

論文

β 線誘起X線計測法によるZr中のトリチウム深さ分布の評価

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Estimation of Tritium Depth Profile in Zirconium by β -Ray-Induced x-Ray Spectrometry

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Abstract

The usefulness of the recently developed β -ray-induced x-ray spectrometry(BIXS) for nondestructive measurements of tritium captured in matrix was investigated using zirconium as a model sample. Two distinct spectra from characteristic and bremsstrahlung x-rays were clearly observed for the Zr sample exposed to tritium gas at room temperature. The former x-rays showed a sharp intense peak, while the latter x-rays formed a broad continuous spectrum. The intensity of both peaks decreased sharply with vacuum heating. At the same time, the top of the bremsstrahlung x-ray peak shifted to the higher energy side. These results indicate that the absorbed tritium diffused into the bulk by heating in vacuo. The changes were analyzed by computer simulation. The computer simulation could reproduce the observed spectra quite well. BIXS is therefore thought to be a highly promising technique for nondestructive determination of tritium inventories and depth profiles in materials.

1. Introduction

It is indispensable for safe handling of a large amount of tritium in thermonuclear fusion reactors to determine quantitatively tritium inventory and its local distribution in material. For this purpose, a variety of methods has been developed and applied so far; for example, direct β -ray counting, Rutherford backscattering, nuclear reaction analysis and so on. These methods, however, require complicated sample handling and procedures or are limited for measurements in a shallow sub-surface region below 0.1 μm .

Recently developed β -ray-induced x-ray spectrometry has been a highly promising technique for this purpose [1]. This method is based on the fact that β -rays emitted from tritium captured in a material interact with the constituent atoms to produce characteristic and bremsstrahlung x-rays. This means that tritium trapped in a deep region of the material can be detected by these x-rays because of their considerably larger escape depth than tritium β -rays. In addition, it has been also pointed out that depth profiles of tritium in materials could be determined nondestructively by this method in combination with computer analyses of the observed x-ray spectra. This is because the escape depth of a photon is determined by photon energy, constituent atoms and density of the material. Both of the spectral intensity and shape give direct information about the amount and the depth profile of tritium. There should be a one-to-one correspondence between the depth profile and the β -ray-induced x-ray spectrum.

This paper describes nondestructive measurements of β -ray-induced x-ray spectra, their changes with vacuum heating and analyses by computer simulation. Zirconium was selected as a model material for demonstrating the applicability of this method to the nondestructive determination of tritium inventory and its distribution.

2. Experimental

2.1. Apparatus

Figure 1 shows a schematic drawing of the experimental apparatus used in the present study. It consisted of vacuum, tritium supply-recovery, and x-ray measuring systems. The vacuum system comprised a sputter ion pump(SIP) and a turbo molecular pump(TMP) backed with an oil-sealed rotary pump(RP), which was connected to a tritium removal system(TRS). A quadrupole mass spectrometer(QMS) and an ionization gauge(IG) were also

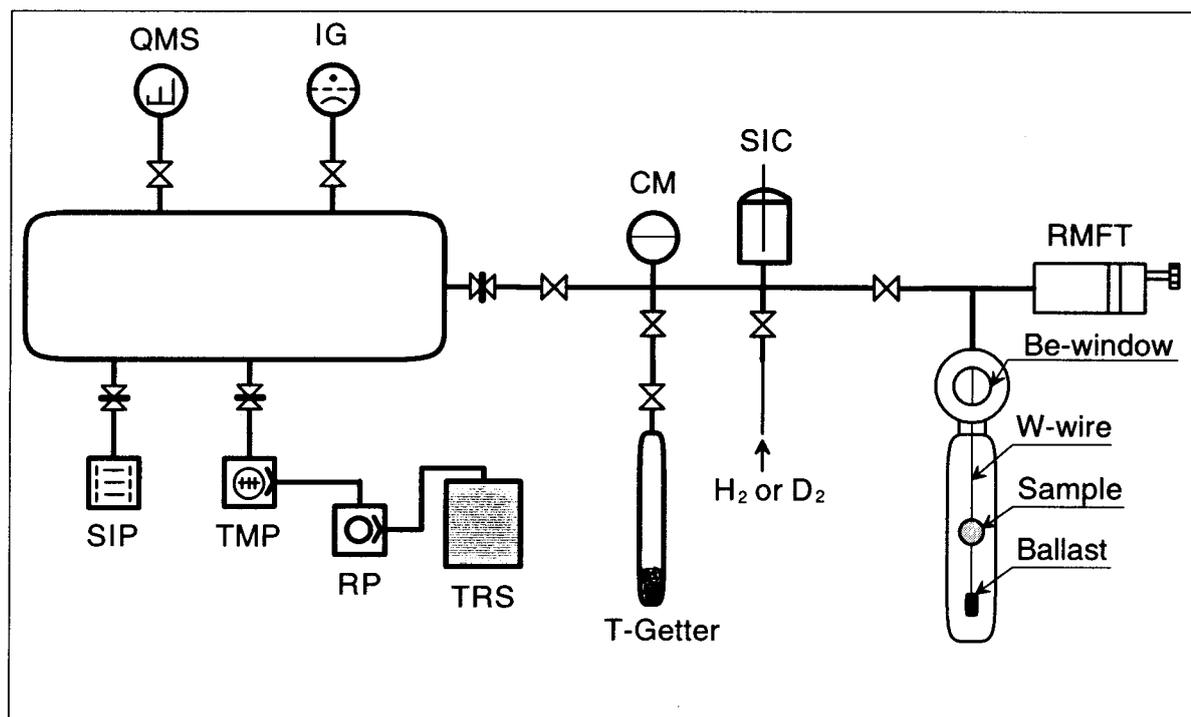


Fig. 1. Experimental apparatus used to expose a Zr sample to tritium gas and to measure changes in x-ray spectra with time and temperature.

installed. The residual pressure of the vacuum system was routinely below 6×10^{-6} Pa, where the main impurities were hydrogen, water vapor, and carbon monoxide. The tritium supply-recovery system was fitted with a capacitance manometer (CM: lower detection limit was 0.1 Pa), a small ionization chamber (SIC) specially designed for measuring high level tritium [2], and a tritium storer (T-Getter), for which ZrNi powder was used. Hydrogen and deuterium cylinders were also connected to this system. The x-ray spectra measuring system consisted of a beryllium window (Be-window) attached to a double-sided Con-Flat flange, a sample tube made of quartz glass, and a rotary motion feedthrough (RMFT). The Be-window was prepared from a beryllium plate whose inner surface was coated with a thin evaporated gold film. The thickness and the diameter of the beryllium plate were 150 μm and 25 mm, respectively. A sample disc was hung from RMFT with a very fine W-wire coated with gold to move the sample up and down. In addition, a small ballast was hung from the sample with the same W-wire for smooth vertical motion of the sample.

An ultra-low energy germanium detector (CANBERRA: Model GUL0055P) was used for detection of x-rays emitted from a sample. Nominal energy resolution of the detector was 150 eV at 5.9 keV. The active diameter of the detector was 8.0 mm and the protection window of germanium was made of a thin beryllium membrane of 8 μm in thickness. Energy calibration of the detector was performed by using ^{57}Co , ^{133}Ba , ^{137}Cs and ^{241}Am .

2.2. Materials

Two zirconium disks(sample 1 and sample 2) were used as samples. Sample 1 was employed for examination of annealing effects on tritium distribution. They were cut from a zirconium plate delivered from Nilaco Co. The nominal purity of the zirconium plate was 99.7%. The size of each disc was 10.4 mm in diameter and 0.5 mm in thickness. Tritium used was diluted with hydrogen, whose specific activity was 38.6 GBq/cm³(40.4 % in tritium concentration).

All of the reagents used for the etching of Zr samples were purchased from Wako Pure Chemicals (reagent grade).

2.3. Procedures

Each sample was mechanically polished with three different polishing papers of successive series numbers, and then rinsed in acetone. It was spot-welded to a W-wire to connect to the rotary motion device. After the sample being set in the sample tube, the measuring system was evacuated below 10⁻⁶ Pa at room temperature and the sample was heated at 873 K for 2 hours to gain an active surface of the samples for absorption of tritium.

After the activation, the sample was exposed to tritium gas at room temperature for a given time. The tritium gas was supplied from the T-getter heated at 625 K, and the initial pressure of tritium gas was set at 133 Pa. After the tritium exposure, tritium remaining in the gas phase was recovered by the T-getter at room temperature and then pumped for a short time by the SIP

X-rays emitted from the sample were measured firstly by lifting it up to the fixed position in front of the Be-window. After this measurement, the sample was put down to the heating part, and heated in vacuo for 1 hour at a given temperature from 473 to 573 K. Then it was again lifted up to observe changes in the x-ray spectrum.

The proper depth profiles of tritium in matrix were determined by electrolytic etching and counting method after a series of x-ray measurements, where a mixed solution of glycerin, nitric acid and hydrofluoric acid(20:2:1) was used to etch electrolytically the zirconium disc containing tritium. The etching of a Zr sample was carried out under the conditions of 5V and 40 mA. The tritium concentration in the etching solution was followed at a regular time interval by using a liquid scintillation counter. In the control experiment, the etching rate had been evaluated from weight loss as 0.20-0.23 μm/min.

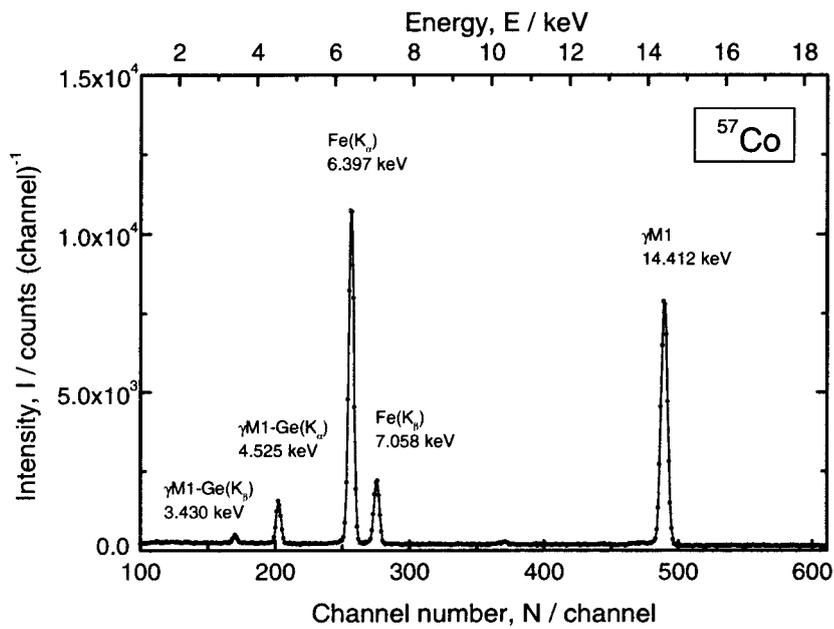


Fig. 2. Low energy spectrum from ^{57}Co measured to evaluate the resolution of the present x-ray detector.

3. Results

3.1. Energy resolution of the x-ray detector

Because the characteristic and bremsstrahlung x-rays induced by tritium β -rays should appear in the energy region below 18.6 keV, the energy resolution of the x-ray detector in the low energy region is of a great importance for analysis of spectral shape of the β -ray-induced x-rays. Therefore, the energy resolution of the x-ray detector used was determined in advance by employing the characteristic x-rays and γ -rays emitted from ^{57}Co source. Five peaks were observed in the energy region of interest. They were assigned as escape peaks, characteristic x-rays from Fe and γ -rays as indicated in Fig. 2. The energy resolution determined from these peaks, $\Delta E/E$ (E is the energy of a peak and ΔE is the full width at half maximum of the peak), was 3.1% at 4.525 keV, 2.2% at 6.397 keV and 1.2% at 14.41 keV. Namely, the x-ray detector used has a sufficient energy resolution for analyzing the β -ray-induced x-ray spectra.

3.2. Spectral changes at room temperature

Figure 3 shows a typical example of β -ray-induced x-ray spectrum, which was observed for the Zr sample exposed to tritium gas at room temperature. The measurement was carried out for 40 minutes to minimize a relative standard error of x-ray intensity. Two distinct peaks can be seen in the figure. One makes a sharp intense peak centered at 2.0 keV,

and the other comprises a broad peak. The former agreed quite well with the characteristic x-rays of $Zr(L\alpha_1)$ and $Zr(L\alpha_2)$ at 2.0424 and 2.0399 keV [3], respectively, although they could not be distinguished by the present detector. The broad peak is due to the bremsstrahlung x-rays emitted from bulk of the sample.

Figure 4 shows the x-ray spectra observed for the sample kept in vacuum at room temperature for given times after the tritium exposure. Although there appeared no appreciable change in the spectral shape, there arose a slight reduction in the peak intensities. Figure 5 summarizes the changes in the intensities of characteristic and bremsstrahlung x-rays with time, where each intensity was normalized to that measured at 1 hr after the tritium exposure. The intensities of both peaks decreased sharply within 1 hr, but showed only a small reduction in additional 14 hours. In addition, there appeared a feature of increasing intensities with time beyond this point. The peak intensity of the characteristic x-rays was always larger than that of the bremsstrahlung x-rays. Since the peak intensity of the characteristic x-rays is much dependent on the amount of tritium near the surface owing to their low energies, the observations suggest that most of the tritium absorbed in the

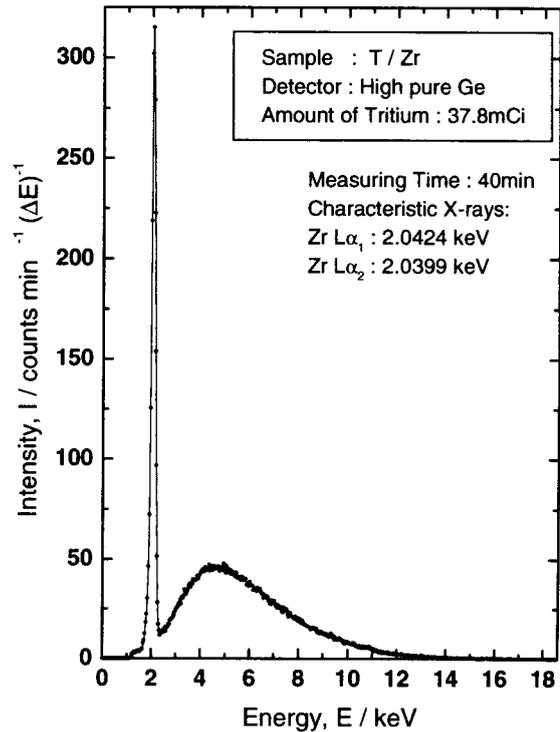


Fig. 3. Typical spectrum from Zr sample exposed to tritium gas.

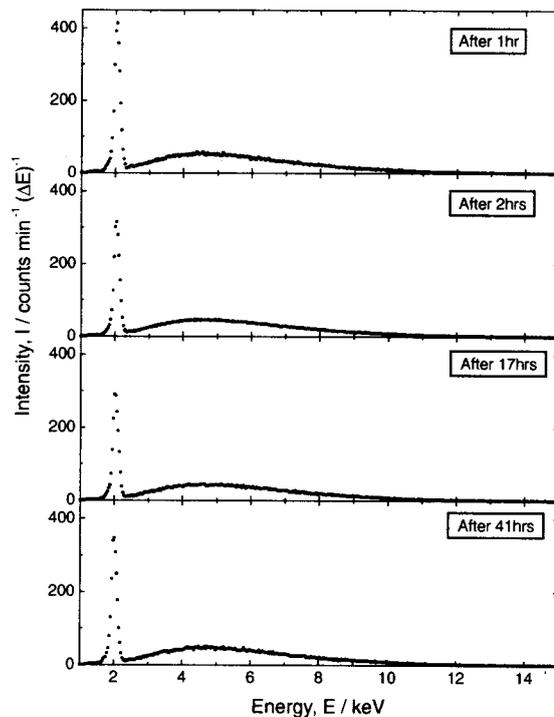


Fig. 4. Change in the spectra with time at room temperature.

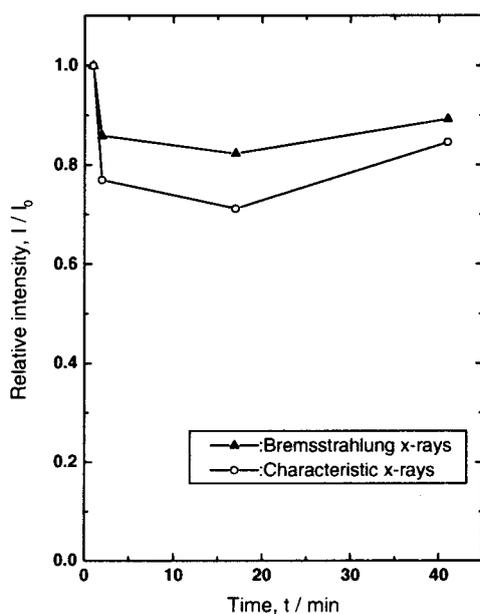


Fig. 5. Changes in each x-ray intensity with time.

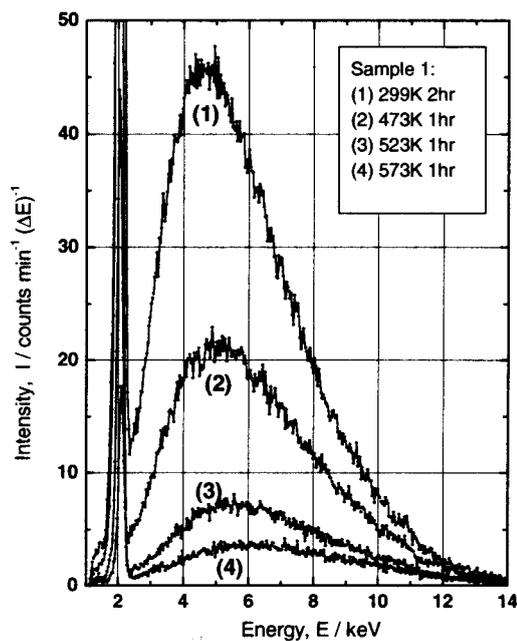


Fig. 6. Change in the characteristic x-ray spectra with annealing temperature.

sub-surface layers of the sample was not mobile sufficiently to diffuse into the bulk at room temperature.

3.3. Spectral changes at higher temperatures

More pronounced spectral changes can be expected at higher temperatures because of enhanced tritium mobility. Then, the x-ray spectra were measured for a sample, which had been exposed to the tritium gas at room temperature, before and after the annealing at given temperatures up to 573 K for 1 hr without evacuation. No detectable tritium was released from the sample during this procedure. Figure 6 shows the change in the bremsstrahlung x-ray peaks, all of which were measured at room temperature. It is seen that the intensity of the bremsstrahlung x-rays considerably decreased by annealing at elevated temperatures and the top of a bremsstrahlung x-ray peak shifted to higher energy side. The intensity of the characteristic x-rays also drastically decreased with increasing temperature. These observations indicate that the depth profile of tritium in the sample changed by the heating, suggesting that the tritium absorbed in the sub-surface layers diffused into the bulk.

Figure 7 shows the changes in the peak intensities of characteristic and the bremsstrahlung x-rays with heating temperature. Both the peaks decreased their intensities with increasing temperature, and then reached the values of about 1/10 of the respective initial intensities. On the other hand, the ratio of the peak intensity of the former to the latter

increased with temperature. It was especially noticeable at temperatures above 500 K. The weakening of the intensities is due to the reduction in the amount of tritium absorbed in the sub-surface layers, within the penetration depths of these x-rays. Namely, these observations indicate that the tritium desorption or diffusion into the bulk was enhanced considerably at elevated temperatures. In the case of the characteristic x-rays, the reduction of the absorbed tritium plays a dominant role, while the absorption of low energy x-rays by the media contributes much to the decrease of bremsstrahlung x-ray intensity.

3.4. Simulation of the bremsstrahlung x-ray spectrum

A bremsstrahlung x-ray spectrum can be calculated by numerical computation with a given depth profile of tritium in a matrix. The method of numerical calculation has been reported in detail elsewhere [4]. The main components of the calculation program comprise the production of the tritium β -ray spectrum, the energy conversion of β -rays to x-rays, and the absorption of photons by the matrix during their traveling. The similar computation can be applied to the characteristic x-ray spectrum by use of the conversion probability of β -rays to characteristic x-rays given by theoretical models [5].

Figure 8(A) shows bremsstrahlung x-ray spectra obtained by the computation for

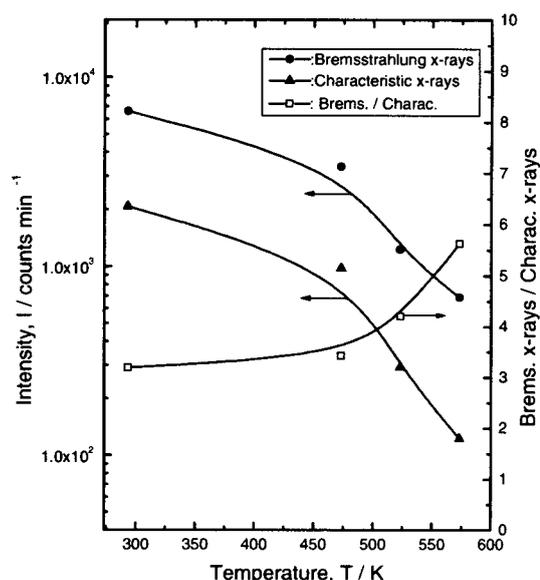


Fig. 7. Changes in the x-ray intensities and the ratio between both the intensities with temperature.

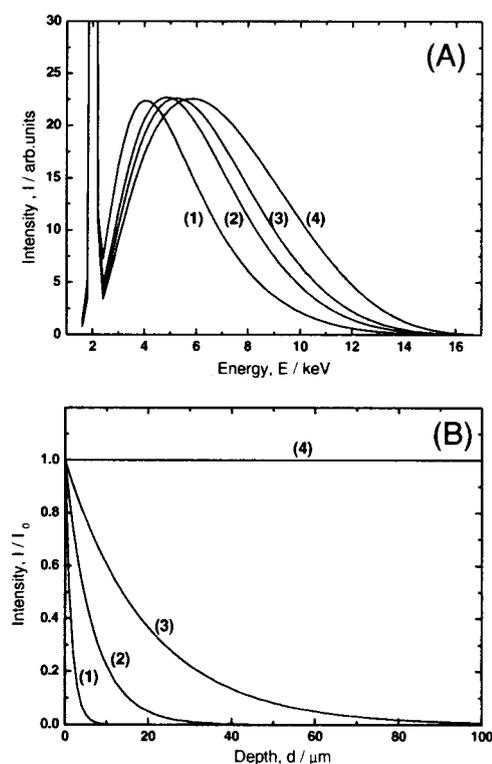


Fig. 8. Simulation of bremsstrahlung x-ray spectra(A) based on the corresponding depth profiles of tritium(B).

the respective depth profiles shown in Fig. 8(B). A common number is used for the depth profile and the corresponding spectrum in Fig. 8(A) and (B). In Fig. 8(A), the maximum intensity of a respective spectrum was normalized to compare the spectral shape clearly. It can be seen from this figure that a sharp depth profile in thin layers gives a narrow bremsstrahlung x-ray spectrum at a low energy side, while a flat depth profile extended over thick layers results in a broad spectrum with the peak at a higher energy side.

4. Discussion

4.1. Effect of gaseous tritium on x-ray spectra

Although it was expected to be minor, the Be-window itself might contributed to the production of x-rays owing to the interaction with contaminant tritium adsorbed on the inner wall of the measuring system or with tritium in the residual gas. To examine the extent of this effect, a given amount of tritium gas was introduced into the measuring system without a sample, and the x-ray spectrum was measured.

Figure 9 shows a typical spectrum of the x-rays causing by interactions of β -rays from gaseous tritium with the surface of the Be-window, where the measuring time was 5 min. Two characteristic features should be noted here. One is the appearance of three characteristic x-ray peaks and the other is the shape of the bremsstrahlung x-ray spectrum. The characteristic x-ray peaks were assigned to Au(L α), Au(M α) and Ni(K α) [3], which were not detected in the spectra from the Zr samples. This indicates that little tritium gas existed in the measuring system during the measurements of x-ray spectra. In addition, the bremsstrahlung x-ray spectrum was peaked at 4 keV, being much lower than the peak for the Zr sample.

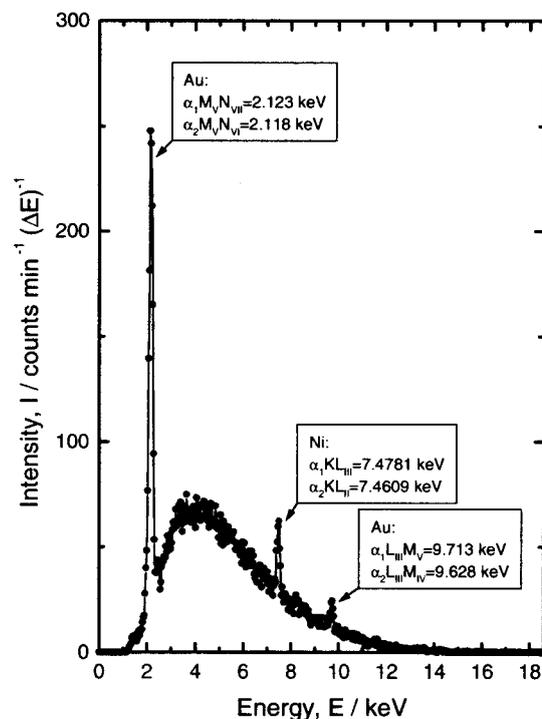


Fig. 9. Typical x-ray spectrum induced by gaseous tritium

4.2. Change of x-ray spectra at room temperature

The energies of the characteristic x-rays of $Zr(L_{\alpha 1})$ and $Zr(L_{\alpha 2})$ are so low that these x-rays are strongly attenuated in a short traveling distance. Namely, they are only sensitive for tritium on the surface or in the sub-surface layers. On account of this fact, it is concluded that the slight change in the intensity of the characteristic x-rays with time at room temperature shown in Figs. 4 and 5 was due to the presence of immobile tritium on the surface.

This conclusion, however, contradicts to the average diffusion distance of tritium at room temperature in α -Zr predicted by the diffusion coefficients determined by many groups. For example, Sugisaki et al. has reported [6] that diffusion coefficient of tritium in α -Zr is $D(\text{cm}^2/\text{s}) = 3.14 \times 10^{-3} \exp(-42.7(\text{kJ}/\text{mol})/\text{RT})$. From this diffusivity, the average diffusion distance is evaluated to be about 80 μm at room temperature within 41 hours. On the other hand, hydrogen can hardly diffuse in zirconium oxide at room temperature according to the reported diffusion data [7]. In fact, the sample surface showed a faint color change after the initial activation procedure at 873 K. Then it is plausible that the tritium immobilization was caused by the formation of zirconium oxide layers on the surface.

4.3 Temperature dependence of peak profile

The steep reduction of the characteristic x-ray's intensity with annealing temperature indicates that the amount of tritium on the sub-surface layers decreased sharply with elevating temperature. This should be due to the diffusion of tritium into bulk, because no pressure increase was observed during the annealing. The reduction of the bremsstrahlung x-ray's intensity can be also attributed to the tritium diffusion, but a matter of concern in this case is the tritium presented in the sub-surface layers. The peak shift of the bremsstrahlung x-rays to the higher energy side with temperature reflects also that the tritium absorbed in the sub-surface layers migrated into deeper region. This is because the low energy photons are attenuated more strongly than high energy ones in a given traveling distance, causing the peak shift to the higher energy side. Namely, all of these observations indicate that the high temperature annealing gave rise to tritium diffusion into bulk and caused to change tritium depth profile.

The depth profiles were calculated by assuming a semi-infinite media using the diffusion constant of tritium reported in ref. 6. It can be seen in Fig. 8 that the peak top moves toward the higher energy side with increasing thickness of tritium contained in sub-surface layers. This is one of the characteristic features of the observed bremsstrahlung x-ray spectra.

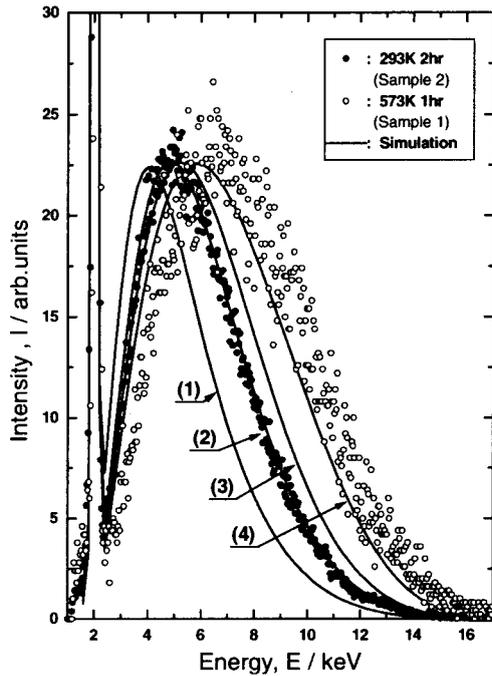


Fig. 10. Comparison of the observed bremsstrahlung x-ray spectra with those obtained from simulation.

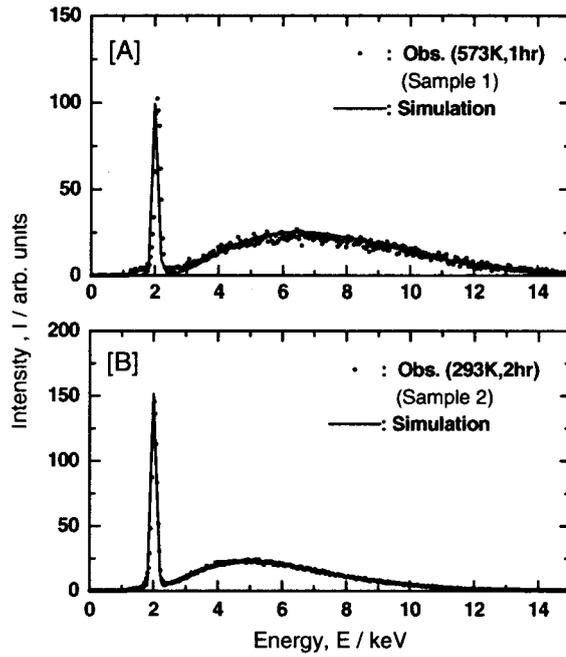


Fig. 11. Simulation of the observed characteristic x-ray spectra.

Furthermore, the calculated spectra are compared with those for the samples with and without high temperature annealing in Fig. 10. The observed spectra agree quite well with the calculated ones for the depth profiles of No. 2 and 4 shown in Fig. 8(B). It should be also mentioned that the characteristic x-ray spectra could be reproduced very well by computer simulation as shown in Fig. 11. These figures indicate that the tritium depth profiles of No. 2 and 4 are most likely for the observed characteristic x-ray spectra.

To confirm the reliability of simulation of x-ray spectra, the tritium depth profiles of samples 1 and 2 were determined by the electrolytic etching and counting method. As shown in Fig. 12, the observed depth profile coincide well with the assumed profiles applied for calculation. Then, it can be concluded that the β -ray-induced x-ray

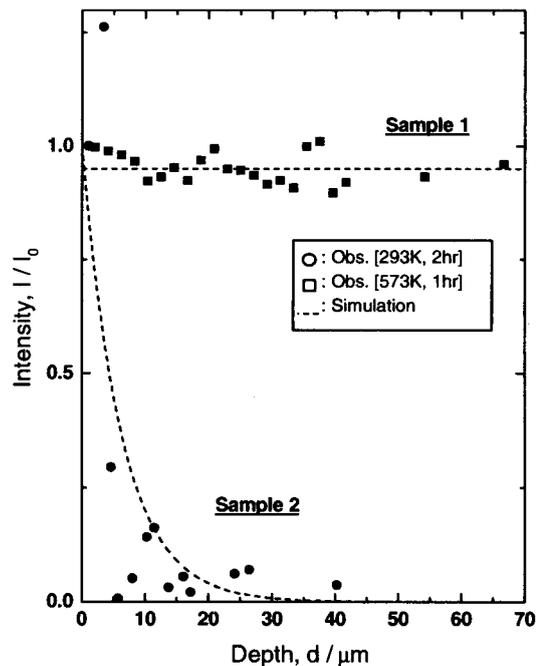


Fig. 12. Determination of tritium depth profiles by an electrolytical etching method.

spectrometry has high potential for in-situ and nondestructive measurements of tritium depth profiles in materials.

5. Conclusions

Nondestructive evaluation of a tritium depth profile in metallic materials was carried out by using β -ray-induced x-ray spectrometry(BIXS). As a first step, the newly developed BIXS was applied to the Zr samples as model material absorbed a given amount of tritium. Both of characteristic and bremsstrahlung x-ray spectra were observed for the samples. The former x-ray peak, which was sharp and strong, appeared at 2.04 keV, while the latter spectrum showed a broad peak. It was expected from those peak profiles that most of the absorbed tritium was trapped in the sub-surface layers of the Zr sample at room temperature. Furthermore, changes in both x-ray spectra were followed for 41 hours at room temperature after tritium exposure in order to examine the behavior of tritium. Only a little decrease of both x-ray intensities was observed during measurements, indicating that the absorbed tritium was strongly fixed in the sub-surface layers of the Zr sample. With heating the sample, however, drastic changes of the spectra were observed; the intensities of both peaks decreased and the peak top of bremsstrahlung x-rays shifted to higher energy side with a temperature rise. It could be seen from such spectral changes that a part of tritium in the sub-surface layers diffused into bulk of the Zr sample.

To evaluate nondestructively tritium depth profiles in the Zr sample at temperatures of 293 and 573 K, bremsstrahlung x-ray spectrum measured at each temperature was compared with that obtained from computer simulation, assuming tritium depth profiles in a sample. The observed spectra agreed quite well with the calculated ones, which were based on two distinct tritium depth profiles: that is, it was suggested from the computer simulation that the tritium concentration at 293 K exponentially decreased and extended to about 30 μm , whereas the concentration at 573K was almost uniform. Verification of the expected depth profiles was carried out by using a conventional etching method. As a result, the depth profiles obtained from the etching method were consistent with those expected from the computer simulation. It was revealed, therefore, that the BIXS is highly promising for nondestructive evaluation of tritium depth profiles and inventories in materials.

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