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# Hydride dissociation and hydrogen evolution behavior of electrochemically charged pure titanium

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## Abstract

A commercially pure α-titanium was electrochemically charged with hydrogen in a 5% $H_2SO_4$ solution at a current density of 5 kA $m^{-2}$ for 14.4 ks (4 h), and the dissociation process of the electrochemically formed hydride and the evolution behavior of hydrogen from the samples were investigated by means of high temperature X-ray diffractometry, thermal desorption spectroscopy (TDS) and differential thermal analysis (DTA). The electrochemical charging produced δ-titanium hydride; this dissociated completely at temperatures around 600 K; $(\alpha+\beta)$ titanium then appeared, indicating that the hydride formed eutectoidally. The DTA detected the dissociation of the hydride (or $(\alpha+\delta)$–$(\alpha+\beta)$ boundary in the titanium–hydrogen system) as an endothermic peak. The TDS analysis, however, revealed that the accelerated hydrogen evolution could not be found at the dissociation temperature of the hydride but could be at higher temperatures. It was suggested that the hydride dissociation, $(\alpha+\delta)$, into $(\alpha+\beta)$ two-phase region was not accompanied by hydrogen evolution from the samples, but the free hydrogen owing to the hydride dissociation was diffused into the samples. The peak temperatures of both DTA and TDS analyses shifted to lower temperatures with decreasing heating rate. The Kissinger plots fitted these results fairly well and indicated that the apparent activation energies for δ-hydride dissociation and hydrogen evolution were estimated to be about 106 kJ $mol^{-1}$ and about 49 kJ $mol^{-1}$ respectively.

*Keywords:* Titanium; δ-hydride; Electrochemical charging; Thermal analyses; X-ray diffraction

## 1. Introduction

Hydrogen in metals and alloys is known to cause embrittlement. For titanium and titanium alloys, it has been reported that the presence of hydrogen and titanium hydride enhanced the fracture by localized plastic deformation and brittle fracture respectively [1].

Recently, in the titanium–hydrogen system as shown in Fig. 1, three kinds of titanium hydride (δ, ϵ, γ) have been reported to form [2,3]. The δ-hydride has an f.c.c. unit cell with the hydrogen atoms occupying the tetrahedral interstitial site ($CaF_2$ type structure). At high hydrogen concentrations, the δ-hydride transforms into ϵ-hydride which has an f.c.t. ($c/a<1$) structure at temperatures below about 310 K. At low hydrogen concentrations (1–3 at.% H), the metastable γ-hydride, which has an f.c.t. ($c/a>1$) structure with an ordered arrangement of hydrogen, forms. The equilibrium hydride phase is the δ-titanium hydride; there have been several reports on precipitation (formation) and orientation characteristics of δ-hydride in α-titanium [4–7] but less on hydride dissociation and hydrogen evolution characteristics.

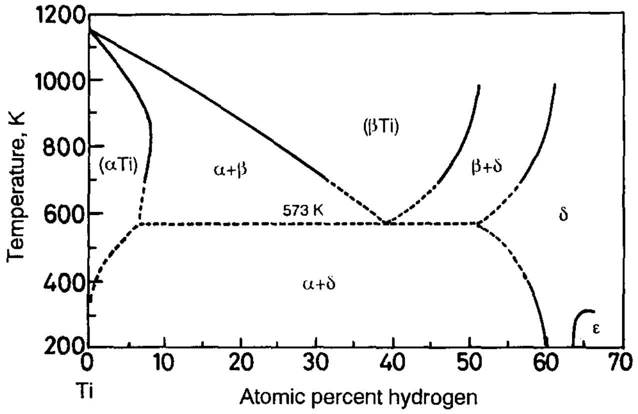

Fig. 1. The titanium–hydrogen phase diagram [9].

In this study, dissociation behavior of an electrochemically formed titanium hydride and hydrogen evolution behavior from the samples were investigated;

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the effect of heating rate on these behaviors is also discussed.

## 2. Experimental procedure

The material used for this study was a commercially pure (nominally 99.99%) titanium ingot which was electron beam melted in a vacuum condition. The ingot was cold rolled and then samples of dimensions 10 × 10 × 0.4 mm$^3$ were cut, mechanically ground and polished. No treatment was performed for the samples before hydrogen charging. Hydrogen charging was carried out electrochemically at room temperature using platinum counter electrodes in a 5% $H_2SO_4$ solution. The current density was maintained at 5 kA m$^{-2}$ and the charging time was 14.4 ks (4 h). The microstructural change during heating was examined by a JEOL JDX-3530 X-ray diffractometer with Cu K$\alpha$ radiation operated at 40 kV and 40 mA. A high temperature attachment was used for the in situ high temperature X-ray diffraction measurement under an argon gas flow. The thermal desorption spectroscopy (TDS) was performed in an ultra-high vacuum condition (10$^{-6}$ Pa) with an ULVAC QMS-400 quadrupole mass analyzer. The details of the TDS system and the analysis have already been reported [8]. Differential thermal analysis (DTA) was performed by a DuPont 910 differential scanning calorimeter under a nitrogen gas flow. All measurements and analyses were performed at heating rates between 5 K min$^{-1}$ and 20 K min$^{-1}$.

## 3. Results

Fig. 2 shows the results of high temperature X-ray diffraction measurement for electrochemically charged titanium (heating rate: 20 K min$^{-1}$), in which the result before heating (at 303 K) is also included. At 303 K, the f.c.c. $\delta$-titanium hydride is observed with a matrix phase ($\alpha$-titanium). The diffraction peaks corresponding to the $\delta$-hydride, particulary the diffraction peak from (220)$\delta$, shift to higher diffraction angles during heating and disappear at temperatures less than 573 K. At a temperature of 573 K, the strong diffraction peak from (110) of $\beta$-titanium, as well as the weak diffraction peak from (200)$\beta$, is observed with diffraction peaks from $\alpha$-titanium. However, this strong peak disappears at 673 K and then reappears at temperatures above 773 K. There are some unindexed peaks in Fig. 1, particulary at 873 K, that are probably owing to an oxidation product. To determine the amount of hydride remaining during the heating process, the ratio of the (220)$\delta$ integrated intensity at each temperature to that at room temperature is calculated. The diffraction from (220)$\delta$ is the only peak which is not interfered with those from $\alpha$- or $\beta$-titanium in a given diffraction angle range. Fig. 3 shows the variation of the remaining hydride with temperature at heating rates of 5 K min$^{-1}$ and 20 K min$^{-1}$; this indicates that the remaining hydride is dependent on heating rate. For a heating rate of 20 K min$^{-1}$, most of the $\delta$-hydride is seen to be stable at temperatures up to 470 K, whereas for a heating rate of 5 K min$^{-1}$, the hydride is only stable at temperatures up to about 325 K. For both heating rates, most of the $\delta$-hydride completely dissociates at temperatures below 600 K. Isothermal high temperature X-ray diffraction measurements were also carried out at 373 K and 473 K in order to examine the thermal stability of the hydride. These isothermal rates of dissociated hydride (calculated in a manner similar to that stated for Fig. 3) as a function of holding time are shown in Fig. 4; the hydride dissociates faster at 473 K than at 373 K. Half of the hydride dissociates in a holding time of about 500 s at 473 K, and in about

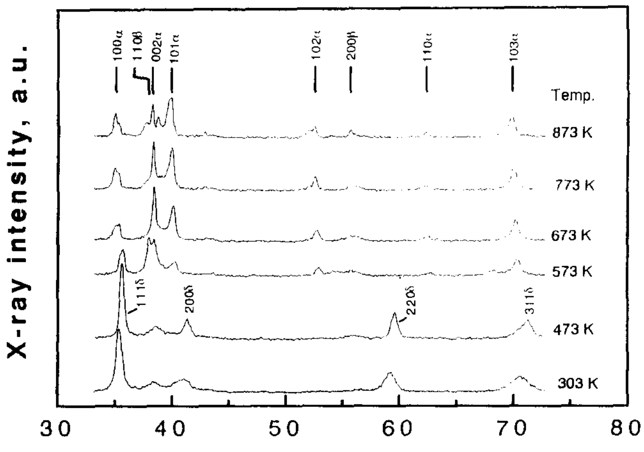

Fig. 2. High temperature X-ray diffraction profiles of electrochemically charged $\alpha$-titanium.

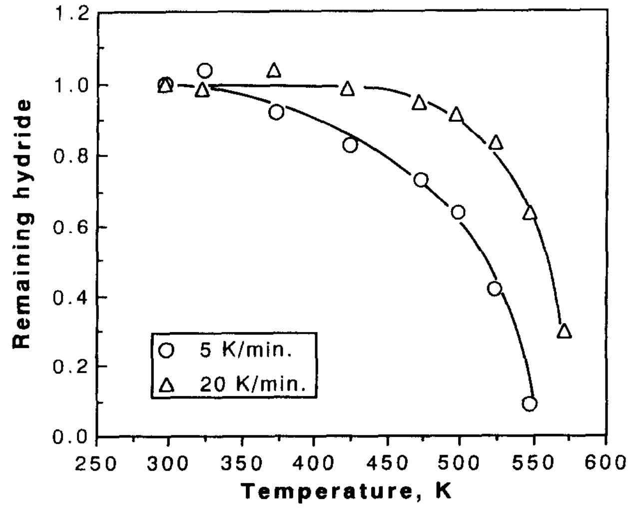

Fig. 3. Temperature variations in remaining $\delta$-hydride.

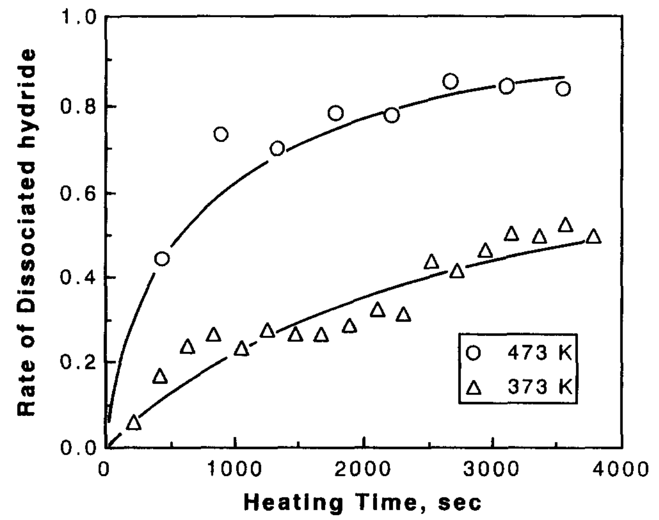

Fig. 4. Thermal stabilities of δ-hydride for isothermal heating at 373 K and 473 K.

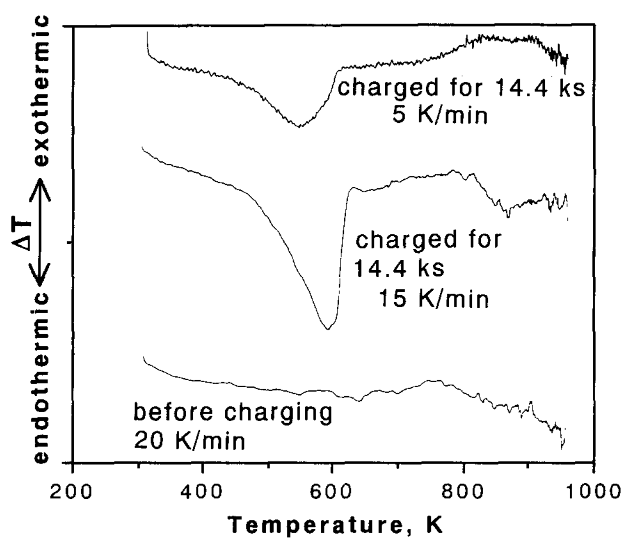

Fig. 5. Results of differential thermal analyses for α-titanium before and after electrochemical charging.

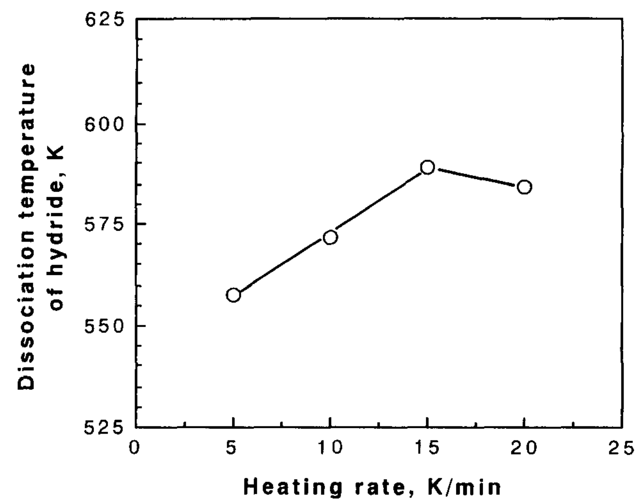

Fig. 6. Dissociation temperatures of δ-hydride as a function of heating rate.

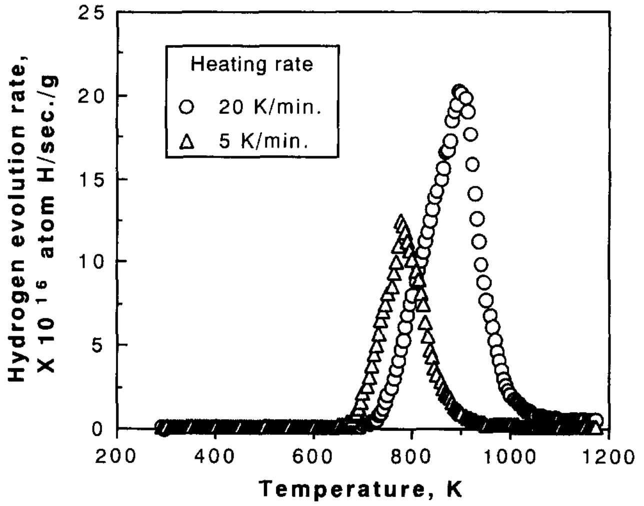

Fig. 7. Thermal desorption spectra for electrochemically charged α-titanium.

3.5 ks at 373 K .Thus, the δ-hydride is unstable even at temperature of 373 K.

Typical results of DTA analyses for the samples before and after hydrogen charging are shown in Fig. 5. The sample before charging shows no typical peak. However, for samples after charging, an endothermic peak is found at about 600 K (for heating rate of 15 K $\min^{-1}$). This peak temperature is good agreement with the above result of high temperature X-ray diffraction measurement. Therefore, the endothermic reaction detected by the DTA is a result of the δ-hydride dissociation. The initiation temperature of the δ-hydride dissociation can be determined to be about 480 K for a heating rate of 15 K $\min^{-1}$ from the point of intersection of the base curve with a tangent to the peak curve. The peak temperature is also found to be dependent on heating rate, as shown in Fig. 6. The peak temperature increases with increasing heating rate up to 15 K $\min^{-1}$ and then decrease slightly at 20 K $\min^{-1}$.

Fig. 7 shows the TDS spectra for the electrochemically charged titanium at heating rates of 5 K $\min^{-1}$ and 20 K $\min^{-1}$. Accelerated hydrogen evolution is found at about 900 K for a heating rate of 20 K $\min^{-1}$ and at about 750 K for 5 K $\min^{-1}$. Hydrogen evolution for a heating rate of 5 K $\min^{-1}$ initiates at a slightly lower temperature (about 650 K) than that for 20 K $\min^{-1}$ (about 700 K). No hydrogen evolution from the samples can be observed at temperatures less than about 600 K. The integrated intensities of the TDS spectra give the total number of hydrogen atoms evolved from the samples. The rates of evolved hydrogen as a function of temperature for heating rates of 5 K $\min^{-1}$ and 20 K $\min^{-1}$ are shown in Fig. 8; more hydrogen is evolved from the sample at lower temperatures for a heating

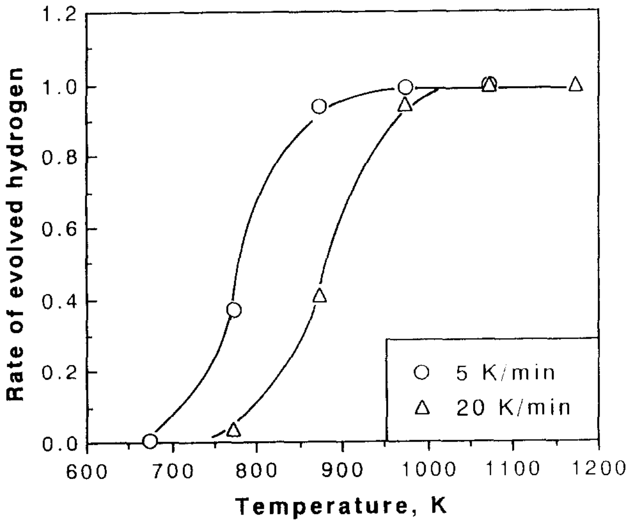

Fig. 8. Rate of evolved hydrogen as a function of temperature.

rate of 5 K $min^{-1}$ than for 20 K $min^{-1}$. Half of the total hydrogen evolved up to 1123 K is evolved at temperatures up to each peak temperature.

## 4. Discussion

From the results shown above, we now consider the relationship between hydrogen evolution and microstructural change. Comparing with the titanium–hydrogen system [9] shown in Fig. 1, the peak temperature at about 600 K (the dissociation temperature of $\delta$-hydride) obtained by DTA agrees well with the eutectoid temperature (boundary of $(\alpha+\delta)$–$(\alpha+\beta)$). The $\delta$-hydride was unstable even at temperatures lower than the eutectoid temperature (Fig. 3 and Fig. 4) but the TDS results showed no hydrogen evolution from the sample (Fig.7) at temperatures less than the eutectoid temperature. This indicates that the hydrogen atoms which can be free from the $\delta$-hydride lattice due to the dissociation are dissolved (diffused) into the sample, so that the hydrogen could not be evolved from the sample. McKinsey et al. [10] also observed by a microscopy that a hydride layer, formed electrochemically on a predominantly $\alpha$-titanium, was dissociated and some hydride extended into the sample core (diffusion). Above the eutectoid temperature, the results of X-ray diffraction measurement indicated that the microstructure of the sample changed from $(\alpha+\beta)$ to single $\alpha$ and then $(\alpha+\beta)$ region again with increasing temperature. Thus, it is considered that the peak temperature obtained by the TDS analysis could indicate the $(\alpha+\beta)$–$\alpha$ or the $(\alpha+\beta)$–$\beta$ boundary in the titanium–hydrogen system; this means that the accelerated hydrogen evolution could occur at the $(\alpha+\beta)$–$\alpha$ or the $(\alpha+\beta)$–$\beta$ boundary. Therefore, the initial hydrogen concentration level for the present charging condition could be at the titanium rich side in the $(\alpha+\delta)$ two-phase region from the eutectoid point of the titanium–hydrogen system. However it is difficult to determine the actual initial hydrogen level of the sample in the titanium–hydrogen system at this stage. It could also be concluded that the DTA detects only the $(\alpha+\delta)$–$(\alpha+\beta)$ boundary whereas the TDS analysis does not detect the $(\alpha+\delta)$–$(\alpha+\beta)$ boundary but detects only the $\alpha$–$(\alpha+\beta)$ or the $(\alpha+\beta)$–$\beta$ boundary in the titanium–hydrogen system. In our preliminary DTA and TDS analysis for a commercially available $TiH_2$ powder, which was also a $\delta$-type hydride, both analyses detected the peak at about 800 K for heating rate of 20 K $min^{-1}$, which was considered to correspond to a $\delta$–$(\beta+\delta)$ boundary in the titanium–hydrogen system.

The peak temperatures obtained from the DTA and the TDS shifted to lower temperatures with decreasing heating rate. The apparent activation energies of hydride dissociation and hydrogen evolution can be estimated from the Kissinger method [11] from the shifts of peak temperatures. This method uses a solid to gas decomposition reaction of any order on the corresponding DTA pattern, and is also applied to any other thermal

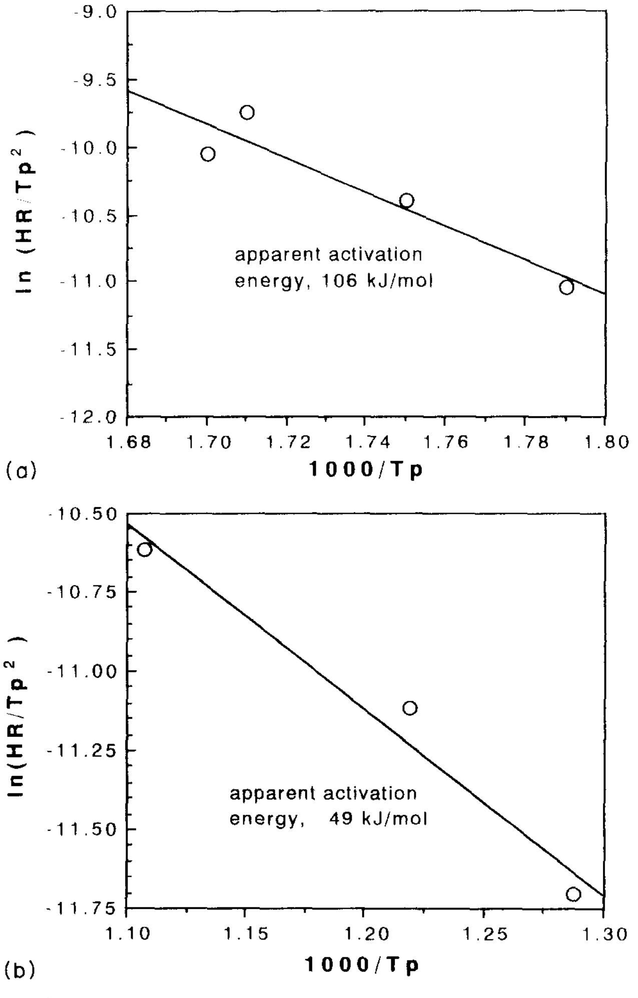

Fig. 9. The Kissinger plots obtained from (a) DTA and (b) TDS.

analyses, such as the gas chromatograph technique and TDS analyses [12,13]. This method involves application of the equation

$$\ln(HR/T_p^2) = -(E/K_BT_p) + A$$

where $HR$ is heating rate in K min$^{-1}$, $T_p$ the peak temperature in K, $E$ the activation energy in kJ mol$^{-1}$ and $A$ is a constant. If the heating rate and peak temperatures are known, the activation energies can be calculated from the slope of a $\ln(HR/T_p^2)$ vs. $(1/Tc_p$ plot. The Kissinger plots for DTA and TDS analyses are shown in Fig. 9. Both plots can be expressed fairly well with the Kissinger method. The apparent activation energy obtained from DTA (for δ-hydride dissociation) is estimated to be about 106 kJ mol$^{-1}$; that from the TDS analysis (for hydrogen evolution) is about 49 kJ mol$^{-1}$. The difference in these activation energies also indicates that the peak temperatures obtained from the DTA and the TDS analyses show different types of phenomena.

## 5. Conclusions

(1) The electrochemically formed δ-hydride was thermally unstable even at 373 K. It dissociated completely at temperatures up to 600 K, but the hydrogen evolution from the sample could not occur during the dissociation process. The hydrogen evolution from the sample was accelerated at about 900 K for a heating rate of 20 K min$^{-1}$.

(2) The DTA detected only the $(\alpha+\delta)$–$(\alpha+\beta)$ boundary whereas the TDS detected only the $\alpha$–$(\alpha+\beta)$ or the $(\alpha+\beta)$–$\beta$ boundary in the titanium–hydrogen system.

(3) The peak temperatures obtained from the DTA and the TDS were dependent on heating rate. From the shifts of the peak temperatures, the apparent activation energies for dissociation of δ-hydride and for hydrogen evolution were estimated to be about 106 kJ mol$^{-1}$ and about 49 kJ mol$^{-1}$ respectively.

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