Effects of heat treatment on trapping and release of tritium from He pre-irradiated tungsten

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Abstract

The effects of heating on retention of tritium implanted into tungsten pre-irradiated with helium have been examined by β-ray-induced X-ray spectrometry (BIXS), which gives information about changes in the amount and depth profile of tritium retained on/in materials. Tritium implantation and isochronal heating of the helium pre-irradiated and un-irradiated tungsten samples were repeated as a series of experiments, and changes in the X-ray spectra were measured in each heating cycle. Quite different decreasing behavior between Ar(Kα) and W(Mα) X-ray intensities for both samples was observed in the heating process, and it was seen that the majority of tritium implanted into the helium pre-irradiation sample was trapped by the radiation defects rather than in helium bubbles.
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1. Introduction

High-Z materials such as tungsten and its alloys are promising candidates for plasma-facing materials (PFMs) in a future fusion reactor. PFMs are exposed to high energy particles of helium and hydrogen isotopes. From the viewpoints of fuel control and tritium safety, it is of a great importance to understand any effect of helium irradiation on the trapping and release behavior of hydrogen isotopes in high-Z materials. In addition, since these materials are also exposed at high temperatures, it is important to examine the effects of heating on the retention of tritium that was implanted into the helium pre-irradiated materials. An overview on the hydrogen interactions with defects, bubbles and impurities in tungsten has been recently given by Ogorodnikova et al. [1].

To examine the trapping and release behavior of hydrogen isotopes, the technique of thermal desorption spectroscopy (TDS) is widely used. This gives valuable information about the desorption kinetics of hydrogen isotopes, but it does not give direct information about the residual amount of hydrogen isotopes on the surface of a material. Recently, it has been shown by Matsuyama et al. [2–4] that the amount and depth profile of tritium trapped on/in various materials can be evaluated nondestructively by β-ray-induced X-ray spectrometry (BIXS). The basic principle of BIXS lies in utilization of the characteristic and bremsstrahlung X-rays induced by β-rays from the trapped tritium atoms, and it is a useful feature that allows independent determination of amounts of tritium trapped on the surface and in the bulk. As a recent application of BIXS to the studies on PFMs [5], the diffusion coefficient of tritium in tungsten was determined to be 2.4×10^{-19} m^2/s at room temperature from changes in the β-ray-induced X-ray spectra with time.

In this study to examine the effects of He pre-irradiation on trapping and release behavior of tritium by BIXS, two kinds of tungsten samples were used: one is a pre-irradiated sample with a fixed amount of helium

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(described as 'He pre-irradiated sample'), and the other is an un-irradiated sample (described as 'as-received sample'). Tritium implantation and heating of these tungsten samples were repeated in a series of experiments. The present study focuses attention on effects of heating on the retention of tritium implanted into a tungsten sample that was pre-irradiated with helium ions.

2. Experimental

2.1. Materials

Thin polycrystalline tungsten plates fabricated by powder metallurgy were prepared as sample, in the present study, and the purity and the size of them were 99.95% and $10 \times 10 \times 0.02$ mm^3, respectively. Prior to the implantation of tritium ions, a fixed amount of helium ions was implanted at room temperature: energy and fluence of helium ions were 8 keV and 5×10^{21} ions/m^2, respectively. It is reported that the distribution of helium was in the range from near surface to 80 nm in depth [6]. Tritium diluted in deuterium with the concentration of about 0.8% was used for the ion implantation. The purity of deuterium was 99.6% and that of argon used for X-ray measurements was 99.999%.

2.2. Implantation of tritium ions

Tritium ions were implanted into both the He pre-irradiated and as-received samples by using a specially designed tritium implantation device. The tritium implantation device mainly consisted of a tritium storage–supply–recovery part, an implantation part equipped with a conventional ion gun, a high vacuum system, and a sample transfer system. The detailed construction and specifications of the tritium implantation device are described elsewhere [5].

A sample holder was fixed in the implantation part equipped with the ion gun, and a sample was sandwiched between a shielding plate having a hole of 6 mm diameter and a thin molybdenum plate. A chromel–alumel thermocouple was attached to the molybdenum plate. A heater made of W–Re wire was fixed with a thin mica foil beneath the molybdenum plate. To measure ion current during tritium implantation, the sample holder was isolated and biased +18 V to prevent secondary electron emission.

2.3. Measuring device of β-ray-induced X-rays

A high purity Ge detector for an ultra-low energy X-ray detection, which was purchased from CANBERRA, was used to measure X-ray spectra induced by β-rays from tritium atoms. Since the major component of the energy distribution of the β-ray-induced X-rays is below 10 keV, a specially designed thin beryllium foil (8 μm) was used as an entrance window of the X-ray detector. In addition, both the X-ray detector and the sample were placed in an argon atmosphere to convert efficiently β-rays from surface tritium to X-rays, and they were sandwiched between two lead bricks to lower the effects of natural radioactivity. The flow rate of Ar was 40 cm^3/min.

2.4. Experimental procedures

The tungsten samples were evacuated for one week at room temperature in the tritium implantation device. Prior to the first tritium implantation, the tungsten sample was degassed at 673 K in vacuum. Subsequently, the sample was cooled down in vacuum to room temperature and then used for the implantation of tritium ions. The tritium implantation was carried out with acceleration energy and implantation time kept at 1 keV and 15 min, respectively. During the implantation, the total pressure in the tritium implantation device was kept at 4 Pa.

To lower the release of tritium species from the walls of the tritium implantation device when the sample is taken out, the tritium implantation device was evacuated for one week after the implantation. Just before taking out the sample, the tritium implantation device was decontaminated furthermore using a conventional tritium removal system. After this decontamination, the sample was transferred to the front of the X-ray detector, and measurements of the X-ray spectrum were started. The distance between the sample and beryllium window was kept at 5 mm.

To examine the retention behavior of tritium at elevated temperatures, the sample was heated stepwise in vacuum for 30 min at a temperature range from 373 to 973 K. At each step the sample was cooled down to room temperature for X-ray spectrum. This heat treatment was conducted using another conventional vacuum device to avoid cross contamination. Most X-ray spectra were measured for 12 h. After heating to the maximum temperature (973 K) in the first run, the same sample was again supplied to a second implantation of tritium ions. The same heat treatments in vacuum, tritium implantation, and measurements of X-ray spectra were repeated.

3. Results and discussion

3.1. First tritium implantation and heating

Fig. 1 shows the X-ray spectra observed for He pre-irradiated and as-received samples. Three characteristic X-ray peaks appeared in the spectra, although the
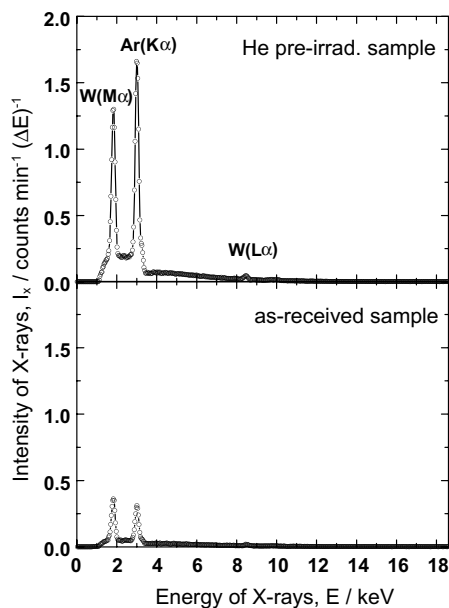
Fig. 1. Initial X-ray spectra observed for the He pre-irradiated and as-received samples after the first tritium implantation.

intensity of a W(Lα) peak was very weak in comparison with the other two peaks. This is due to a small population of β-rays that can excite the electrons in the L-shell of tungsten atoms.

In these spectra, the intensity of an Ar(Kα) peak corresponds to the amount of tritium trapped in a sub-surface region shallower than 20 nm, and that of a W(Mα) peak corresponds to the amount of tritium trapped up to a depth of 500 nm. In addition, the intensity of the W(Lα) peak depends on the amount of tritium trapped in a region up to 10 μm deep. The intensity ratios of W(Mα) to W(Lα) as well as of Ar(Kα) to W(Mα) are give a qualitative guide to the shape of a tritium depth profile: namely, those ratios increase with a relative decrease of tritium concentration in bulk. The depth profile of tritium is also reflected in the shape of the bremsstrahlung X-ray spectrum. Maximum intensity in the bremsstrahlung X-ray spectrum shifts to higher energy with an increase in the amount of tritium in bulk.

The X-ray spectrum intensity of the He pre-irradiated sample was several times larger than that of the as-received sample. Since the implantation time of tritium was the same for both samples, it is clear that the difference is not due to a difference in tritium fluence. In addition, the intensity ratio of Ar(Kα) to W(Mα) for the as-received sample was smaller than 1, while that in the He pre-irradiated sample was larger than 1. It is suggested, therefore, that a large part of the tritium in sub-surface regions of the as-received sample was reemitted during an implantation and/or desorbed after the implantation, and that diffusion and/or recombination of tritium were strongly impeded by the pre-irradiation with helium ions.

Table 1 shows X-ray intensities of Ar(Kα), W(Mα) and W(Lα) and ratios of Ar(Kα)/W(Mα) and W(Mα)/W(Lα) after tritium implantation at room temperature and heating at 973 K. After the implantation of tritium, the ratio of Ar(Kα)/W(Mα) for the He pre-irradiated sample was 1.7 times larger than that for the as-received sample, indicating that fraction of the amount of tritium trapped in a sub-surface region of the former sample is larger than that of the latter sample. However, this ratio became almost the same after heating at 973 K, indicating a similar depth profile for both samples. The reasons for the difference in intensities of Ar(Kα) and W(Mα) after heating at 973 K are an open question.

Fig. 2 shows the change in Ar(Kα) and W(Mα) intensities by isochronal heating of the He pre-irradiated sample. The intensity of Ar(Kα) X-rays began to decrease at about 400 K and mostly disappeared above 800 K. W(Mα) peak intensity behaved quite differently. Namely, the W(Mα) peak intensity kept nearly constant up to 623 K. Above 623 K, significant reduction appeared in a narrow temperature region, indicating the rapid release of tritium atoms trapped in a deeper region. It is known that the pre-irradiation with helium ions under the present conditions give rise to structural defects such as vacancies, dislocation loops and helium bubbles distributing in/near the irradiation zone of the tungsten sample. According to the experiments by temperature desorption spectroscopy, Eleveld and van Veen [7] ascribed the desorption peak of deuterium at around 650 K to release from helium bubbles. If the helium bubbles trap the implanted tritium, it is expected that

Table 1
Summary of the intensity and ratio of characteristic X-rays observed for both samples in the first isochronal heating

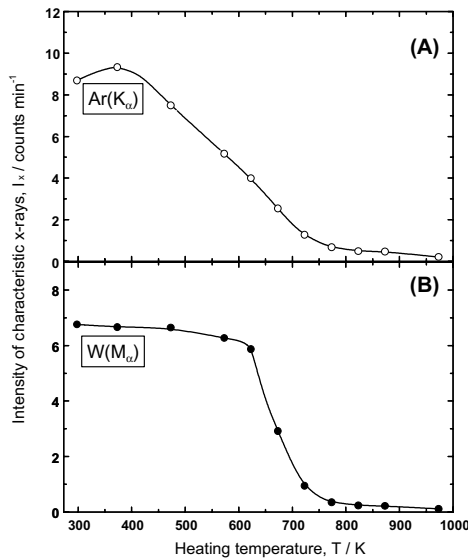|	As-received sample					He pre-irradiated sample				
	Ar(Kα) (cpm)	W(Mα) (cpm)	W(Lα) (cpm)	$\frac{Ar(K\alpha)}{W(M\alpha)}$	$\frac{W(M\alpha)}{W(L\alpha)}$	Ar(Kα) (cpm)	W(Mα) (cpm)	W(Lα) (cpm)	$\frac{Ar(K\alpha)}{W(M\alpha)}$	$\frac{W(M\alpha)}{W(L\alpha)}$
After irrad. at RT	1.75	2.05	0.06	0.85	34.2	10.5	7.29	0.16	1.44	45.6
After heating at 973 K	0.88	0.44	–	2.00	–	0.17	0.09	–	1.89	–

Fig. 2. Change in Ar(Kα) and W(Mα) intensities by isochronal heating for the He pre-irradiated sample in the first run.
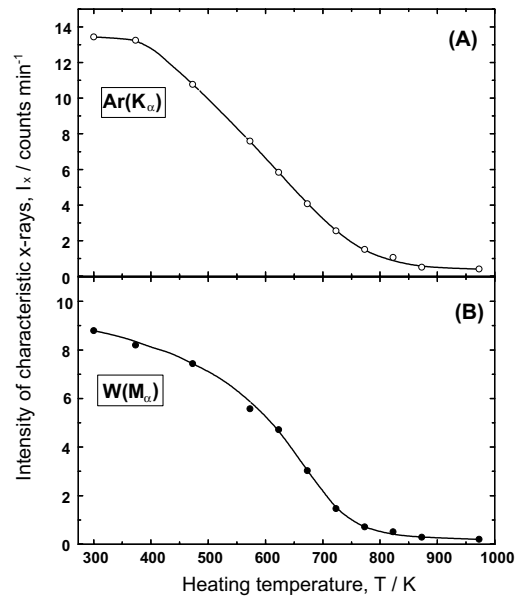

Fig. 3. Change in Ar(Kα) and W(Mα) intensities by isochronal heating for the He pre-irradiated sample in the second run.

the same changes in W(Mα) intensity would appear again in the second run.

3.2. Second tritium implantation and heating

Table 2 illustrates the result of changes in the X-ray intensities for the second tritium implantation. All X-ray intensities increased in the second tritium implantation. However, the difference of the X-ray intensities in both samples became smaller than that observed in the first run. This is mainly due to the increase of the X-ray intensities in the as-received sample. The ratio of Ar(Kα)/W(Mα) was larger than 1 for both samples, and they were almost the same. These intensity changes show a possibility that a similar surface condition was reached on heating in the first run for each sample.

Figs. 3 and 4 show changes in the X-ray intensities obtained by the second isochronal heating of the He pre-irradiated and as-received samples, respectively. For the former sample, changes in Ar(Kα) intensity in the sec-

ond run were the same as that in the first run, while the W(Mα) intensity began to decrease at 373 K, indicating that the mobility of tritium became high. This decreasing behavior is quite different from that in the first experiment. Namely, it is suggested that the number of a strong trapping site decreased by the first heating up to 973 K. On the other hand, for the as-received sample the decreasing behavior of Ar(Kα) intensity was almost identical to that in the first run, and that of W(Mα) intensity was also similar. W(Mα) intensity of the as-received sample was a little smaller than that of the He pre-irradiation sample. This indicates that He pre-irradiation effects did not completely disappear by heating at 973 K. These observations show that the majority of tritium implanted into the He pre-irradiation sample was trapped by the radiation defects and not by helium bubbles. Namely, it can be stated that radiation defects rather than irradiated helium atoms or bubbles play an important role in the trapping and release of tritium.

Table 2
Summary of the intensity and ratio of characteristic X-rays observed for both samples in the second isochronal heating

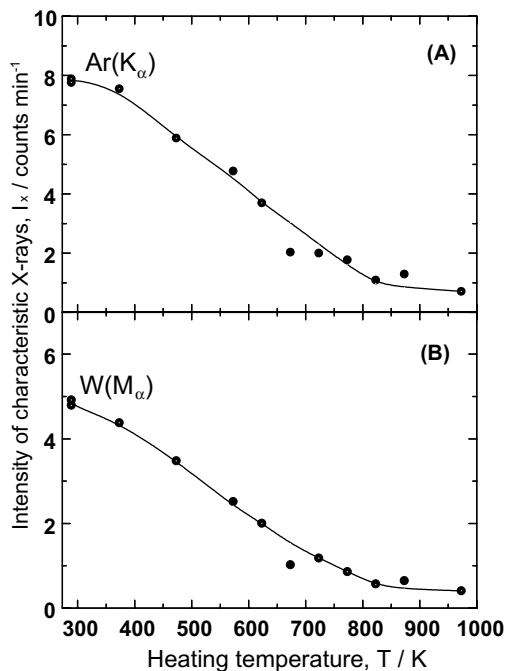|	As-received sample					He pre-irradiated sample				
	Ar(Kα) (cpm)	W(Mα) (cpm)	W(Lα) (cpm)	$\frac{Ar(K\alpha)}{W(M\alpha)}$	$\frac{W(M\alpha)}{W(L\alpha)}$	Ar(Kα) (cpm)	W(Mα) (cpm)	W(Lα) (cpm)	$\frac{Ar(K\alpha)}{W(M\alpha)}$	$\frac{W(M\alpha)}{W(L\alpha)}$
After irrad. at RT	7.87	4.78	0.13	1.65	36.8	13.4	8.80	0.25	1.52	35.2
After heating at 973 K	0.71	0.41	–	1.73	–	0.41	0.20	–	2.05	–

Fig. 4. Change in Ar(Kα) and W(Mα) intensities by isochronal heating for the as-received sample in the second run.

4. Conclusions

To examine the effects of heating on the retention of tritium implanted into tungsten pre-irradiated with helium, tritium implantation and isochronal heating of the helium pre-irradiated and un-irradiated samples were repeated as a series of experiments. For these experiments, β-ray-induced X-ray spectrometry (BIXS), which gives information about changes in the amount and depth profile of tritium retained on/in materials, was employed, and changes in the X-ray spectra were measured in each heating process. Quite different behavior between Ar(Kα) and W(Mα) intensities for both samples was observed in the isochronal heating process. It was seen that a major part of tritium implanted into the helium pre-irradiation sample was trapped by the radiation-created defects rather than in helium bubbles.

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