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Effects of Helium Pre-Irradiation on Tritium Release from Thin Boron Film Deposited on Stainless Steel type 316

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Abstract

The effects of helium pre-irradiation on trapping and release behavior of tritium implanted into thin boron films deposited on a plate of stainless steel type S316 were examined by an isothermal heating method and β-ray-induced spectrometry (BIXS). BIXS results showed that the helium pre-irradiation caused an increase in the trapping amount of surface tritium. Isothermal heating of the samples was carried out at temperatures in the range of 473 to 723K, and the decreasing rate of surface tritium was measured by tracking changes in the intensity of X-rays induced by β-rays. It was found that the decreasing rate of residual tritium obeyed first order reaction kinetics, indicating that the helium pre-irradiation has no influence on the tritium release kinetics. Apparent activation energy of the decreasing rate was determined to

be 0.3 eV from temperature dependence of the decreasing rate constant, which was about two-times larger than that measured without pre-irradiation of helium.

1. Introduction

It is well known that the plasma facing materials (PFMs) play an important role for control of impurities as well as fuel particles in the reactor core of a magnetic fusion device. A coating technique of the first wall surfaces with low-Z materials such as lithium, beryllium and boron is widely employed to reduce the oxygen partial pressure and the high-Z metallic impurities in the plasma. Effectiveness of boron coating for remarkable improvement of plasma parameters has been reported so far [1-3], but dynamic behavior of tritium in boron materials has not been clarified yet. In addition, energetic helium particles produced by the thermonuclear reactions impinge on the surfaces of PFMs along with fuel particles. Therefore, it is indispensable to understand the effects of helium irradiation on trapping and release behavior of tritium.

In the previous study [4], we examined the release and diffusion behavior of tritium ions irradiated thin boron films, which were deposited on a stainless steel plate. The examinations were carried out by isochronal and isothermal heating methods. As a result, it was found that most of the desorbed tritium was in an oxidized form and the residual amount of tritium in the surface layers decreased exponentially with time in the isothermal heating to 723 K. It was suggested, therefore, that the decreasing rate obeys first order reaction kinetics and the rate-determining step is the diffusion of tritium in boron. Furthermore, the Arrhenius plot of the decreasing rate constants showed a good linear fit and from this relation apparent activation energy of the diffusion of tritium was determined to be 0.17 eV.

In this study, effects of helium pre-irradiation on tritium retention in a thin boron film deposited on stainless steel plates were examined using β-ray-induced X-ray spectrometry (BIXS) and isothermal heating.

2. Experimental

2.1. Materials

Prior to coating of a boron film, plates of stainless steel type 316 (described as SS316), which were used as a model substrate, were finally polished on buff after polishing on a series of polishing papers, and then rinsed with water and acetone. A thin boron film was prepared by RF-assisted DC glow discharge using a mixture of helium and decaborane gas (95:5), and it was deposited on a plate of SS316 (described as B/SS316). Size of the SS316 plate was 15x15x0.5 mm^3, and thickness of the boron film was about 0.1 μm. Purity of the boron films prepared was about 90% and the details were described elsewhere [4].

Tritium gas used for ion irradiation was diluted with deuterium, and the concentration of tritium was about 0.7 %. Purity of helium used for pre-irradiation was 99.99995%, and the main impurities were nitrogen and oxygen.

2.2. Preparation of the irradiation samples

Tritium ions were irradiated using the tritium irradiation device that was specially designed for the irradiation of hydrogen isotopes. The pre-irradiation of helium ions were also conducted with the same device. The detailed structure of the irradiation device was described elsewhere [5]. At first, a B/SS316 sample was fixed on an irradiation stage in the irradiation device. Then the sample was evacuated at ambient temperature for two days and subsequently degassed to below 10^{-5} Pa at 673K. After degassing, an ion irradiation was carried out. Two kinds of irradiation samples were prepared in this study: namely, one was irradiated with only tritium ions, and the other was irradiated with helium ions prior to tritium irradiation. Irradiations of tritium and helium ions were carried out at 1 keV for 15 min at room temperature. During an irradiation, total pressures of tritium and helium gases were kept constant at 4 and 1.3 Pa, respectively, and the ion current in each irradiation was recorded to estimate the fluence of each ion. Average ion currents of tritium and helium were 1.0 and 0.3 μA, respectively. After the irradiation with tritium ions, the irradiated sample was evacuated for about one week to avoid the severe release of tritium species from the irradiation chamber walls when the sample is taken out of the irradiation device.

2.3. Isothermal heating of the irradiation samples

The irradiation samples were subjected to examination of isothermal heating. It was carried out using a separate vacuum device as shown in Fig. 1. An irradiation sample was hung by using a cage made of a fine metallic wire, and then evacuation to below 10^{-5} Pa was conducted at room temperature. The sample set in the cage was initially separated from the heating part surrounded by a furnace, and it was brought down after the heating part reached at a given temperature. The sample was heated for 30 min, and the released gases were evacuated during heating at a constant temperature. After a given time, the sample was again lifted, and it was cooled down to the room temperature. After this, the sample was detached from the vacuum device, and subjected to measurements of an X-ray spectrum induced by β-rays in the argon atmosphere.
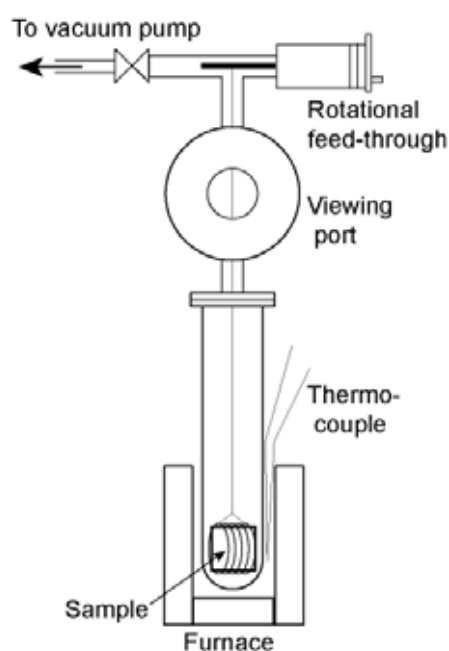

Fig. 1. Schematic drawing of the device used for isothermal heating of samples.

The sample was again set in the vacuum device after the measurements and it was heated under the same conditions. Namely, heating of an irradiation sample and measurements of an X-ray spectrum were repeated. The isothermal heating was carried out at temperatures in the range of 473 to 723K.

2.4. Measurements of an X-ray spectrum induced by β-rays

A high purity Ge detector was applied to measure the X-ray spectra induced by β-rays in the argon atmosphere. Argon was used as working gas to evaluate the residual amount of tritium in surface layers of the B/SS316 samples irradiated with tritium. The flow rate of argon was kept at 40 cm^3/min. All of the X-ray spectra were measured at room temperature after heating under the given conditions of temperature and time.

3. Results and discussion

Small angle X-ray diffraction analyses were applied to examine a crystal structure of the thin boron film deposited on a SS316 plate. Angle of incident X-rays was kept at one degree. The observed diffraction pattern for B/SS316 is shown in Fig. 2 along with that for the SS316 plate. Quite similar diffraction pattern appeared in both X-ray diffraction analyses, and no characteristic diffraction peaks for boron crystals were observed. That is, all the diffraction peaks observed were attributable to the structure of stainless steel. This suggests that the structure of the boron films prepared under the present conditions is a state of amorphous.

Figure 3 shows the comparison of the observed X-ray spectra with and without helium pre-irradiation. Several intense and sharp peaks appeared in both spectra, and they were ascribed to the Ar(Kα),

Fig. 2. XRD patterns for SS316(upper) and boron-coated SS316(lower) samples

Cr(Kα), Fe(Kα) and Ni(Kα) lines as shown in the figure. The appearance of Ar(Kα) line is due to a reason that the tritium irradiated samples were measured in an argon atmosphere. The intensity of Ar(Kα) line corresponds to the amount of tritium trapped in the surface layers of a tritium-irradiated B/SS316 sample. The Ar(Kα) intensity in the case of He pre-irradiation was about 1.5 times greater than that of no helium pre-irradiation [4]. This increase was beyond the limitation of experimental error. It is considered, therefore, that the increase is due to production of a variety of defects such as dislocation and vacancy by He pre-irradiation. A
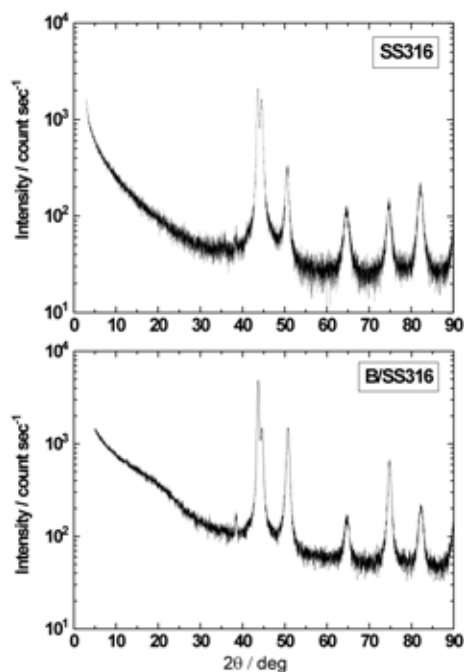
great increase, ca. 5 times, was observed for tungsten pre-irradiated with helium ions, but the difference in effect of the increase was mainly due to the fluence and energy of helium ions [6].

Characteristic X-ray peaks ascribed to the constituent elements of stainless steel was observed for B/SS316 samples though their surfaces are coated with the thin boron film. Maximum range of β-rays in boron is estimated to be about 1 μm, assuming that the range is closed to that in carbon. Namely, a half part of β-rays emitted in the boron films can strike the surface of a stainless steel substrate, because thickness of the boron films was about 0.1 μm. This is a reason why three characteristic X-ray peaks ascribed to Cr, Fe and Ni atoms appeared in the B/SS316 sample.

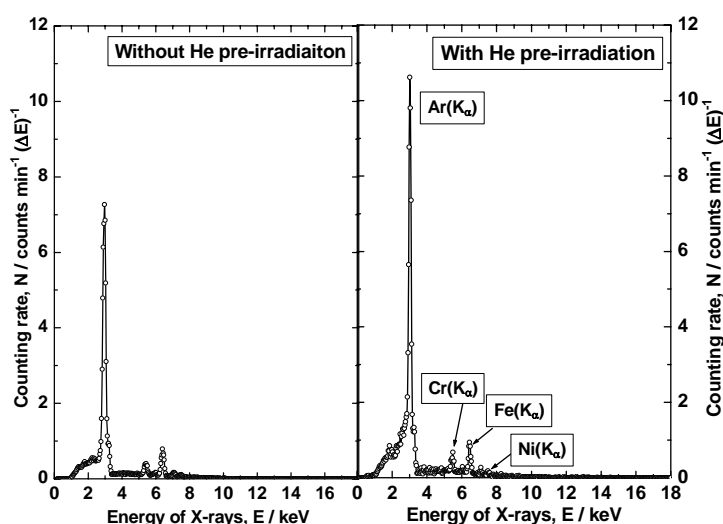Figure 4 shows the comparison of X-ray spectra observed before and after heating

Fig. 3. X-ray spectra observed for B/SS316 samples with and without He pre-irradiation.
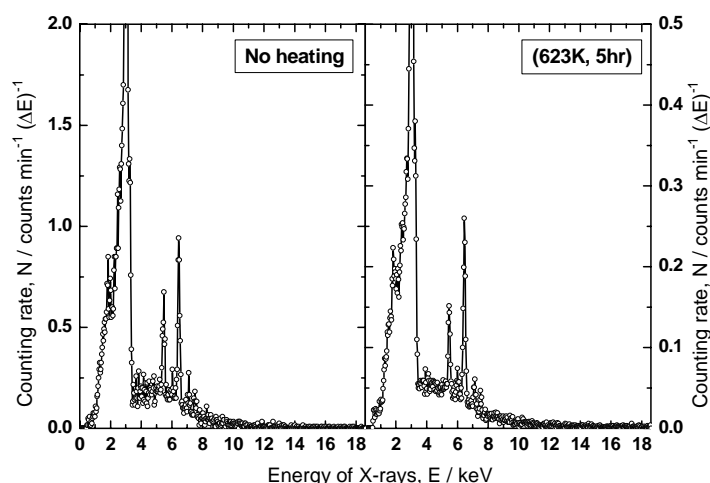
Fig. 4. Effects of heat treatment on the shape and intensity of X-ray spectrum.

at 623 K for 5 hours. The intensity of X-rays decreased to 25% of the initial intensity by heating, but shape of both X-ray spectra was quite similar as a whole. This indicates that most of tritium desorbed from the boron film by heating and the diffusion of tritium into the substrate is negligibly small. If considerable amount of tritium diffused into the substrate by heating at high temperatures, the shape of bremsstrahlung X-ray spectrum should change as the maximum shifts to the higher energy side and intensities of characteristic X-rays of Cr and Fe become larger. Namely, it is suggested that the interface between the boron film and the substrate acted as a diffusion barrier of tritium.

Such diffusion behavior of tritium at higher temperatures can be also understood from changes in intensity ratios of Cr(Kα) and Fe(Kα) to Ar(Kα) line with heating time. If the

surface tritium atoms diffuse into the stainless steel, one can observe an increase in intensity ratios of them. Figures 5 and 6 show changes in the intensity ratio of X-rays with heating time at all the examination temperature. It can be seen from both figures that the intensity ratios of X-rays are constant within experimental error, indicating that the irradiated tritium did not diffuse into the substrate of stainless steel during heating. This agrees with the previous result [4].

To examine the release behavior of tritium at room temperature, the intensity of an X-ray spectrum was tracked for a long period prior to the isothermal heating of the tritium-irradiated B/SS316 samples. A gradual decrease in the intensity was observed. Most of the desorbed tritium species was in an oxidized form and the elemental form was quite small.

Figure 7 shows the changes in the residual amount of tritium with isothermal heating for the helium pre-irradiated B/SS316 samples at elevated temperatures. Each symbol in the figure describes the X-ray intensity normalized by setting the initial intensity of Ar(Kα) line in each sample to unity, and the solid lines were drawn by a similar exponential function as shown in the previous result [4]. In this figure, two-times examinations were carried out at 473 K, and reproducibility of the decreasing curve was observed although initial intensities of Ar(Kα) line for both samples were different from each other. As seen clearly from the figure, decreasing rate of X-ray intensity increased with an increase in temperature, indicating that release rate of tritium trapped
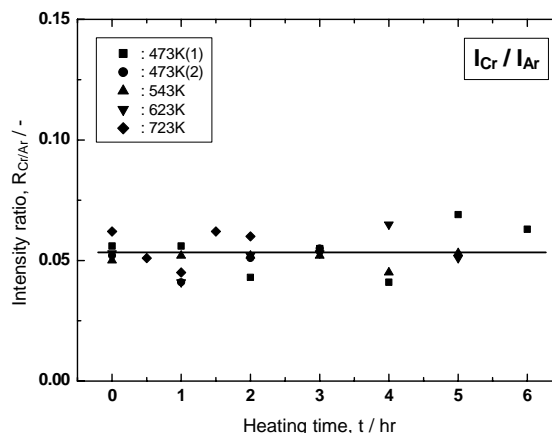

Fig. 5. Change in intensity ratio of characteristic X-rays of Cr to those of Ar.
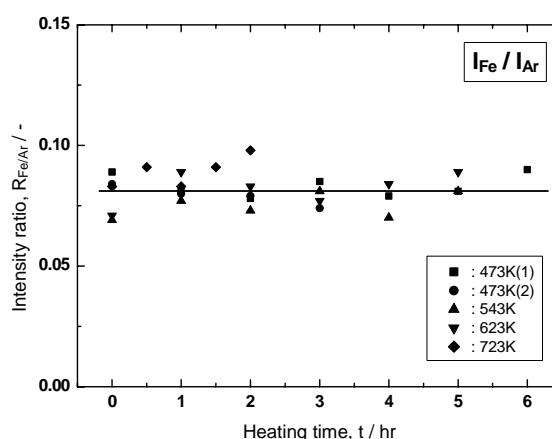

Fig. 6. Change in intensity ratio of characteristic X-rays of Fe to those of Ar.
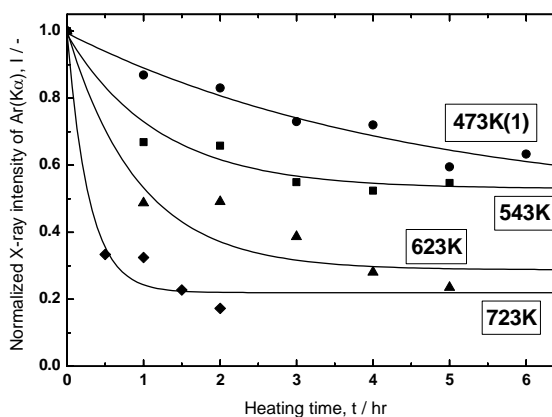

Fig. 7. Changes in the X-ray intensity of Ar with heating time.

in the surface layers was accelerated by heating because the residual amount of tritium corresponds to the intensity of an Ar(Kα) line.

The time-course of the tritium reduction could be reproduced by the following exponential function:

$$N(t) - N(\infty) = \{N_0 - N(\infty)\}\exp(-kt),$$

where $N(t)$ represents the residual amount of tritium at t, N_0 the initial amount of tritium, $N(\infty)$ the final amount of tritium remaining in the surface layers of the sample, and k the decreasing rate constant. $N(\infty)$ was dependent on the heating temperature. It is suggested that the decreasing rate of residual tritium obeys first order reaction kinetics. It was seen, therefore, that the helium pre-irradiation has no influence on the tritium release kinetics.

Figure 8 shows the tempera- ture dependence of decreasing rate constants determined from Fig. 7 along with the previous results measured without helium pre- irradiation for the same B/SS316 sample. A good linear relation appeared in the temperature range from 473 to 723 K, and apparent activation energy was determined to be 0.30 eV from the ramp of the line. The present activation energy was about two times larger than the previous result (0.17 eV) [4]. It is considered that the increase in the activation energy is due to formation of strong trapping sites such as a B-T terminal bond by helium pre-irradiation.
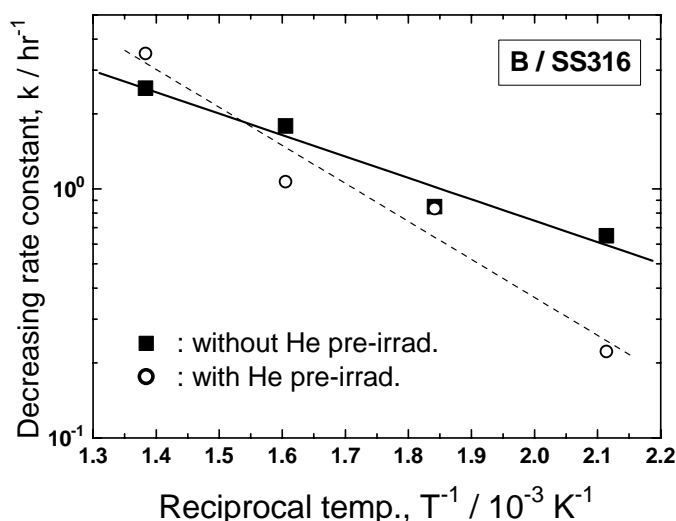

Fig. 8. Temperature dependence of the decreasing rate constant for the residual amount of tritium.

4. Summary

Plasma facing materials (PFMs) play an important role for control of impurities as well as fuel particles. Low-Z materials such as lithium, beryllium, boron and carbon are promising materials as PFMs. These materials are exposed to energetic helium particles as well as fuel particles. From this viewpoint, effects of helium pre-irradiation on trapping and release behavior of tritium were examined under the condition of isothermal heating. Thin boron films were prepared by plasma chemical vapor deposition on a substrate of stainless steel type 316, and those were used as samples.

The amount of tritium retained in surface layers was measured with β-ray-induced X-ray

spectrometry (BIXS). The amount of tritium trapped in thin boron films increased to 1.5 times by He pre-irradiation. The amount of tritium implanted by ion irradiation decreased with a time of isothermal heating. It was seen from the changes in X-ray spectra that the decreasing behavior is due to the tritium release from the surface but not diffusion into the stainless steel.

From the changes in the Ar(Kα) line, the decreasing rate of residual tritium obeyed first order reaction kinetics, which was the same kinetics as the case of no helium irradiation. It was seen, therefore, that the helium pre-irradiation has no influence on the tritium release kinetics. From the temperature dependence of the decreasing rate constant, the apparent activation energy of tritium release was determined to be 0.30 eV, and it was about two times larger than the previous result of no helium pre-irradiation.

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