

Studies on the Characteristic of Titanium-Tritium Reaction

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Abstract: The *p-c-T* curves of tritium absorption and desorption of titanium were measured using the method of step equilibrium by stepping up the tritium quantity on an experimental apparatus of metal hydride. The *p-c-T* curves for tritium have one plateau at temperature below 300 K and two plateaus at temperature above 300 K. The thermodynamic parameters of the different phases were determined according to the van't Hoff equation. The hysteresis effect was not observed in reversible process of tritium absorption and desorption of titanium on our experimental condition. The tritium absorption behavior of titanium in the temperature ranging from 550 K to 750 K and desorption behavior of titanium in the temperature ranging from 350 K to 550 K have been investigated in a constant volume system. A method of the reaction rate analysis was proposed and examined for determining the rate constant. The apparent activation energy obtained by this analysis for the absorption and the desorption were (155.5 ± 3.2) kJ/mol and (62.1 ± 1.6) kJ/mol respectively.

Key words: titanium, tritium, thermodynamics, kinetics

1. Introduction

Titanium is an important hydrogen-storage^[1,2] material which is widely used in tritium technology^[3,4] because of its high storage capacity. So titanium-tritium reaction and its parameters are concerned for the fuel cycle of fusion reaction. although many works have been done about titanium-protium^[5,6] and titanium-deuterium^[7] system, little work has been published on the titanium-tritium system due to the risk in handling tritium. So in the present work, the tritium absorption and desorption behavior of titanium on thermodynamics and kinetics is investigated.

2. Experimental

2.1 Specimen and apparatus

A titanium sheet of 1 mm thickness with purity of 99.99% was utilized as a specimen. The sheet was cut into rounds(6mm), mechanically polished, degreased by boiling 10 min and repeating it two times in the solution of sodium hydroxide, deoxidized in the solution of hydrofluoric acid until the surface of specimen showed its argent metal luster. Then the specimen was washed in acetone for getting rid of the water and then it can be used for experiment. The purity of the tritium used for the absorption and desorption experiment was 98.0%.

The experiment was carried out in a vacuum metal system. A titanium specimen was laid in a metal salver in the sample chamber made of quartz glass and was heated by a resistance furnace. The sample chamber was separated from the vessel by a valve and the system can be evacuated by a molecular pump system. The ultimate pressure of this system can be below 10^{-6} Pa. A change of the tritium pressure in the system during the absorption and the desorption experiments was measured with two diaphragm manometers.

2.2 Experimental procedure

2.2.1 Measurement of absorption and desorption p - c - T curves

As the first step of the tritium absorption experiment a specimen was out-gassed from 20 to 700 slowly and kept at 700 for 30 min in the sample chamber under vacuum in the order of 10^{-4} Pa. Then the specimen was activated until it can absorb tritium easily at room temperature. The specimen then was heated to a desired temperature and absorbed determinate tritium which had been desorbed from the uranium bed until titanium tritide was saturated.

The atomic ratio of tritium and titanium can be calculated using the following formula:

$$n(T)/n(Ti) = \frac{2M}{mR} \left[\frac{V_1(P_1 - P_3)}{T_1} + \frac{V_2(P_2 - P_3)}{T_2} \right] \quad (1)$$

Here, $n(T)/n(Ti)$ is the atomic ratio of tritium and titanium, M is the atomic weight of titanium, m is the mass of specimen, R is the gas constant, p_1 , p_2 and p_3 are the initial pressure of vessel, the initial pressure of sample chamber and the equilibrium pressure of reaction respectively. V_1 is the volume of the vessel. V_2 is the volume of sample chamber. T_1 is the temperature of the vessel and T_2 is the temperature of the specimen. So from the measured atomic ratio and the equilibrium pressure, the absorption isotherms were plotted. p - c - T curves of desorption were measured with the contrary process of absorption.

2.2.2 p - t curves of tritium absorption

The sample chamber and vessel was isolated from the pumping equipment when the pressure was under 10^{-4} Pa. The specimen was heated to a desired temperature in the sample chamber and tritium gas which was stored in vessel was introduced into the sample chamber up to the pressure 3.4×10^3 Pa for each run. A change of tritium pressure following the time due to the absorption (p - t curve) was measured until thermodynamic equilibrium was attained at the given temperature. The tritiated specimen was then heated to a higher temperature and the released tritium was reclaimed with uranium bed. When tritium in the specimen was released entirely, the specimen was heated to another desired temperature to carry out another absorption-desorption cycle.

2.2.3 p - t curves of tritium desorption

The sample chamber and vessel was isolated from the pumping equipment when the pressure was under 10^{-4} Pa after the specimen was saturated with tritium gas at room temperature, the valve between the sample chamber and the vessel was closed and the vessel was evacuated. The specimen was then heated at the desired temperature in the sample chamber for 10 min. Then the valve between the sample chamber and the vessel was reopened and a change of the tritium pressure following the time due to the desorption was measured until thermodynamic equilibrium was attained at the given temperature. Subsequently the specimen was cooled and re-absorbed the tritium gas in vessel and sample chamber. Then the specimen was heated to another desired temperature to carry out the same process.

4. Results and discussion

4.1 Thermodynamics of tritium absorption of titanium

The p - c - T curves of tritium absorption of titanium obtained in the temperature ranging from 250 to 550 are shown in Fig.1. It was found that there was only one plateau when tritium absorption of titanium at 250 with the equilibrium pressure of 4 Pa and there were two plateaus when tritium absorption of titanium between 500 and 550. According to the phase chart of titanium-hydrogen system^[8] the plateau of p - c - T curve at 250 is in accord with ($\beta + \gamma$) phases and the two plateaus from 500 to 550 are in accord with ($\beta + \delta$) phases and ($\delta + \epsilon$) phases respectively since there is little effect of H-D-T isotope on phase chart of titanium-hydrogen system. The plateau at 250 are very smooth and the atomic ratio of T/Ti reaches 1.95 which is nearer to the theoretical value 2.0 of tritium absorption of titanium. This fact shows that titanium has favorable capability of storing tritium. For the reaction rate, it was found during the experiment that the speed of tritium absorption of titanium is faster at β phase, ($\beta + \gamma$) phases and δ phase than at ($\beta + \delta$) phases obviously, namely, when β phase transformed to δ phase its reaction speed slowed down. This fact indicates that there is obvious effect for rate of absorbing tritium in titanium when β phase of titanium tritide transforms to δ phase.

The thermodynamic parameters of tritium absorption of titanium between 500 and 550 can be calculated with the equation of van't Hoff.

$$\ln P_{H_2} = \Delta H^0 / RT - \Delta S^0 / R \quad (2)$$

here, P_{H_2} is the equilibrium pressure of plateau, ΔH^0 is the standard enthalpy of reaction, ΔS^0 is the standard entropy of reaction.

The parameters of ΔH^0 and ΔS^0 show in table 1. There are different ΔH^0 and ΔS^0 at different phases and the absolute value of ΔH^0 and ΔS^0 at the second plateau are larger than at the first plateau, this means that the reaction releases more caloric and the chaos degree of system decreases at the second plateau and this means that titanium tritide of the second plateau is steadier than titanium tritide of the first plateau.

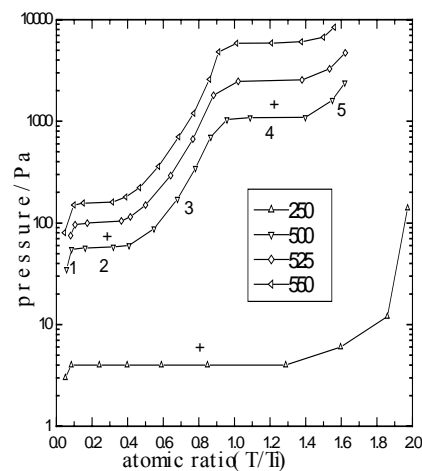


FIG.1. The p - c - T curves of tritium absorption of titanium

TABLE : THERMODYNAMIC PARAMETERS OF TITANIUM-TRITIUM REACTION

Plateau	ΔH^0 (kJ.mol ⁻¹)	ΔS^0 (J.K ⁻¹ .mol ⁻¹)	Form of Phases
The first plateau	- 101.5 ± 1.9	- 165.3 ± 1.9	+
The second plateau	- 179.6 ± 5.6	- 290.3 ± 7.1	+

4.2 Thermodynamics of tritium desorption of titanium

p - c - T curves of tritium desorption of titanium are shown in Fig.3. They are presented in company with the p - c - T curves of tritium absorption for comparison. From Fig.3. It can be seen that the hysteresis effect was not observed during the absorption-desorption cycle on the experimental condition. This means that titanium can absorb tritium with high storage capacity easily and desorbs tritium with little amount of residual tritium. This characteristic is very important for titanium as a tritium storage and supply material.

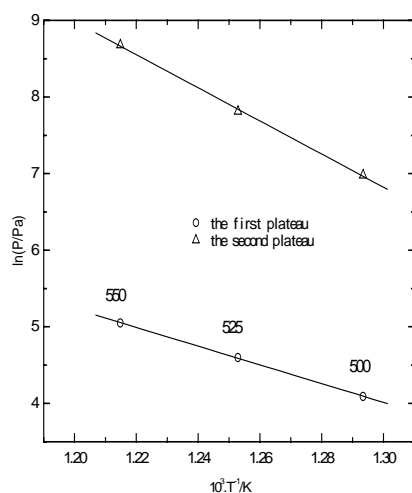


FIG2.Relation between absorption equilibrium pressure and temperature of tritium absorption of titanium

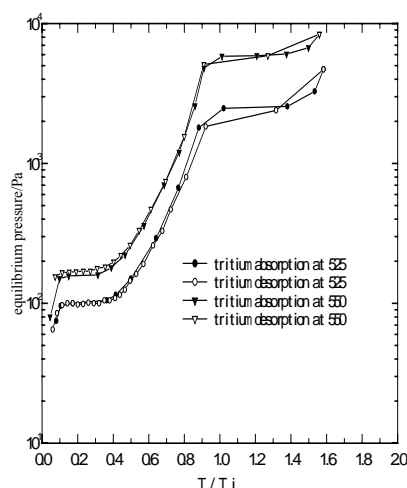


FIG3. p - c - T curves of tritium desorption of titanium

4.3 Kinetics of tritium absorption and desorption

4.3.1. Kinetic theory

Y.Hirooka^[9] proposed a method of rate analysis for dealing with the reaction of titanium-hydrogen system in the constant volume system. The method is based the assumption that the reaction rate to reach equilibrium is proportional to the deviation from the equilibrium. In the present work the tritium absorption and desorption experiments were carried out in a constant volume system. This means that the tritium pressure in the system changes owing to the reaction until thermodynamic equilibrium is attained at the given temperature. The tritium absorption and desorption rates are proportional to the difference between the tritium pressure, p_t , in the system at arbitrary time, t , and that at the final

equilibrium state, p_{eq} . The reaction rate in this case can be expressed by the rate of the tritium pressure change due to the absorption or the desorption, dp/dt . Thus the following rate equations are valid for the tritium absorption:

$$-dp/dt = k_a(p_t - p_{eq}) \quad (3)$$

And for the tritium desorption:

$$dp/dt = k_d(p_{eq} - p_t) \quad (4)$$

The constants k_a and k_d are defined as the absorption and the desorption rate constant, respectively. Supposed that these constants are independent of p , eqs. (3) and (4) are solved as following:

$$\ln[(p_t - p_{eq}) / (p_0 - p_{eq})] = -k_a t \quad (5)$$

$$\ln[(p_{eq} - p_t) / (p_{eq} - p_0)] = -k_d t \quad (6)$$

Here p_0 is the initial tritium pressure. The values of k_a and k_d are determined by the slopes of the straight lines given by plotting the lefthand values of eqs. (5) and (6) against time respectively.

According to the law of chemical reaction speed :

$$k_a = A e^{-E_a / RT} \quad (7)$$

$$k_d = A e^{-E_d / RT} \quad (8)$$

Here A is a constant factor, E_a and E_d are activation energy of absorption and desorption respectively, R is the gas constant, T is Kelvin temperature.

Eqs. (9) and (10) can be obtained from making logarithm to eqs. (7) and (8):

$$\ln k_a = \ln A - \frac{E_a}{RT} \quad (9)$$

$$\ln k_d = \ln A - \frac{E_d}{RT} \quad (10)$$

So the activation energy of absorption and desorption can be obtained by a set of reaction speed constants at different temperature.

4.3.2 Kinetics of tritium absorption

Tritium absorption curves obtained at the temperature ranging from 550 to 750 are shown in Fig.4. The initial tritium pressure was 3.4×10^3 Pa on each run. The curves show that the tritium pressures decrease quickly and eventually reach the equilibrium value at the given temperature and the time of reaching equilibrium became shorter with the equilibrium pressure increasing when the temperature increased. This suggests that the reaction rates of absorption tritium turns rapid when the temperature increases.

The absorption curves were analyzed using eq.(5) and the result obtained is shown in Fig.5. Since a good linear relation between $\ln[(p_t - p_{eq}) / (p_0 - p_{eq})]$ and time was obtained, the above mentioned method is confirmed to be applicable to analyze the absorption tritium behavior of titanium.

The Arrhenius plot of the absorption rate constants is shown in Fig.6 and the activation energy for the absorption was determined as (155.5 ± 3.2) kJ.mol⁻¹.

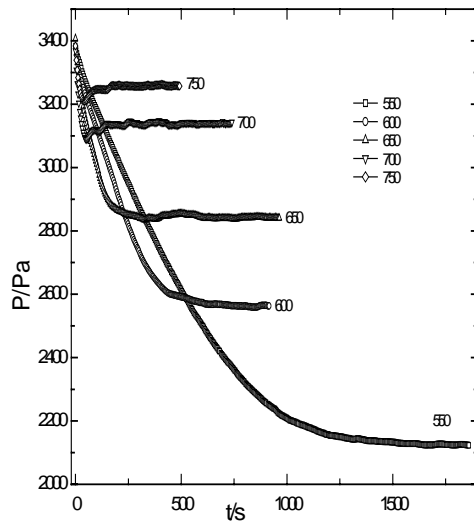


FIG.4. The p - t curves of titanium tritiation

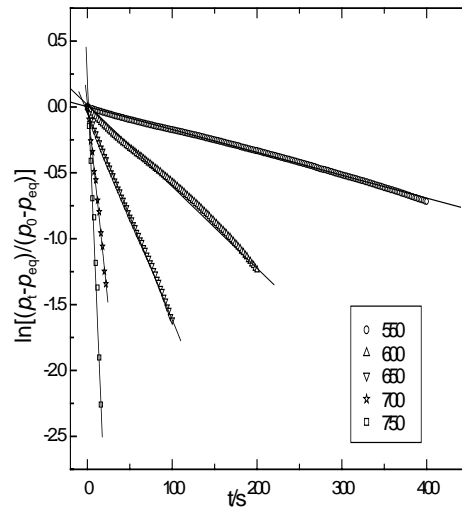


FIG.5. Kinetic curves of titanium tritiation

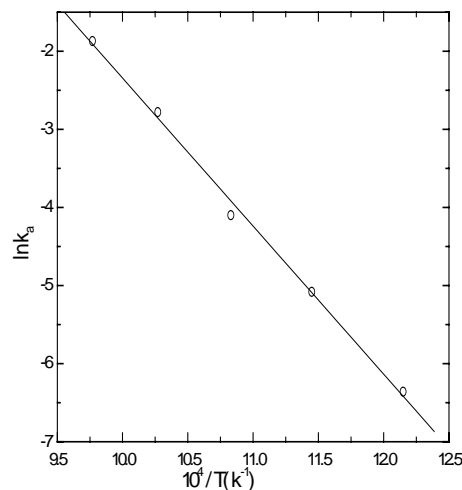


FIG.6. Relationship between $\ln k_a$ and $1/T$ for tritiation of titanium

4.3.3 Kinetics of tritium desorption

The tritium desorption curves obtained at the temperature ranging from 350 to 550 are shown in Fig.7. The initial tritium concentration (T/Ti) in the specimen was 1.7 in this case. As seen in this figure, the tritium pressure increases quickly and eventually reaches the equilibrium value at the given temperature and the time of reaching equilibrium was shorter with the higher equilibrium pressure at the higher temperature. This means that the reaction rates of desorption tritium turns rapid when the temperature increases.

The analysis of the desorption curves was made using eq.(6) on the condition of different initial tritium pressure, p_0 . The result obtained is shown in Fig.8. The good linear relation between $\ln[(p_{eq}-p_t)/(p_{eq}-p_0)]$ and time suggests that the method of rate analysis was applicable to analyze the desorption behavior.

The arrhenius plot of the rate constants is shown in Fig.9 and the activation energy for the desorption was determined as (62.1 ± 1.6) kJ/mol.

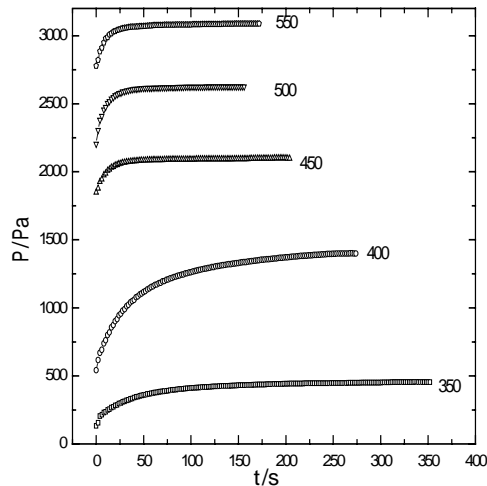


FIG.7. Desorbing p - t curves of titanium tritide

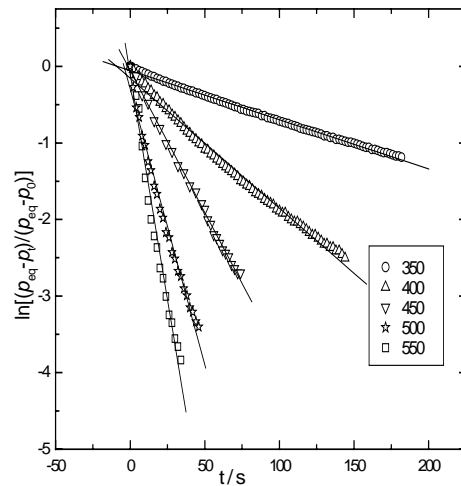


FIG.8. Desorbing kinetics curves of titanium tritide

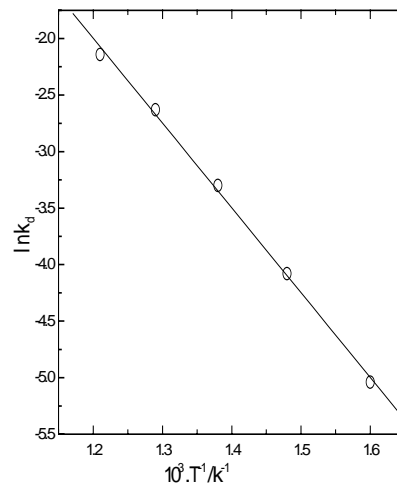


FIG.9. Relationship between $\ln k_d$ and $1/T$ for titanium tritide

4.4 Reaction mechanism

In this experiment, the specimen was outgassed and activated before absorption and desorption, the adsorptive oxygen on specimen surface was desorbed when outgassed and deoxidized in the ambience of hydrogen when activated, so the surface oxide has little effect on absorption and desorption process. the hydrogen absorption^[10] and desorption kinetics were finished^[11] before this experiment with the same conditions and the absorption and desorption activation energies were in accord with values for hydrogen diffusion in α -Ti and β -Ti respectively^[12], this suggests that the hydrogen absorption and desorption rate are controlled by the hydrogen diffusion in the specimen bulk and this means that the tritium absorption and desorption rate are controlled by the tritium diffusion in the bulk of titanium.

Compared with the reported data^[10] of hydrogen absorption and deuterium absorption, the activation energy for the tritium absorption is somewhat larger and the desorption activation energy has the same instance. This can be explained by theory of hydrogen isotope effect of kinetics.

5. Conclusion

The following conclusion are obtained from the present work on the titanium-tritium system:

(1) The p - c - T curves and the relation between equilibrium pressure and temperature of tritium absorption and desorption by Ti are measured at 250,500,525 and 550 . Equilibrium pressures of the absorption and desorption at different temperature of Titanium are given and then the thermodynamic parameters and the tritium absorption capacity are determined according to Van't Hoff equation. There are different changes of enthalpy and entropy when titanium tritide changing to different phases. The changes of enthalpy in the first and second plateau are $-101.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $-179.6 \text{ kJ}\cdot\text{mol}^{-1}$ respectively and the changes of entropy in the first and second plateau are $-165.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $-290.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ respectively. The hysteresis effect is not found when tritium desorption by titanium.

(2) A method of rate analysis for hydrogen was introduced for analyzing the tritium absorption and desorption behavior by titanium in a constant volume system. the activation energy values obtained by this analysis for the absorption and the desorption were $155.5 \text{ kJ}\cdot\text{mol}^{-1}$ (550 to 750) and $62.1 \text{ kJ}\cdot\text{mol}^{-1}$ (350 to 550) respectively. It is suggested that the absorption and desorption process are probably controlled by the tritium diffusion in titanium.

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