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Dependence of surface oxidation on hydrogen absorption and desorption behaviors of Ti–6Al–4V alloy

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Abstract

The hydrogen absorption and desorption behaviors of surface oxidized and degassed Ti–6Al–4V alloys under a condition of hydrogen pressure near to the pressure during glow discharge conditioning in reactor were evaluated by thermal desorption spectroscopy (TDS). The equilibrium hydrogen concentration, C_{eq}, of degassed Ti–6Al–4V alloy decreased with increase of temperature. The C_{eq} was about half of that of pure Ti in the temperature region of 673–873 K. The desorption peak of degassed Ti–6Al–4V alloy appeared at the temperature of 790 K. The peak temperature was almost the same even when the absorption amount changed. The absorption amount, C_{ab}, of surface oxidized alloy largely decreased with the increase of atomic ratio (O/Ti) on the top surface and the thickness of the oxide layer when adsorption time was 1 h. In addition, the desorption peak shifted to a higher temperature region with the increase of O/Ti ratio. In the surface oxidized Ti–6Al–4V alloy with an oxide layer of about 10 nm, the C_{ab} was two orders of magnitude smaller than that of the degassed sample when the absorption temperature and time were kept at lower than 650 K and 1 h, respectively. However, the C_{ab} of surface oxidized alloy became comparable with that of degassed sample when the absorption temperature was higher than 800 K because the oxide layer disappeared in the higher temperature region. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen; Absorption; Desorption; Oxidation; AES; XPS

1. Introduction

Titanium alloy may be used for vacuum vessel, first wall and blanket in a fusion reactor because of its low radioactivity [1,2]. However, it may be a problem if the embrittlement of Ti alloy due to hydride formation takes place. It is reported that the mechanical strength of Ti–6Al–4V alloy was drastically weakened, when the absorption amount of hydrogen exceeds approximately 1000 wppm [3]. Davis et al. [4] estimated the equilibrium hydrogen concentration, the C_{eq}, of Ti–6Al–4V alloy, comparing with the C_{eq} of pure Ti [5] or Ti–Al alloy [6]. The C_{eq} of Ti–6Al–4V alloy was 60% of that of pure Ti. It is also reported that the retention properties of hydrogen were largely changed by the irradiation of atomic hydrogen [7], hydrogen (deuterium) ion [8–10] or neutron [11] for Ti, Ti-alloy and other metals. In particular, the hydrogen concentration in the vicinity of the projected range of hydrogen ion exceeded the solution limit at a lower temperature [12]. The hydrogen absorption behavior is strongly affected by impurities or coatings at the surface, such as oxygen and nitrogen [8,13–17].

In our previous research, the C_{ab} of mechanical polished Ti–6Al–4V alloy was observed to be very small at temperatures lower than 650 K. Here, the hydrogen absorption experiment was conducted under a hydrogen pressure of 0.3 Pa for 48 h [18]. In the present study, the hydrogen absorption and desorption behaviors of surface oxidized and degassed Ti–6Al–4V alloys were investigated under a condition of hydrogen pressure near the pressure during glow discharge conditioning in a reactor, by using thermal desorption spectroscopy (TDS). Based on this study, the effect of the thick oxide layer as a diffusion barrier on hydrogen absorption was examined.

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2. Experimental

The Ti–6Al–4V alloy with a final treatment of dipping in HNO_3 – HF mixed acid was used as the sample. Sample geometry was a slab with a size of 10 mm × 20 mm × 0.4 mm. As received sample was mechanically polished by both using Emery paper and Al_2O_3 powder, and rinsed by ethanol in an ultrasonic bath. Polished sample was degassed at 973 K for 10 min in a vacuum ($\sim 5 \times 10^{-6}$ Pa). In this paper, this sample is named as the 'degassed sample'. The degassed sample was oxidized for about 10 min at temperatures of 323, 623 and 873 K in the oxygen atmosphere with a pressure range from 5×10^{-3} to 5 Pa. The oxygen exposure in this condition was $(0.44–16) \times 10^{19}$ O_2/cm^2. This second sample is named as the 'surface oxidized sample'. We prepared 10 polished samples, 10 degassed samples and 20 surface oxidized samples for the measurements of hydrogen absorption property and its reproductivity and surface property of samples.

Hydrogen absorption experiments were carried out in the TDS apparatus for the polished sample, degassed sample and the surface oxidized sample, under the condition of temperature ($T_s = 423–873$ K), hydrogen pressure ($P_{H2} = 10$ Pa) and absorption time ($t_s = 0.5–50$ h, Typical t_s was 1 h). This TDS apparatus was also used for the oxidation of the alloy. The components of TDS apparatus were made by SS. But, only the sample tube (30 mm ϕ × 300 mm) was made by quartz. In order to avoid the surface oxidation due to residual gases during the hydrogen absorption, hydrogen gas was pumped by using a turbo molecular pump (TMP). After the hydrogen absorption, hydrogen desorption behavior was measured by the TDS. No micro-cracks occur on the surface of oxidized samples after cooling. The sample was heated from room temperature to 973 K with a constant ramp rate of 0.5 K/s, and held for 10 min at 973 K. An infrared furnace was used for the heating. The temperature was monitored by a thermocouple spot-welded on the sample.

The surface morphology, atomic composition and chemical bonding states of samples were analyzed by using techniques of scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), respectively.

3. Results

3.1. Surface property

Fig. 1 shows the depth profiles of atomic ratio (O/Ti) for polished, degassed and surface oxidized samples. The depth profile was obtained by AES analysis. Here, oxidation was conducted under the oxygen exposure of $(5–8) \times 10^{18}$ O_2/cm^2. The depth scale was estimated from the sputtering yield of Ti with 2 keV Ar^+ ion. The thickness of the oxide layer was determined from a cross point of two dashed lines drawn in Fig. 1. The O/Ti ratio on the top surface increased with the oxidation temperature. Compared with the case of the degassed sample, in the surface oxidized samples, the O/Ti ratio on the top surface and the thickness of oxide layer largely increased. In particular, in the sample oxidized at 873 K, the thickness of oxide layer became about 10 nm. It is surprising that the O/Ti ratio and thickness of the oxide layer for the polished sample was the largest in these samples. From SEM observation, it was found that there were many polishing traces with the interval of sub-micron on the surface of the polished sample.

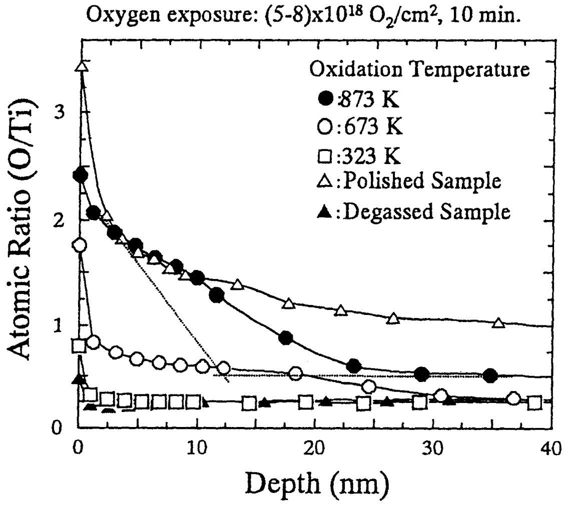

Fig. 1. Depth profiles of atomic ratio, O/Ti, for polished, degassed and surface oxidized samples.

Fig. 2 shows the binding energies (E_B) of core levels for $Ti2p_{2/3}$, Al2p and V2p levels in the near surface of the samples. These results were obtained by XPS analysis. In the surface oxidized and degassed samples, the depth profiles of E_B were very similar to the results of O/Ti ratio measured by AES analysis. Surface segregation of Al was observed in the sample oxidized at 873 K. Vanadium concentration slightly decreased with increase of oxidation temperature. It is presumed that the vapor pressure of vanadium oxide, e.g., V_2O_5, is higher than those of other metal oxides. In the polished sample, the depth profiles of E_B for $Ti2p_{3/2}$ and V2p were similar to those of degassed samples. However, Al oxide was observed in the deep depth, and this change of E_B for Al2p was similar to that of the sample oxidized at 673 K.

3.2. Desorption property of hydrogen

Fig. 3 shows a typical desorption spectra of the polished sample. Major outgassing species were H_2, H_2O, CO

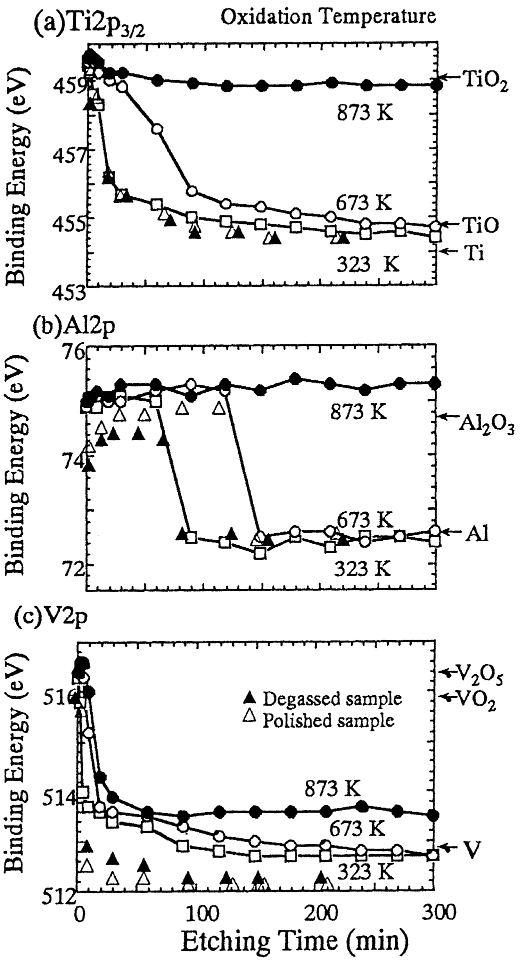

Fig. 2. Depth profiles of binding energy for core level of Ti2p$_{3/2}$ (a), Al2p (b) and V2p (c).

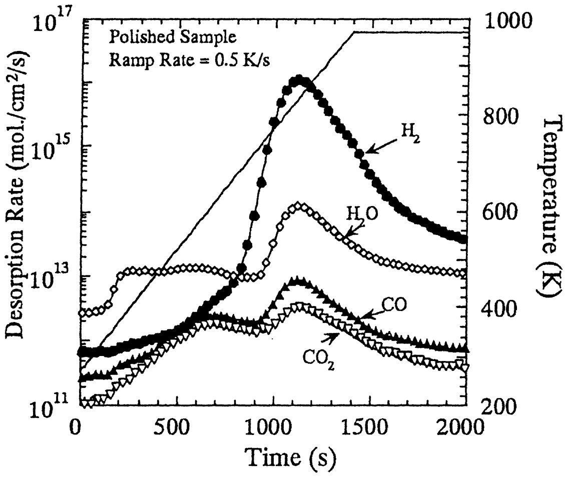

Fig. 3. Thermal desorption spectra of gases desorbed from a polished Ti–6Al–4V alloy.

and CO_2. It is seen that the desorption rate of hydrogen significantly increased at the temperature of about 650 K and had a peak at about 820 K. The peak temperature (T_p) of other gas species were also observed at 820 K. The amount of desorbed hydrogen, i.e., initial hydrogen concentration, was 110 ± 10 wppm, which was two or three orders of magnitude larger than those of other gas species.

Fig. 4 shows hydrogen desorption spectra of both the degassed and surface oxidized samples after hydrogen absorption for 1 h when P_{H2} and T_s were kept 10 Pa and 673 K, respectively. Here, the oxidation was conducted under a condition of temperature of 673 K and oxygen exposure with a range of $(0.054–1.1) \times 10^{20}$ O_2/cm^2. In the desorption curve of the degassed sample, the T_p was 790 K, which was 30 K lower than that of the polished sample. It can be seen that the desorption rate was roughly symmetric with respect to the T_p. This peak temperature remained the same even if the absorption amount was changed from 200 to 1100 wppm.

On the contrary, in the case of surface oxidized samples, the T_p shifted to a higher temperature region with increase of oxygen exposure. Similar tendencies were observed for samples oxidized at 323 and 873 K as shown in Fig. 5. It is presumed that the diffusion coefficient becomes small due to the effect of oxide thickness, and/or the recombination rate of hydrogen atom on the surface is reduced by both the small content of hydrogen and the increase of oxygen concentration. Here, T_p was not proportional to the oxygen exposure. It is presumed that the thickness of oxide and the concentration of oxygen on the top surface were not linearlly proportional to the oxygen exposure, i.e. oxygen pressure.

3.3. Absorption property of hydrogen

The absorption amounts (C_{ab}) of hydrogen for degassed and surface oxidized samples were obtained by

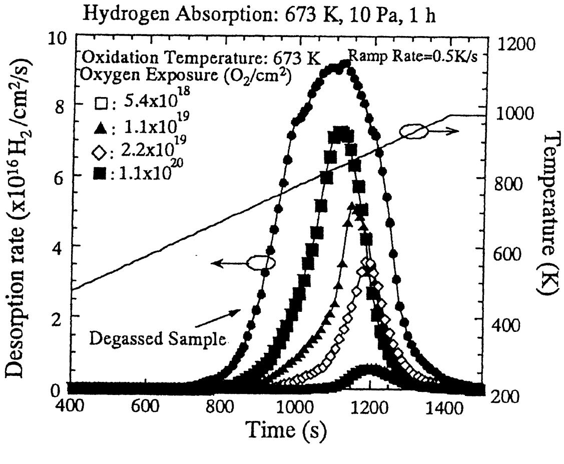

Fig. 4. Hydrogen desorption spectra of degassed and surface oxidized samples after hydrogen absorption.

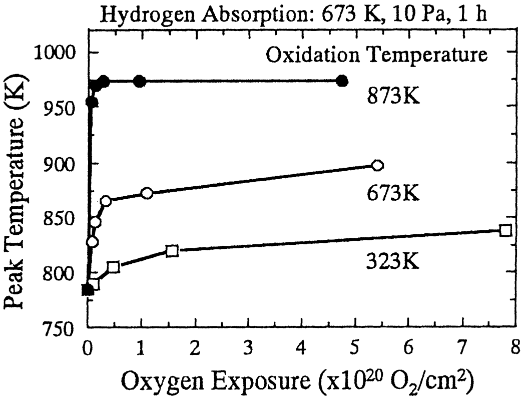

Fig. 5. Peak temperature in the hydrogen desorption curve as a function of oxygen exposure, when the ramp rate was 0.5 K/s.

time-integration of desorption rate shown in Fig. 4. Fig. 6 shows the C_{ab} as a function of oxygen exposure. Absorption experiments were carried out at the temperature of 673 for 1 h. Here, oxidation temperatures were 323, 673 and 873 K. The C_{ab} decreased with increase of oxygen exposure in all oxidized samples. The C_{ab} of the samples oxidized at 673 and 873 K was two orders of magnitude smaller than that of degassed sample when the oxygen exposure was higher than 1×10^{20} O_2/cm^2. It is presumed that the sticking probability of hydrogen on metals is reduced by the surface coverage [19].

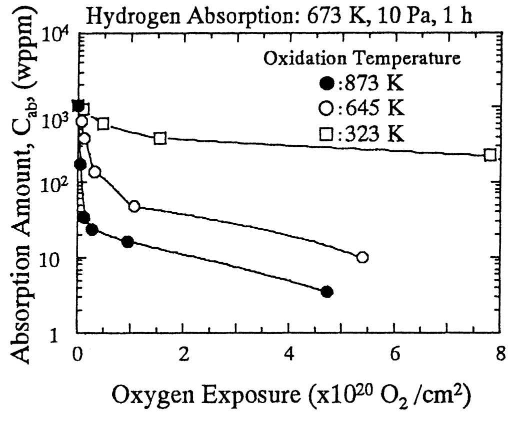

Fig. 6. Hydrogen absorption amounts, C_{ab}, versus oxygen exposure.

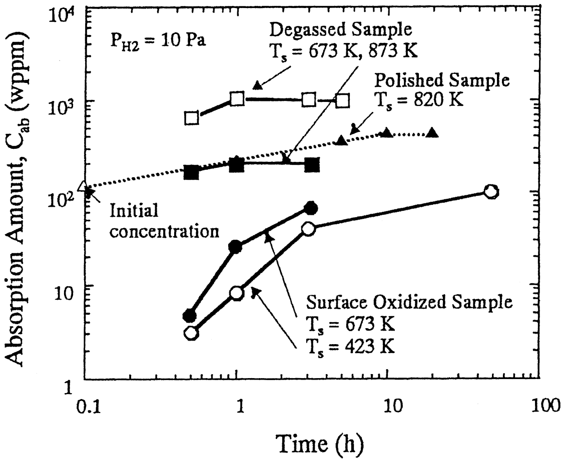

Fig. 7. Hydrogen absorption amounts (C_{ab}) of hydrogen for polished sample, degassed sample and surface oxidized sample as a function of absorption time. Surface oxidation condition: (5–8) × 10^{18} O_2 /cm^2, 873 K, 10 min.

Fig. 7 shows the C_{ab} as a function of absorption time for the polished sample [18], degassed sample and the surface oxidized sample (oxidation condition: 873 K, 10 min, (5–8) × 10^{18} O_2/cm^2). The C_{ab} of the polished sample increased from initial concentration (~100 wppm) to ~400 wppm and saturated when absorption time exceeds 10 h at 820 K. The C_{ab} of the degassed sample saturated when absorption time exceed 1 h at 673 and 873 K. We evaluated these C_{ab} as the equilibrium concentration of hydrogen (C_{eq}). The C_{eq} of Ti–6Al–4V alloy was about half of that of pure Ti [5] in the temperature region of 673–873 K. However, the C_{ab} for the surface oxidized sample increased with increase of absorption time and did not saturate yet. Therefore, if the absorption time is kept for a long time ($t_s = \infty$), the C_{ab} of the surface oxidized sample will become the C_{eq}. In the present data, it is difficult to estimate the time period when the C_{ab} approaches the C_{eq} at a low temperature region, since such a long absorption time was not taken.

The dependence of absorption temperature on the C_{ab} for samples with and without oxidation was examined when P_{H2} and t_s were kept 10 Pa and 1 h, respectively. Fig. 8 shows the C_{ab} for degassed sample and the surface oxidized sample. The surface oxidized sample was prepared at the temperature of 873 K for 10 min when oxygen exposure was kept (5–8) × 10^{18} O_2/cm^2. The depth profiles of O/Ti for this sample is shown in Fig. 1. Data of the polished sample are also plotted in this figure [18]. Here, hydrogen absorption time for the polished sample was 5 h. In Fig. 8, the C_{eq} estimated by Davis et al. [4] was also shown. In the case of the polished sample, the C_{ab} was very small and was almost the same as the initial concentration (bulk concentaraion, ~110 wppm) at the temperature in the range lower than 723 K due to the effect of surface oxide. But, at 820 K, the C_{ab} increased and approached that of Davis's data. In the degassed sample, it is seen that the absorption amount decreased with increase of absorption temperature in the range higher than 650 K. In this temperature

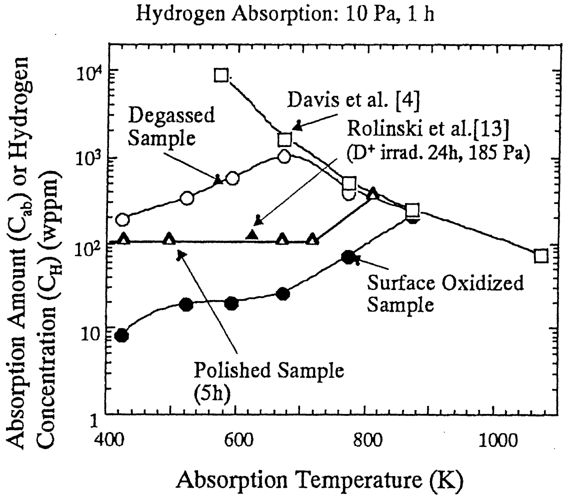

Fig. 8. Absorption amounts of hydrogen for polished sample, degassed sample and surface oxidized samples as a function of absorption temperature. Surface oxidation condition: (5–8) × 10^{18} O_2/cm^2, 873 K, 10 min. □: Hydrogen concentration extrapolated from the data reported by Davis et al at $P_{H2} = 10$ Pa [4], ▲: Concentration of H + D after 800 eV D^+ irradiation obtained by Rolinski [13].

region, the C_{ab} saturated at absorption time of 1 h as shown in Fig. 7. This dependence of absorption temperature on the C_{ab} is due to the fact that Ti and V are metals of exothermic occluders for hydrogen [20]. This equilibrium concentration of hydrogen was approximately half of that of pure Ti [5] and slightly smaller than the value estimated by Davis et al. [4]. This means that the C_{eq} of hydrogen for V [21] is smaller than that of α-Ti.

In the temperature region lower than 650 K, the C_{ab} increased with increase of absorption temperature. It is presumed that the small content of oxygen on the surface strongly affects the hydrogen diffusion at the low temperature region. This result also means that the C_{ab} did not saturate within the absorption time of 1 h. Therefore, if absorption time is kept a long time, the C_{ab} will increase with increasing of absorption temperature like Davis' data.

In the surface oxidized sample, the C_{ab} was very low in the temperature region lower than 673 K. However, in the temperature region higher than 800 K, the absorption amount was almost the same as that of the degassed sample. This means that the effect of the oxide layer as a diffusion barrier on hydrogen absorption disappeared at the high temperature region (800 K). After the hydrogen absorption at 873 K, the depth profiles of O/Ti ratio were examined. The oxide layer disappeared and the O/Ti ratio became similar to that of the degassed sample. This change may be due to the diffusion of oxygen into the bulk. Similar tendency was observed for Ti-alloy or stainless steel [22,23].

In a reactor, since Ti-alloy is irradiated by deuterium (tritium) ion with high fluence [1,13], the amount of retained hydrogen might be larger than that of the absorption amount of molecular hydrogen. Rolinski et al. investigated the amount of retained deuterium for nitrided and bare Ti–6Al–4V alloys when deuterium ion fluence was 2×10^{25} D^+/m^2 at 623 K. Here, irradiation time and deuterium pressure were 24 h and 185 Pa, respectively. The maximum amount of H+D in the bare Ti-alloy was only 130 wppm (Fig. 8). They reported that the Ti-alloy with protective oxide layer did not pick up a large amount of deuterium. Therefore, if oxide layer is not disappeared by ion irradiation or heat load, or Ti-alloy can be rapidly re-oxidized, the time period until the amount of retained hydrogen reaches the critical concentration which is required to affect the mechanical property of Ti-alloy, can be extended.

4. Conclusion

The hydrogen absorption and desorption properties for Ti–6Al–4V alloy were examined under hydrogen pressure near the pressure during glow discharge conditioning of the fusion reactor. Typical and maximum hydrogen exposure times were 1 h and 50 h, respectively. The equilibrium hydrogen concentration for Ti–6Al–4V alloy was estimated as about half of that of pure α-Ti. The desorption peak shifted to a higher temperature region, as the increase of O/Ti ratio.

In the temperature region lower than 650 K, the absorption amount of the surface oxidized sample was two orders of magnitude smaller than that of the degassed sample under a limited absorption time (1 h). Similar results were shown in the polished sample with oxide layer. However, the effect of the oxide layer as a diffusion barrier on hydrogen absorption disappeared in the temperature region higher than 800 K.

If absorption time is kept for an extended time, absorption amount of hydrogen for surface oxidized and polished Ti–6Al–4V alloy will reach that of the critical concentration where mechanical property of Ti-alloy become weakened. But, there is a possibility that this time period can extend due to the surface oxidation. However, if Ti–6Al–4V alloy is directly irradiated by a hydrogen plasma in a reactor, the hydrogen concentration in the near surface might exceed the solution limit, and hydrogen might accumulate at the stress points. Therefore, based on many studies for these properties, Ti–6Al–4V alloy or surface modified Ti-alloy with oxidation or nitridation [1,13] etc., must be evaluated as the material for a reactor.

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