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Hydrogen absorption and desorption by Ti, Ti-5Cr and Ti-5Ni alloys

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Abstract

The hydrogen absorption and desorption kinetics and the *p–C–T* relationships of Ti, Ti-5Cr(at.%) and Ti-5Ni(at.%) alloys have been studied in the temperature range of 880 to 1050 K and in the pressure range of 1.3 to 13.3 kPa. The relative partial molar enthalpies for hydrogen solution in β phase obtained from the *p–C–T* relationships are found to be −71.0, −68.3 and −59.7 kJ/mol for Ti, Ti-5Cr and Ti-5Ni alloys, respectively. The constant volume method of the reaction rate analysis is used to determine the rate constants for hydrogen absorption and desorption. The activation energies for hydrogen absorption by Ti, Ti-5Cr and Ti-5Ni alloys are 110.1, 91.0 and 89.5 kJ/mol, respectively. The activation energies for hydrogen desorption are 67.0 and 61.8 kJ/mol for Ti and Ti-5Cr alloys, respectively. The hydrogen absorption is controlled by the α/β phase interface process, whereas the rate controlling step for desorption is the hydrogen transport through the surface oxide film.

Keywords: Hydrogen absorption and desorption; Kinetics; *p–C–T* relationship; Titanium alloy

1. Introduction

Owing to the good reversibility of hydrogen absorption and desorption, titanium has been used to construct a hydride temperature sensor and a fire detector. In this application area, the appropriate thermodynamic and kinetic properties are required. It is expected that the thermodynamic and kinetic properties of the Ti–H reaction could be improved by adding some alloying elements to titanium. Recently, Wang [1] has summarized and evaluated the thermodynamic functions of the Ti–H system from 400 K to 1010 K. Efron et al. [2] studied the kinetics and mechanism of titanium hydride formation at temperatures of 370 to 520 K, while the hydrogen absorption and desorption kinetics of titanium in the temperature range of 720 to 1070 K were investigated by Hirooka et al. [3]. However, there are no data available on the influence of an alloying element on the thermodynamic and kinetic properties of the Ti–H reaction in the literature. In the present work, the hydrogen absorption and desorption kinetics and the *p–C–T* relationships of Ti, Ti-5Cr(at.%) and Ti-5Ni(at.%) alloys are studied in the temperature range of 880 to 1050 K. The reaction rate constants, the activation energies for hydrogen absorption and desorption, and the relative partial molar enthalpies for hydrogen solution are determined. The rate controlling steps for hydrogen absorption and desorption are discussed.

2. Experimental

2.1. Specimen and experimental procedure

Materials used for the specimen preparation were sponge titanium, electrolytic nickel and chromium. The principal impurities were 0.06 Fe, 0.06 O, 0.02 C and 0.02 N (wt.%). The Ti, Ti-5Cr(at.%) and Ti-5Ni(at.%) alloys were melted in a nonconsumable electrode arc furnace. In order to obtain a homogeneous ingot, magnetic stirring was utilized during melting, then the button-like ingot was turned over and remelted twice. Alloy sheets of about 1.2 mm thickness were cut from the ingot by electrodischarge machining. Specimens with dimensions of about $1\times10\times10$ mm were mechanically ground and then ultrasonically cleaned in acetone.

In the hydrogen absorption experiment, a specimen was introduced into the reaction vessel made of quartz glass. The reaction vessel was first evacuated by an oil diffusion pump, and then filled with ultrapure hydrogen (99.9999%) which was supplied by an ultrapure hydrogen generator made of palladium. After the evacuated and filled cycle was repeated two to three times, ultrapure hydrogen was

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introduced into the system upto a pressure of 13.3 kPa (the initial hydrogen pressure) for each experiment. The reaction vessel was then moved into a resistance furnace kept at the desired temperature, and the pressure change due to the absorption was continuously measured by means of a capacitance manometer until thermodynamic equilibrium was attained at the given temperature.

For the hydrogen desorption experiment, specimens were precharged with hydrogen by heating them in hydrogen gas. The initial hydrogen content in specimen was between 0.6 and 1.0 H/M. After introducing the precharged specimen into the reaction vessel, the cycle evacuated and filled with hydrogen was also repeated twice or three times. The system was evacuated to a pressure below 10^{-3} Pa (the initial pressure for the desorption experiment) and then it was isolated from the pumping equipment. By heating the specimen at the desired temperature, the hydrogen desorption was started.

2.2. Kinetic analysis method

In the present work, the hydrogen absorption and desorption experiments were carried out in a constant volume system. Hirooka et al. [3] proposed a method of reaction rate analysis in the constant volume system. This method is based on the assumption that the reaction rate to reach equilibrium is proportional to the deviation from the equilibrium. Thus, the hydrogen absorption and desorption rates are proportional to the difference between the hydrogen pressure, p, at arbitrary time, t, and that at the equilibrium state, p_e. The reaction rate can be expressed by the rate of the hydrogen pressure change, dp/dt, due to the absorption or the desorption. Therefore, the rate equations for the absorption and the desorption are obtained:

$$-dp/dt = k_a(p - p_e) \tag{1}$$

$$dp/dt = k_d(p_e - p) \tag{2}$$

where k_a and k_d are the rate constants for absorption and desorption, respectively. These two equations are solved as follows:

$$\ln[(p - p_e)/(p_i - p_e)] = -k_a t \tag{3}$$

$$\ln[(p_e - p)/(p_e - p_i)] = -k_d t \tag{4}$$

where p_i is the initial hydrogen pressure. If the reaction fraction, F, is defined as $F = (p_i - p)/(p_i - p_e)$ for the absorption, or $F = (p - p_i)/(p_e - p_i)$ for the desorption, then a unified reaction equation for both absorption and desorption is obtained:

$$-\ln(1 - F) = kt \tag{5}$$

where k is the reaction rate constant (i.e. k_a for absorption and k_d for desorption).

3. Results

3.1. The p–C–T relationship

In the present work, the equilibrium hydrogen concentration in Ti, Ti-5Cr and Ti-5Ni alloys has been measured in the temperature range of 880 to 1050 K and in the pressure range of 1.3 to 13.3 kPa. According to the phase diagram of the Ti–H system, the equilibrium phase under the experimental conditions used in this study is the hydrogen solution in the β phase with BCC lattice. Recently, Wang [1] proposed on the basis of a modified form of Sieverts law that the hydrogen dissolution behavior in β-Ti can be described by the following p–C–T relationship:

$$\ln p = \alpha + \beta C + 2\ln[C/(2 - C)] + \gamma/T \tag{6}$$

where α, β and γ are constants. By applying this equation to the databases for hydrogen solution in β-Ti, he obtained:

$$\ln p = 15.84 + 0.7C + 2\ln[C/(2 - C)] - 16.0 \times 10^3/T. \tag{7}$$

In Eq. (7), hydrogen pressure and hydrogen concentration are given in atm and H/M (the hydrogen-to-metal atom ratio), respectively. We assume that Eq. (6) is applicable to the β phase of both pure Ti and titanium alloy. Introducing a parameter Z,

$$Z = \ln p - 0.7C - 2\ln[C/(2 - C)] \tag{8}$$

the p–C–T relationship of hydrogen solution in β phase could be expressed as follows:

$$Z = \alpha + \gamma/T. \tag{9}$$

Table 1 summarizes the experimental results and the plots of Z vs. $1/T$ are shown in Fig. 1. It is found that, for pure titanium, all data points measured by either the hydrogen absorption method or the hydrogen desorption method are on the same straight line. (Only the absorption method was used for Ti-5Cr and T-5Ni alloys.) The following p–C–T relationships are derived from these experimental results:

$$\text{Ti: } \ln p = 17.02 + 0.7C + 2\ln[C/(2 - C)] - 17.08 \times 10^3/T \tag{10}$$

$$\text{Ti-5Cr: } \ln p = 17.25 + 0.7C + 2\ln[C/(2 - C)] - 16.43 \times 10^3/T \tag{11}$$

$$\text{Ti-5Ni: } \ln p = 14.84 + 0.7C + 2\ln[C/(2 - C)] - 14.36 \times 10^3/T \tag{12}$$

where hydrogen pressure and concentration are given in atm and H/M, respectively. The relative partial molar enthalpies for hydrogen solution in the β phase, $\Delta\bar{H}$,

Table 1
The p–C–T relationship

(a) Ti	T (K)	881	933	968	985	998	1052
	Z^a	−2.318	−1.276	−0.615	−0.466	−0.106	0.879
	Measured method[b]	D	A	A	D	A	D
(b) Ti-5Cr	T (K)	933	958	986			
	Z^a	−0.376	0.142	0.578			
(c) Ti-5Ni	T (K)	891	929	964	1003		
	Z^a	−1.222	−0.692	−0.017	0.539		

[a] $Z = \ln p - 0.7C - 2 \ln [C/(2 - C)]$ where p and C are given in atm and H/M, respectively.

[b] A and D denote hydrogen absorption and desorption, respectively.

obtained from the above equations are −71.0, −68.3 and −59.7 kJ/mol for Ti, Ti-5Cr and Ti-5Ni alloys, respectively. The value of ΔH for pure titanium found in the present work is slightly more negative than that given by Wang [1] (−66.5 kJ/mol).

3.2. Kinetics of hydrogen absorption and desorption

The kinetic experiments of hydrogen absorption were carried out at an initial pressure of 13.3 kPa and in the temperature range of 880 to 1010 K. The hydrogen absorption plots of Ti analyzed using Eq. (5) are shown in Fig. 2. Since a good linear relation between $-\ln (1-F)$ and t was obtained, the method described in Section 2.2 is confirmed to be applicable to analyze the absorption behavior. The absorption plots of Ti-5Cr and Ti-5Ni alloys are similar straight lines. The rate constants for hydrogen absorption, k_a, determined from the slope of these lines are listed in Table 2. The Arrhenius plots of the absorption rate constants are shown in Fig. 3 and the activation energies for hydrogen absorption by Ti, Ti-5Cr and Ti-5Ni alloys are found to be 110.1, 91.0 and 89.5 kJ/mol, respectively.

The kinetics of hydrogen desorption was studied at 890–1040 K using the precharged specimens. Fig. 4 shows the desorption plots of titanium analyzed in terms of Eq. (5). It is found that the plots of $-\ln (1-F)$ against t are straight lines for Ti as well as for Ti-5Cr and Ti-5Ni alloys, indicating that Eq. (5) can also be used to describe

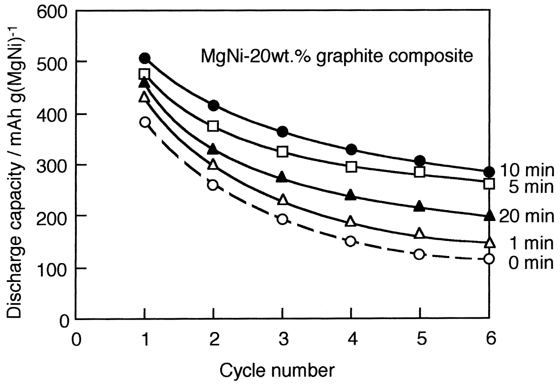

Fig. 1. The p–C–T relationship.

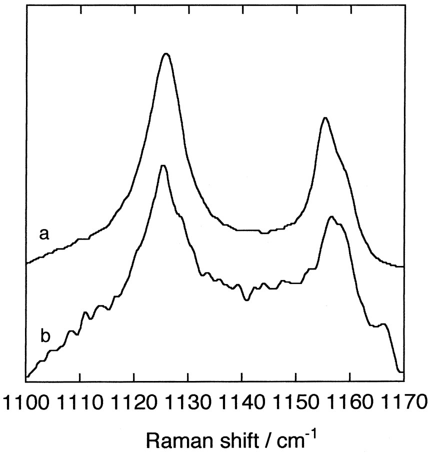

Fig. 2. Hydrogen absorption plots.

Table 2
The rate constant for hydrogen absorption

(a) Ti	T (K)	885	934	968	996
	k_a (min^{-1})	0.666	1.482	2.388	3.560
(b) Ti-5Cr	T (K)	885	933	958	
	k_a(min^{-1})	0.815	1.429	2.130	
(c) Ti-5Ni	T (K)	907	939	1008	
	k_a(min^{-1})	0.918	1.392	3.035	

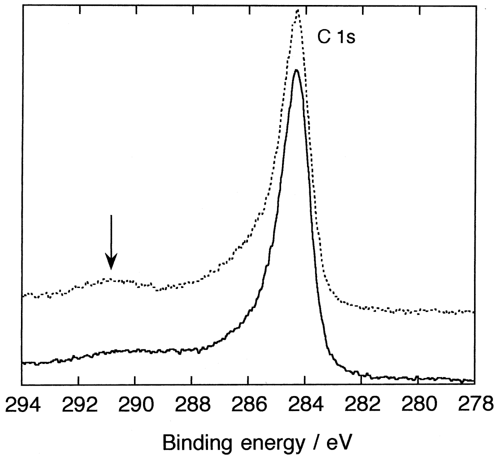

Fig. 3. The Arrhenius plots of hydrogen absorption and desorption.

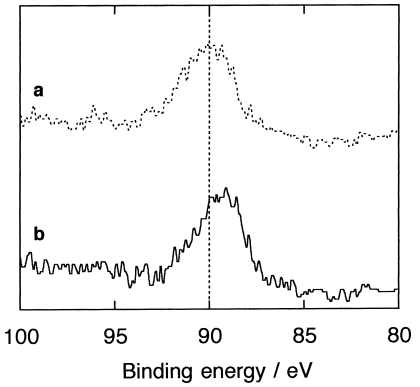

Fig. 4. Hydrogen desorption plots.

the desorption behavior. Table 3 summarizes the desorption rate constants, k_d, and the Arrhenius plots of the rate constants for hydrogen desorption are shown in Fig. 3. The activation energies for hydrogen desorption from Ti and Ti-5Cr are 67.0 and 61.8 kJ/mol, respectively.

4. Discussion

Before hydrogen absorption, the initial phase in the titanium specimen is the α phase with HCP lattice. After hydriding under the experimental conditions used in the present work, the product is the hydrogen solution in the β phase with BCC lattice. A phase transformation of α→β takes place during hydrogen absorption. The metallographic examination showed by using the partially hydrided specimen that a product envelope of the β phase was formed in the outer region of the specimen while the α phase remained in the inner region. During hydrogen absorption, the thickness of the β layer increases due to hydrogen diffusion through the β phase and the α/β phase interface advances to the specimen interior. Therefore, the rate controlling step for hydrogen absorption would be one of the following three processes: the surface process, the hydrogen diffusion process through the product envelope, and the α/β phase interface process.

Wasilewski and Kehl [4] first investigated the hydrogen diffusion in titanium and reported the activation energies for diffusion in α-Ti and β-Ti to be 51.8 and 27.8 kJ/mol, respectively. The corresponding diffusion activation energies of 42.2 and 36.4 kJ/mol were given by Someno and Nagasaki [5]. Using nuclear magnetic resonance, Korn and Zamir [6] found that the activation energies for hydrogen diffusion in α-Ti and β-Ti are 54.4 and 27.8 kJ/mol, respectively. The activation energy for hydrogen absorption obtained in the present work is much higher than that for hydrogen diffusion, indicating that the hydrogen diffusion process is not the rate controlling step for hydrogen absorption. As to the surface process, the experimental system was repeatedly cleaned with ultrapure hydrogen before carrying out the hydrogen absorption experiment and the specimen surface was found to be very bright after finishing the experiment. Therefore, it is expected that the hydrogen transport through the surface oxide film is not the rate controlling step for hydrogen absorption either. Thus, we believe that the hydrogen absorption in titanium would be controlled by the α/β phase interface process, i.e. the phase transformation of α→β. This argument is further supported by the experimental results of hydrogen absorption kinetics in zirconium which is quite analogous to titanium. Bloch [7] studied the hydriding kinetics and morphology in Zr and a high activation energy of 165 kJ/mol for hydrogen absorption by Zr above the eutectoid temperature was obtained. This is comparable to the absorption activation energy of 110 kJ/mol for Ti found in the present work. The high activation energies are consistent with the fact that the α→β phase transformation in Ti–H and Zr–H systems is expected to be very sluggish [8].

Since the activation energy for hydrogen desorption obtained in the present work is higher than that for hydrogen diffusion in the α phase or the β phase, the hydrogen desorption is not controlled by the hydrogen diffusion. On the other hand, the activation energy for hydrogen desorption is much lower than that for hydrogen absorption and, as mentioned above, the hydrogen absorption is controlled by the α→β phase transformation. Therefore, the α/β interface process is not the rate controlling step for hydrogen desorption either. Thus, there is only one possible rate limiting step left: i.e. the surface process. It is noted that the specimens for the hydrogen desorption experiment used in this study are heated twice (first precharged with hydrogen at an elevated temperature and then discharged at the desorption temperature) and an oxide film will easily be formed on the specimen surface at high temperatures. Hence, we suggest that the hydrogen transport through the surface oxide film would be the rate controlling step for hydrogen desorption. In a study of hydrogen absorption and desorption by titanium, Hirooka et al. [3] also found that the absorption process may be affected by the surface oxide. Using a lower pure hydrogen (99.9%) in their absorption experiment, they obtained an absorption activation energy of 74 kJ/mol, which is close to the desorption activation energy of 67 kJ/mol found in the present work.

Table 3
The rate constant for hydrogen desorption

(a) Ti	T (K)	901	968	1033
	k_d (min^{-1})	0.787	1.386	2.480
(b) Ti-5Cr	T (K)	887	980	1029
	k_d (min^{-1})	0.690	1.385	2.247
(c) Ti-5Ni	T (K)	963	1036	
	k_d (min^{-1})	1.121	2.426	

5. Conclusions

1. The p–C–T relationship for hydrogen solution in the β phase of all three alloys can be expressed by the following equation:

   $$\ln p - 0.7C - 2\ln[C/(2-C)] = \alpha + \gamma/T$$

   where α and γ are two constants. The relative partial molar enthalpies for hydrogen solution in the β phase obtained from this equation are −71.0, −68.3 and −59.7 kJ/mol for Ti, Ti-5Cr and Ti-5Ni alloys, respectively.
2. The activation energies for hydrogen absorption by Ti, Ti-5Cr and Ti-5Ni alloys are 110.1, 91.0 and 89.5 kJ/mol, respectively. The activation energies for hydrogen desorption from Ti and Ti-5Cr alloys are found to be 67.0 and 61.8 kJ/mol, respectively.
3. The hydrogen absorption is controlled by the α/β phase interface process, whereas the rate controlling step for the desorption is the hydrogen transport through the surface oxide film.

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