

Tritium Tracking by BIXS in Contamination and Decontamination Processes

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ABSTRACT

The β -ray-induced X-ray spectrometry(BIXS) was applied to evaluate contamination and decontamination behavior of tritium for four kinds of metallic materials. Two kinds of charging methods were employed for tritium contamination: irradiation with tritium ions at room temperature and exposure to molecular tritium at elevated temperatures.

The order of contamination level due to the irradiation of tritium ions was as follows:

Hastelloy < SS-316 Tungsten < B/SS-316,
where most of the irradiated tritium was retained on the surface and/or in subsurface layers. For the decontamination tests of the B/SS-316 sample, it was recognized that moisture in the air plays an important role for decontamination process at room temperature.

On the other hand, it was estimated from computer simulation of the X-ray spectra that the SS-316 sample exposed to molecular tritium at 473K was uniformly contaminated up to the bulk. The dissolved tritium into the bulk could be removed about 40% by heating for 2 hours at 473K, although the surface kept high tritium activity.

I. INTRODUCTION

In a thermonuclear fusion reactor, the plasma facing components and construction materials are exposed to ionic and/or molecular tritium having a vari-

ety of kinetic energy. A part of such energetic tritium species adsorbs on the surfaces of those materials and diffuses into the bulk. Those tritium will affect not only the recycling efficiency of the fuel in a reactor core but also the safe waste management. From viewpoints of decrease of tritium contamination and effective decontamination of the contaminated materials, it is of great importance to understand basic tritium behavior such as adsorption, desorption, dissolution and diffusion on the surface and/or in the bulk of materials.

Although there are several methods for evaluation of the adsorption amount of tritium on the surface and of a depth profile of tritium in the bulk, those are not still enough for nondestructive and quantitative evaluation of tritium behavior in contamination and decontamination processes. This is a reason why development of a new tritium measuring method is required. From this viewpoint we have proposed a new measuring method for nondestructive determination of tritium on the surface and/or in the bulk¹: i.e., β -ray-induced X-ray spectrometry(BIXS). The BIXS has been employed for determination of the considerably small amount of tritium on an ALT-II limiter tile exposed to D-plasma in TEXTOR², and also for evaluation of diffusion behavior of tritium in bulk of Pd and Zr³.

In this paper, the present measuring technique was applied to evaluate contamination level of tritium by ion irradiation and molecular tritium exposure to some kinds of materials. In addition, after tritium charges

into the materials to examine decontamination behavior, changes in the X-ray spectra at room and elevated temperatures were also observed, and the tritium depth profiles in the bulk were evaluated by analyzing the X-ray spectra by means of computer simulation.

II. EXPERIMENTAL

1. Materials

Four kinds of materials were employed in the present study: namely, stainless steel type 316 (described as SS-316), SS-316 coated with a thin boron film (described as B/SS-316), Hastelloy C-276, and tungsten. The thickness of these materials was 0.5 mm except for tungsten of which thickness was 20 μm . The SS-316 and tungsten samples were used without further treatments except for the rinse by acetone, and the Hastelloy C-276 sample was polished with a paper and fine abrasives before tritium charge. Boron coating on the polished SS-316 was prepared by means of glow discharge in a mixed gas of diborane and helium by using a specially designed device, and the thickness of a boron film was controlled to be about 200 nm.

Tritium used for ion irradiation was diluted with deuterium, and the tritium concentration was about 0.8 %. On the other hand, molecular tritium exposure was carried out using a mixture of hydrogen and tritium, and the tritium concentration was 32 %.

2. Devices for tritium charges and removal

Devices used for tritium charges by means of ion irradiation and molecular tritium exposure basically consisted of an ultra-high vacuum system and tritium supply-recovery-storage system equipped with a hydrogen storage material of Zr-Ni alloy powder. Details of these devices are described elsewhere⁴.

The device used for tritium removal tests was con-

structed with a flow control system of argon, and a heating system, and a collecting apparatus of tritium released from a sample. Details of this device are described elsewhere⁵.

3. Devices for X-ray and released tritium measurements

An X-ray spectrum from the tritium-containing sample was measured by using a semiconductor detector equipped with a high pure Ge element. During a measurement, the detector and sample were kept in an argon atmosphere, and those were sandwiched with two lead bricks to reduce a background level of the detector. The detailed configuration of the X-ray measuring device is described elsewhere².

During heating of a tritium-containing sample, the tritium released from the sample was purged by a constant flow rate of argon and it was separately collected by two water bubblers to distinguish a chemical form of the tritium species, i.e., elemental and oxidized tritium. Activity of the collected tritium was measured with a liquid scintillation counter.

4. Experimental procedures

After the initial polishing and cleaning of the samples, each was installed in the tritium irradiation device or the molecular tritium exposure device. Before tritium charge, all the samples were outgassed in vacuum at 673 K.

Tritium ions were irradiated for 15 minutes at room temperature, and the ion energy and current were kept at 1 keV and about 0.7 μA , respectively. Before removing an irradiation sample from the sample holder in the irradiation device, evacuation for one week needed to prevent contamination of the air due to tritium released from inner wall surface of the irradiation

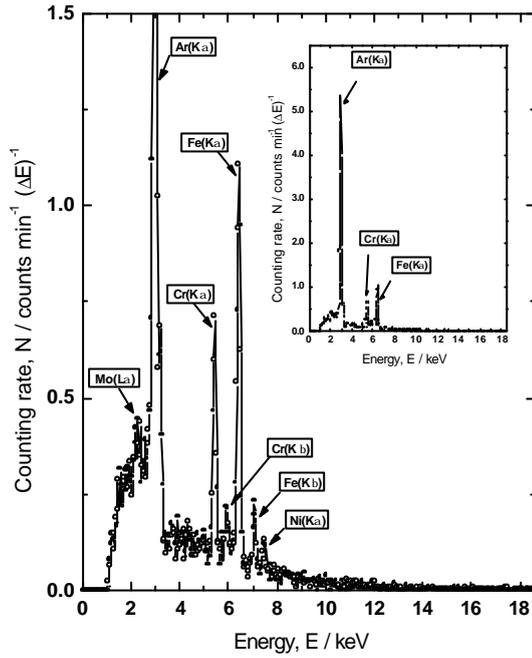


Fig. 1. Example of the X-rays spectra for the SS-316 sample irradiated with tritium ions at room temperature.

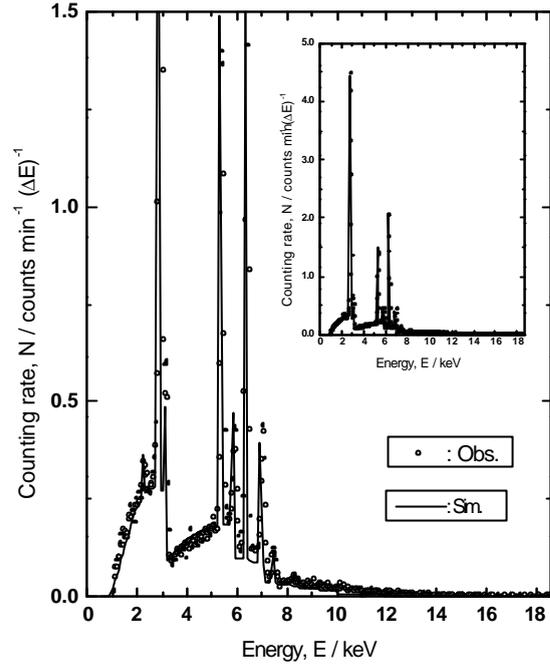


Fig. 2. Example of the X-rays spectra for the SS-316 sample exposed to molecular tritium at 523 K for 3 hours.

device.

On the other hand, molecular tritium was exposed to the SS-316 samples at 523 K for 3 hours. After the tritium charge, to reduce tritium release from the exposure device the samples were cooled down and evacuated at room temperature for about one week. After decontamination of the device, the samples were taken out and used for observation of the X-ray spectra and/or tritium removal examinations.

III. RESULTS AND DISCUSSION

1. Examples of the b-ray-induced X-ray spectra for the SS-316 samples

A tritium-containing sample emits characteristic and bremsstrahlung X-rays from bulk of the sample. These X-ray emissions are resulted in the interactions between β -rays and constituent atoms of the sample. Similarly, if the sample is kept in an argon atmosphere, additional characteristic X-ray peaks of argon appear.

Although conversion efficiency of β -rays to the X-rays for argon is not so high, argon is a practically useful probe as a conversion gas of β -rays from viewpoints of safety and economy.

An example of a typical X-ray spectrum is shown in Fig. 1, where SS-316 irradiated with tritium ions at room temperature was measured. As seen from the figure, the most intense peak was the characteristic X-ray peaks of argon, which consisted of main K(α) and minor K(β) lines though it was hard to divide clearly into two peaks. In addition, K(α) and K(β) lines from constituent atoms of stainless steel such as Fe, Cr, Ni and Mo and a broad bremsstrahlung X-ray peak appeared.

The characteristic X-rays of argon are produced by not only the collision with β -rays emitted from surface tritium but also photoelectric interactions with X-rays from the bulk. In this sample, the former contribution is fairly larger than the latter one, because intensity of the characteristic and bremsstrahlung X-rays higher

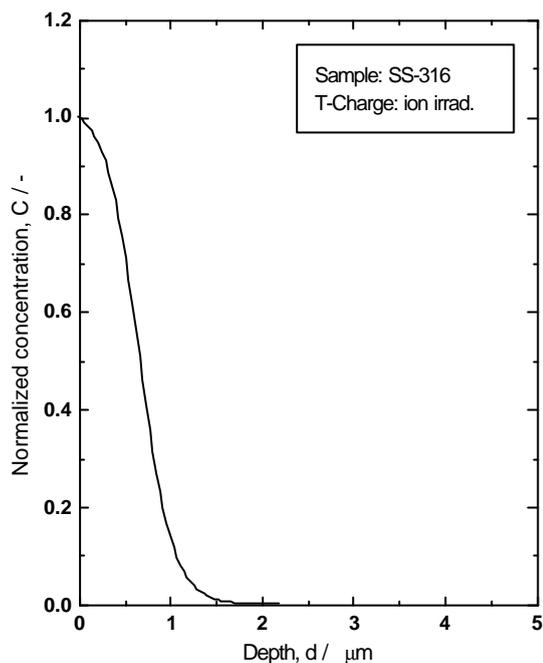


Fig. 3. Tritium depth profile estimated by computer simulation for the SS-316 sample irradiated with tritium ions.

than the transition energy of the argon $K(\beta)$ line is weak. This indicates, therefore, that intensity of the characteristic X-rays of argon gives information about the amount of tritium retained on the surface and in sub-surface layers of SS-316.

The maximum thickness of sub-surface layers corresponds to escape depth of β -rays, depending on the atomic number and density of a tritium-containing sample. In the case of SS-316 the thickness was estimated as about $0.1 \mu\text{m}$. Therefore, intensity of the characteristic X-rays of argon reflects the amount of tritium being retained within a region of about $0.1 \mu\text{m}$ beneath the surface.

On the other hand, intensities of characteristic and bremsstrahlung X-rays from bulk depend on not only the amount of tritium in the bulk but also depth profile of tritium. In addition, the shape of a broad bremsstrahlung X-ray peak gives information on the depth profile of tritium.

Figure 2 shows an example of the X-ray spectra

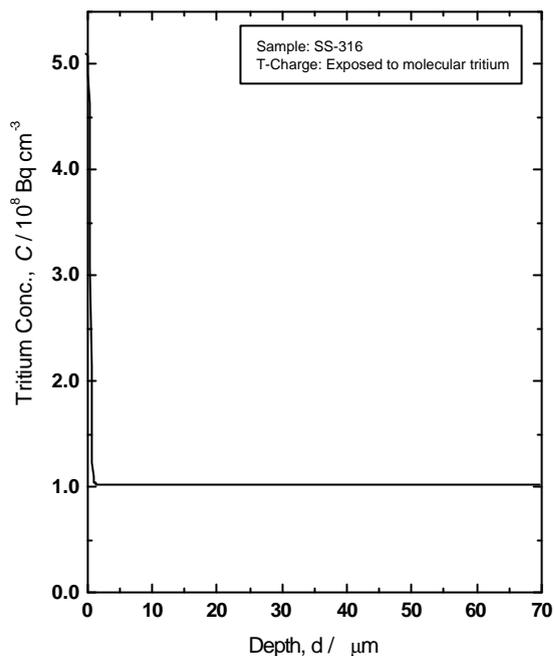


Fig. 4. Tritium depth profile estimated by computer simulation for the SS-316 sample exposed to molecular tritium.

observed for SS-316 exposed to molecular tritium at 523 K for 3 hours. The solid line is a simulation spectrum calculated by basing on a given depth profile which will be described later. The intensity of characteristic X-rays of argon was the almost same as that of the spectrum shown in Fig. 1, which suggests that the surface tritium activity of both SS-316 samples was an equivalent level in spite of different tritium charges. However, the shape of the bremsstrahlung X-ray peak was quite different. This indicates that the tritium depth profile of the SS-316 exposed molecular tritium fairly differs from that of the SS-316 irradiated with the ions.

A tritium depth profile in the bulk can be semi-empirically estimated by analyzing the X-ray spectra with computer simulation. The details are described elsewhere¹. Figures 3 and 4 illustrate the depth profiles obtained by analyzing the spectra shown in Figs. 1 and 2, respectively. Quite different depth profiles were obtained: tritium charged by the ion irradiation

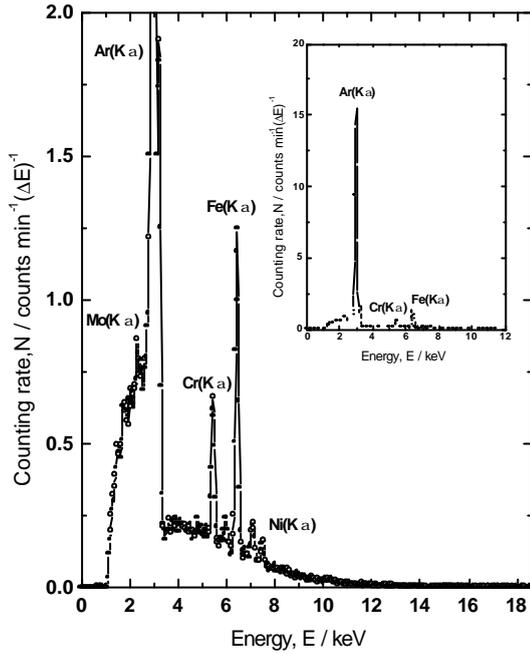


Fig. 5 Example of the X-rays spectra for the B/SS-316 sample irradiated with tritium ions at room temperature.

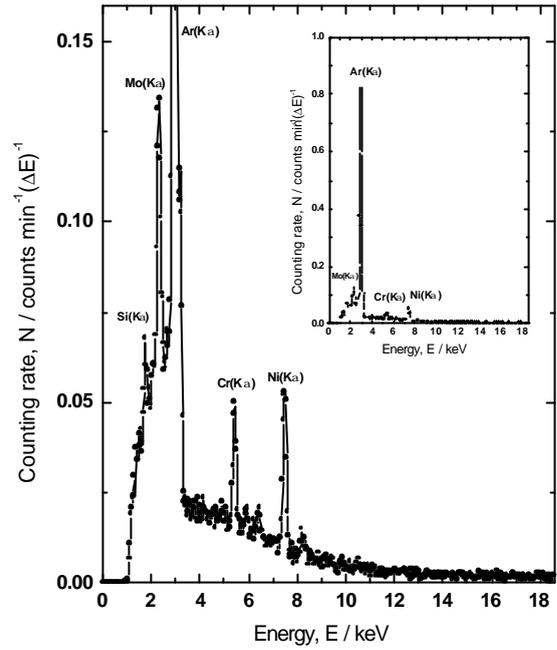


Fig. 6 Example of the X-rays spectra for the Hastelloy sample irradiated with tritium ions at room temperature.

was retained within 1 μm , but that by the molecular tritium exposure uniformly distributed above 70 μm along with a high concentration region near surface. Namely, the X-rays induced by β -rays in a tritium-containing material gives important information about contamination level such as tritium activity on the surface and tritium distribution in the bulk.

2. Examples of the β -ray-induced X-ray spectra for the B/SS-316, Hastelloy, and W samples

Figures 5, 6 and 7 describe the X-ray spectra observed for B/SS-316, Hastelloy and W irradiated with tritium ions at room temperature. The same irradiation conditions were applied to all the samples mentioned above. For B/SS-316 sample, weak characteristic X-rays of the base material appeared in spite of coating with boron film. It seems that this is due to the contribution of backscattering of β -rays.

The intensity of Ar K(α) line from B/SS-316 was

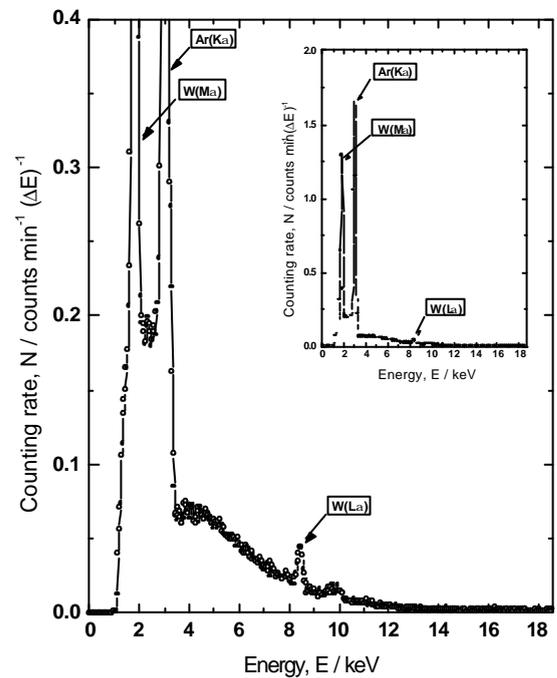


Fig. 7 Example of the X-rays spectra for the tungsten samples irradiated with tritium ions at room temperature.

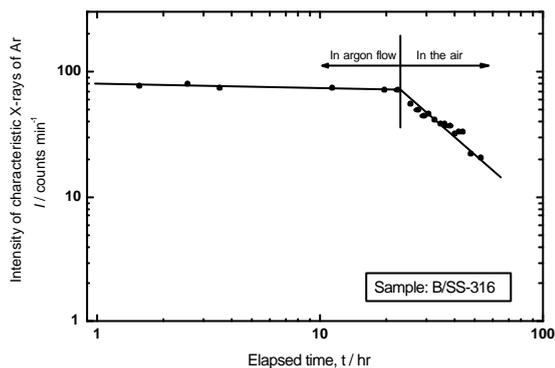


Fig. 8. Change in intensity of the characteristic X-rays of argon with time in an argon flow and in the air at room temperature. The flow rate of argon was 40 cm³/min.

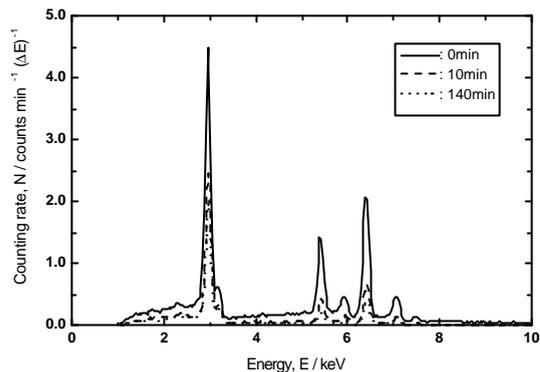


Fig. 9. Change in X-ray spectrum by the isothermal heating at 473 K for the SS-316 sample exposed to molecular tritium.

the highest in the three samples: 20 times greater than Hastelloy, and 10 times greater than W. Irradiation area of W was about 5 times smaller than that of B/SS316 sample. This is the main reason why the intensity for W sample is remarkably smaller than that for B/SS-316. In addition, it is considered that very weak intensity for Hastelloy is due to desorption in the evacuation process for one week after tritium irradiation.

Although the intensity of the bremsstrahlung X-ray spectra was greatly different, there was a little difference in shape for three samples, indicating a fairly small different depth profile near surface region. It is suggested, therefore, that most of the irradiated tritium in these materials did not diffuse into the bulk and it remained near surface region.

3. Tracking of a decontamination process by BIXS

The present measuring method was applied to examination of the desorption behavior of the irradiated tritium. Change in the amount of surface tritium was followed from change in the intensity of characteristic X-rays of argon with time at room temperature.

An examination was carried out using the B/SS-316 sample irradiated with tritium ions, and the result was shown in Fig. 8. The X-ray measurements were continuously conducted in an argon flow with a given time interval from the initial measurement for 24 hours, and after that the sample was stored in the air except for measuring time of the X-rays.

Decrease of the X-ray intensity in the argon flow was very small, but it was accelerated by the storage in the air. There are two possibilities for the decrease of the X-ray intensity: one is due to desorption from the surface, and another is due to diffusion into the bulk. For the present case, the former possibility is dominant behavior. If the latter possibility is advantageous, a large difference in the decreasing behavior will not be expected in the different atmosphere.

The decreasing curves in Fig. 8 could be apparently described by the following equation:

$$I_x = k t^{-n}, \quad \text{----- (1)}$$

where I_x represents the intensity of the characteristic X-rays of argon, k the proportional constant, t the time and n the factor of time dependency. The value of n in the argon flow was estimated to be -2.6×10^{-2} , and that in the air was -1.3 . Namely, this indicates the decrease in the amount of surface tritium was assisted 50 times by exposure to the air containing suitable moisture.

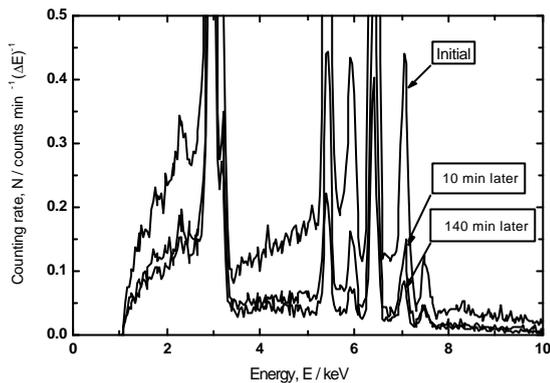


Fig. 10. Enlarged spectra of bremsstrahlung X-rays shown in Fig. 9.

Effects of moisture in argon on desorption rate of tritium are similarly recognized for other materials⁵.

Figure 9 shows change in an X-ray spectrum by the isothermal heating at 473 K for the SS-316 sample exposed to molecular tritium. Enlarged spectra are also illustrated in Fig. 10. Although spectral intensity totally decreased with time by desorption of the dissolved tritium, shape of the bremsstrahlung X-ray spectra was not similar. It is clearly seen in the energy region from 3.5 to 5 keV, where the ramp of curves becomes gentle with heating time. This indicates that the tritium concentration became low near surface region.

All the intensities of the characteristic X-rays of constituent atoms in SS-316 decreased similarly with heating time, which is shown along with the fraction of remaining tritium in Fig. 11. The fraction of remaining tritium was evaluated from the total desorption amount which was finally determined by heating the sample at 1073K. It should be noticed that a steep decrease appeared in the intensity of Mo(K α) line though the fraction of remaining tritium gradually decreased, indicating that tritium concentration did not uniformly decrease. Namely, it is suggested that only tritium concentration near surface region became re-

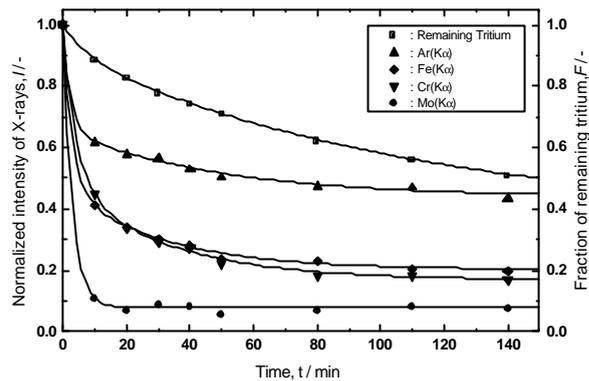


Fig. 11. Changes in intensity of the characteristic X-rays and tritium inventory observed for the SS-316 sample during the isothermal heating at 473K.

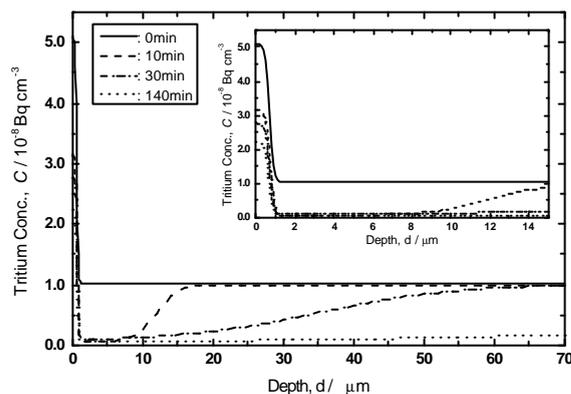


Fig. 12. Change in tritium depth profile estimated by analyzing the X-ray spectra shown in Fig. 9

markably low. This agrees with the change in shape of the bremsstrahlung X-ray spectra shown in Fig. 10.

Figure 12 demonstrates the tritium depth profiles estimated by analyzing the X-ray spectra shown in Fig. 9. The initial depth profile shows that the dissolved tritium uniformly distributed up to 70 μm excepting near surface region. After heating at 473 K for 10 min, however, considerably low concentration appeared in a wide region from about 1 to 10 μm though a subsurface region below 1 μm was still kept at high concentration. In addition, it was seen that high concentration near surface region has remained even after heating for

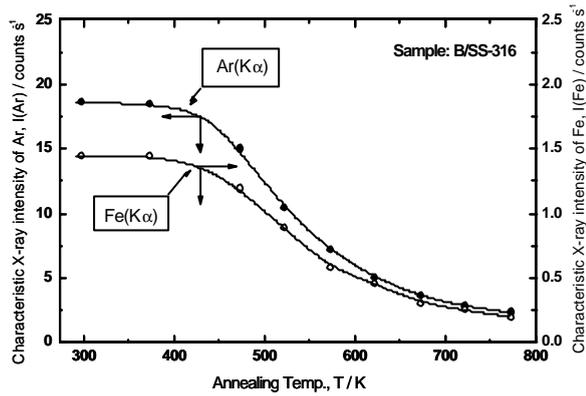


Fig. 13. Changes in intensity of the characteristic X-rays observed for the B/SS-316 sample during the isochronal heating.

140 min. This indicates that tritium trapped near surface region was strongly fixed by trap sites such as OH groups formed on metallic oxides.

Examination of isochronal heating was conducted for the B/SS-316 sample irradiated with tritium ions. The result is shown in Fig. 13. Heating in vacuum was carried out for 30 min at each annealing temperature. The intensity of Ar(K α) line as well as Fe(K α) line began to decrease at about 500 K, and it reached about 15% of the initial intensity at 773 K. Similar results were obtained for boron coating graphite. Furthermore, the bremsstrahlung X-ray spectra indicated no diffusion into the base plate of stainless steel. Namely, it was seen that the irradiated tritium on the boron film can be removed by heating at a relative low temperature and boron coating is useful for the decrease of tritium inventory for stainless steel.

IV. SUMMARY

The β -ray-induced X-ray spectrometry (BIXS) was applied to examine contamination and decontamination behavior of tritium for four kinds of metallic materials. Two kinds of tritium charges were employed for contamination of the materials, and the decon-

tamination process was examined at room temperature and elevated temperatures, i.e. isothermal and isochronal heating. From these examinations, the following results were obtained:

(1) Almost same amount of tritium ions was irradiated at room temperature, but the amount of tritium retained in the materials significantly differed. The order of the retained amount was as follows.

Hastelloy < SS-316 Tungsten < B/SS-316

(2) Exposure of molecular tritium to SS-316 was conducted at 523 K for 3 hours, and a uniform depth profile in the bulk was established, although a considerably high concentration region existed near surface.

(3) From the decontamination test of B/SS-316 in the ambient air, it was suggested that moisture in the air play an important role for decontamination efficiency. In addition, decontamination at elevated temperatures indicated that it is possible to remove tritium relatively low temperatures.

(4) An interesting change in the tritium depth profiles appeared in a decontamination process at 473 K for SS-316. Further investigations are needed to elucidate the decontamination mechanism in detail.

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