

# Hydrogen desorption from pure titanium with different concentration levels of hydrogen

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Received 10 October 2006; received in revised form 29 April 2007; accepted 30 April 2007

Available online 3 May 2007

## Abstract

Hydrogen evolution behaviors for pure titanium plate samples, in which hydrogen has been thermally charged with gas phase hydrogen at a pressure of 0.1 MPa, were investigated by means of thermal desorption spectroscopy (TDS). Hydrogen concentration in the samples were varied from an extremely low level to a high one, as to form the hydride, by changing the charging times (up to 20 h) and temperatures (398–773 K). After hydrogen dissolution of low concentration level at the initial stage of the dissolution, four kinds of hydrogen evolution peaks were found at 850, 900–950, 1050 and 1150 K in TDS spectra. The hydride formation occurred abruptly at charging temperatures more than 680 K and at the hydrogen concentration level of more than 15–16 at.%, leading final hydrogen concentration of more than 47 at.% hydrogen. For the sample with high hydrogen concentration level as to form the hydride, another TDS peak at 750 K was observed in addition to that at 850 K. The sample hydrogenated evolved a large amount of hydrogen accompanying with a TDS peak from 550 to 900 K. The composition of the hydride was estimated to be  $\text{TiH}_x$  ( $x:1.1$ ).

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**Keywords:** Metal hydrides; Gas-solid reaction; Thermal analysis

## 1. Introduction

Titanium and its alloys are attractive structural materials because of their high strength-to-weight ratio and their high chemical stability. Because titanium exhibits very strong interaction with hydrogen as well known, it is used as one of hydrogen storage elements [1]. It has been reported that the presence of hydrogen and titanium hydride enhanced the fracture by localized plastic deformation and brittle fracture, respectively [2].

There have been many reports on hydrogen diffusion and hydride formation in  $\alpha$ -titanium [3–8], and it has been known that three kinds of titanium hydride ( $\delta$ ,  $\varepsilon$ ,  $\gamma$ ) are formed. The  $\delta$ -hydride, which is an equilibrium hydride phase, transforms into  $\varepsilon$ -hydride at high hydrogen concentrations, and the metastable  $\gamma$ -hydride forms at low hydrogen concentrations (1–3 at.% H)

[1,9,10]. However, the formation process of the hydride has not yet been clear [11]. There are some reports on the hydrogen evolution characteristics for the titanium sample hydrogenated with acidic solutions at room temperature [12,13]. In these reports, the hydrogenation of titanium has only occurred in the vicinity of the surface of sample because of the hydrogen charging at low temperature. Therefore, in order to understand the formation process of hydride at high temperature, it seems to be important to investigate the building-up process of hydrogen concentration in titanium, under a charging condition accompanying with thermal diffusion of hydrogen to the central part of sample.

In this study, hydrogen evolution behaviors for the titanium samples, which were thermally charged with gas phase hydrogen, were investigated in detail. The hydrogen concentration level varied from an extremely low level to a high one, so as to form the hydride. The variation of hydrogen evolution peaks observed in thermal desorption spectra (TDS) were also discussed in connection with the hydrogen concentration levels and the charging conditions.

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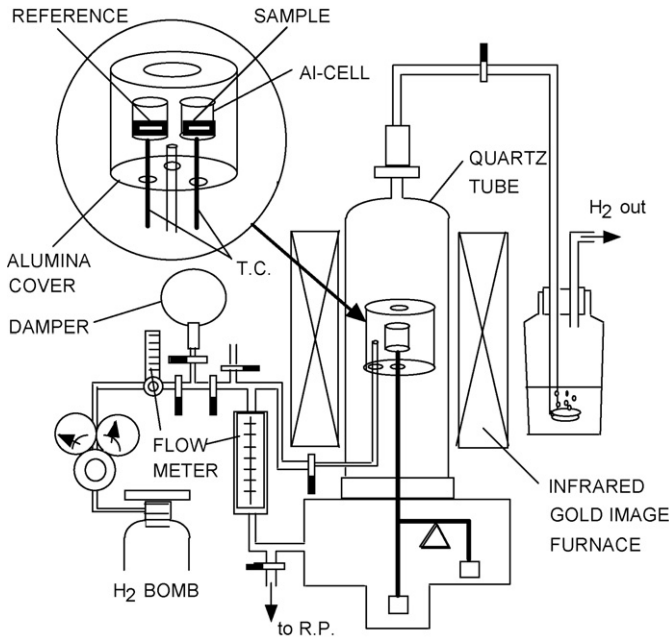


Fig. 1. A modified TG-DTA system for hydrogen charging under 0.1 MPa hydrogen gas flow.

## 2. Experimental procedure

The material used in this study was a commercially pure (nominally 99.99%, Mitsubishi Material Co. Ltd.) titanium ingot which was electron beam melted in a vacuum. The ingot was cold rolled and then samples (about  $10\text{ mm} \times 5\text{ mm} \times (0.4\text{--}0.8^t)\text{ mm}$ ) were mechanically cut. Their surfaces were polished by an emery paper of #3000 and rinsed with acetone in an ultrasonic bath. Before hydrogen charging, the samples were heat-treated at a temperature of 1123 K for 1 h under an ultra-high vacuum of  $10^{-6}\text{ Pa}$ , in order to adjust the initial condition for the microstructure of the titanium sample and to remove the intrinsic hydrogen already dissolved in the samples during the preparatory process.

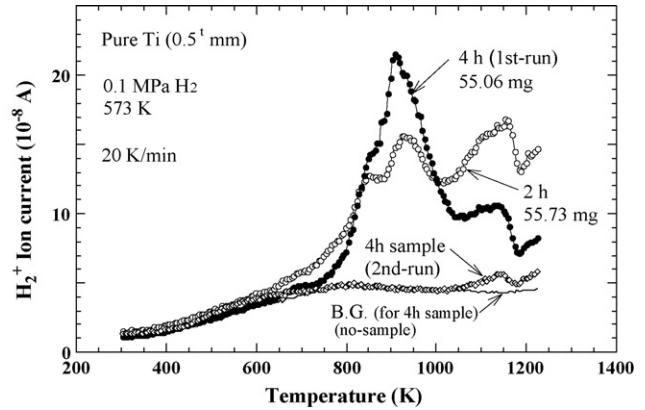


Fig. 3. TDS spectra of hydrogen for the samples charged for 2 and 4 h at a temperature of 573 K.

Hydrogen charging was performed with gas phase hydrogen by using a modified TG-DTA (ULVAC Co. Ltd., Japan) system, as shown in Fig. 1. The sample was inserted in an aluminum cell and heated from a temperature of 398 to 773 K under 0.1 MPa hydrogen gas flow (heating rate: 10 K/min). During the charging, the thermal gravimetric analysis (TG) and the thermal differential analysis (DTA) were performed. The hydrogen charging time was in the range from 5 min to 20 h in this study. Samples were removed from the cell and exposed to the atmosphere after cooling to room temperature.

Charged sample was set on an alumina boat and placed inside a quartz tube of an infrared gold image furnace. The quartz tube was, then, evacuated to  $10^{-6}\text{ Pa}$ . Thermal desorption spectrum (TDS) of the hydrogen evolution was measured as a function of the sample temperatures from 303 to 1273 K (heating rate: 20 K/min) by using a quadrupole mass analyzer (ULVAC Co. Ltd., MSQ-400, Japan) attached with an ultra-high vacuum system, as shown in Fig. 2.

## 3. Results and discussion

The amount of hydrogen dissolved into sample generally increases with hydrogen charging time and temperature. Fig. 3 shows typical TDS spectra of hydrogen from the samples charged for 2 and 4 h at 573 K. In each spectrum, three TDS

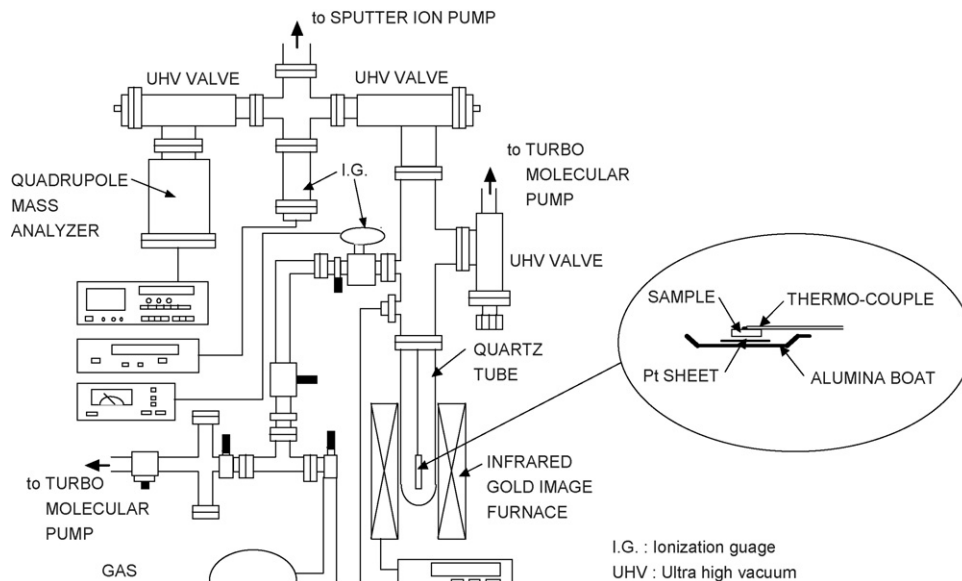


Fig. 2. A set-up for the measurement for thermal desorption spectrum (TDS) of hydrogen.

peaks are observed at about 850 (shoulder), 920 and 1150 K. The peak at 1150 K is considered to be caused by a sudden decrease in the hydrogen evolution rate due to the phase transition of the titanium ( $\alpha \rightarrow \beta$  at 1155 K) because the  $\beta$ -Ti dissolves much hydrogen than the  $\alpha$ -Ti. The evolution curve for the 2nd-run was obtained from the sample after keeping it in air at room temperature for 2 days after 1st-run measurement. Most of the hydrogen dissolved in sample have desorbed in the 1st-run. The apparent hydrogen concentrations in these samples, estimated from the TDS spectra, were in the range from 0.01 to 0.02 at. %.

Such a multi peaked structure was indistinct in the TDS spectra from the sample charged for long time (12 and 20 h) at 573 K, because of a large TDS peak at 850 K. The samples only with lower hydrogen concentration, in other words, being in the initial stage of hydrogen dissolution, exhibit such multi peaked TDS structure. This would suggest that there are two kinds of existing sites of hydrogen in the  $\alpha$ -Ti.

Fig. 4 (a and b) shows the TDS spectra of hydrogen for the samples charged for 2 h at several temperatures ranging from 520 to 673 K, as indicated in the figure. For the sample with extremely low hydrogen concentration (about 0.002 at. %), a broad evolution peak is observed at about 1050 K. With increasing the charging temperature, it becomes obvious that the dominant TDS peak in each spectrum shifts to lower temperature. And, at charging temperatures of more than 623 K, two peaks, at about 850 K (at the charging temperature of 673 K) and 900–950 K (at that of 623 K), become more clear as shown in

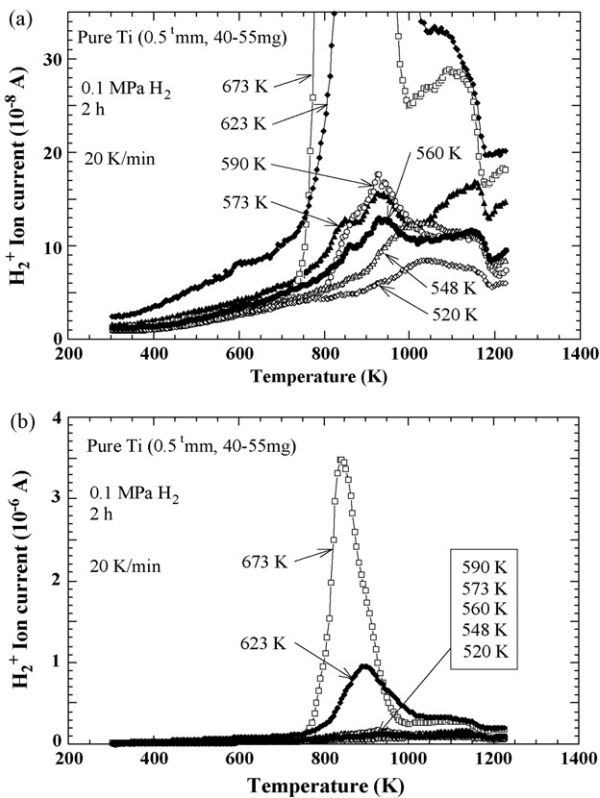


Fig. 4. TDS spectra of hydrogen for the samples charged for 2 h at several temperatures ranging from 520 to 673 K, (a) Enlarged spectra (vertical axis about 100 times larger than that of (b)). (b) whole spectra.

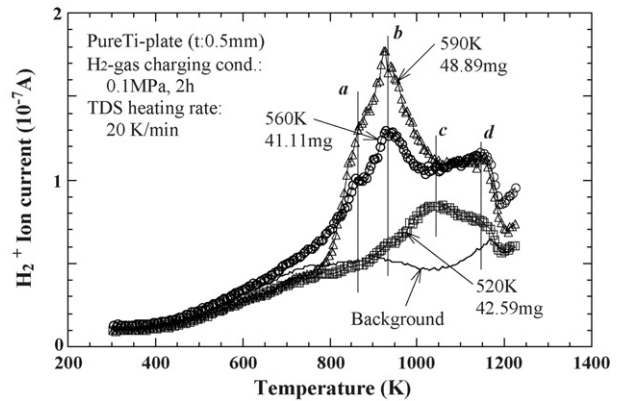


Fig. 5. Characteristic four evolution peaks of hydrogen observed after an initial stage of hydrogen dissolution.

Fig. 4(b). After the initial stage of hydrogen dissolution into titanium, four hydrogen evolution peaks (*a–d*) are characterized, as shown in Fig. 5. Here, the peak marked with *d* is due to the phase transformation of titanium, as is mentioned above. The peak *b* is a dominant evolution peak observed only for the samples with low hydrogen concentration, generally charged for less than 4 h and at temperatures less than 590 K. On the other hand, the peak marked with *a* dominates in the samples with high hydrogen concentration. Therefore, *a* is a dominant peak in high hydrogen concentration, *b* is a dominant peak in low hydrogen concentration, *c* is in the lowest hydrogen concentration and *d* is due to the phase transition of titanium sample. These results would suggest that there are three kinds of the existing states of hydrogen in titanium.

It has been suggested that, in the hydrogen desorption, the shift of TDS peak to higher temperatures is occurred by the corrosion product on surfaces of sample [13]. While, in the present experiment, the sample surfaces have been exposed to a reduced atmosphere during hydrogen charging and have still kept their original metallic reflection even after hydrogen charging, except the samples charged for longer time so as to form the hydride. The present results, therefore, show that the shifts of TDS peak are corresponding to the trapping states of hydrogen in titanium, though these states have not yet been able to be clarified.

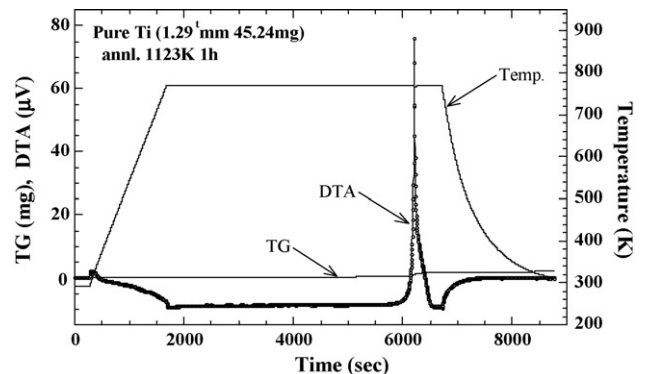


Fig. 6. A typical TG–DTA result after hydrogen charging at a temperature of 773 K. The  $\gamma$ -hydride formation has occurred.

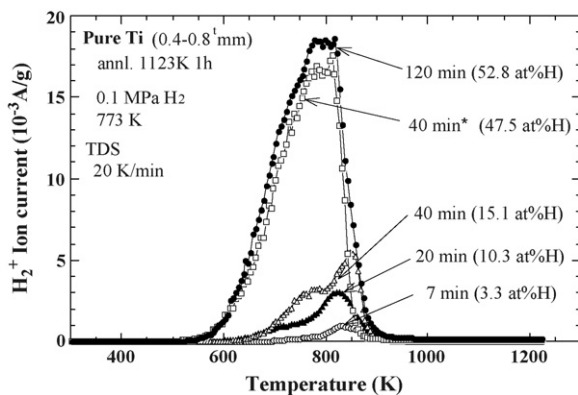


Fig. 7. Hydrogen evolution for the titanium samples charged for several charging times (7–120 min) at the temperature of 773 K. The evolution for the sample hydrogenated is marked with (\*), in order to distinguish from that for the no hydrogenating sample charged for almost same charging time of 40 min.

The hydride formation of titanium, in this study, has occurred at higher charging temperatures more than 690 K, which has depended on the thickness of sample under a given heating condition. Fig. 6 shows a typical TG–DTA result for hydrogenation process to form the hydride at the charging temperature of 773 K. It is observed that a rapid hydrogenation of titanium sample is occurred exothermally (in DTA) and that the mass of sample starts increasing (in TG).

Hydrogen evolution spectra for the titanium samples charged for several charging times (7–120 min) at 773 K are shown in Fig. 7. Here, the sample hydrogenated is marked with (\*), in order to distinguish from another sample, no hydrogenating, for the almost same charging time of 40 min. The hydrogenation has occurred abruptly at the hydrogen concentration more than 15.1 at.%. A large amount of hydrogen (47.5 at.%) has disso-

ciated from the sample hydrogenated, which is seen in TDS spectra for the sample charged for 40 min\*, as shown in Fig. 7. The hydrogen evolution peak at 750 K, as well as the peak at 850 K, clearly exists when hydrogen concentration in the sample reaches so high as to form the hydride. After the hydrogenation, the amount of evolved hydrogen, which shows a large and broad TDS peak between 550 and 900 K, has not increased, remarkably, in spite of the charging for long time of 120 min as shown in Fig. 7. Results of the X-ray diffraction (XRD) analysis for the samples after several charging times at 773 K are shown in Fig. 8. The hydride formed in this study is confirmed to be the  $\gamma$ -type.

#### 4. Conclusions

Hydrogen evolution behaviors and hydrogenation process for pure titanium plate samples with various concentration level of hydrogen were investigated by means of thermal desorption spectroscopy. The concluding remarks are summarized as follows:

- (1) At the initial stage of dissolution of hydrogen into titanium, a characteristic TDS evolution pattern was observed. The TDS peaks were observed at about 850, 920, 1050 and 1150 K. With increasing the hydrogen concentration, the main evolution peak shifted to lower temperatures.
- (2) A rapid hydrogenation of titanium has occurred at hydrogen concentration more than 15.1 at.% at the charging temperature of 773 K. In this case, the TDS peak of hydrogen desorption at 750 K became to be dominant.
- (3) After hydrogenation, titanium samples formed the  $\gamma$ -hydride, which desorbed more than 47.5 at.% hydrogen.

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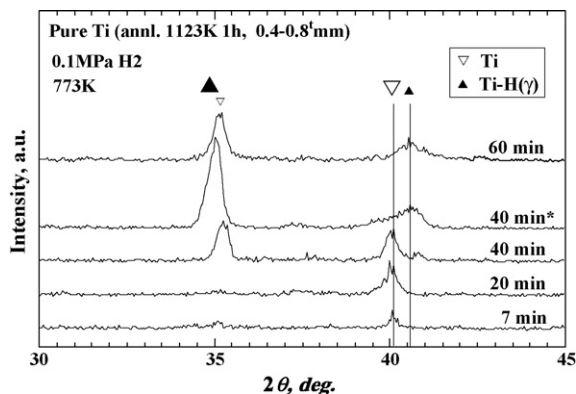


Fig. 8. Results of the X-ray diffraction (XRD) analysis for the samples after hydrogen charged for several charging times.