Deuterium retention in V–4Cr–4Ti alloy after deuterium ion irradiation

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Abstract

The deuterium retention properties of vanadium alloy, V–4Cr–4Ti, were investigated by thermal desorption spectroscopy after deuterium ion irradiation. The deuterium ion irradiation was carried out at 380, 573 and 773 K with ion energy of 1.7 keV. Deuterium retained in the sample was desorbed in the forms of D_2, HD, HDO and D_2O. The amount of retained deuterium at 380 K increased with the ion fluence, and did not saturate to a fluence up to 1×10^{19} D/cm^2. In addition, more than 100% of implanted D was retained at high deuterium fluence. The retained amount at 380 K was one and two orders of magnitude larger than graphite and tungsten, respectively. For the irradiation at 773 K, the amount of retained deuterium decreased with increase in ion fluence in the high fluence region, and the retained amount was almost the same as that for graphite or tungsten.
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1. Introduction

Vanadium alloy is an attractive structural material for fusion reactor, because of its low induced radioactivity and the good thermal and mechanical properties at high temperatures [1]. The development of various vanadium alloys and the evaluation of their performances for fusion application have been widely carried out [2]. The vanadium alloy, V–4Cr–4Ti, is a promising material, because it showed excellent mechanical tolerance to neutron damage [2]. One of important concerns in the vanadium alloy is a large retention of tritium (deuterium) introduced by gas absorption and ion implantation. This may become important to the viewpoints of safety, tritium inventory and hydrogen embrittlement. In the present study, the deuterium retention properties of V–4Cr–4Ti alloy sample has been examined by using thermal desorption spectroscopy, TDS. The sample was irradiated by deuterium ions at

temperatures of 380, 573 and 773 K, and the retained deuterium was subsequently measured by TDS.

2. Experiments

V–4Cr–4Ti samples with low impurity contents [3], NIFS-HEAT-1, were prepared by National Institute for Fusion Science (NIFS). The sample size was 25 mm × 5 mm × 0.25 mm. A flow chart of the experimental procedure is shown in Fig. 1. The sample was mechanically polished with Al_2O_3 powder. After that, the sample was degassed at 1273 K for 1 h in an Electron Cyclotron Resonance (ECR) ion irradiation apparatus [4]. Fig. 2 shows depth profile of atomic composition of the degassed sample analyzed by X-ray photoelectron spectroscopy. The surface impurity layer containing oxygen and carbon existed at the surface of the degassed sample. The thickness of the impurity layer was approximately 30 nm. After degassing, the sample was irradiated by deuterium ions at various temperatures at ion energy of 1.7 keV and ion flux of 1×10^{15} D$^+$/cm^2 s. The irradiation temperatures were an ambient temperature (∼380 K), 573 and 773 K. The first wall temperature in ITER is estimated to be approximately 573 K [5]. On the other

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Mechanical polishing of vanadium alloy sample (NIFS-HEAT-1)

Degassing (1273 K, 1hr)

Deuterium ion irradiation (1.7 keV, D⁺)

TDS measurement (RT-1273 K, 0.5 K/s)
→ *Evaluation of deuterium retention*

Deuterium gas absorption (1×10⁻³ Pa)
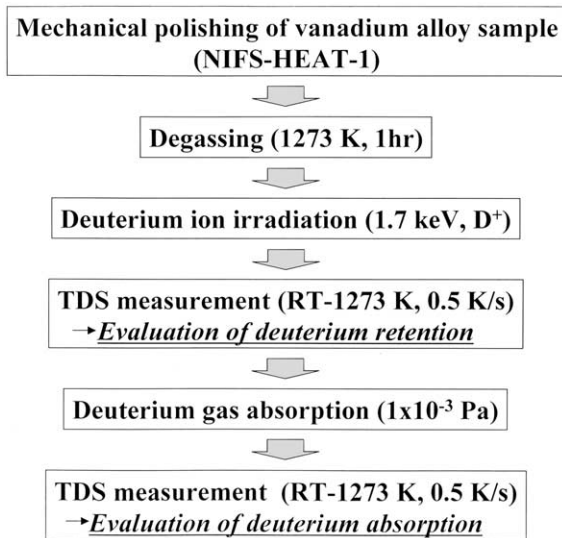
TDS measurement (RT-1273 K, 0.5 K/s)
→ *Evaluation of deuterium absorption*

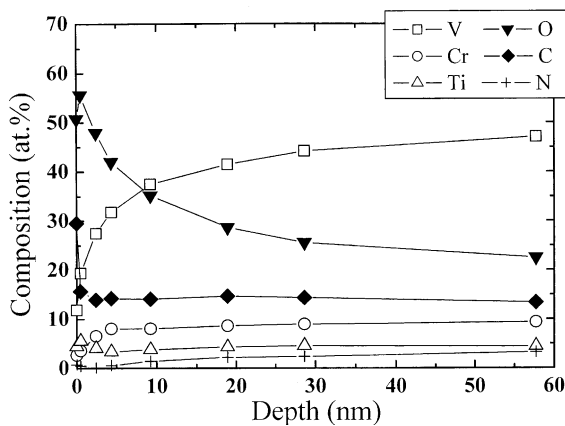Fig. 1. Flow chart of experimental procedure.

Fig. 2. Depth profile of atomic composition of the degassed sample. The atomic compositions were analyzed by X-ray photoelectron spectroscopy.

hand, operating temperatures of blankets using vanadium alloy in a fusion reactor are expected to be from 673 to 923 K [6]. Therefore, we selected this temperature range for the experiments. After the ion irradiation, the amount of retained deuterium in the sample was measured by TDS. The sample was resistively heated to 1273 K with a ramp rate of 0.5 K/s. The sample was held at 1273 K for 60 min. During the heating, the desorption of gas was monitored by a quadrupole mass spectrometer, QMS. The retained amount of deuterium was obtained by integrating the desorption rate for gases containing D over the heating time. The desorption rates of the gases were obtained quantitatively [7] using standard leaks.

Since it is difficult to obtain standard leaks for gases such as HD, HDO and D_2O, the average value of calibration factors for those of D_2 and H_2 was used for HD, and the calibration factor for H_2O was used as the calibration factor for D_2O or HDO. Deuterium gas was also absorbed into the samples during the ion irradiation. In order to evaluate the amount of absorbed deuterium gas during the irradiation, we carried out an absorption experiment for the same sample at the same condition of temperature, pressure and time, but without the irradiation.

3. Results and discussion

Fig. 3(a) shows thermal desorption spectra of gases from the sample after deuterium ion irradiation to a fluence of 5×10^{18} D/cm² at 380 K. Major gases desorbed thermally from the sample after the irradiation were D_2, HD, HDO and D_2O. In particular, the amount of desorbed D_2 was exceptionally large. The desorption spectrum of D_2 had a sharp peak at 650 K and a shoulder at 800 K.

Fig. 3(b) shows thermal desorption spectra of desorbed gases after deuterium gas absorption at 380 K but without irradiation. The pressure of deuterium gas and the fluence of deuterium gas were similar to those for the deuterium ion irradiation experiment for Fig. 3(a). The gas species of D_2, HD, HDO and D_2O were desorbed from the sample, although the desorbed amount was significantly smaller than that for the irradiated sample. This result indicates the retention at the traps induced by the ion irradiation was dominant for the irradiated sample.

Fig. 4 shows thermal desorption spectra of D_2 for V–4Cr–4Ti alloy samples after deuterium ion irradiations at 773 K for several ion fluences. The desorption rates of D_2 gradually increased with the fluence up to 8×10^{18} D/cm², but then the desorption rate at the fluence of 1×10^{19} D/cm² was significantly decreased. Also, the peak temperature at low temperature region became low at the fluence of 1×10^{19} D/cm². This result suggests that, during the irradiation, the recombination coefficient might have increased owing to the reduction of a surface impurity layer containing oxygen and carbon by the ion sputtering [8]. The spectrum for V–4Cr–4Ti alloy samples after deuterium gas absorption at 773 K with a gas fluence of 1.2×10^{20} D_2/cm² is also shown in Fig. 4. Comparison between the spectrum after the ion irradiation and that after the gas absorption shows that the contribution of absorbed deuterium due to D_2 gas is larger at 773 K than for the irradiation at 380 K.

Fig. 5 shows the dependence of the amount of retained deuterium at various temperatures on the deuterium ion fluence. The data shows the amount of deuterium retained only from the ion irradiation, i.e.,
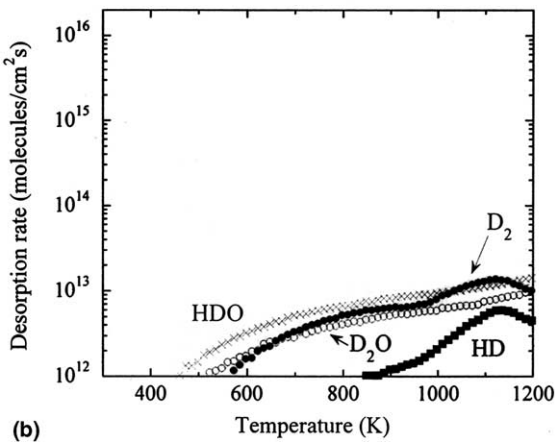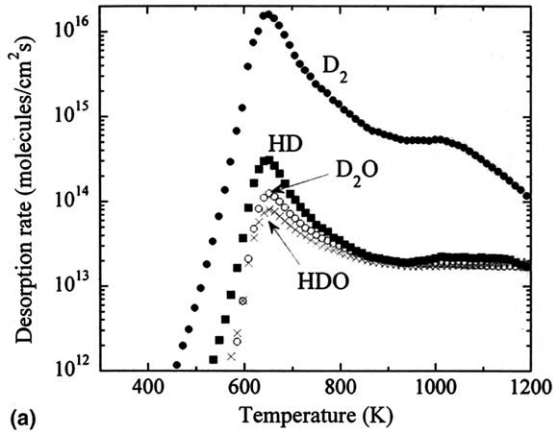
Fig. 4. Thermal desorption spectra of D_2 for V–4Cr–4Ti alloy samples after deuterium ion irradiations at 773 K for several ion fluences. The spectrum for V–4Cr–4Ti alloy samples after deuterium gas absorption at 773 K with a gas fluence of 1.2×10^{20} D_2/cm² is also shown.

Fig. 3. Thermal desorption spectra of gases containing deuterium for V–4Cr–4Ti alloy sample after deuterium ion irradiation at 380 K (a) and after deuterium gas absorption at 380 K (b).

Fig. 5. The amounts of retained deuterium in the vanadium alloy sample, graphite [10] and tungsten as a function of deuterium ion fluence. The amounts of graphite and tungsten at 773 K are the values extrapolated from the data in reference [11].

after the contribution of absorption by the gas phase was subtracted. The amount of retained deuterium in the sample after irradiation at 380 K did not show saturation at the highest fluence and exceeded 100% of the implanted deuterium at high fluence. This result suggests that enhanced absorption from the gas phase may occur during the ion irradiation. The enhancement of the deuterium absorption during the ion irradiation results in an overestimation of deuterium retention in the present study. One of the possible reasons of the enhancement of absorption was the reduction of the surface impurity layer owing to ion sputtering. This layer, containing high oxygen concentration, acts as a diffusion barrier for deuterium [9].

For the case of irradiation at 573 K, the amount of retained deuterium was approximately 1.8×10^{18} D/cm², nearly independent of the ion fluence. At the irradiation temperature of 773 K, the amount of retained deuterium
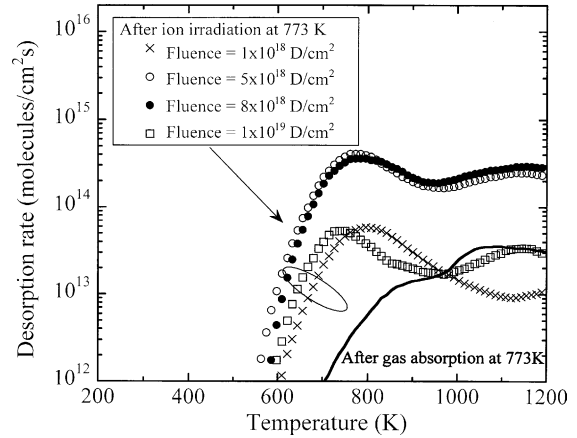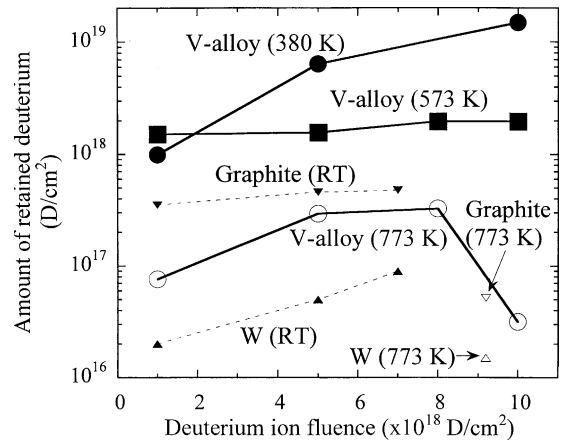
decreased with increase in fluence in the high fluence region, i.e., from 3% to 0.1% of the fluence. This decrease of the amount of retained deuterium may be caused by the reduction of surface impurity layer and the absence of oxygen at the surface, discussed as follows.

Oxygen in the surface impurity layer diffuses into the bulk in the vanadium alloy at 773 K. The barrier effect on deuterium diffusion became weaker owing to absence or decrease of oxygen content at the surface [9]. Consequently, the amount of absorbed D_2 gas during the ion

irradiation is similar to that estimated by the absorption experiment without ion irradiation due to less of oxygen at the surface. This is in contrast to the experiments at 380 K.

In addition, the surface impurity layer may have many lattice defects that can serve as the trapping sites for the deuterium retention. So, the reduction of the impurity layer by the ion sputtering causes a decrease in the number of the trapping site for deuterium. In addition, the more deuterium not from ion implantation (absorbed deuterium from the gas phase) may occupy more trapping sites in the surface layer at 773 K than that at 573 K or ambient temperature (Figs. 3 and 4). Hence, the amount of deuterium retained only from ion implantation decreases at the high fluence region.

In Fig. 5, the amounts of retained deuterium in isotropic graphite [10] and polycrystalline tungsten were also plotted. The amounts of retained deuterium in graphite and tungsten at 773 K are values extrapolated from the data in reference [11]. The amount retained in the vanadium alloy at ambient temperature was one and two order of magnitude larger than that for graphite and tungsten, respectively. This difference in the amount of retained deuterium between these samples depends on the trapped state. For graphite, implanted D mainly binds with broken π-bonds of the graphite. Therefore, the atomic ratio, D/C, becomes approximately 0.4 [12]. For tungsten, deuterium is trapped in defects [13]. In addition, tungsten hydride does not form. The vanadium alloy sample has a high solubility for deuterium at low temperatures [14], and vanadium hydride may form. At the irradiation temperature of 773 K, which is a possible operating temperature of the blanket, the retained amount of deuterium for the vanadium alloy sample was almost the same as that for graphite or tungsten at high fluence region.

4. Conclusions

The deuterium retention properties of vanadium alloy, V–4Cr–4Ti, were investigated by thermal desorption spectroscopy after deuterium ion irradiation. The amount of retained deuterium in the vanadium alloy sample irradiated at 380 K did not saturate up to 1×10^{19} D/cm^2, and then more than 100% of implanted D was retained in the samples at high fluences. This result may indicate the underestimation of the absorption amount from the gas phase during the ion irradiation experiment, which was estimated by the absorption experiment without ion irradiation. The enhanced absorption may be caused by the reduction of the surface impurity layer.

In addition, the amount of retained deuterium at 380 K was one and two orders of magnitude larger than that of graphite and tungsten, respectively. On the other hand, when the deuterium ion irradiation was carried out at 773 K, which temperature was chosen to simulate the retention of hydrogen isotopes in the blanket of the fusion demonstration reactor, the amount of retained deuterium in the vanadium alloy sample was 0.1–3% of the total deuterium ion fluence, similar to that in graphite or tungsten.

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