# Deuterium retention of V–4Cr–4Ti alloy exposed to the JFT-2M tokamak environment

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## Abstract

Vanadium alloy (V–4Cr–4Ti) samples were exposed to JFT-2M tokamak environment during deuterium plasma discharges including 200 divertor shots for 9 months operation period. In this environment, the samples are not directly exposed to deuterium plasma, and are exposed to high-energy particles, i.e., D and $D_2$ including impurity species. The deuterium amount retained was $2 \times 10^{17}$ $D/cm^2$ (1.3 wppm), which is only one order of magnitude larger than that found in the exposed SS304 sample. This concentration is sufficiently low not to cause the hydrogen embrittlement. A layer about 200 nm which was found to contain Ti, O, C, Fe and Cr was observed on the surface of the exposed sample. To investigate the effect of oxidation unexposed V-alloy samples were oxidized under a condition of low oxygen pressure (0.05 Pa) and low temperature ($\leqslant 723$ K). After the oxidation, titanium segregation in the surface region was observed. The content of absorbed hydrogen in the oxidized sample having a thick Ti-oxide layer ($\geqslant 100$ nm) was one order of magnitude smaller than that of unoxidized sample under a given absorption condition. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Vanadium alloys have been proposed as structural materials for fusion reactor because of their low neutron activation and good thermal and mechanical properties in the high temperature region [1]. For fusion application, research and development had been widely conducted [2]. One important concern is the embrittlement of V-alloy due to oxygen [3] and hydrogen absorption. DiStefano et al. [4] reported that the embrittlement of V-alloy occurs, when the amount of absorbed hydrogen exceeds approximately 400 wppm for pure V-alloy and 35–160 wppm for V-alloy with high oxygen concentration. Oxygen and hydrogen have a strong synergetic effect on the embrittlement of

V-alloy. In addition, it is well known that the absorption of hydrogen is strongly affected by impurities on the surface.

In the present study, V–4Cr–4Ti samples were exposed to JFT-2M tokamak environment for a long duration. Since the samples were placed in a region far from the divertor plasma, the samples are not directly exposed to deuterium plasma, but the samples are exposed to energetic particles. The amount of absorbed deuterium and the depth profiles of atomic composition of the exposed samples were examined by thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The hydrogen (deuterium) content of exposed V-alloy sample was compared with those of the unexposed samples and of the exposed SS304 samples.

The effect of surface oxidation on hydrogen absorption and desorption behaviors for V-4Cr-4Ti alloys was also investigated under a hydrogen pressure of 10 Pa.

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## 2. Experimental

The V–4Cr–4Ti slab samples were manufactured by General Atomics (GA) [5] and had a size of 10 mm × 10 mm × 1 mm. Two slab samples were placed on a sample bed provided with a heater of SS304 together with other test samples for the investigation of the mechanical properties [6]. The sample bed was placed under the baffle plate in the outward region of JFT-2M tokamak which was far from the divertor plasma as shown in Fig. 1. In this region, the samples are exposed to high-energy particles, i.e., D and $D_2$, including impurity species. These samples were received to about 2200 discharges including 200 lower-single-null divertor shots over a period of 9 months operation. Typical operation parameters were: plasma current, $I_p = 200$ kA; toroidal magnetic field, $B_t \sim 1.3$ T; electron density and electron temperature near the divertor plate, $n_e = (1–4) \times 10^{19}$ m$^{-3}$, $T_e = 5–15$ eV; average discharge duration, $t_{dis} = 1$ s; typical neutral pressure, $P_{dis} = 0.1–0.2$ Pa. The sample temperature was kept at ∼573 K for lower-single-null divertor shots.

After the exposure to tokamak plasma, the V-alloy and the sample holder of SS304 having a size of 48 mm × 5 mm × 2 mm were received. The deuterium retained in the V-alloy and the SS304 samples was examined by thermal desorption spectroscopy (TDS). These samples were heated from RT up to 1273 K with a constant ramp rate of 0.5 K/s, and held for 60 min at 1273 K. The amounts of hydrogen retained were determined by integrating the desorption rate for $H_2$, $D_2$ and HD over time. The pumping speed ($S$) and the sensitivity of the mass spectrometer ($K$) for $H_2$ and $D_2$ were measured using a standard leak. For HD, an average value between $H_2$ and $D_2$ was used. To compare the absorption behavior of energetic deuterium particles and thermal $D_2$ gas, an absorption experiment with $D_2$ was also conducted for unexposed V-alloy under similar divertor discharge conditions, i.e., $T_{ab} = 573$ K, $P_{D2} = 0.2$ Pa, $t_{ab} = 30$ min.
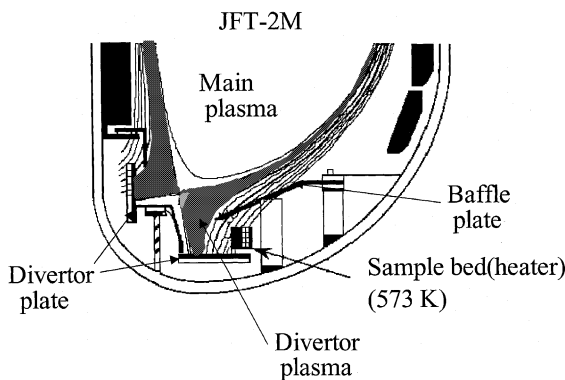
The effect of a surface oxidation on the absorption behavior of hydrogen of the V-alloy was also investigated. After mechanical polishing and degassing at 1273 K for 10 min under vacuum ($10^{-6}$ Pa), the sample was oxidized in the TDS apparatus by changing the oxidation temperature from 373 to 723 K at $P_{O_2} = 0.05$ Pa over a period of $t_{oxi} = 10$ min. Then, the absorption hydrogen was conducted under glow discharge conditions, i.e., $T_{ab} = 523$ K, $P_{H_2} = 10$ Pa, $t_{ab} = 60$ min. After that, the absorption content of hydrogen was determined by TDS.

The surface morphology, atomic composition and chemical bonding states of the exposed and oxidized samples were analyzed by scanning electron microscopy (SEM), AES and XPS.

## 3. Results

### 3.1. Deuterium retention and surface properties of a V-alloy exposed in JFT-2M tokamak environment

#### 3.1.1. Deuterium retention in an exposed sample

Fig. 2 shows thermal desorption spectra of gases desorbed from the exposed V-alloy sample. Major gas species were $H_2$, HD, $D_2$, $H_2O$, CO and $CO_2$. It is seen that the desorption rates of $H_2$, HD, $D_2$ significantly increased at a temperature of about 670 K, and reached a maximum at about 833 K. The amount of desorbed $H_2$ was 8.2 wppm, which is approximately half of that of unexposed sample (17.5 wppm), since the samples were heated at 573 K during the exposure. The desorption amounts of HD and $D_2$ were 1.7 and 0.12 wppm, respectively. The total D content versus geometrical surface area for the exposed V-alloy was $2 \times 10^{17}$ D/cm$^2$, which corresponds to deuterium concentration of 1.3 wppm. The hydrogen content was 10.02 wppm, which was smaller than that before the exposure. The value was sufficiently low not to cause hydrogen embrittlement [4]. The mechanical properties of the exposed sample
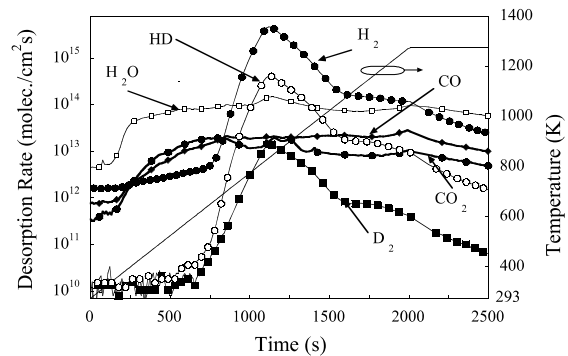


Fig. 1. Location of the sample bed in the JFT-2M tokamak device.



Fig. 2. Thermal desorption spectra of gases with a ramp rate of 0.5 K/s from the V–4Cr–4Ti alloy exposed in JFT-2M.

were not significantly affected by the exposure [6]. The deuterium content was approximately one order of magnitude larger than that of the exposed SS304 sample ($1.6 \times 10^{16}$ D/cm$^2$). The deuterium content of the V-alloy after D$_2$ gas absorption was 0.085 wppm($= 1.28 \times 10^{16}$ D/cm$^2$). On the assumption that deuterium is mainly retained in the samples during divertor shots, i.e., no deuterium absorption occurs during main discharges at RT, this result indicates that the energetic deuterium particles were retained to a higher degree in the sample than thermal D$_2$ molecules.

### 3.1.2. Surface properties of exposed sample

Fig. 3 shows the atomic depth profile of the exposed V-alloy sample as obtained by AES analysis. The depth scale was estimated from the sputtering yield of V with 3 keV Ar$^+$. The concentration of C, Ti, Fe and O at a depth of 100 nm (in the deposition layer) were formed to be 33 at.%, 28 at.%, 16 at.% and 19 at.%. The atomic concentration of carbon was evaluated using the relative sensitivity factor of carbide [7]. The thickness of the deposition layer was about 200 nm. In the JFT-2M device, a Ti-flashing was used to reduce the residual gas. But Ti did not directly deposit on the sample during the Ti flashing because the sample bed is located behind the baffle plate. It is believed that the impurity elements including Ti, resulted from a redeposition of species eroded by the plasma from the first wall, divertor or baffle plate materials. Other metal impurities such as Cr, should have been deposited on the surface. However a small concentration of Cr could not be clearly assigned due to overlapping with an Auger transition of V. By XPS analysis, however a very small amount of Cr was observed [6]. The color of the surface of the exposed specimen was red–yellow suggesting formation of metal oxides, e.g., TiO$_x$ and FeO$_x$. On the other hand, the shape
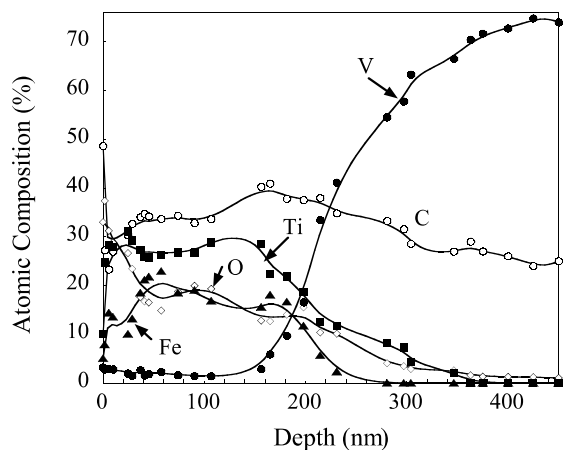
of C Auger differential spectrum (d$N$/d$E$) was similar to that of transition metal-carbide [7]. Accordingly, it is presumed that Ti-oxide, Fe-oxide and TiC were formed in the deposition. The thickness of the interface of the exposed sample was about 100 nm which was large in comparison to the unexposed sample (30 nm). At a depth of more than 300 nm, high concentrations of carbon were observed. A similar result was observed for an unexposed sample. Based on XPS analysis, the binding energies ($E_B$) of C1s near the surface of the unexposed sample corresponded to that of VC [9] as shown in Fig. 4(c). Therefore, both AES and XPS analyses indicate the presence of vanadium carbide near the surface region.

### 3.2. Effect of surface oxidation on the hydrogen absorption behavior

### 3.2.1. Surface properties of oxidized and unoxidized samples

The effect of surface oxidation on the hydrogen absorption behavior of the V-alloy was investigated by changing of oxidation temperature.
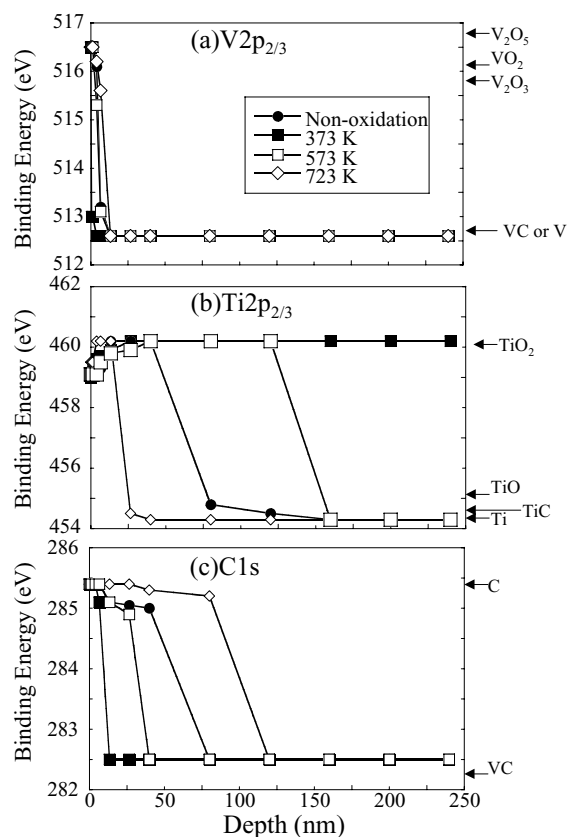


Fig. 3. Depth profiles of atomic composition for the exposed V-alloy sample measured by AES analysis.



Fig. 4. Changes of the binding energies for V 2p$_{3/2}$ (a), Ti 2p$_{3/2}$ (b) and C1s (c) near the surface of unoxidized and oxidized V-alloys.

Table 1
The concentration of Ti and O, the thickness of Ti-oxide layer and graphite layer and the absorption amount of hydrogen ($C_{ab}$) for unoxidized and oxidized V-alloy samples for various oxidation temperatures, $T_{oxi}$

| $T_{oxi}$ (K) | Ti conc.* (at.%) | O conc.* (at.%) | Ti-oxide layer (nm) | Graphite layer (nm) | $C_{ab}$ (wppm) |
|---|---|---|---|---|---|
| Non-oxidation** | 1–2 | 23 | 60∼80 | 50–80 | 0.601 |
| 373 | 7–10 | 27 | >250 | 13 | 0.062 |
| 573 | 4–6 | 33 | ∼140 | ∼40 | 0.075 |
| 723 | 2–4 | 35 | ∼30 | 90–130 | 46.700 |

* O and Ti conentrations were measured at a depth of more than 150 nm and near surface region, respectively.
** This sample was heated at 1273 K for 10 min in vacuum of $\sim 10^{-6}$ Pa.

After the oxidation, three characteristic surface properties were found, i.e., (1) the carbon concentration significantly changed from 12 at.% to 1.5 at.%, (2) the titanium concentration near the surface region increased from ∼1 at.% to ∼10 at.% , and the Ti segregation increased at lower oxidation temperatures, (3) and the oxygen concentration at the surface of every sample was almost the same. The oxygen concentration increased slightly with increasing oxidation temperature at depths above 150 nm. The results are summarized in Table 1.

Fig. 4 shows the binding energies ($E_B$) [8,9] for V $2p_{3/2}$, Ti $2p_{3/2}$ and C1s in the near surface of the oxidized and unoxidized samples as a function of the thickness. It is seen that the $E_B$ of V $2p_{3/2}$ changed from 516.5 (V-oxide) to 512.7 eV (VC and/or V) within a depth of 25 nm in every sample. Similar result was observed for Cr. The $E_B$ of Ti$2p_{3/2}$ changed from 460.2 (TiO₂) to 454.3 eV (TiC and/or Ti). The thickness of the Ti-oxide layer largely varied with the oxidation temperature (Table 1). It is seen that, (1) the thickness of the Ti-oxide layer decreases with increasing oxidation temperature, and (2) that the oxide layer of the sample oxidized at 673 K was thinner than that of the unoxidized sample. Under the condition of high temperature and low oxygen pressure, oxygen quickly diffuses into the bulk. Consequently, a thick oxide layer could not be formed in the near surface region. In every sample, the $E_B$ of C1s varied from graphite to vanadium carbide. The thickness of the graphite layer increased with oxidation temperature (Table 1).

### 3.2.2. Absorption and desorption properties of hydrogen for oxidized sample

Fig. 5 shows the thermal desorption curves of hydrogen of oxidized and unoxidized samples. In comparison with the case of an unoxidized sample, the peak temperature ($T_p$) of surface-oxidized samples at 373 and 573 K shifted to a higher temperature region, i.e., >1273 K. It is presumed that the diffusion coefficient of hydrogen becomes small due to the effect of oxide thickness, and/or the recombination rate of hydrogen atom on the surface is reduced by a small content of hydrogen.

The amount of absorbed hydrogen, $C_{ab}$ is summarized in Table 1. The $C_{ab}$ values decreased with in-
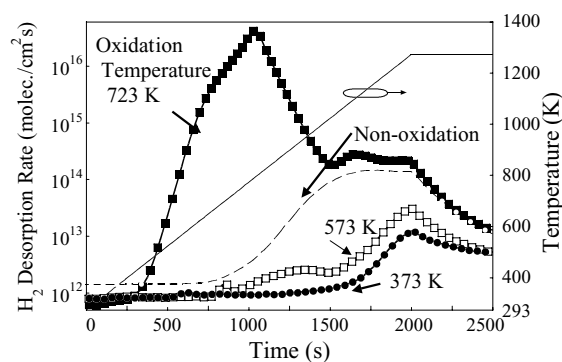


Fig. 5. Thermal desorption spectra of hydrogen with a ramp rate of 0.5 K/s from surface oxidized and unoxidaized V-alloys after hydrogen absorption.

creasing thickness of the Ti-oxide layer. The $C_{ab}$ values of the samples oxidized at 373 and 573 K are one order of magnitude smaller than that of unoxidized sample under a given absorption condition (523 K, 10 Pa, 60 min). These results indicate that the Ti-oxide layer is an effective diffusion barrier for hydrogen.

However, in the case of the sample oxidized at 723 K, the $C_{ab}$ value is about 80 times larger than the unoxidized sample, and $T_p$ is observed at lower temperature (∼790 K). Presumably the thickness of the Ti-oxide layer of this sample becomes thin as shown in Fig. 4 and Table 1. Shkolnik et al. [10] reported that the diffusion coefficient of hydrogen in V-alloy becomes large after the oxidation and annealing. Therefore, another reason for the large content of hydrogen observed in the sample oxidized at 723 K is the increase of diffusion coefficient. It was also reported that the critical concentration of hydrogen drastically decreased with high oxygen content [4]. If V-alloy is exposed to oxygen for a long time under high temperature condition (>723 K), the absorption rate of hydrogen increases gradually and the mechanical properties degrade due to hydrogen embrittlement. Thermal stability of the Ti-oxide layer is therefore very important for the embrittlement and mechanical properties.

## 4. Conclusion

For V–4Cr–4Ti alloy samples exposed to tokamak environment and the surface oxidation, the deuterium (hydrogen) content, the deposition of impurity near the surface and the effect of oxidation on hydrogen absorption behavior were investigated. The main results were:

1. During 200 divertor discharge shots, out of 2200 total discharge shots, a small content of deuterium (1.3 wppm) was retained in the V-alloy, and was sufficiently low not to cause hydrogen embrittlement.
2. The absorption rate of hydrogen in a V-alloy with a thick Ti-oxide layer (>100 nm) was one order of magnitude smaller than that of the unoxidized sample at 523 K.
3. At high oxidation temperatures, the hydrogen absorption rate becomes large.

On the viewpoint of hydrogen content, even if V-alloy is exposed for further long term, no embrittlement due to hydrogen will occur. In addition, Ti-oxide layer or deposition acts as a diffusion barrier of hydrogen under the glow discharge conditioning of the tokamak. In the temperature range of application of V-alloys [2], i.e., 400–600°C, the presence of oxygen will strongly enhance the absorption rate of hydrogen. Further investigations are needed for the developments of V-alloy.

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