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論　文

β線誘起X線計測法による硼素コーティング黒鉛材料のトリチウム保持に関する検討

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Examination of Tritium Retention in Boron-Coated Graphite by β-Ray-Induced X-ray Spectrometry

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Abstract

Tritium retention in boron-coated graphite (B/Graphite) irradiated with tritium ions at room temperature and at higher temperatures was examined by β-ray-induced X-ray spectrometry (BIXS). The results of analyses by X-ray diffraction and X-ray photoelectron spectroscopy for an unirradiated sample suggested that boron coated on the graphite surface formed an amorphous structure and that it contained impurities such as oxygen and carbon. Both a sharp intense peak and a broad weak peak induced by β-rays appeared in the observed X-ray spectra. It was seen from the X-ray spectra that most of tritium implanted into the B/Graphite at room temperature was retained on the surface and in subsurface layers. In addition, it was seen that the implanted tritium can be easily removed at a relatively low temperature and that the retention amount decreased to 1/3 by heating at 300 °C for 30 min. However, a considerable increase in tritium retention was observed when the irradiation temperature was increased to more than 300°C, indicating adsorption of tritium on the bare surface of graphite.

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1. Introduction

It is widely recognized that the plasma-facing materials (PFMs) in fusion devices play an important role for control of impurities and fuel particles. To reduce impurities such as heavy metals and oxygen, low-Z materials like beryllium, boron and carbon have been employed so far in many fusion devices. Effects of boron coating on an impurity reduction and a confinement improvement of plasmas were confirmed in various large experimental devices such as TEXTOR[1-2], DIII-D[3], TFTR[4], JT-60U[5-6], and ASDEX-Upgrade[7]. Especially, it is concluded from examinations by these devices that the boron coating is valuable for better confinement of plasmas due to a fair reduction of oxygen impurity. However, effects of boron coating on tritium retention have not been thoroughly clarified yet.

For the examinations of tritium retention, a nondestructive measuring method is required from a viewpoint of safe handling of the tritium-containing samples. For this purpose, Matsuyama et al.[8] have recently proposed a new measuring technique of tritium which is trapped on the surface and/or in the bulk of materials, which is called β-ray-induced X-ray spectrometry (BIXS). This is based on measurements of characteristic and bremsstrahlung X-rays induced by β-rays from tritium retained on and/or in materials. The main advantageous features of the present method are as follows: the first point is that it is possible to measure nondestructively the amount of tritium on the surface, and the second point is to be able to estimate separately a tritium depth profile from surface tritium activity.

In the present paper, trap and release of tritium have been examined for boron-coating graphite (described as B/Graphite) irradiated with tritium ions at room and elevated temperatures. In addition, the irradiated B/Graphite was isochronally heated and change in the tritium retention was examined. For evaluation of changes in the amount of tritium on the surface, the BIXS was applied to those examinations.

2. Experimental

2. 1. Materials

As a sample, a graphite plate coated with a thin boron film was prepared by a glow discharge in a mixture gas of helium(95%) and diborane(5%). The graphite plates used were

isotropic graphite IG-430U delivered from Toyo Tanso Co. Prior to the boron coating, the graphite plates were polished with a fine abrasive paper and rinsed with acetone. Size of a graphite plate was 15x15x0.5 mm^3, and thickness of the boron film was about 200 nm. Tritium was diluted with deuterium, and the concentration was 0.8 %.

2. 2. Device for tritium irradiation

Implantation of tritium ions into a boron coating sample was carried out by using the tritium irradiation device which was specially designed for this purpose. Main components of the tritium irradiation device consisted of a tritium storage-supply-recovery part, an irradiation part equipped with a conventional ion gun, a high vacuum system and a sample transfer system. The detailed construction and specifications of the tritium irradiation device is described elsewhere[9].

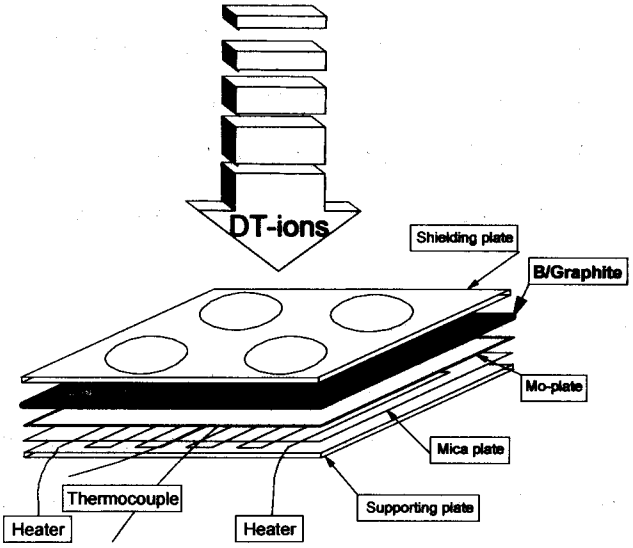

Fig. 1. Schematic of a sample holder for the implantation of tritium ions.

Figure 1 shows the detailed drawing of a sample fixture used for tritium implantation. The sample was sandwiched between a thin molybdenum plate attached with a K-thermocouple and a shielding plate having four holes of 6 mmϕ in diameter. The molybdenum plate was used to ensure thermally uniform transmission from a heater, which was made of W-Re alloy and was fixed with a thin mica foil beneath the molybdenum plate. The sample fixture was electrically disconnected from the ground level using an insulating material to measure ion current. During the measurement of ion current, the sample was applied +18V to prevent emission of secondary electrons due to the tritium ion irradiation.

2. 3. Device for X-ray measurements

A high pure Ge detector, which was purchased from CANBERRA, was used to measure X-rays induced by β-rays. Since major energy distribution of the X-rays is considerably lower than 18.6 keV which corresponds to the maximum energy of β-rays from tritium, a window of the X-ray detector consisted of a specially designed thin beryllium plate (8 μm) to gain effective penetration

efficiency of low energy photons. In addition, to lower natural radioactivity during a measurement, the detector and sample was sandwiched with two lead bricks of 5 cm in thickness.

2. 4. Device for characterization of boron coating

An X-ray photoelectron spectroscopy (XPS) was applied to characterize the surface states of a boron film, which equipped a double pass cylindrical mirror analyzer (PHI 04-191). A magnesium anode was used at 400 W for XPS measurements. Furthermore, a crystallographic analysis for the sample was carried out by X-ray diffraction (XRD) used a diffractometer of Philips PW1820 with Cu-K_α. The X-ray diffraction pattern was measured at an incident angle of 0.5° with respect to the horizontal, because the boron coating was very thin.

2. 5. Procedures

After a B/Graphite sample was installed in the tritiuim irradiation device, evacuation of the tritium irradiation device carried out for about one week at room temperature. After the evacuation, the sample was degassed at 400 °C in vacuum and it was heated till the residual pressure reached below 10^{-7} Torr. Then the sample was cooled to a given temperature for the irradiation of tritium ions. Tritium irradiation was carried out under the following conditions: although most of irradiation temperature was set at room temperature, an irradiation at elevated temperatures was applied to examine the effects of irradiation temperature. In addition, acceleration energy and irradiation time of tritium ions were kept at 1 keV and 15 min, respectively. During the irradiation, the total pressure in the irradiation device was kept constant at 0.03 Torr. The project range of tritium ions in boron is estimated to be around 10 nm under the present energy condition.

After the tritium irradiation, to minimize tritium release from wall surfaces of the irradiation device when the irradiation device was opened to take out the irradiation sample, the irradiation device was additionally evacuated for about one week. Just before taking out the sample, the irradiation chamber was finally processed by a special tritium removal system to prevent the contamination of ambient atmosphere. After these processings, the measurement of an X-ray spectrum of the irradiation sample was started at room temperature under the flowing condition of Ar. The flow rate of Ar was 40 cm^3/min.

To examine the retention behavior of tritium at elevated temperatures, an irradiated sample was isochronally heated in vacuum for 30 min at the temperature range from 300 to 500 °C. The X-ray measurements were carried out at room temperature after heating at each temperature.

3. Results and discussion

3. 1. Analyses of boron coating by XRD and XPS

Figure 2 shows the X-ray diffraction pattern observed for an unirradiated B/Graphite sample. Although there appeared some diffraction peaks, all the diffraction angles of them perfectly agreed with those of the diffraction peaks observed for a graphite base plate. If the rhombohedral structure of crystalline boron was formed on graphite, one can observe the diffraction peaks at 21.2°(111), 22.0°(010), 35.5°(121), and 43.1°(111). However, no diffraction peaks related to crystalline boron was observed, indicating that boron film coated on the graphite plate may form an amorphous structure.

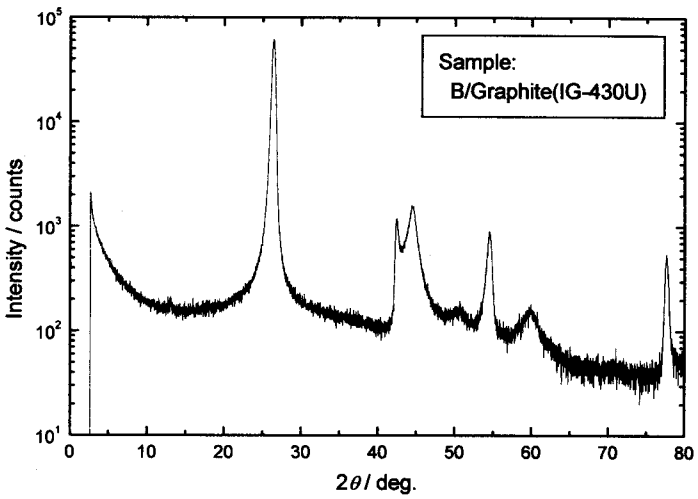

Fig. 2. The X-ray diffraction pattern observed for the unirradiated B/Graphite.

Although no existence of crystalline boron could be confirmed by the XRD analyses, an XPS spectrum indicated the existence of boron atoms on the surface as shown in Fig. 3. According to a narrow range spectrum, the chemical shift of 1 eV from the peak position for pure boron to the higher binding energy side was observed, indicating an oxidized state of boron. In addition to boron, carbon and oxygen also appeared in the spectrum. It was seen that the ratio of carbon to boron atoms was determined as 5:3 taking into account sensitivity.

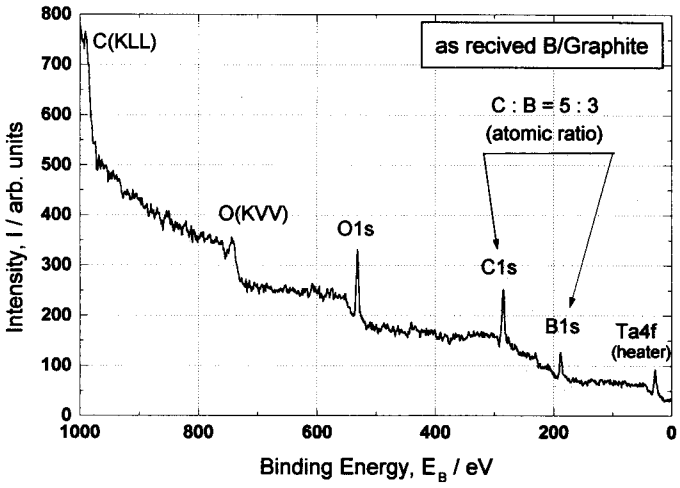

Fig. 3. The XPS spectrum measured for the unirradiated B/Graphite.

3. 2. Example of β-ray-induced X-ray spectra

Figure 4 shows an example of β-ray-induced X-ray spectra observed for a B/Graphite

sample irradiated with tritium. An intense sharp peak overlapped with a weak broad peak. The former one was attributed to the characteristic X-rays of argon, i.e., Ar(K_α) and Ar(K_β). Since the X-ray energy difference of both peaks is very small and intensity of the Ar(K_β) peak is considerably weaker than that of the Ar(K_α) peak, it was hard to separate clearly both peaks. On the other hand, the latter peak was attributed to the bremsstrahlung X-rays induced in argon and a boron film. The inset illustrated an enlarged drawing of the bremsstrahlung X-ray spectrum.

Intensity of the characteristic X-rays of argon is proportional to the amount of tritium on the surface and/or in subsurface layers of a material as reported elsewhere[10]. In the present spectrum, the intensity was evaluated to be 9.64 counts/min, which corresponds to 39.5 kBq. This tritium activity was equivalent to about 85% of that calculated from the ion current observed during an irradiation, indicating that most of the irradiated tritium ions were captured on the surface and in subsurface layers. Comparison with the spectrum observed for a graphite sample without a boron film is shown in Fig. 5. Although the characteristic X-ray intensity for B/Graphite was a little smaller than that for the bare graphite sample, shape of the bremsstrahlung X-ray peak was quite similar. Namely, this suggests that for both samples the depth profiles of tritium are the almost same and that the sticking coefficients of tritium ions are little difference in both samples.

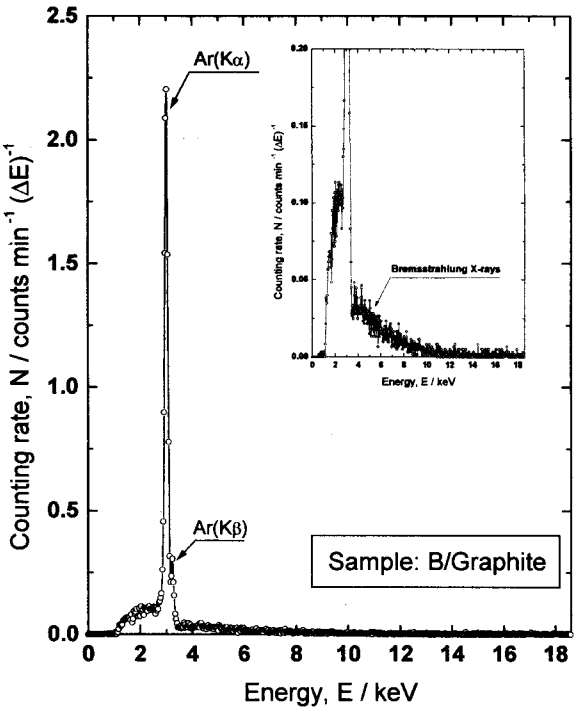

Fig. 4. An example of β-ray-induced X-ray spectra observe for the B/Graphite samples irradiated with tritium.

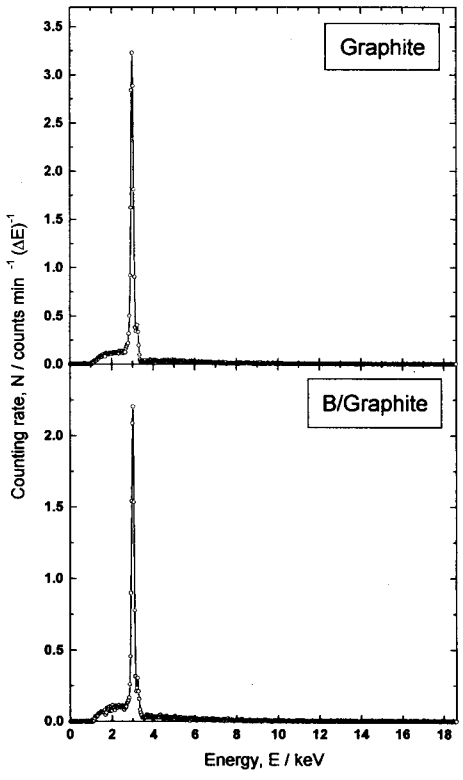

Fig. 5. Comparison of the spectra observed for samples with and without boron coating.

3. 3. Effects of irradiation temperature on tritium retention

Energetic fuel particles in a magnetic fusion device continuously strike at surfaces of the plasma-facing components of the elevated temperatures as well as room temperature. It is of practically important to examine changes in the retention of tritium with temperature. Figure 6 represents change in intensity of the X-ray spectrum with an irradiation temperature for B/Graphite. It is clear that increase in the irradiation temperature brought about increase in the characteristic X-ray intensity of argon. The X-ray intensity at 400 °C was about 5 times greater than that at room temperature in spite of no large increase in an ion current during the irradiation. Increase in the X-ray intensity suggests that molecular tritium existing in the irradiation chamber during the irradiation reacted with boron and/or graphite. Tritium retention above 300 °C for B/Graphite should decrease with a temperature rise as described later, while the tritium retention for bare graphite little changes below 500 °C. It is expected, therefore, that the increase of tritium retention in the present experiment is due to a reaction with bare surface of graphite. Since a graphite plate used as a base of the boron coating is a porous material as shown in Fig. 7, during an irradiation period thermal tritium molecules will attack and adsorb on the bare graphite surfaces.

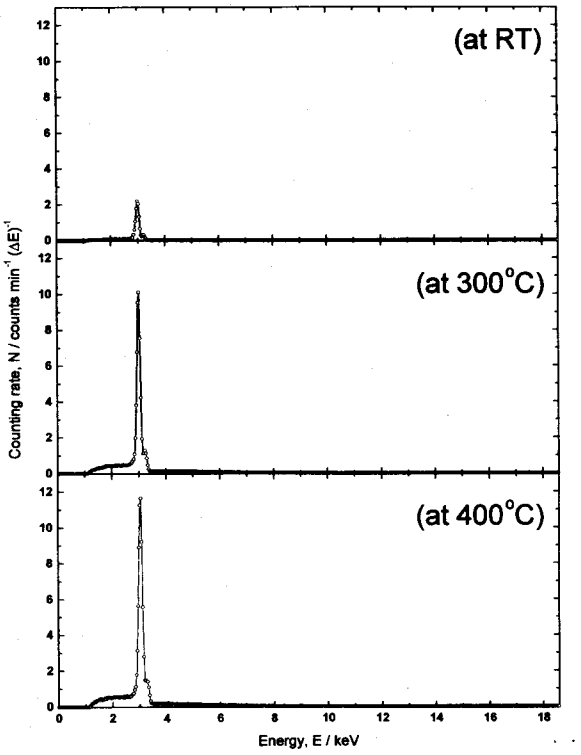

Fig. 6. Change in intensity of the X-ray spectrum with an irradiation temperature.

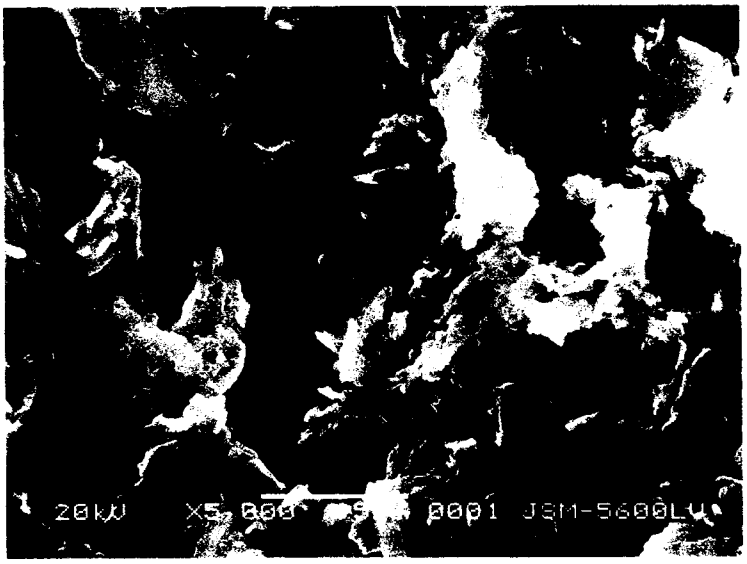

Fig. 7. Photograph of the surface of B/Graphite by a scanning electron microscope.

3. 4. Retention of tritium at elevated temperatures

Figure 8 shows the change in intensity of the X-ray spectra observed during an isochronal heating after the tritium irradiation for B/Graphite. As seen from the figure, with a temperature rise the intensity of the X-ray spectrum decreased fairly, indicating the decrease in tritium retention on the surface and/or in subsurface layers. Both tritium release from the surface and diffusion of tritium into the bulk give rise to the decrease in X-ray intensity. Although the amount of tritium released by heating in a vacuum device could not be measured, the present decrease should be mainly attributed to the desorption of tritium from the surface, because shape of all the X-ray spectra was quite similar.

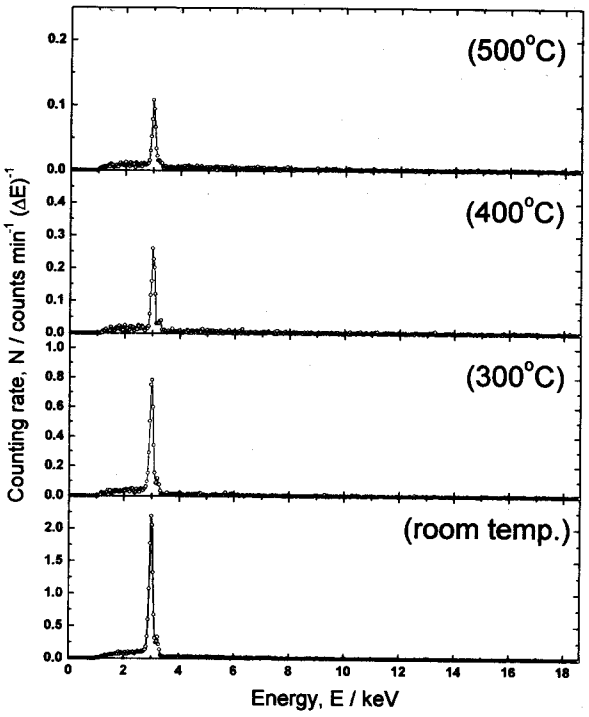

Fig. 8. Change in intensity of the X-ray spectra observed during an isochronal heating.

Intensities of the characteristic and the bremsstrahlung X-rays with temperature similarly decreased as shown in Fig. 9. Namely, ratios of both X-ray intensities were almost constant within a region of experimental temperatures. This indicates that the tritium concentration in B/Graphite decreased with a temperature rise but the depth profile of tritium did not change. The amount of tritium remained at 300 °C lowered at about 1/3 in comparison with the initial amount, and at the maximum temperature it decreased below 4 %. Such behavior is favorable for decrease of the tritium inventory in PFMs.

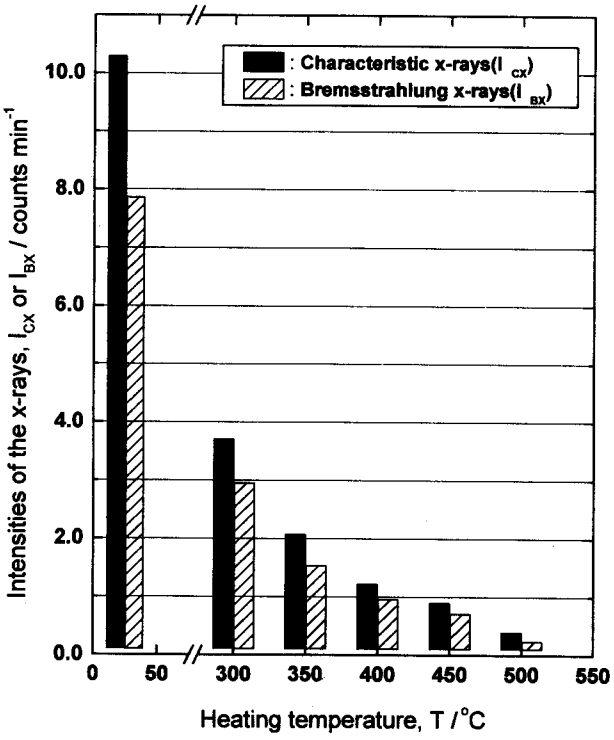

Fig. 9. Changes in intensity of the characteristic and bremsstrahlung X-rays with temperature.

Jimbou et al. [5] reported that deuterium retained in B_4C was released at lower temperatures than that in graphite as shown in Fig. 10. In this figure the present result is also illustrated, although

the experimental conditions in both results differed in some points. Main difference was the heating time at each temperature: our experiments were kept for 30 min at a given temperature, but the reference data were obtained from the heating for 5 min. Even though taking into account such difference, advantage of the boron coating will not change. Namely, it was concluded that the boron coating will play an important role for decrease of the tritium inventory in PFMs in a thermonuclear fusion reactor.

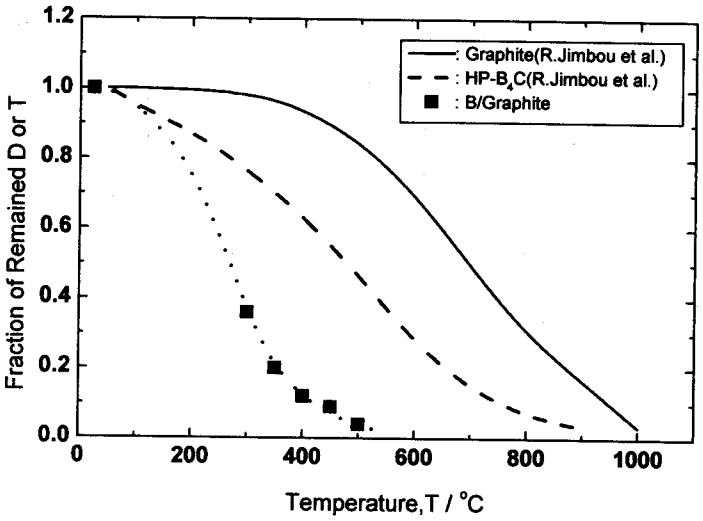

Fig. 10. Comparison of tritium retention for low-Z materials.

4. Summary

It is indispensable to lower the tritium inventory in plasma-facing components (PFMs) from viewpoints of tritium safety and control of the fuel particles in a reactor core of the magnetic fusion devices. For this reason characteristics of a thin boron film coated on graphite (B/Graphite) were examined with respect to retention of tritium by means of β-ray-induced X-ray spectrometry (BIXS). As a consequence, the following results were obtained:

(1) According to the analyses by X-ray diffraction and X-ray photoelectron spectroscopy, it was suggested that the boron film coated on a graphite surface formed an amorphous structure and it contained impurities such as oxygen and carbon.

(2) The X-ray spectrum induced by β-rays consisted of a sharp intense peak and a broad weak peak: the former peak depending on the amount of tritium on the surface and/or in subsurface layers is the characteristic X-rays of argon, and the latter peak depending on a tritium depth profile is the bremsstrahlung X-rays. It was seen that most of tritium implanted into B/Graphite at room temperature was retained on the surface and in subsurface layers.

(3) Tritium retention considerably increased when an irradiation temperature was elevated above 300°C. It is considered that this is due to tritium adsorbed on the surface of bare graphite. If boron is coated on a flat non-porous material, tritium retention in the material may be able to lower.

(4) Tritium implanted into B/Graphite at room temperature easily desorbed at a relatively low temperature of 300 °C, and the amount of tritium estimated from the X-ray intensity decreased to 1/3 by heating for 30 min.

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