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Heat conductions due to electrons and phonons for titanium hydride and deuteride

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Abstract

Thermal conductivities of titanium hydride and deuteride (TiH_x and TiD_x: $1.64 \leq x \leq 1.98$) in the temperature range from room temperature to 570 K have been calculated from the relation of thermal diffusivities, which are measured by means of a laser flash method, the literature data of their densities and specific heats. The calculation results showed that the thermal conductivities of TiH_x and TiD_x increased with increasing temperature and composition and were higher than that of Ti. On the basis of Wiedemann–Franz rule, the heat conductions due to electrons and phonons have been estimated from the temperature and composition dependences of the thermal and electrical conductivities measured using a four-contact DC method. Both phonons and electrons play an important role in the thermal conductivities of TiH_x and TiD_x at 570 K.

Keywords: Titanium hydride and deuteride; Thermal diffusivity; Thermal conductivity; Electrical resistivity; Electrical conductivity; Isotope effect

1. Introduction

Development of a hydrogen–air fuel cell which consists of proton-conducting oxides as a solid electrolyte and hydrogen storage metals as a hydrogen source have been proposed recently [1,2]. This closed-type fuel cell, making unnecessary the supply of hydrogen gas from outside, is promising as a compact electric-power generating system satisfying the increasing ecological demands.

The fuel cell using proton-conducting oxides has advantages under application at high temperatures. There, temperature profiles in the hydrogen storage metals will greatly influence hydrogen migration and transport. The rate of hydrogen transport to the fuel cell is one of the most important rate-determinant processes in the closed-type fuel cell. Thus, it is essentially important to understand the thermal properties of the hydrogen storage metals with changing hydrogen concentrations and temperatures. However, reported data are very scarce concerning the thermal conductivity of hydrogen storage metals in a wide range of temperatures and of hydrogen concentrations. Furthermore, the hydrogen transport itself may contribute to the heat transport, thus, the study of the hydrogen-isotope effects in the thermal conductivity will be important.

In the present study, the titanium hydrides and deuterides (TiH_x, TiD_x) with various hydrogen isotope concentrations were prepared and their thermal diffusivity was experimentally evaluated in the temperature range from 295 to 570 K. With the experimentally measured electrical conductivity and the reported reference data of the specific heat and the density, the thermal conductivity of the hydrides and the deuterides was calculated, separating the contributions of free electrons and phonons to the heat conductivity. The electrical conductivity of the hydrogen storage metals itself is an important parameter for a closed-type fuel cell, as the hydrogen storage metal will compose a part of the electrical circuit in the system.

The migration of the hydrogen (protons) in the hydrogen storage metals will also contribute to the electrical and the thermal conductivity. In the present study, isotope effects were studied, through comparing the thermal conductivity of the hydrides and the deuterides, having similar chemical compositions. The isotope effects are discussed mainly in terms of their influence on the electronic and phonon heat

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conduction. At elevated temperatures, mobility of the hydrogen (protons) is substantial and the isotope effects in the thermal conductivity will be complicated. The further detailed analysis on the isotope effects will be reported separately [3].

2. Experiments

The TiH_x and TiD_x specimens with various compositions of $1.64 \leq x \leq 1.98$ were prepared by adjusting the gas pressure and the temperature by means of a Sieverts apparatus. The hydrogen isotope concentrations in TiH_x and TiD_x were determined by the mass gain or the pressure changes after the hydrogenation. The dimensions of the specimens were $\phi 10.0 \times 1.0$ mm^3 for the thermal diffusivity measurement and $1.0 \times 1.0 \times 20.0$ mm^3 for the electrical resistivity measurement. The crystal structures of the composition with $x < 1.9$ are face-centered cubic (δ-phase) within the experimental temperatures of 280–570 K, while those with $x \geq 1.9$ transform from face-centered tetragonal (ε-phase) to face-centered cubic roughly between 280 and 320 K [4–6]. Hydrogen atoms in the ε- and δ-phases are located in vacant tetrahedral interstices with only a very small fraction in octahedral holes [7]. Scanning electron microscope micrographs showed that there existed a little microcrack in the specimens.

The thermal diffusivity and the electrical resistivity measurements were made using laser-flash [8] and four-contact DC [9] methods, respectively. For both measurements, the specimens were heated up to 570 K, because TiH_x and TiD_x quickly decompose at temperatures above 600 K. Each measurement was performed on heating and cooling of the specimens.

3. Results and discussion

3.1. Thermal diffusivities of titanium hydride and deuteride

The thermal diffusivities of $TiH_{1.77-1.97}$ and $TiD_{1.64-1.96}$ are plotted against the temperatures from room temperature to 570 K in heating and cooling regimes in Figs. 1(a) and (b). The dashed curve represents the thermal diffusivity of Ti. The data obtained on heating were consistent with those obtained on cooling. These results indicate that the hydrogen isotope loss from TiH_x and TiD_x in the experimental temperature range is negligible. The thermal diffusivities of TiH_x and TiD_x increased as the composition increased and as the temperature decreased. $TiH_{1.97}$ is the only compound with better thermal diffusivity than Ti in the temperatures up to 570 K. In the compositions with $x > 1.9$ cases, the values of the thermal diffusivities scattered due to the ε–δ transformation at about 300 K. The temperature dependence of the thermal

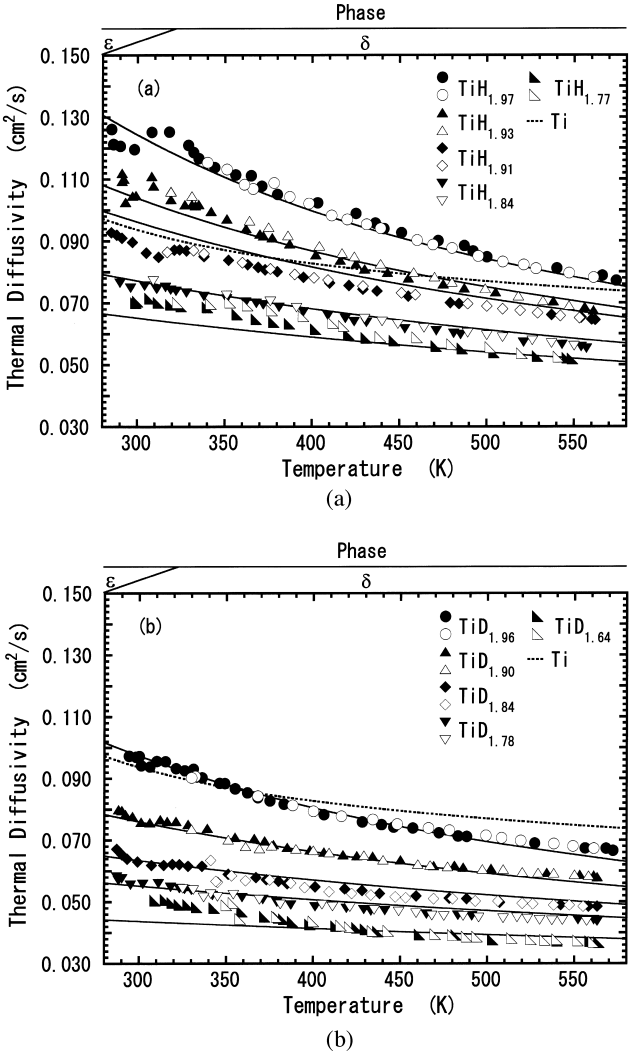

Fig. 1. Temperature dependence of thermal diffusivities for (a) $TiH_{1.77}$, $TiH_{1.84}$, $TiH_{1.91}$, $TiH_{1.93}$, $TiH_{1.97}$ and (b) $TiD_{1.64}$, $TiD_{1.78}$, $TiD_{1.84}$, $TiD_{1.90}$, $TiD_{1.96}$, as compared with that for Ti. The solid curves are computed with the empirical Eqs. (1) and (2), respectively, as functions of the temperature and the hydrogen isotope concentration.

diffusivities for TiH_x and TiD_x (α_{TiHx} and α_{TiDx} [cm^2/s]) was expressed with the following empirical equations as functions of the temperature T ($280 \leq T \leq 570$) (K) and the composition x ($1.64 \leq x \leq 1.98$);

$$\alpha_{TiHx} = \frac{40.4}{\{T + 2.00 \times 10^3 (2.00 - x)\}} + 1.20 \times 10^{-2} \quad (1)$$

$$\alpha_{TiDx} = \frac{32.2}{\{T + 2.28 \times 10^3 (2.00 - x)\}} + 1.50 \times 10^{-2} \quad (2)$$

To observe clearly the isotope effect in the thermal diffusivities for the various compositions in Figs. 1(a) and (b), the effect of the composition on the thermal diffusivities of TiH_x (●) and TiD_x (○) at 350 K and TiH_x

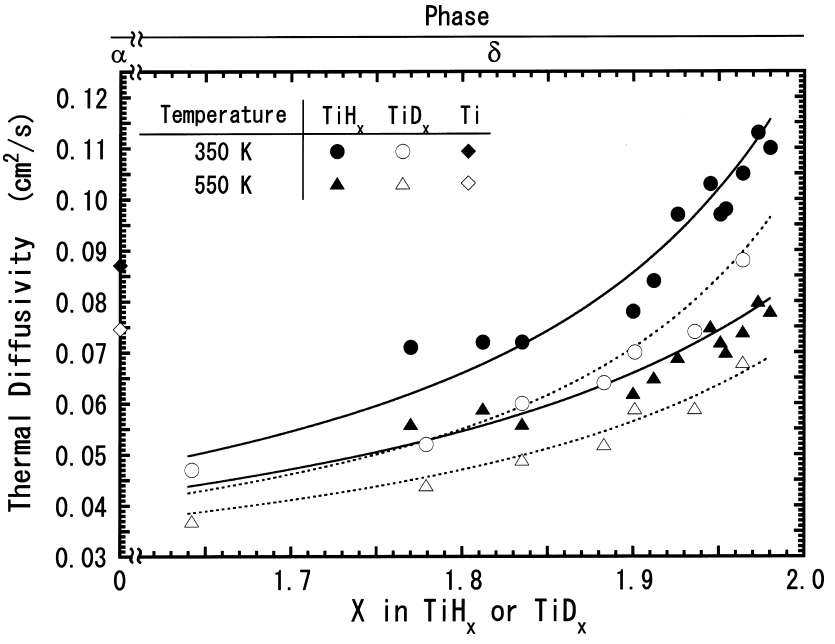

Fig. 2. Composition dependence of thermal diffusivities at temperatures of 350 and 550 K.

(▲) and TiD_x (△) at 550 K is shown in Fig. 2. The solid and dashed curves in Fig. 2 are fitted with Eqs. (1) and (2), respectively. The isotope difference reduced a little as the temperature increased and the composition decreased.

3.2. Evaluation of thermal conductivity

Figs. 3(a) and (b) shows thermal conductivities ($\lambda_{TiH1.92}$, $\lambda_{TiD1.93}$ and λ_{Ti}) of $TiH_{1.92}$, $TiD_{1.93}$ and α-Ti, which were obtained with the empirical equations of the thermal diffusivities (Eqs. (1) and (2)). The $\lambda_{TiH1.92}$ and $\lambda_{TiD1.93}$ were higher compared with λ_{Ti} in the temperatures of 280–570 K. The thermal conductivities (λ_i: $i = TiH_x$, TiD_x, Ti) of TiH_x, TiD_x and Ti were calculated from the relations of $\lambda_i = \alpha_i Cp^i d_i$, where Cp^i and d_i represented the specific heat and the densities of i. In the present study, the values of Cp^{TiHx}, Cp^{TiDx}, Cp^{Ti}, d_{TiHx}, d_{TiDx} and d_{Ti} were expressed as functions of temperature (280 K$\leq T \leq$570 K) and composition ($1.64 \leq x \leq 1.98$) with $Cp^{TiHx} = 0.116 + 1.69\times10^{-3}T$, $Cp^{TiDx} = 0.262 + 1.69\times10^{-3}T$, $Cp^{Ti} = (9.94\times10^{-2} + 7.78\times10^{-5}T)\times4.184$ [J/g·K], $d_{TiHx} = 4.02 - 0.112x$, $d_{TiDx} = d_{TiHx} + 0.141$ and $d_{Ti} = 4.41$ [g/cm^3], which were derived from the literature [6,10,11].

The thermal conductivities of TiH_x, TiD_x and Ti by electronic conduction (λ_e^i) were estimated from the relations of $\lambda_e^i = L_e^i \sigma_i T$, according to the Wiedemann–Franz rule. σ_i are the electrical conductivities of i, which were measured at the same experimental conditions as the thermal diffusivity by the four-contact DC method. L_e^i are the Lorenz numbers for the electronic conduction of i, which are assumed as $L_e^i = (\pi^2/3)(k_B/e)^2 \fallingdotseq 2.45\times10^{-8}$ [WΩ/K^2], where k_B and e are the Boltzmann constant and elementary electric charge. A small isotope difference between $\lambda_e^{TiH1.92}$ and $\lambda_e^{TiD1.93}$ in Fig. 3(a) is interpreted by the difference in the electron–phonon scattering, where the optical mode plays an important role.

Finally, the thermal conductivities of TiH_x, TiD_x and Ti by phonon conduction (λ_p^i) were determined by subtracting λ_e^i from λ^i. It was found in Figs. 3(a) and (b) that the heat conductions for TiH_x, TiD_x at the higher temperatures were due to both free electrons and phonons, while that for Ti was due to free electrons only. At lower temperatures, the contribution by the phonons was greater than that by the electrons. The isotope difference in the thermal conductivities of TiH_x and TiD_x corresponds to the difference in the electron–phonon and phonon–phonon scatterings. Therefore, the isotope effects in the thermal diffusivities at 350 and 550 K in Fig. 2 are ascribed to the electron–phonon scattering by the optical mode and to the phonon–phonon scattering.

4. Summary

In order to estimate the electronic and phonon heat conductions of TiH_x and TiD_x, the thermal diffusivities and electrical resistivities were measured by means of the laser-flash and the four-contact DC methods, respectively. The thermal conductivities were calculated from the experimental data of the thermal diffusivity and the literature data for the specific heat and the density, while the electrical ones were derived from the electrical re-

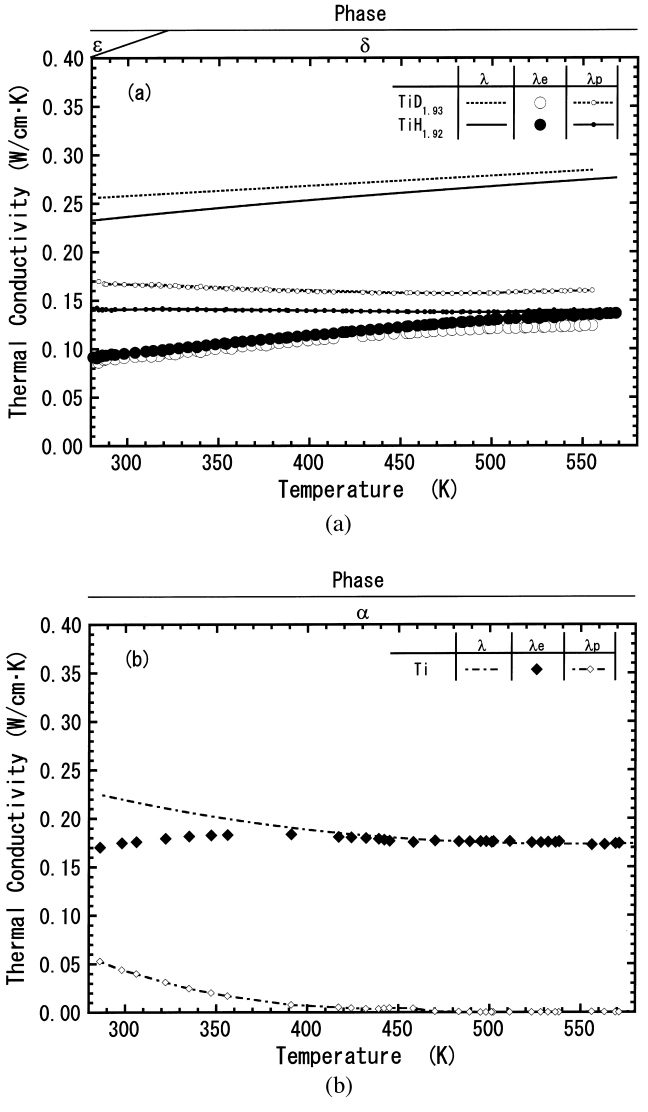

Fig. 3. Temperature dependence of thermal conductivities for (a) $TiH_{1.92}$ and $TiD_{1.93}$ and (b) Ti. λ, λ_e and λ_p represent the experimental data of the thermal conductivity, the thermal conductivities due to free electrons and phonons, respectively.

sistivities. The thermal diffusivities of TiH_x and TiD_x decreased with increasing temperature and decreasing composition, while the electrical resistivities increased. Isotope effects in the thermal and electrical conductivities were observed. From the temperature dependences of the thermal and electrical conductivities and the Lorenz number of the electronic conduction for the Wiedemann–Franz rule, the heat conductions due to the electrons and phonons were separated. It was found that both electrons and phonons played a role in the thermal conduction in the temperature range up to 570 K. The electron–phonon scattering by the optical mode and the phonon–phonon scattering greatly contribute to the isotope effect in the thermal conductivities of TiH_x and TiD_x.

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