{1/2}$)) [7]. Peak of oxide assigned to the latter species shifted to the lower binding energy side with depth. This indicates that decrease in the amounts of FeO(OH) and Fe₂O₃ is larger than that of FeO with depth. Great difference in two analyzed spots is the fraction of metallic iron as mentioned above. Metallic iron, which is known as one of catalysts available for the adsorption of hydrogen, will contribute to the adsorption of tritium [8]. In addition, existence of iron carbide was also suggested from a C(1s) spectrum as described later.

The observed spectra for chromium are illustrated in Fig. 9. It was seen that chemical forms of chromium are metallic chromium (574.1 eV ($2p_{3/2}$) and 583.6 eV ($2p_{1/2}$)) and its oxides such as Cr₂O₃ and CrO(OH) (576.6 eV ($2p_{3/2}$) and 586.2 eV ($2p_{1/2}$)), although intensities of these peaks are fairly weaker than that of iron peaks. Fraction of metallic chromium increased with the increase in depth. This is a similar tendency to the changes in a peak intensity of iron.

The observed spectra for titanium are illustrated in Fig. 10. Only a weak peak appeared in the spectra. It was seen that a chemical form of titanium is TiO₂ (458.5eV ($2p_{3/2}$)), but metallic titanium (453.8 eV ($2p_{3/2}$)) can not be found within a depth of 21 nm. However, an intense X-ray peak of titanium appeared as is shown in Fig. 1 (B), where the sample was heated at 673 K in vacuum and exposed to tritium gas at 296 K. It is considered that titanium atoms diffuse from bulk to the surface by vacuum heating, and tritium concentration near titanium atoms becomes high by annealing at high temperature in vacuum. Further investigations by XPS are required about the diffusion of titanium after vacuum heating at 673 K.

As is shown in Fig. 5, most of the surface was covered with carbon and oxygen atoms. Figure 11 shows the changes in C(1s) peak with depth. Two peaks apparently appeared in each spot. The peak of 283.2 eV was assigned to iron carbide [9], which may not contribute to the tritium adsorption. The higher energy peak (284.9 eV for the spot [A], 284.5 eV for the spot [B]) consists of plural peaks, and they were assigned to chemical forms such as graphite/aromatics and (-CH₂-) [10]. There was a large difference in the as-received surface: namely, carbon content in the spot [A] is appreciably larger than that in the spot [B], and carbon species in the spot [B] consist of chemical forms of graphite, (-CH₂-) and carbide, although the content and chemical form of carbon in bulk is similar to each other. Tritium retention in point [B] was several times larger than

that in point [A] as is shown in Figs. 3 and 4. It is considered, therefore, that the amount of carbon on the surface of deposition layers is one of key factors for tritium retention.

Figure 12 shows the changes in O(1s) peak with depth. At least, the peak of O(1s) consists of two kinds of oxygen species: O²⁻ (530.1 eV) and OH⁻ (531.5 eV) [11]. Assignment of these peaks coincides with that of oxide peaks of iron and chromium observed in Figs. 8 and 9. There are not large differences in a chemical state of oxygen for both analyzed spots.

4. Summary

Tritium retention behavior on the surface of a stainless steel plate, which was previously exposed to plasmas at the location of 6.5L in the Large Helical Device (LHD) during one cycle, has been studied. To clarify the effects of plasma exposure, the plasma-exposed sample along with a bare sample were exposed to tritium gas under the given temperature conditions. Three different temperature conditions of the vacuum heating and tritium exposure were applied to these samples.

It was seen from the BIXS and IP measurements that the amount of tritium retained in the plasma-exposed surface was larger than that in the bare surface irrespective of temperature conditions and it remarkably increased in increasing temperatures of vacuum heating and tritium exposure. Large heating effects for tritium retention appeared in the plasma-exposed sample than the bare sample of stainless steel. Furthermore, significantly intense X-ray peak of titanium was observed by vacuum heating at 673 K, although it did not appear at 296 K.

Non-uniformity of tritium distribution on the plasma-exposed surface was confirmed by the images of IP irrespective of temperatures of the vacuum heating and tritium exposure. XPS analyses of the as-received surface of the 6.5L sample indicated the existence of metallic chromium and iron, although the surface was exposed to ambient atmosphere after exposure to plasmas. It is considered, therefore, metallic species in the deposited layers are responsible for the non-uniformity of tritium distribution. This will be clarified by further XPS analyses of the sample processed at high temperatures.

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