



# Suppression of hydrogen absorption to V–4Cr–4Ti alloy by TiO<sub>2</sub>/TiC coating

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## Abstract

Titanium oxide film was coated on the surface of a V–4Cr–4Ti alloy to reduce hydrogen absorption at low temperature region. Titanium oxide was deposited by rf reactive magnetron sputtering with a titanium target using oxygen as sputter gas. The film consisted of a mixture of TiO<sub>2</sub> and TiC. The content of TiO<sub>2</sub> was approximately 80%. The atomic composition remained the same in the temperature range below 873 K. The film thickness also remained the same in the temperature region below 773 K. At the temperature higher than 973 K, the oxygen concentration decreased due to diffusion into the bulk of V-alloy, and the carbon concentration increased due to diffusion from the bulk of V-alloy. The hydrogen absorption rate of Ti-oxide coated V-alloy decreased with increase of the film thickness. In the case of the film with the thickness of 0.5 μm, the absorption rate was much smaller than that of non-coated V-alloy at the absorption temperature of 573 K.

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## 1. Introduction

Vanadium alloy has been proposed as a structural material for fusion reactors because of its lower neutron induced activation and more rapid decay than other candidate materials and good thermal–mechanical properties in the high temperature region [1]. For the fusion application, research and development have been widely conducted for the use of V-alloy [2,3]. One of important concerns is embrittlement of V-alloy due to hydrogen absorption. The hydrogen absorbs into V-alloy by exothermic reaction, and it was reported that the equilibrium absorption amount of hydrogen in the V-alloy was almost the same as that in pure V [4,7]. The absorption amount becomes large at low temperatures

and high hydrogen pressures. Therefore, embrittlement of V-alloy may occur when the V-alloy is exposed to hydrogen under high pressure and low temperature environment for a long time period. It was reported that embrittlement of V-alloys are affected by oxygen [4–7]. In these reports, it was found that, (1) the ductility of V–4Cr–4Ti alloy without oxygen reduced drastically at the hydrogen concentrations ( $C_H$ ) > 400–500 wppm and complete embrittlement occurred at  $C_H$  > 700 wppm, and (2) the embrittlement of V–4Cr–4Ti alloy with oxygen pickup of 850 wppm at 500 °C, the embrittlement occurred at  $C_H$  of 35–130 wppm [5], and (3) the embrittlement of V–5Cr–5Ti alloy with the oxygen pickup of 172 wppm occurred at  $C_H$  ~ 45 wppm [4,5], and (4) deterioration of the ductility of V–4Cr–4Ti alloy due to hydrogen absorption were different from grain size, temperature of heat treatment [4,7]. In our previous study, titanium segregation in the surface region was observed after oxidation of the V–4Cr–4Ti alloy at low temperature [8]. In this case, titanium was oxidized as

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TiO<sub>2</sub>. The hydrogen absorption rate of such the oxidized sample was one order of magnitude smaller than that of non-oxidized sample.

In the present study, titanium oxide was coated on the surface of V–4Cr–4Ti alloy to reduce hydrogen absorption in the low temperature region. First, thermal stability of the Ti-oxide film was examined by heating in vacuum. The heating temperature was changed in the range from 573 to 973 K. After the heating, the changes of the atomic composition and film thickness were measured by ex-situ Auger electron spectroscopy (AES) analysis. In order to examine the effect of the coating on hydrogen absorption, Ti-oxide coated V–4Cr–4Ti sample was exposed in hydrogen atmosphere for a long time. The absorption rate of hydrogen was measured, and compared with that of non-coated sample. The samples with different Ti-oxide film thickness were prepared, and the dependence of the hydrogen absorption rate on the film thickness was obtained.

## 2. Experiments

V–4Cr–4Ti sample (NIFS-HEAT-1) with low impurity contents [9], was prepared by National Institute of Fusion Science, NIFS, and the sample size was  $10 \times 10 \times 1$  mm<sup>3</sup>. After mechanical polishing and degassing at 1273 K for 60 min in vacuum ( $\sim 10^{-6}$  Pa), the titanium oxides coating was made on V-alloy in an rf magnetron sputtering apparatus with a Ti target. Oxygen was used as the sputtering gas. The background pressure of the sputtering apparatus was approximately  $2 \times 10^{-4}$  Pa. The rf power was 1 kW. The gas flow rate and pressure of oxygen were kept 2 sccm and 3 Pa, respectively. The temperature of the sample was approximately 523 K during the coating. Ti-oxide was coated on all surfaces of the V-alloy. The thickness of the Ti-oxide film was measured by using a surface profile meter. The growth rate of Ti-oxide film was 4.2 nm/min. The thickness of Ti-oxide film was changed from 0.12 to 1.1  $\mu$ m. The crystal structure and depth profile of atomic composition of the Ti-oxide films were analyzed by X-ray diffraction with CuK $\alpha$  ray and ex-situ AES, respectively. In the AES analysis, Ar<sup>+</sup> ion with energy of 3 keV was used for sputtering.

The thermal stability of Ti-oxide film was examined by heating. The heating temperature was changed from 573 to 973 K. The heating time was 5 h. After the heating, the changes of the atomic composition and film thickness were measured by ex-situ AES.

In order to absorb hydrogen into the Ti-oxide coated sample, the sample was extracted from the sputtering apparatus, and installed in a TDS apparatus. The ultimate pressure of the TDS chamber was approximately  $1 \times 10^{-6}$  Pa. Hydrogen gas was admitted into the chamber with a volume of  $1.2 \times 10^{-3}$  m<sup>3</sup>. Before hydrogen

absorption, the initial hydrogen pressure was kept 10 or 40 Pa. The equilibrium hydrogen concentration of V-alloy with high impurity concentration exceeds the critical value for the embrittlement if the temperature is lower than approximately 700 K and the hydrogen pressure is 10 Pa, as it is shown in the next section. In addition, the equilibrium concentration increases with decrease of heating temperature. Then, in the present experiment, the absorption temperature was kept constant, 573 K, by heating the sample using an infrared light furnace. During the heating, the change of the pressure was monitored by a diaphragm vacuum gauge. The absorption amount of hydrogen was calculated from pressure difference.

## 3. Results

### 3.1. Thermal stability of titanium oxide film

Fig. 1 shows the depth profiles of atomic composition of the Ti-oxide coated sample before (a) and after the heating at 973 K (b). The atomic composition of Ti, O, C and N in the Ti-oxide film were 35, 55, 7 and 3 at.%, respectively. Since Auger spectrum of C was carbide type, the atomic concentration of carbon was determined using the relative sensitivity factor of carbide [10]. The spectrum of N overlapped with typical spectrum of Ti. Then, we tried to separate N and Ti by using other spectrum of Ti. A small content of Cr contained in the V-alloy was not clearly observed due to overlapping with spectra of O and V. By XPS analysis, the concentration of Cr in the surface region of V-alloy was obtained as 9 at.%. The atomic composition of Ti contained in the V-alloy was also obtained as 4 at.%. The atomic composition of the film was roughly uniform in the entire film region (Fig. 1(a)). If we assume that all C atoms bind to Ti atoms as TiC, the atomic ratio of O to Ti becomes O/Ti = 2, i.e. TiO<sub>2</sub> is formed. The content of TiO<sub>2</sub> was approximately 80%. From XRD results, the diffraction pattern of a tetrahedral TiO<sub>2</sub> (Anatase TiO<sub>2</sub>) oriented to (200) was observed. The thickness of TiO<sub>2</sub> film measured by a surface profile meter was 120 nm. After the heating at 973 K for 5 h in vacuum, we observed the change of atomic composition. The atomic composition of oxygen largely decreased from 55 to 37 at.% and that of carbon largely increased from 7 to 23 at.%. The changes of C and O resulted in the increase of atomic composition of Ti. In the present study, L<sub>3</sub>M<sub>23</sub>M<sub>45</sub> Auger transition of Ti (Auger electron energy is 419 eV) which does not overlapped to N was used for the calculation of the atomic composition. Although this Auger transition of Ti is affected by oxygen, we used a relative sensitivity of Ti in TiO<sub>2</sub> against all heated samples. Therefore, in the case of the sample heated at 973 K, there is a possibility that the sensitivity of Ti is different from that of TiO<sub>2</sub>, i.e.

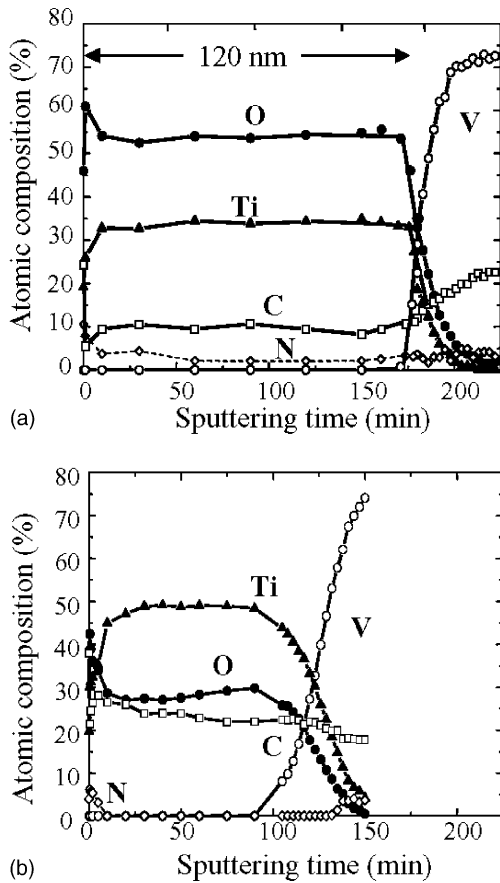


Fig. 1. Depth profiles of the atomic composition of titanium oxide coated samples before (a) and after heating at 973 K for 5 h (b).

the sensitivity became small, and the atomic composition of Ti may be large. Since it is very difficult to determine the sensitivity of Ti with different concentration of oxygen, we used the sensitivity of Ti in  $TiO_2$ . Even if the Ti concentration of the sample heated at 973 K is the same as that of as-coated sample, it is clear that the oxygen concentration decreased and the carbon concentration increased after heating.

Fig. 2 shows the atomic composition at the center of the Ti-oxide film as a function of the heating temperature. In the temperature range below 873 K, the atomic composition of oxygen decreased and that of carbon increased with increase of the heating temperature. At the temperature higher than 900 K, the changes of the atomic composition became large. From the depth profiles of oxygen and carbon, it is seen that the oxygen diffused into the V-alloy, although the carbon diffused in the Ti-oxide film from the V-alloy. The XPS analysis showed that the carbon was contained in the V-alloy as vanadium carbide.

Based on the assumption that sputtering yield of  $Ar^+$  ion remains the same for the heated sample, apparent

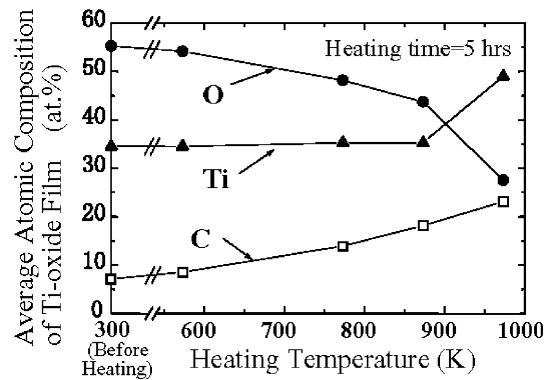


Fig. 2. Atomic composition of Ti-oxide films at a center of the film as a function of heating temperature.

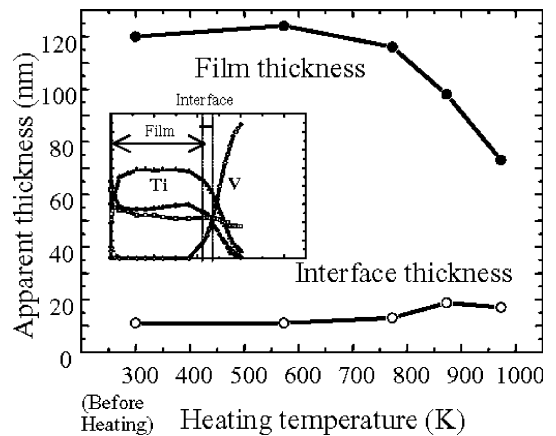


Fig. 3. Apparent thickness of Ti-oxide films as a function of heating temperature.

film thickness of the sample after heating was obtained by sputtering time. Fig. 3 shows the apparent thickness of Ti-oxide film and the thickness of the interface between the coating and V-alloy as a function of the heating temperature. The depth of the film was estimated by comparing sputtering time for the heated sample with that for the sample before heating. The thickness remained the same after the heating at the temperature below 773 K. At the temperature higher than 800 K, the thickness decreased. The thickness of the interface increased at temperature higher than 800 K. However the decrease of the thickness of the coating was considerably larger compared with that of the interface. As Ti is not emitted from the coatings becomes of low vapor pressure at 973 K, Ti must diffused into the V-alloy to decrease the thickness of the coating. But the thickness of the interface slightly increased. From Figs. 1 and 2, the atomic composition of the coating changed after heating. Especially, after heating at 973 K, the

coating was consisted of TiO + TiC or Ti + O + C. In this case, the sputtering yield of the coating might change. Therefore, there is a possibility that the thickness of the coating after heating was overestimated. Although the thickness of the coating heated at higher temperature can not accurately evaluate, at least, the thickness of the coating remained the same in the temperature range below 773 K. From the results of the atomic composition and the thickness of the coating, it is regarded that the Ti-oxide coating is stable at the temperature lower than 773 K.

### 3.2. Hydrogen absorption of Ti-oxide coated V-alloy

To investigate the reduction of hydrogen absorption by Ti-oxide coating, Ti-oxide coated samples with different film thickness were prepared. The deposition was repeated to coat all surfaces of the V-alloy. The thickness of Ti-oxide film was changed from 0.13 to 1.1  $\mu\text{m}$ . Fig. 4 shows the change of the hydrogen pressure for non-coated and Ti-oxide coated samples as a function of absorption time. The initial pressure of hydrogen was 40 Pa. After that, the sample was heated up to 573 K with a ramp rate of 200 K/min. The pressure of the chamber increased due to gas desorption from the sample, because the chamber was not evacuated by a pump. Fig. 5 shows a typical thermal desorption spectrum of gases desorbed from the Ti-oxide coated sample. At the temperature range around 573 K, main desorbed gas species were H<sub>2</sub>O, CO and CO<sub>2</sub>, but H<sub>2</sub> did not desorb because the V-alloy was heated at 1273 K for 60 min before coating. Therefore, hydrogen did not contain in this desorption. In the beginning of absorption, the pressure of the chamber is determined by both the desorption and the absorption. Therefore, the absorption rate seems apparently zero at the beginning of the absorption experiment. It was found that the pressure decreased lin-

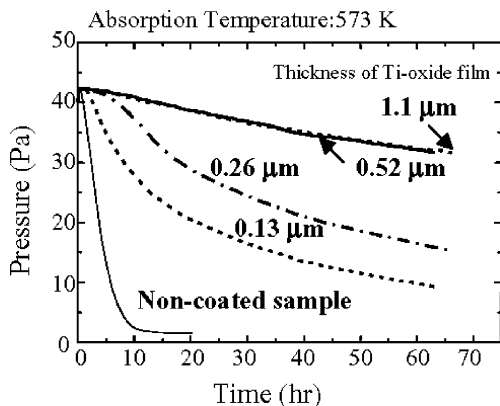


Fig. 4. Change of hydrogen pressure of Ti-oxide coated and non-coated samples as a function of absorption time. Initial pressure = 40 Pa.

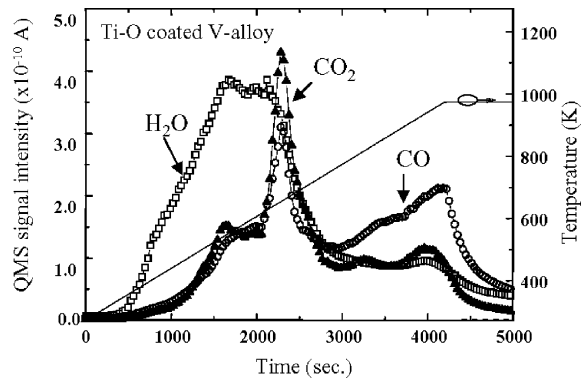


Fig. 5. Typical thermal desorption spectrum of the Ti-oxide coated sample with Ti-oxide thickness of 120 nm.

early with the absorption time at an initial stage of absorption ( $P < 40$  Pa), and then the change of pressure became small. In the case of non-coated sample, the pressure rapidly decreased with the absorption time, and became constant, 1.52 Pa, after 10 h. The amount of adsorbed hydrogen was obtained and the hydrogen concentration was estimated as 58.5 wppm, which was the same as the equilibrium concentration of H in pure V at 1.52 Pa. Here, the equilibrium concentration of pure V was calculated by using Siverts' law. This amount of adsorbed hydrogen in non-coated V-alloy was also confirmed by thermal desorption spectroscopy. For the Ti-oxide coated samples, it is seen that the absorption rate of hydrogen decreased with increase of the film thickness. For the reduction of the hydrogen absorption rate, there may be reasons as follows: (1) the recombination coefficient of hydrogen becomes larger on the surface of the Ti-oxide, and (2) the diffusion coefficient of H in Ti-oxide film is much smaller than that in V-alloy. However, the absorption rate of coated sample with the thickness of 1.1  $\mu\text{m}$  was almost the same as that of 0.52  $\mu\text{m}$ . For the sample with the thickness of 1.1  $\mu\text{m}$ , surface roughness was measured by a surface profile meter. In this film, several cracks with the size of the sub-micron were observed. If a more dense and thick Ti-oxide film is coated on the V-alloy, the hydrogen absorption rate may be more reduced.

The gradient of pressure decrease in the linear region,  $\Delta P/\Delta t$ , for the Ti-oxide coated samples with the thickness of 0.5 and 1.1  $\mu\text{m}$  became approximately 3 orders of magnitude smaller than that of non-coated sample, i.e. the Ti-oxide coating was largely reduced the absorption rate. Thus, the lifetime of V-alloy determined by hydrogen absorption can be largely lengthened by Ti-oxide coatings.

### 3.3. Equilibrium hydrogen concentration of V-alloy

Since the V-alloy contains contents of Ti and Cr, the equilibrium hydrogen concentration of V-alloy may

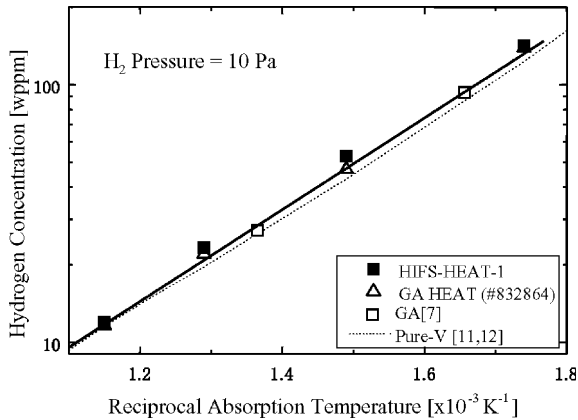


Fig. 6. Equilibrium concentration of hydrogen of V-4Cr-4Ti samples vs. temperature.

differ from that of V-metal. The equilibrium concentration was measured for V-alloys prepared by NIFS and GA, and this value was compared with the value for pure V [11,12]. The temperature was changed from 573 to 873 K in the measurements. Fig. 5 shows the equilibrium concentration ( $C_{eq}$ ) of hydrogen as a function of absorption temperature at 10 Pa. These data were obtained by extrapolating the experimentally measured concentrations to those at 10 Pa, using Sieverts' law. The hydrogen concentration in NIFS-HEAT-1 V-alloy, and that in V-4Cr-4Ti alloy (GA-HEAT,#832864) both measured in the present study, were compared with the data reported by Röhrig et al. [7] and data of pure V [11,12]. It is found that the equilibrium hydrogen concentration of V-4Cr-4Ti alloy is almost the same as that of pure V. Since the critical hydrogen concentration for embrittlement of V-4Cr-4Ti alloy is reported as 400 wppm in the case of pure V-alloy and 35–160 wppm in the case of oxidized V-alloy with high concentration, the embrittlement does not occur in the environment with the pressure lower than 1 Pa and temperature higher than 673 K. However, V-alloy may be used in the environment with the temperature below 673 K. In this case, the Ti-oxide coating is quite effective to reduce the hydrogen absorption rate, or to lengthen the lifetime of the construction (Fig. 6).

#### 4. Conclusion

Titanium oxide was coated on the surface of a V-4Cr-4Ti alloy to reduce the hydrogen absorption rate in the low temperature region. Thermal stability of Ti-oxide and the absorption rate of hydrogen were investigated. The major results were as follows:

- (1) The Ti-oxide was thermally stable at the temperature range lower than 773 K from the viewpoint of the atomic composition and thickness of the coating.
- (2) The hydrogen absorption rate of Ti-oxide coated V-alloy decreased with increase of Ti-oxide thickness at the absorption temperature of 573 K.
- (3) In the case of 0.5  $\mu\text{m}$ , the absorption rate was observed to be much smaller than that of non-coated V-alloy.

If a dense and thick Ti-oxide film without cracking can be coated on the surface of V-alloy, the lifetime of V-alloy might be enlarged.

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