In-situ measurements of tritium desorption from a vanadium alloy by β-ray-induced X-ray spectrometry (BIXS)

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Abstract

Thermal release of tritium from a vanadium alloy was investigated by means of β-ray-induced X-ray spectrometry (BIXS). The sample tested was a V-4Cr-4Ti alloy recrystallized by annealing at 1000 °C for 2 h. A tritium gas diluted with hydrogen was characterized with a quadrupole mass spectrometer and a small ionization chamber, and the concentration of tritium was evaluated to be 0.14%. The sample was exposed to the tritium gas at 400 °C. The total concentration of hydrogen isotopes absorbed in the sample was 0.17 at%, and the corresponding tritium concentration was 2.4 appm, respectively. Tritium started to desorb at 350 °C. The duration of time required for desorption was much longer than that expected from the diffusion coefficient of tritium in the alloy, indicating that the rate of tritium release was controlled by a surface recombination process.

1. Introduction

Vanadium alloys, in particular V-4Cr-4Ti alloy, are considered as promising candidates of structural materials for fusion reactors [1]. Trapping and thermal desorption behaviors of hydrogen isotopes will be crucial issues for their applications in fusion energy systems because the behaviors of hydrogen isotopes will be closely related to the D-T fuel control and the mechanical properties of the alloys. BIXS (β-ray-induced X-ray spectrometry) [2,3] is a newly developed technique to detect the

tritium distribution in the surface layers (here the surface layers denote the region of the escaped depth of β particles in materials) and in the bulk of materials (the distance depends on the attenuation of X‑rays in the materials and usually exceeds 100 μm).

Up to now, many kinds of materials containing tritium have been examined by BIXS to characterize the X-ray spectra and the depth profiles of tritium, e. g. carbon based materials [4], stainless steel [5] and tungsten [6]. Vanadium alloys, however, have not been investigated so far. In the present work, thermal desorption of tritium from a V-4Cr-4Ti alloy was examined by using tritium gas diluted with hydrogen. Firstly, the tritium gas used was characterized with a quadrupole mass spectrometer (QMS) and a small ionization chamber. The recrystallized V-4Cr-4Ti alloy sample was exposed to the tritium gas at 400 °C, and the depth profile of tritium concentration was measured *in-situ* by a technique of BIXS. Finally, the release behavior of tritium in the alloy was investigated by raising the sample temperature step by step from room temperature (RT) to 450 °C.

2. Experimental

2.1 Characterization of tritium gas

A quadrupole mass spectrometer (QMS) was used to characterize the tritium gas released from a getter material (Zr-Ni alloy) at 250 °C. Fig. 1 shows the mass spectrum of the tritium gas. This figure shows a small peak at mass number 3 and large one at mass number 2, indicating tritium was diluted with hydrogen. From the intensity ratio between the peaks at mass numbers 2 and 3, the concentration of tritium in the released gas was roughly estimated to be 0.1%.
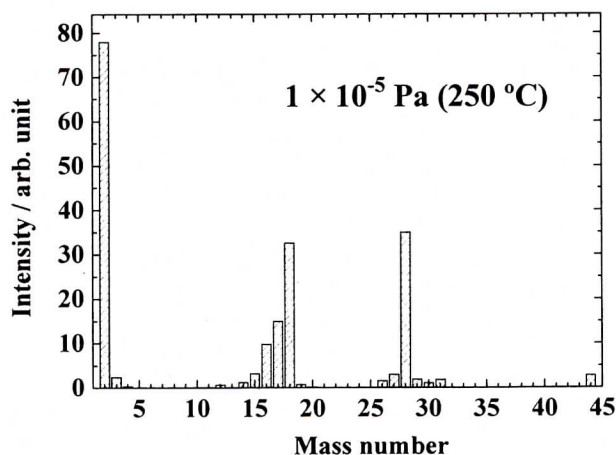

Fig.1 Mass spectrum of tritium gas diluted with hydrogen.

In order to estimate the tritium concentration more accurately, another technique was employed. In this case a small ionization chamber was used as the tritium monitor. The detailed experimental arrangement and processing method can be found in Ref. [7]. Table 1 shows the experimental conditions and results. Tritium concentration was evaluated with an empirical formula obtained by standard samples. Based on the characterization tests, tritium content in the hydrogen isotope gas released from the getter material at 250 °C was determined to be about 0.14 %.

Table 1 Tritium concentration in the gas released from getter material (Zr-Ni alloy).

Getter Temperature (°C)	Pressure (Pa)	Current (pA)	T-concentration (%)
250	5320	30.00	0.139
270	7679	59.50	0.146
290	10262	100.00	0.148
310	13200	157.00	0.150

2.2 Hydrogen isotope absorption and thermal release experiments

A sheet of V-4Cr-4Ti alloy (NIFS-HEAT-2) (99.5 % cold worked and 0.5 mm in thickness) was supplied by the National Institute for Fusion Science, NIFS. The samples with size of $15 \times 10 \times 0.5$ mm^3 were cut from this sheet. After mechanical polishing by Al_2O_3 powder with size of 0.06 μm and cleaning with acetone in an ultrasonic bath, the samples were annealed at 1000 °C for 2 h in vacuum for recrystallization. Finally, one of the samples was placed on a thin molybdenum heater mounted on a transfer rod, and then this device was connected to the main vacuum system for tritium desorption experiments with in-situ BIXS
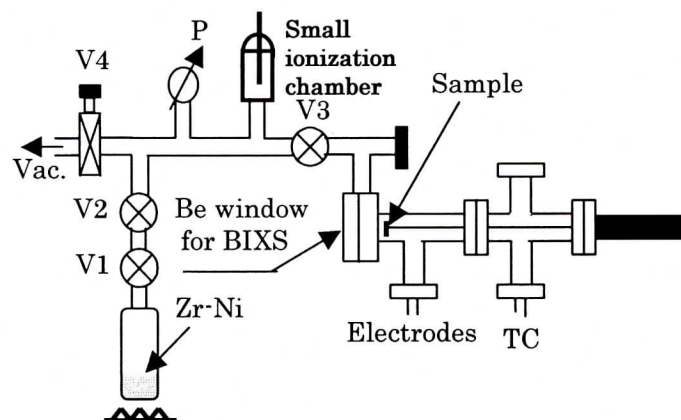

Fig. 2 A sketch drawing of apparatus for tritium desorption experiments and *in-situ* BIXS measurements.

analysis as shown in Fig. 2. In order to detect low energy β-particles, a thin beryllium window (150 μm in thickness) was set up in the front of a Si detector. A very thin Au film was coated on the beryllium window to prevent the tritium contamination of Be.

After heating the getter material to 250 °C, the valves 1 and 2 were opened, while the valves 3 and 4 were closed to make a given volume of tritium gas. Then the valve 3 was opened to introduce tritium gas into the sample chamber for absorption. The sample temperature was kept at 400 °C. An equilibrium pressure was obtained after 2h absorption. From the extent of pressure change, the total concentration of hydrogen isotopes in the sample and the corresponding tritium concentration were evaluated to be 0.17 at% and 2.4 appm, respectively. After cooling down the sample to room temperature (RT), the residual hydrogen isotope gas was recovered by the getter material. BIXS measurements were conducted to measure depth profile of tritium in the sample.

In order to investigate the thermal desorption of tritium, the sample was heated in vacuum step by step from 250 to 450 °C with a step of 50 °C. In every cycle the sample was kept at the given temperature for 1h, and then cooled down to RT. The depth profiles of tritium remaining in the sample were obtained by analyzing the observed X-ray spectra.

3. Results and discussion

3.1 β-ray-induced X-ray spectra of V-4Cr-4Ti alloy

Figure 3 shows a typical example of BIXS spectra obtained at RT after tritium absorption. The observed spectrum indicated by dot marks consists of characteristic X-ray peaks of V, Ti and Cr (sharp peaks) and broad bremsstrahlung X-rays. The intensities of Cr(Kα) and Ti(Kα) peaks were evaluated to be 4 % of intensity of V(Kα) peak. These intensity ratios correspond to the composition of the alloy. Since Cr(Kα) peak was overlapped with V(Kβ) peak, the intensity of the former was evaluated by subtracting the contribution of the latter by assuming that the intensity ratio of vanadium peaks, $I(K\beta)/I(K\alpha)$ is 2/15. Solid line in this figure indicates a spectrum obtained by simulation assuming uniform tritium distribution in the specimen. Details
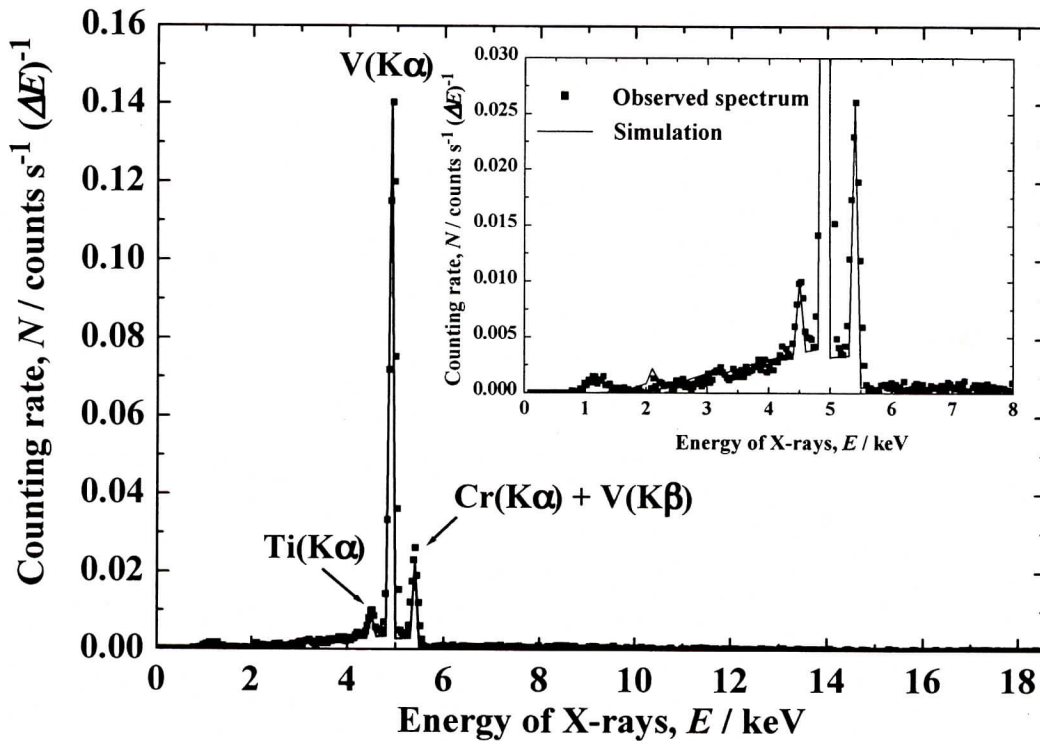
Fig. 3   Typical example of BIXS spectra of V-4Cr-4Ti alloy. Channel width, ΔE, of Si detector was 34.18 eV

of the simulation method are described elsewhere [8]. In this simulation, absorption coefficients of photons in V-4Cr-4Ti alloy are important parameter to calculate the attenuation of X-rays, which affect the shape and intensity of X-ray spectra. According to Ref. [9], the absorption edge of K-shell in vanadium is 5.4639 keV. The energy dependence of absorption coefficient in vanadium given in Ref. [10] could be expressed as $8363.9E^{-2.77503}$ below the absorption edge and as $78493E^{-2.80386}$ in higher energy region, where E is the photon energy. The spectrum thus obtained by the simulation agreed fairly well with the observation as shown in Fig. 3. This agreement indicates that tritium distribution in the sample was uniform at least up to the depth of about 100 μm (the maximum detection depth of BIXS).

3.2 Thermal desorption of tritium from V-4Cr-4Ti alloy

As mentioned in Section 2.2, the sample was heated at temperatures from 250 to 450 °C (with step of 50 °C) for 1 h, and the tritium desorption was examined by means

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of BIXS after every heating step. The change in V(Kα) peak intensity is plotted against annealing temperature in Fig. 4 as a measure of tritium content in the sample. No significant tritium desorption was observed below 300 °C, while the tritium content
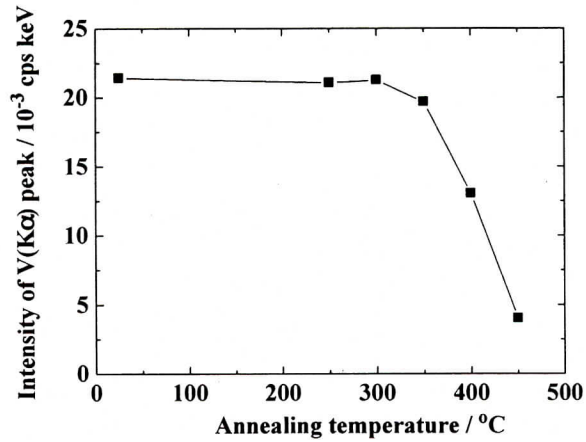
Fig. 4 Change in V(Kα) peak intensity with annealing temperature.

clearly decreased with increasing temperature in higher temperature region. After annealing at 450 °C, most of tritium was released. This result indicates that a baking temperature of 400 °C or higher is strongly required for tritium decontamination from this type of alloy. No systematic change was observed in the intensity ratios between Cr(Kα) and V(Kα) peaks, and Ti (Kα) and V(Kα) peaks during desorption.

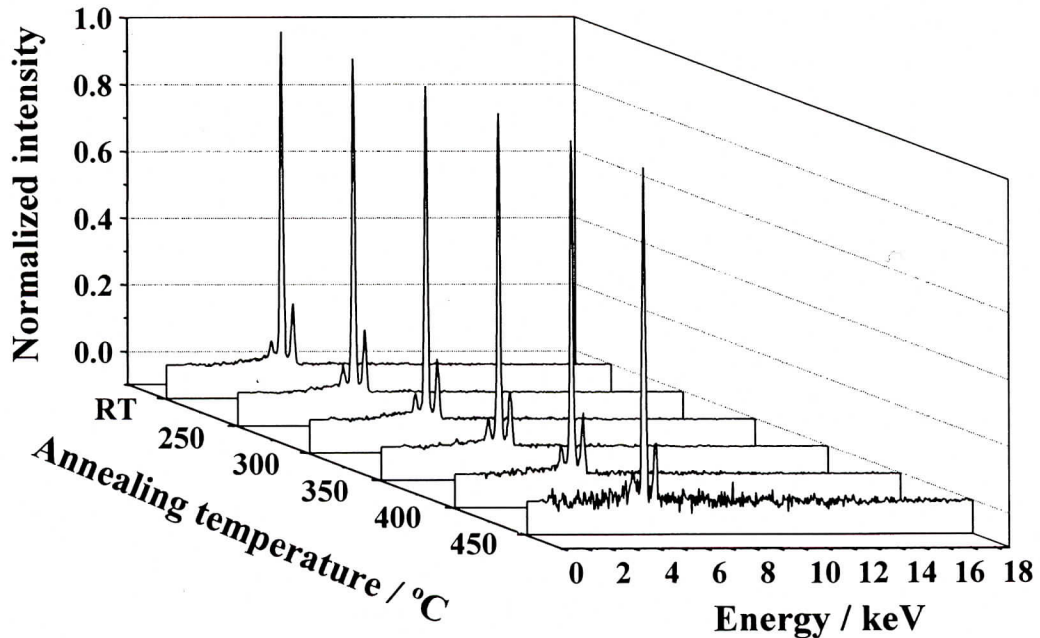The duration of time necessary for desorption was much longer than the critical

Fig. 5 Normalized BIXS spectra of V-4Cr-4Ti alloy after thermal desorption process.

time of tritium diffusion in the sample, which can be roughly estimated by the expression of $L^2/6D_T$, where L is the thickness of samples (0.5 mm), and D_T is the diffusion coefficient of tritium. According to Hashizume et al. [11], the diffusion coefficient of tritium in the present alloy is expressed as

$$D_T = (7.5 \pm 0.2) \times 10^{-4} \exp (- 0.13 \text{ (eV)} /kT),$$

where k is the Boltsmann constant. The critical time was evaluated to be about 10 seconds even at 250 °C and much shorter than 1 h. Hence, it was concluded that desorption rate was controlled not by diffusion process but by surface recombination process. Namely, the trapping effect in the bulk was weaker than the effect of surface barrier against recombination under the present conditions. As shown in Fig. 5, the shape of bremsstrahlung X-ray spectrum after desorption did not show a significant change in comparison with the initial one, although the reduction in tritium content due to desorption resulted in poorer signal-to-noise ratio. The uniform depth profile of tritium should be maintained during desorption process, if desorption rate is fully controlled by the surface process. Hence, this observation is consistent with the above-mentioned conclusion.

4. Summary

In-situ measurements of tritium desorption from a V-4Cr-4Ti alloy were carried out by using β-ray-induced X-ray spectrometry (BIXS). Tritium started to desorb at 350 °C. The period of time required for tritium desorption was much longer than that expected from diffusion coefficient. It was therefore concluded that the tritium release rate was controlled not by diffusion process but by surface recombination process under the present experimental conditions.

Acknowledgements

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