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Behavior of tritium release from thin boron films deposited on SS316

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Abstract

Release and diffusion behavior of tritium implanted into thin boron films were examined by isochronal and isothermal heating. For comparison, a polycrystal boron plate was also employed for the same examinations. Changes in the residual amount of tritium with heating were measured by β-ray-induced X-ray spectrometry (BIXS). Most of the tritium desorbed at room temperature was in HTO form, and the residual amount decreased to 20–30% of the initial amount loaded at 773 K. The time-course of the tritium reduction was well represented by an exponential function, suggesting that the tritium release obeys first order reaction kinetics and the rate-determining step is a diffusion process. The apparent activation energy of diffusion was determined to be 0.17 eV. Both the depth profiles calculated from a diffusion equation and determined by computer simulation of X-ray spectra agreed quite well for polycrystal boron.

1. Introduction

It is recognized that plasma-facing materials in fusion devices play an important role in control of impurities and fuel particles. To reduce the partial pressure of oxygen species as well as the concentration of metallic impurities in the plasma, it is widely adopted to coat the first wall surfaces with low-Z materials such as beryllium and boron. It has been reported so far that the boron coating is very effective for the improvement of plasma performance [1–5]. However, the desorption behavior of hydrogen isotopes from the boron-coated materials has not yet been thoroughly evaluated.

Thin boron films deposited on stainless steel plates (named as B/SS316) were prepared and implanted with tritium ions. The diffusion and release behavior of tritium was examined. Changes in the amount of tritium remaining in B/SS316 with isochronal and isothermal heat treatments were evaluated by applying a recently developed technique, the β-ray-induced X-ray spectrometry (BIXS) [6–8]. This technique is useful for nondestructive measurement of the amount and depth profile of tritium retained in surface layers and/or bulk of materials.

2. Experimental

2.1. Materials

Boron films were prepared on stainless steel plates (SS316) by RF-assisted DC glow discharge using a mixture of helium (95%) and decaborane (5%). The size

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of SS316 plates was $15 \times 15 \times 0.5$ mm^3, and thickness of the boron films was 100–200 nm. A polycrystal boron plate ($10 \times 10 \times 1$ mm^3) was also used for comparison. For both of the boron films and the polycrystal boron, impurities such as carbon, oxygen and nitrogen were measured by X-ray photoelectron spectroscopy. The impurity levels depending on a temperature of SS316 and vacuum conditions during a preparation were as follows: for the boron films atomic ratios (B:C:O:N) were 50:25:17:8 and 90:6:4:0, and these films are named as B/SS316-50 and B/SS316-90, respectively. For the polycrystal boron, the ratio was 94:3:2:1. To examine the influence of the impurities, these two kinds of boron films that purity was different were prepared.

2.2. Tritium implantation

Implantation of tritium ions was carried out using a specially designed tritium implantation device [6]. One of the boron samples was installed in the implantation device and then the device was evacuated for about 1 week at room temperature. After the evacuation, the sample was degassed to below 10^{-5} Pa at 673 K. Tritium ions were implanted at 1 keV for 15 min at room temperature, where the source gas was a mixture of tritium and deuterium (0.7% tritium). Average range of tritium implanted into a boron film was about 15 nm. After the implantation, the boron sample was kept under evacuation for about 1 week to decontaminate the device.

2.3. Measurements of X-ray spectra

X-ray spectra induced by β-rays were measured using a high purity Ge detector in an argon atmosphere. During the X-ray measurements, desorbed tritium was collected by water bubblers and measured by a liquid scintillation counter. To examine the release behavior of tritium at elevated temperatures, isochronal and isothermal heating of the boron films were carried out in vacuum. For the isochronal heating, the temperature was elevated with steps of 50 K in the range from 373 to 773 K, and the sample held for 30 min at each temperature. The isothermal heating was carried out in the range from 473 to 723 K. All of the X-ray spectra were measured at room temperature after heating for a given condition of temperature and time.

3. Results and discussion

3.1. Changes in X-ray spectra with heating

Fig. 1 shows a typical X-ray spectrum observed for B/SS316 implanted with tritium. Two kinds of X-ray peaks appeared: one is the characteristic X-ray peaks of Ar and of constituent atoms of the SS316 substrate, and the other is a broad bremsstrahlung X-ray peak. The characteristic X-ray peak attributable to boron was not observed because of its very low energy (Kα: 0.183 keV). The characteristic X-rays of Ar are mainly induced by tritium existing within a range of the escape depth of β-rays, which corresponds to ≈640 nm in amorphous boron. Therefore, the intensity of characteristic X-rays of Ar is proportional to the amount of tritium retained in the surface layers. This has been confirmed by using another material implanted with tritium [8]. The characteristic X-ray peaks of Fe, Cr, Ni, Mo and Si were also observed. This is due to a fact that the thickness of the boron film is much less than the escape depth of β-rays. Important information is contained in the peak shape of the bremsstrahlung X-ray spectrum, from which one can deduce the tritium depth profile. It can be estimated precisely by computer simulation [7].

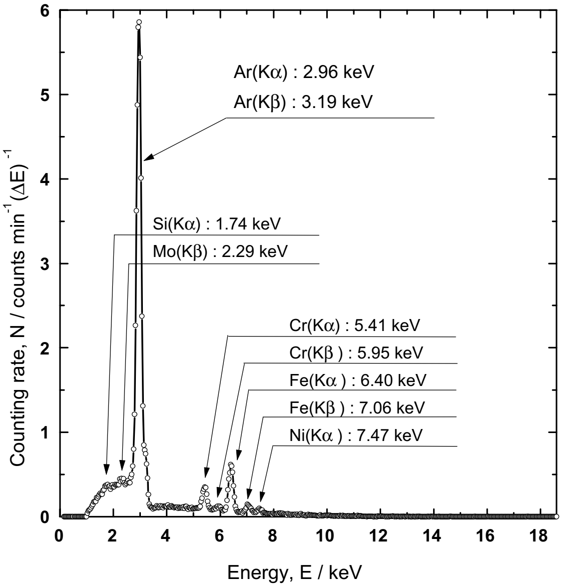

Fig. 1. An example of X-ray spectra observed for the B/SS316 samples implanted with tritium.

Fig. 2(A) and (B) show examples of X-ray spectra observed before and after heating of B/SS316 and polycrystal boron samples, respectively. After heating to 773 K, the intensity of characteristic X-ray peaks as well as the bremsstrahlung X-ray peak decreased for both samples. There are two possibilities for such decrease: one is the release of tritium from surface layers, and the other is the diffusion of tritium deeper into the bulk. The latter behavior should be reflected in the shape change in the bremsstrahlung X-ray spectrum. No change in the shape with heating was observed for B/SS316, whereas the maximum intensity of the bremsstrahlung X-rays for polycrystal boron shifted significantly to higher energies on heating. The former indicates that the release from

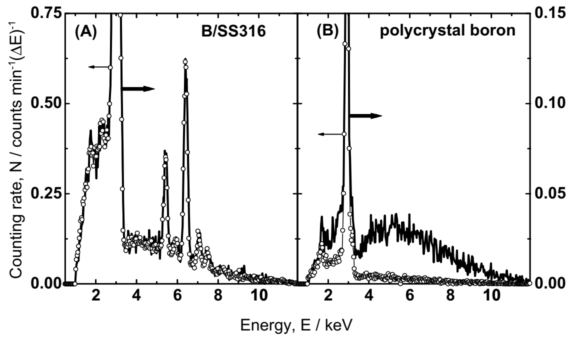

Fig. 2. Comparison of the spectra observed before (–○–, left scale) and after (—, right scale) isochronal heating at 773 K: (A) B/SS316 and (B) polycrystal boron.

the surface is predominant, and the latter is due to the diffusion into the bulk.

3.2. Changes in X-ray intensity with isochronal heating

Fig. 3 shows change in the amount of tritium remaining in the samples after isochronal heatings, where the residual amount was evaluated from the characteristic X-ray intensity of Ar. The residual amount decreased with temperature and reached 20–30% of the initial amount loaded at 773 K for all the boron samples. Even at this temperature, however, the shape of the X-ray spectra for both samples was quite similar to that of the initial spectra. This indicates that the decrease of tritium was not due to diffusion into the bulk of SS316, but mainly due to the desorption from the surface. This is an interesting phenomenon [9] from a viewpoint of tritium permeation barriers. Furthermore, the reduction rate for B/SS316-50 was a little lower than that for B/SS316-90. This may be due to the difference in the impurity levels contained in these boron films. On the other hand, the reduction of tritium from polycrystal boron was faster than that from B/SS316-90, although the impurity level was almost the same. This is mainly due to the diffusion of tritium into the bulk of polycrystal boron as shown in Fig. 2(B).

3.3. Changes in X-ray intensity with isothermal heating

Prior to the isothermal heating, the intensity of an X-ray spectrum was followed for a long period of time, to examine the changes in the residual amount of tritium at room temperature. The majority of the desorbed tritium at room temperature was in an oxidized form, and that in the elemental form such as HT, DT and T_2 was as low as 10–20%.

Fig. 4 shows the changes in the residual amount of tritium with isothermal heating for B/SS316-90 at elevated temperatures. Each symbol in the figure represents the observed values, and the solid lines were drawn by least square fitting. The time-course of the tritium reduction could be described by an exponential function, $N(t) - N(T) = (N_0 - N(T))\exp(-kt)$, where $N(t)$ is the residual amount of tritium at time t, N_0 the initial amount, $N(T)$ the final amount of tritium remaining in the samples, which depends on the heating temperature, k the decreasing constant. It is indicated that the decreasing rate of residual tritium obeys first order reaction kinetics. On the other hand, the shape of all the X-ray spectra was similar, indicating that the reduction of the tritium inventory was due to desorption, not to diffusion into the SS316 substrate. In this case, at least three mechanisms can be considered as the rate-determining-step: the first is the diffusion in the boron film, the second is detrapping from trap sites such as radiation damage formed by tritium implantation, and the third is detrapping from impurity trap sites.

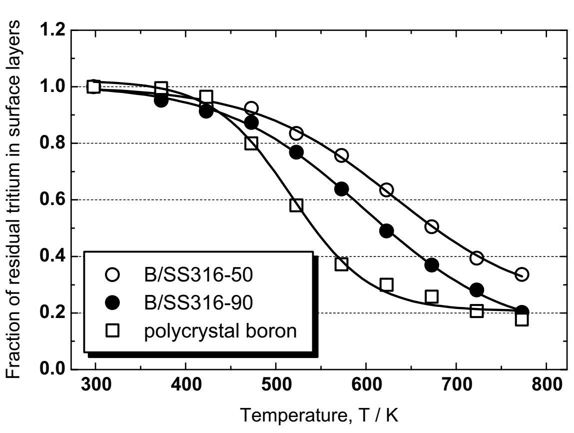

Fig. 3. Changes in the residual amount of tritium with isochronal heating of the B/SS316 and polycrystal boron samples.

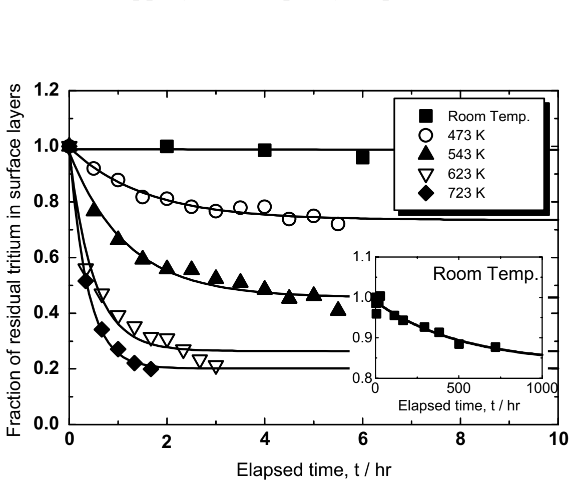

Fig. 4. Changes in the residual amount of tritium with isothermal heating of the B/SS316-90 sample.

Fig. 5 shows the temperature dependence of the decreasing constant determined from Fig. 4. A good linear relation appeared in a temperature range from 473 to 723 K, but the low temperature (RT) data deviated significantly. The straight line can be described by $\ln k = 3.67 - 1.98 \times 10^3/T$, where T is the heating temperature. From this equation, the apparent activation energy was determined to be 0.17 eV. Since the low temperature data were obtained by keeping the sample in an ambient atmosphere at room temperature, it seems to be affected by the effective moisture in the ambient atmosphere for tritium desorption. The decreasing constant for the polycrystal boron was also plotted in Fig. 5, showing quite good agreement with the temperature dependence for B/SS316-90. This indicates that the decreasing rate for polycrystal boron obeys similar reaction kinetics and is independent of the thickness of boron.

Fig. 6 shows tritium depth profiles estimated from both the BIXS analysis and a diffusion model for polycrystal boron after heating at 523 K for 30 min, where the solid line shows the depth profile determined by computer simulation of the X-ray spectra, and the open circles indicate the profile calculated by a diffusion equation using the activation energy mentioned above (0.17 eV). By using the present activation energy, the diffusion coefficient (D) at 523 K was estimated to be 7.67×10^{-7} cm^2/s, and the pre-exponential factor (D_0) was 3.41×10^{-5} cm^2/s. Both of the depth profiles agreed quite well. The apparent activation energy determined from Fig. 5 can be attributed to the diffusion of tritium in boron. In comparison with the data for B_4C by Grossman et al. [10], the present D_0 is quite close to their value, while the activation energy is much lower than that of B_4C (0.73 ± 0.07–3.91 eV).

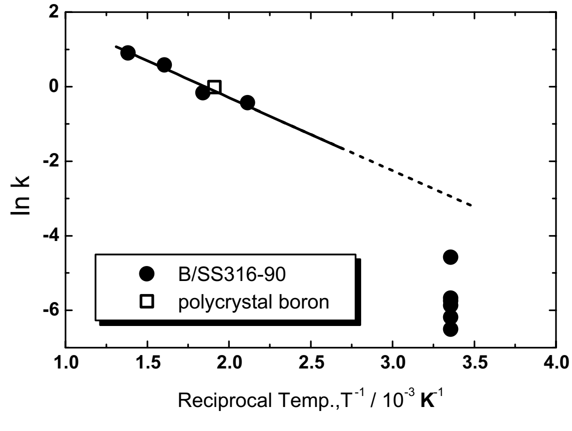

Fig. 5. Temperature dependence of decreasing constant for the residual amount of tritium in the B/SS316-90 and polycrystal boron samples.

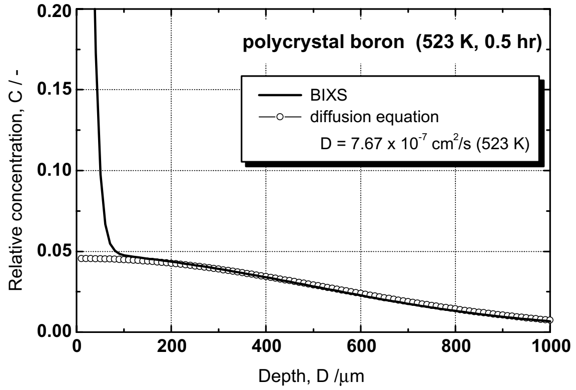

Fig. 6. Comparison of tritium depth profile determined from computer simulation of X-ray spectrum and the diffusion profile given for semi-infinite medium.

4. Conclusions

Release and diffusion behavior of tritium implanted into thin boron films, which were deposited on stainless steel plates, were examined by isochronal and isothermal heatings. For comparison, polycrystal boron plates were also used. Changes in the residual amount of tritium in these boron materials were followed by using the technique of β-ray-induced X-ray spectrometry (BIXS), and the results are summarized as follows:

(1) By the isochronal heating up to 773 K, the residual amount of tritium decreased to 20–30% of the initially loaded amount, and depended on impurity levels in the boron films. The decreasing behavior of tritium for the polycrystal boron was largely different from that for B/SS316-90, although purity of both of these samples was almost the same.

(2) At room temperature, most of the desorbed tritium was in an oxidized form and that of elemental form was 10–20%. In the isothermal heating to 723 K, the residual amount of tritium in the surface layers decreased exponentially with time, indicating that the decreasing rate obeys first order reaction kinetics. It is concluded that the rate-determining step is the diffusion of tritium in boron.

(3) The Arrhenius plot of the decreasing coefficient of residual tritium showed a good linear fit except for the data at room temperature. The apparent activation energy of tritium diffusion was 0.17 eV.

(4) The tritium depth profile estimated from computer simulation of an X-ray spectrum agreed quite well with that from a simple diffusion equation based on a semi-infinite medium.

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