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Journal of Nuclear Materials 344 (2005) 298–300

journal of nuclear materials

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Thermal properties of titanium hydrides

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Abstract

Thermal properties of the TiH_x ($1.53 \leqslant x \leqslant 1.75$) were measured in the temperature range from 323 to 673 K. The Debye temperatures for the TiH_x compounds were smaller than those for the metal. The heat capacities of the titanium hydrides were larger than that for the metal because of hydrogen vibration. The thermal diffusivities for the titanium hydrides were smaller than that for the metal. The thermal conductivities were estimated. The dependency of thermal conductivity on temperature was slightly changed by hydrogenation. However a significant difference between the values for titanium and the titanium hydrides was not found.

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1. Introduction

Metal hydride fuels are considered as target materials to transmute actinide wastes that are generated in nuclear fuels. For example, the U–Ti–H or U–Zr–H system is proposed as the actinide hydride target in the core of the fast breeder reactor containing mixed oxide fuels. However, the change of hydrogen concentration affects thermal and mechanical properties of the hydride target. Since a high reliability of nuclear materials is required under various severe conditions, it is necessary to clarify the influence of hydrogen on properties of the materials. However, there are few reports on their thermal properties. Yamanaka et al. [1–3] reported that the thermal properties of zirconium were considerably changed by hydrogenation. Therefore, it is expected that thermal properties of titanium hydride are quite abnormal, and thus it is necessary to elucidate the characteristics of titanium hydride. In the present study, the thermal properties of titanium hydride were examined.

2. Experimental procedure

The titanium hydrides were prepared by the modified Sieverts' apparatus. A pure titanium (99.9%) polycrystalline pellet (10 mm ∅ × 5 mm l) was used as a starting material. Firstly, the pure titanium was put into the apparatus, which was evacuated down to 10^{-8} Torr, and was annealed at 1073 K for 10 h. Secondly, the titanium was hydrogenated at 0.05 MPa hydrogen atmosphere in the temperature range of 673–1073 K. The absorbed hydrogen had the purity of 7N. The details of the hydrogenation method were described in our previous paper [4]. We succeeded to produce the crack-free titanium hydride bulk samples by this method.

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doi:10.1016/j.jnucmat.2005.04.059

The Debye temperature was estimated by sound velocities, which were obtained by applying the ultrasonic pulse-echo method (Echometer1062, Nihon Matech Corp.). The heat capacity was measured by the DSC method (Triple-cell DSC, ULVAC-RIKO inc.). The thermal diffusivity was measured using a laser flash apparatus (TC-7000, ULVAC) from room temperature to 773 K in vacuum. The thermal conductivity was estimated from the thermal diffusivity, the heat capacity and the density.

3. Results and discussion

The Debye temperature θ_D for the titanium hydride was derived from the sound velocities by using the following equation:

$$\theta_D = \frac{h}{k}\sqrt[3]{\frac{9N}{4\pi V_c}\frac{1}{1/V_L^3 + 2/V_S^3}}, \tag{1}$$

where h is the Planck constant, k is the Boltzmann constant, N is the number of Ti atoms in the unit cell, V_c is the unit cell volume, V_L and V_S are the longitudinal and shear sound velocities, respectively. The change of the Debye temperature is plotted in Fig. 1, as a function of hydrogen content. The θ_D for the titanium hydride is much smaller than that for pure titanium, and decreases with increasing hydrogen content, as follows:

$$\theta_D(K) = 1622 - 806 \times C_H(H/Ti). \tag{2}$$

The present values are consistent with the values by Bohmhammel [5], which have been obtained by the measurement of low temperature heat capacity. It is also found from this figure that decrease of the Debye temperature suggests the decrease of inter-atomic bond strength by hydrogen addition.

Fig. 2 shows the experimental and the calculated values of heat capacities of Ti and TiH_x as a function of temperature. The details of the calculation were described in our previous paper [2]. From the calculation, it is found that the heat capacities for the hydrides were larger than that for the metal because of hydrogen vibration. The results of the calculation are in fair accordance with both of the present experimental and the literature data [6,7]. However, only for the measurement of $TiH_{1.66}$, hydrogen desorption was found to occur at around 550 K. According to Bhosle et al. [8], hydrogen desorption temperature decreased with decreasing of the grain size. This measurements showed that the hydrogen desorption temperature would be affected by the grain size of TiH_x. Although we estimated that the grain size of the titanium hydride was 30 μm [4] by using the optical microscope, further analysis would be required.

Fig. 3 shows the thermal diffusivities of TiH_x as a function of temperature. The diffusivities of the hydrides are smaller than that of the metal. The results of the

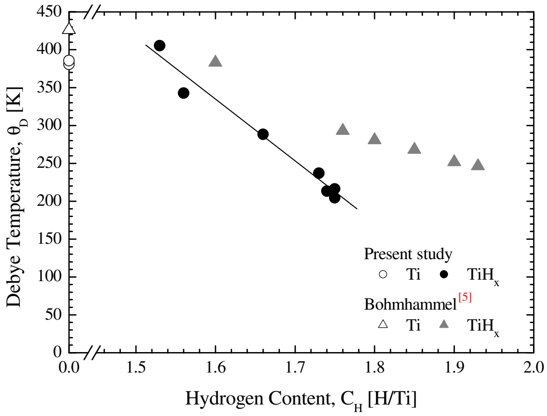

Fig. 1. Change in the Debye temperature θ_D of TiH_x with the hydrogen content C_H.

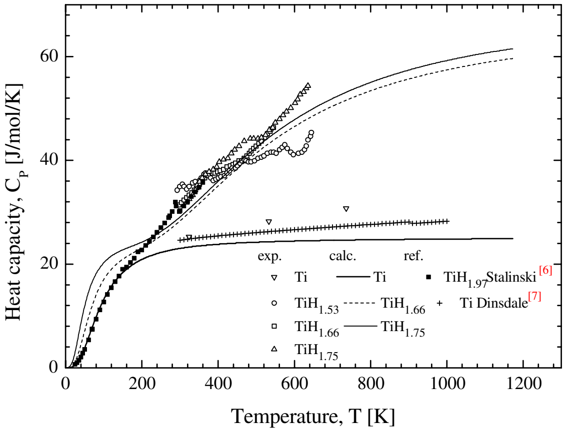

Fig. 2. Temperature dependence of heat capacity C_p of TiH_x.

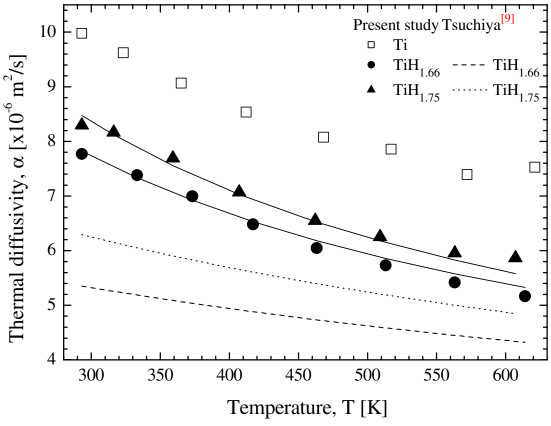

Fig. 3. Temperature dependence of the thermal diffusivity α of TiH_x.

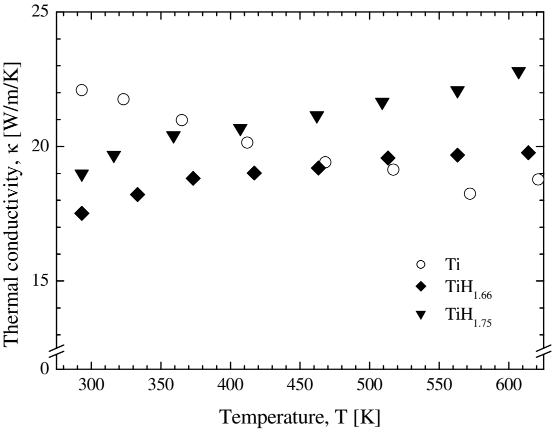

Fig. 4. Temperature dependence of the thermal conductivity κ of TiH_x.

present study are significantly different from those by Tsuchiya et al. [9]. There were no micro-cracks observed by scanning electron microscope in the present study, whereas these had been in the work by Tsuchiya et al. Therefore it is considered that the difference for the diffusivity is due to the amount of the internal micro-cracks or dislocations, which probable causes thermal resistance. The thermal diffusivities of TiH_x for the present study are expressed as follows:

$$\alpha(TiH_x) = \frac{2.82 \times 10^{-3}}{T + 500 \times (2 - x)} + 1.73 \times 10^{-6} (m^2/s). \quad (3)$$

The thermal conductivity κ was derived from the product of the thermal diffusivity α, the heat capacity C_p, and the density ρ. The densities of the pure Ti, $TiH_{1.66}$ and $TiH_{1.75}$ were 4.50, 3.85 and 3.82 g/cm^3, respectively

$$\kappa = \alpha C_p \rho. \quad (4)$$

Fig. 4 shows the thermal conductivity of the titanium and the titanium hydrides. The temperature dependence of the thermal conductivity is opposite for the hydride and metal. These differences would be given by the increased heat capacity. However, these differences are considered not to be significant.

4. Conclusions

Titanium hydride bulk samples were fabricated with no cracks. The Debye temperatures of the titanium hydrides were smaller than that of the metal, and decreased with the hydrogen addition. The heat capacities for the hydrides were larger than those for the metals because of hydrogen vibration. The thermal diffusivities of the titanium hydrides were larger than those from the previous report, the reason for which was considerable to be the internal micro-cracks. The thermal conductivities for both Ti and TiH_x were almost identical.

Acknowledgement

We would like to express our special thanks to Research Associate Dr B. Tsuchiya, for the advice of the development of fabrication of flaw-free bulk titanium hydride.

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