We have investigated the thermodynamic properties of Ti-H system including high concentration region (TiH$_x$: 0 < $x$ < 1.8) by utilizing electrochemical reaction of hydride ion, H', in molten salt. Electrode potential-composition isotherms in three single phases, α, β and δ, and in two coexisting phases, (α+β) and (β+δ), have been measured in a molten LiCl-KCl-LiH system at 673-773 K. The relative partial molar quantities of absorbed hydrogen, $\Delta G_H$, $\Delta H_H$ and $\Delta S_H$, and integral quantities, $\Delta G_f^\theta$(TiH$_2$), $\Delta H_f^\theta$(TiH$_2$) and $\Delta S_f^\theta$(TiH$_2$), were estimated. And it was confirmed that the obtained results were in good agreement with reported values obtained by using other techniques.

INTRODUCTION

There have been numerous investigations concerning thermodynamic properties of metal-hydrogen (M-H) systems for scientific and industrial interests. Thermodynamic data on M-H systems can be derived from pressure-composition-temperature, P-C-T, relationships, from closely equivalent approach of electrode potential-composition-temperature, E-C-T, relationships and from calorimetry. Among them, The electrochemical approach is the most direct one for the determination of thermodynamic data because the relative partial molar Gibbs energy is directly measured. So this approach has been utilized to estimate thermodynamic properties of palladium (1-3), palladium-based alloys (4-7) and hydrogen absorbing alloys for secondary batteries (8-9). In addition, it only needs very simple apparatus and is possible to change hydrogen pressure, even if it is extremely low, instantaneously by controlling the electrode potential. However, the electrochemical approach had critical disadvantage of its limited temperature range as long as using aqueous solutions for the electrolyte. So, the methods utilizing P-C-T measurement have been widely employed for high temperature M-H systems until now.

Concerning the hydrogen source at high temperatures, H' ion can be used for the electrochemical investigations. H' ion is produced by dissolution of a saline hydride like LiH in molten salts, such as LiCl-KCl (10), LiF-NaF-KF (11) and LiI-KI (27) eutectic melts. It is stable in the molten salts and its half cell reaction, represented in eq. 1, has been investigated by several workers (10-12, 27, 28).

$$H^+ = H + e \quad [1]$$
In 1991, Takenaka et al. (12) found that a small amount of hydrogen was absorbed in an iron electrode by electrochemical anodic oxidation of H' ion in LiCl-KCl-LiH melts at 682-787 K. By utilizing similar electrochemical hydrogen absorbing reaction in molten salts, it is possible to investigate metal-hydrogen system at high temperature range. In addition, the use of H' ion never deprives the advantages in the electrochemical approach. For instance, Ito et al. (28) have reported the H₂/H' electrode potential was 0.50 V (vs. Li⁺/Li) in a molten LiCl-KCl-LiH (2.0 mol% LiH added) system at 673 K. If Nernst equation holds for this system, hydrogen pressure is expectingly equivalent to \(8.1 \times 10^{-9}\) atm at electrode potential of 0 V (vs. Li⁺/Li) in a molten LiCl-KCl-LiH (1.0 mol% LiH added) system at 673 K. It is very difficult for conventional vacuum equipment to achieve such low pressure value.

In the present study, the authors have measured detailed E-C-T relationships of Ti-H system (TiHₓ; 0 < x < 1.8) at 673-773 K. In this experimental conditions, there exist three single phases (α, β and δ) and two coexisting phases (α+β and β+δ) according to the phase diagram shown in Fig. 1. Ti-H system is one of the systems whose thermodynamic properties have been extensively investigated. Nevertheless, fewer thermodynamic investigations in high concentration region were conducted than that in low concentration region. In this temperature range, Liaw et al. (13) also measured thermodynamic quantities in α, α+β and β phases of Ti-H system by electrochemical method using LiCl-KCl-LiH melts at 688 K and LiI-KI-LiH melts at 628 K. However, their investigation had lack of the data in high concentration region (β+δ and δ phases). So, in this investigation, partial molar thermodynamic quantities of absorbed hydrogen, including high concentration region, were estimated from the measured E-C-T relationships. And using these quantities, integral thermodynamic quantities of formation of TiH₂. In addition, all of obtained quantities were compared with reported values estimated by using other techniques (14-25).

![Phase diagram of Ti-H system (29).](image-url)
EXPERIMENTAL

Apparatus and chemicals

Reagent grade LiCl and KCl (Wako Pure Chemical Co., Ltd.) were dried under vacuum for more than 72 hours at 473 K in order to remove water. The eutectic mixture (59 mol% LiCl, 41 mol% KCl) were then melted in a high purity alumina crucible (99.5 % Al₂O₃; Nippon Kagaku Togyo Co., Ltd.) under a pure, dry argon atmosphere. After the eutectic mixture was melted, argon gas was bubbled into the melt for 24 hours and pre-electrolysis was carried out with the terminal voltage of 2.5 V in order to remove further small amount of contaminating water. For the pre-electrolysis, a spiral platinum wire and a glassy carbon rod were used as cathode and anode, respectively. When the cathodic current density became less than about 3 \times 10^{-4} \text{ A cm}^{-2}, pre-electrolysis was terminated. LiH (Wako Pure Chemical Co., Ltd.) was used as H⁺ ion source. From our own analysis, the purity of the LiH is 97.0+ %, which is equal to 99.0+ % in mole fraction. Experiments were performed at 673, 698, 723, 748 and 773 K.

Electrodes

A rectangular-shaped plate of titanium (99.9999 %, 5 \times 8 \times 0.4 \text{ mm}, Mitsubishi Mater. Co., Ltd.) was used as a working electrode after mechanical polishing and rinsing with ethanol. The reference electrode was an electrochemically formed TiHₓ electrode in (α+β) coexisting phase state. The equilibrium potential of this electrode is determined by the following reaction.

\[ \alpha\text{-TiH}_{n1} + (n_2-n_1) \text{H}^+ = \beta\text{-TiH}_{n2} + (n_2-n_1) e \]  \[2\]

where \( n_1 \) and \( n_2 \) are the lowest and highest composition values for (α+β) coexisting phase region at corresponding temperature, respectively. The potential of this reference electrode was calibrated with reference to that of 1 atm of H₂ gas measured by using a reversible hydrogen electrode (RHE). Its potential was identified as the stable potential after galvanostatic anodic H₂ gas evolution on a baglike nickel mesh. All potentials in the present paper are given with reference to the RHE potential at each temperature. A counter electrode was the Al-Li alloy (26), which was prepared by electrodepositing lithium on an aluminum plate (99.99 %, 10 \times 40 \times 1 \text{ mm}, Nilaco Co.).

Electrochemical measurement and characterization of formed TiHₓ

Electrochemical measurements were performed using a potentiogalvanostat (Hokuto Denko Co., Ltd.: HZ-3000) connected to a personal computer (Fujitsu, FMVS31673) or a potentiogalvanostat (Solastron: SI1287) connected to a personal computer (Fujitsu, FMV46CES3). The temperature measurement was carried out by the Chromel-Alumel thermocouple with an accuracy of ±1 K. Electrochemically formed TiHₓ was characterized by XRD (JOEL: JDX-8030W).
RESULTS AND DISCUSSION

Electrode potential-composition isotherms of Ti-H system
The electrode potential-composition (E-C) isotherms were measured in the following procedure. After the electrochemical activation treatment, galvanostatic cathodic electrolysis at below $5 \times 10^{-3} \text{ A cm}^{-2}$ was conducted on the electrochemically formed TiH$_x$ ($x \approx 1.8$) electrode intermittently to discharge predetermined quantity of hydrogen from the electrode. Then, open-circuit potential was measured after it became settled within $1 \times 10^{-4} \text{ V}$ in 1 minute. This procedure was repeated till the electrode potential was close to Li$^+$/Li potential. Additionally, H/Ti ratio in the following section was calculated from the total quantity of flowed electricity assuming that the current efficiency was 100%.

![Figure 2 E-C isotherms of Ti-H system at 673, 723 and 773 K.](image)

Figure 2 shows the obtained E-C isotherms at 673, 723 and 773 K. In each isotherm, two potential plateaus were observed, which are considered to correspond to the two phase coexisting state. In order to identify the phases, the samples prepared in A, C and E regions marked in Fig. 2 were analyzed by XRD. The obtained XRD results showed that the regions of A, C and E correspond to α, β and Δ phases, respectively. Therefore, the two potential plateaus in Fig. 2 correspond to the following reactions

(B): $\alpha$-TiH$_{n_1} + (n_2-n_1) \text{ H}^+ = \beta$-TiH$_{n_2} + (n_2-n_1) \text{ e} \quad [3]$

(D): $\beta$-TiH$_{n_2} + (n_3-n_2) \text{ H}^+ = \delta$-TiH$_{n_3} + (n_3-n_2) \text{ e} \quad [4]$

Using the obtained isotherms shown in Fig. 2, E-C-T relationship in each phase region has been examined in detail. Figure 3A shows the measured E-C
isotherms at each temperature in \( \alpha \) phase region. Using the following eq. 5, the activities of absorbed hydrogen, \( a_H \), can be derived from measured \( E \) and are plotted against H/Ti ratio in Fig. 3B.

\[
a_H = \exp\left(-\frac{F}{RT}E\right) \quad [5]
\]

where \( F \) is Faraday constant and \( R \) is gas constant. At each temperature, the activity varies linearly with H/Ti ratio up to nearly the terminal solubility. Assuming Sieverts law behavior for hydrogen dissolution to be held in this region, the relationship between \( a_H \) and the H/Ti ratio is expressed as

\[
K_S = \frac{C}{(P_{H_2})^{1/2}} = \frac{C}{a_H} \quad [6]
\]

where \( K_S \) is the corresponding Sieverts law constant, \( P_{H_2} \) is an equilibrium pressure of hydrogen gas and \( C \) is H/Ti ratio. Since \( P_{H_2} \) is very low in this region, fugacity coefficient is assumed to be 1. Solid curves in Fig. 3A and solid lines in Fig. 3B were determined at each temperature assuming eq. 6. In Fig. 3B, however, the extrapolated lines do not coincide with the origin. It is considered that this was caused by the residual hydrogen in Ti electrode. The \( K_S \) obtained from eq. 6 are then plotted against \( T \), from which the following relationship holds between \( K_S \) and \( T \).

\[
\ln K_S = A + \frac{B}{T} = (-6.71 \pm 0.40) + \frac{(6.04 \pm 0.29) \times 10^3}{T} \quad [7]
\]

The enthalpy of solution of hydrogen can be evaluated from the \( B \) value \(( R \times B )\) in eq. 7, and \( \Delta \bar{H}_H = -50.2 \pm 2.4 \) kJ mol\(^{-1}\) is obtained. Several reported values of \( K_S \) are listed in Table 1. Our result is well consistent with that obtained by Giorgi et al.\(^{16}\)
(ΔH_H = -50.6 kJ mol⁻¹), that operated in close temperature range of this work.

Table 1  Sieverts law constant in α phase where In K_s = ln (C/P^1/2) = ln (C/a) = A + B/T with C, P, a and T the H/Ti ratio, equilibrium pressure of hydrogen, activity of absorbed hydrogen and temperature in Kelvin respectively.

| P / atm | T / K  | A   | B / 1000 | Source |
|--------|--------|------|----------|--------|
| -      | 573, 628, 688 | -5.89 | 5.59     | [13]   |
| 10⁻³-1 | 753-1123 | -5.84 | 5.641    | [14]   |
| 10⁻¹¹-10⁻⁶ | 623-1073 | -6.27 | 6.088    | [16]   |
| 10⁻⁷-10⁻⁵ | 773-1073 | -6.627 | 6.332  | [19]   |
| <=10⁻³ | 873-1123 | -5.83 | 5.487    | [24]   |
| -      | 673-773 | -6.71±0.40 | 6.04±0.29 | This work |

In β and δ single phase regions and in (α+β) and (β+δ) coexisting phase regions, E-C isotherms were also measured at 673, 698, 723, 748 and 773 K. In single phase regions, E is treated as a function of C and T. In coexisting phase regions, E is considered as a function of T. The obtained relations are expressed as

\[ \text{In } \beta \text{ phase} \]
\[ E_\beta = (-0.565 - 0.294C) + (1.61 + 7.98C - 1.13\ln C) \times 10^{-4} T \] \[ [8] \]

\[ \text{In } \delta \text{ phase} \]
\[ E_\delta = (-0.872) + (-1.39 + 2.46C - 3.26\ln C) \times 10^{-3} T \] \[ [9] \]

\[ \text{In } (\alpha+\beta) \text{ phase} \]
\[ E_{\alpha+\beta} = (-0.612 \pm 0.013) + (4.89 \pm 0.18) \times 10^{-4} T \] \[ [10] \]

\[ \text{In } (\beta+\delta) \text{ phase} \]
\[ E_{\beta+\delta} = (-0.938 \pm 0.046) + (1.05 \pm 0.06) \times 10^{-4} T \] \[ [11] \]

Utilizing eq. 8-11, partial molar thermodynamic quantities of absorbed hydrogen, \( \Delta \bar{G}_H \), \( \Delta \bar{H}_H \) and \( \Delta \bar{S}_H \), in each phase were obtained clearly by the following equation.

\[ \Delta \bar{G}_H = -FE = \Delta \bar{H}_H - T\Delta \bar{S}_H \] \[ [12] \]
Integral quantities of TiH₂

Since the $E-C-T$ relationships in each phase have been established in the previous section, integral thermodynamic quantities can be estimated. In the following, the integral Gibbs energy, enthalpy and entropy of formation of TiH₂ were evaluated. Firstly, $\Delta G_f^0(\text{TiH}_2)$ can be expressed by using the *Duhem-Margules* equation as

$$\Delta G_f^0(\text{TiH}_2) = \int_0^C \tilde{G}_H dC = -F \left( \int_{\alpha + \beta} C_{(\alpha + \beta) / \beta} - C_{\alpha / (\alpha + \beta)} \right) E dC + \int_{\beta / (\beta + \delta)} \frac{C_{(\beta + \delta) / \delta} - C_{\beta / (\beta + \delta)}}{E} dC$$

where $E$ values in $1.8 < C < 2$ are extrapolated values from eq. 9. $\Delta G_f^0(\text{TiH}_2)$ calculated from eq. 13 at each temperature are plotted against $T$ in Fig. 4, together with reported values. From our result, the following linear relation between $\Delta G_f^0(\text{TiH}_2)$ and $T$ is obtained.

$$\Delta G_f^0(\text{TiH}_2) = -148 + 0.1527 T \text{ kJ mol}^{-1}$$

From eq. 14, $\Delta H_f^0(\text{TiH}_2)$ and $\Delta S_f^0(\text{TiH}_2)$ were calculated to be -148 kJ mol⁻¹ and -152 J mol⁻¹ K⁻¹, respectively. These values are very close to those of San-Martin and Manchester, who proposed the values at 737 K using reports of Dantzer et al. This indicates that the $E-C-T$ relationships obtained in the previous section have been well established.

![Figure 4](image_url)
CONCLUSIONS

The thermodynamic investigation of Ti-H system (TiH₂; 0 < x < 1.8) was conducted at 673 – 773 K by molten salt electrochemical technique. Accurate E-C-T relationships were obtained for α, α+β, β, β+δ and δ phase regions. From the obtained E-C-T relationships, partial molar thermodynamic quantities of absorbed hydrogen were estimated in all phases including high concentration region. In addition, integral thermodynamic quantities of formation of TiH₂ were calculated from obtained partial molar quantities using Duhem-Margules equation. Calculated integral quantities were in good agreement with reported values obtained by other techniques. These results certify that the molten salt electrochemical technique is highly valuable for thermodynamic investigations of various kinds of M-H system at low to high hydrogen concentration at high temperatures where the suitable electrolytes have hardly been applied until now. Furthermore, by utilizing suitable molten salt and stable hydrogen source, similar electrochemical investigations will be possible in wider temperature range.

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