Journal of Nuclear Materials 294 (2001) 94–98

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Thermal properties of zirconium hydride

Shinsuke Yamanaka [a,*], Kazuhiro Yamada [a], Ken Kurosaki [a], Masayoshi Uno [a], Kiyoko Takeda [b], Hiroyuki Anada [b], Tetsushi Matsuda [c], Shinichi Kobayashi [c]

[a] *Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1 Suita, Osaka 565-0871, Japan*
[b] *Sumitomo Metal Industries, Ltd., Fuso-cho, Amagasaki 660, Japan*
[c] *Nuclear Fuel Industries, Ltd., Ohaza-Noda, Kumatori-cho, Sennan-gun, Osaka 590-04, Japan*

Abstract

Zirconium hydride specimens with hydrogen contents of 1.45–1.70 H/Zr were fabricated directly from zirconium metal in a modified UHV Sieverts apparatus. All the zirconium hydride fabricated in the present study were found from X-ray diffraction analysis to be CaF_2-type δ-ZrH_{2-x}. At temperatures of 350–700 K, the heat capacity of the zirconium hydride was measured using an enthalpy method by means of a differential scanning calorimeter (DSC), and the experimental results were consistent with the values estimated from the sound velocities and the thermal expansion coefficient. In the temperature range of 300–700 K, the thermal diffusivity of the zirconium hydride was examined by a laser flash method. The thermal diffusivity decreased with increasing temperature and was not markedly influenced by the hydrogen content. The thermal conductivity of the zirconium hydride was calculated from thermal diffusivity and heat capacity and found to have slightly lower thermal conductivity than pure zirconium metal. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Zirconium alloys such as Zircaloy and Zr–Nb have been employed as nuclear materials of LWRs and CANDUs. Problems such as embrittlement of the cladding and pressure tube have stirred interest in the characteristics of zirconium hydride. In recent years, the influence of zirconium hydride on the integrity of LWR cladding is also observed with keen interest because of high burnup of nuclear fuel.

Therefore, it is important to understand the physicochemical properties of zirconium hydride such as thermochemical data, mechanical and thermal properties, and transport characteristics. Many studies on the crystallographic properties of zirconium hydride have been reported [1–8]. The thermochemical studies on the Zr–H binary system have been also carried out, and a review paper has been published recently [9]. Limited information is available on thermophysical properties of the zirconium hydride such as heat capacity, thermal conductivity, and elastic moduli. Fundamental properties such as crystallographic and mechanical properties were measured in our previous study [10]. In the present study, thermal properties of zirconium hydride such as heat capacity and thermal conductivity have been examined.

2. Experimental

Zirconium hydride specimens in the form of disks and pellets were directly fabricated from zirconium metal with 99.9% purity in a modified UHV Sieverts apparatus. It was found from microscopic observation that all the hydride specimens have no microcracks or pores. The measured densities of the fabricated hydride specimens indicated 100% theoretical density. The hydrogen content of the specimen ranges from 1.45 to 1.70 H/Zr (δ-ZrH_{2-x}).

The lattice parameters and thermal expansion coefficients were obtained by high-temperature X-ray diffraction analysis. Ultrasonic pulse-echo measurements

---

[*] Corresponding author. Tel.: +81-6 6879 7904; fax: +81-6 6879 7889.

E-mail address: yamanaka@nucl.eng.osaka-u.ac.jp (S. Yamanaka).

PII: S0022-3115(01)00457-3

provided sound velocities and elastic moduli. The Debye temperatures and heat capacities were calculated from these results. The details of these measurements were described in our previous paper [10].

The heat capacity of zirconium hydride was measured by a differential scanning calorimeter (DSC) (DSC-SH-3, ULVAC) using an enthalpy method [11]. The details of the procedure for the enthalpy method have been reported by Asou et al. [11]. Measurement were carried out at intervals of 20 K and heating rates of 5 K/min at temperatures between 350 and 700 K, and the heat capacity at the midpoint of each temperature interval was obtained.

Thermal diffusivity measurements were made for zirconium hydride at temperatures from 300 to 700 K by means of a laser flash apparatus (TC-7000, ULVAC). Thermal conductivity was calculated from the thermal diffusivity, heat capacity and density.

3. Results and discussion

3.1. Fundamental properties

Fundamental properties such as lattice parameter, thermal expansion coefficient and elastic moduli of zirconium hydride, were examined in our previous study [10], and are reviewed briefly here.

X-ray diffraction analysis at room temperature showed that all the zirconium hydrides prepared in the present study were δ-ZrH_{2-x} with a fluorite-type structure. The lattice parameter of the zirconium hydride was found in our previous study [1] to change with the hydrogen content according to the following relationship:

$$a\ (\text{nm}) = 0.4706 + 4.382 \times 10^{-3} C_H(\text{H/Zr}).$$

Although the reported data [1–8] show some scatter, our results were close to the values reported by Bowman Jr. [8] and Beck [3]. The densities of the zirconium hydride were calculated from the lattice parameters. Although the hydride had much lower density than zirconium metal, the density of the δ-zirconium hydride $\rho = 5.66$ mg/m^3 was almost independent of the hydrogen content. Since the calculated X-ray density of the zirconium hydride agreed well with measured density, all the hydride specimens appear to have 100% th.d.

Average volume thermal expansion coefficients α from 300 to 600 K, calculated from the results of high-temperature X-ray diffraction analysis, were found to range from 2×10^{-5} to 3×10^{-5} K^{-1} for the zirconium hydrides, which was larger than that of zirconium metal. The elastic moduli such as the shear modulus, Young's modulus, bulk modulus and Poisson's ratio for the zirconium hydride were derived from the longitudinal and shear sound velocities. Both the Young's and shear moduli of zirconium hydride were larger than those of zirconium metal and slightly decreased with increasing hydrogen content. The compressibility β can be written in terms of the longitudinal sound velocity v_l and the shear sound velocity v_s by

$$\beta = [\rho(3v_l^2 - 4v_s^2)/3]^{-1}.$$

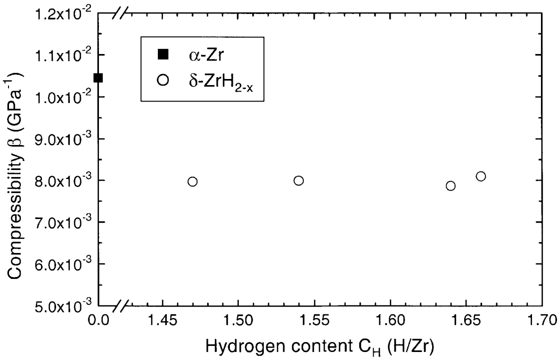

Fig. 1. Change in the compressibility β of δ-ZrH_{2-x} with the hydrogen content C_H.

The change in the compressibility of zirconium hydride with the hydrogen content is shown in Fig. 1. As can be seen in this figure, the compressibility of the hydride ranging from 7.9×10^{-3} to 8.1×10^{-3} GPa^{-1} is not strongly influenced by the hydrogen content and is lower than that of zirconium metal, 1.05×10^{-2} GPa^{-1}.

3.2. Heat capacity

The results of the heat capacity measurement on δ-zirconium hydride by the enthalpy method are revealed in Fig. 2, together with the experimental data for pure zirconium metal. The heat capacities obtained for pure zirconium metal are in good agreement with the literature data [12]. The heat capacity of the zirconium hydride increased with increasing temperature. Zirconium hydride with a hydrogen content of 1.53 H/Zr had a slightly smaller heat capacity than that with 1.58 H/Zr. The heat capacity of zirconium hydride was much larger than that of pure zirconium metal, and the differences in the heat capacity between hydride and metal increased with temperature.

Tomasch [13] has reported the heat capacity of δ-$ZrH_{1.66}$ at temperatures from room temperature to 800 K. The heat capacity above 800 K has been studied by Beck [4] for zirconium hydride with lower hydrogen content. The heat capacity of δ-ZrH_{2-x} has been measured using a drop calorimeter specifically designed for the use with hydride materials by Weeks et al. [14]. As shown in Fig. 2, the heat capacity obtained in the present study is close to the reported values of Tomasch [13] and Weeks et al. [14].

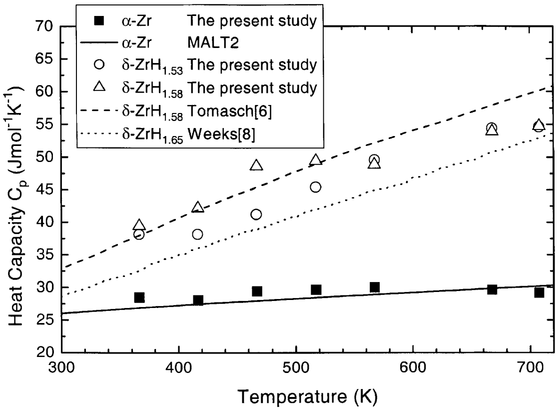

Fig. 2. Temperature dependence of the heat capacity C_P of δ-ZrH_{2-x}.

Although several authors [4,13–15] have studied the heat capacity of zirconium hydride, the dependence of temperature and hydrogen content on the heat capacity of zirconium hydride was not clarified. In the present study, an analysis on the heat capacity has been performed using the experimental and literature data to elucidate various contributions to the heat capacity of zirconium hydride.

The Debye temperature Θ_D was estimated from the longitudinal and shear sound velocities. In the range of 1.45–1.65 H/Zr, the Debye temperature Θ_D of zirconium hydride decreased from 340 to 330 K with increasing hydrogen content, and it was larger than that of zirconium metal at 274 K.

In our previous study [1], the heat capacity C_p of zirconium hydride was calculated from the sum of various contributions:

$$C_p\ (\mathrm{J/mol/K}) = C_v^{Zr} + C_d + C_{el} + C_v^{H},$$

where C_v^{Zr} is the vibrational term of the acoustic mode, C_d the dilatational term, C_{el} the electronic term, and C_v^{H} is the vibrational term of the optical mode. The vibrational term of the acoustic mode was calculated using the experimental values of Θ_D by

$$C_v^{Zr} = 3n_{Zr}RD(\Theta_D/T),$$

where $D(\Theta_D/T)$ is the Debye function, T the temperature in K, n_{Zr} the number of zirconium atoms per molecule, and R is the gas constant. The dilatational term was derived from the experimental data of thermal expansion coefficient α, the compressibility β and the molar volume V_m:

$$C_d = \alpha^2 V_m T/\beta.$$

The electronic term C_{el} was calculated using the coefficient of electronic heat capacity $\gamma = 4.10$ mJ/K^2 mol reported for ε-$ZrH_{2.00}$ [15] by the following equation:

$$C_{el} = \gamma T.$$

Using the vibrational frequency of hydrogen $\nu_H = 3.31 \times 10^{13}\ \mathrm{s}^{-1}$ obtained by neutron scattering measurement for δ-$ZrH_{1.5}$ [16], the vibrational term for the optical mode C_v^{Zr} was evaluated from the following equation:

$$C_v^{H} = 3n_H R(\Theta_E/T)^2 \exp(\Theta_E/T)/[\exp(\Theta_E/T) - 1]^2.$$

In this equation, $\Theta_E = h\nu_H/k$ is the Einstein temperature of hydrogen in δ-zirconium hydride and n_H is the number of hydrogen atoms per molecule.

In Fig. 3, the heat capacity for δ-$ZrH_{1.66}$ calculated in this study is compared with the experimental data obtained in the present study and those reported in the literature [6–9]. The heat capacity of zirconium hydride with the δ-phase calculated in the present study is in good agreement with the experimental values.

Though at lower temperatures the acoustic mode of lattice vibration mainly contributed to the heat capacity, above room temperature, the hydrogen vibration, that is the optical mode, markedly increases the heat capacity. At a given temperature, the heat capacity increased with increasing hydrogen content due to hydrogen vibrational contribution. On the basis of the analysis, the change in the heat capacity with the hydrogen content and temperature was found to obey the empirical equation [10]:

$$\begin{aligned} C_p = {} & 25.02 + 4.746 \times C_H \\ & + (3.103 \times 10^{-3} + 2.008 \times 10^{-2} \times C_H)T \\ & - (1.943 \times 10^5 + 6.358 \times 10^5 \times C_H)/T^2. \end{aligned}$$

At room temperature, the heat capacities of zirconium hydride were close to that for zirconium metal, irrespective of the crystal structure. This suggests that the heat capacity of the hydride at room temperature is

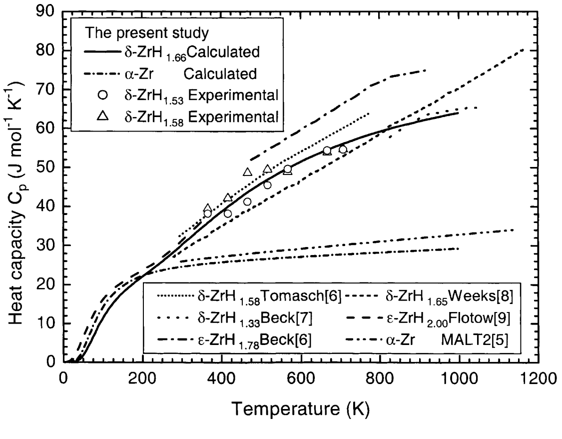

Fig. 3. Comparison of the calculated heat capacity C_P of δ-ZrH_{2-x} with the experimental values.

determined by the vibration of zirconium lattice. The marked difference in the heat capacity between hydride and metal at higher temperatures appears to result from hydrogen vibrational contribution, that is the optical mode of lattice vibration of zirconium hydride. As indicated in Fig. 3, there is no marked difference in the heat capacity between δ- and ε-hydride phase. The heat capacity of zirconium hydride appears to be mainly determined by vibrational contributions. Since the dilatational and electronic contributions are much smaller than vibrational ones, it appears that at higher temperatures the heat capacity of ZrH_{2-x} approaches 70 J/K mol and the temperature dependence is smaller. It should be noted that the calculated heat capacity of zirconium hydride is consistent with the experimental values obtained by DSC and drop calorimetry. This implies the validity of the change in the heat capacity with the hydrogen content and temperature given by the empirical equation.

3.3. Thermal conductivity

The thermal diffusivity δ of zirconium hydride obtained at room temperature is illustrated in Fig. 4 as a function of the hydrogen content. As is obvious from this figure, the thermal diffusivity of zirconium hydride is slightly lower than that of pure zirconium metal and almost independent of the hydrogen content. The thermal diffusivity of zirconium hydride obtained in the present study agrees with the values reported by Weeks et al. [14]. For δ-zirconium hydride with hydrogen contents of 1.45–1.65, the thermal diffusivity ranges from 9×10^{-6} to 1×10^{-5} m²/s.

Fig. 5 indicates the change in the thermal diffusivity of zirconium hydride with temperature, together with the experimental results of pure zirconium metal. As shown in this figure, the thermal diffusivity of pure zirconium metal obtained in the present study agrees with the values reported by Murabayashi et al. [17] and Takahashi et al. [18]. The thermal diffusivity is found from Fig. 5 to decrease with increasing temperature. No marked influence of the hydrogen content on the thermal diffusivity is observed.

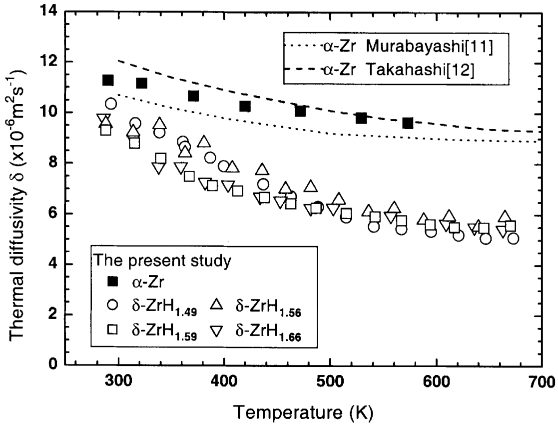

Fig. 5. Temperature dependence of the thermal diffusivity δ of δ-ZrH_{2-x}.

The thermal conductivity κ of zirconium hydride was evaluated by the following relationship:

$$\kappa = \delta C_p \rho.$$

The heat capacity C_p calculated by the empirical equation was employed for the thermal conductivity evaluation. Fig. 6 shows the variation in the thermal conductivity of zirconium hydride at room temperature with the hydrogen content. This figure shows that zirconium hydride has a slightly lower thermal conductivity

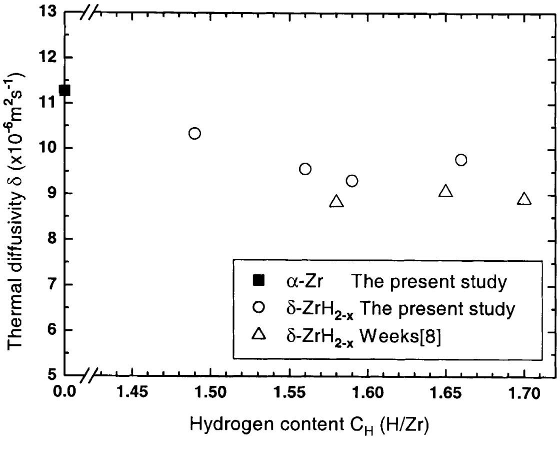

Fig. 4. Change in the thermal diffusivity δ of δ-ZrH_{2-x} at room temperature with the hydrogen content C_H.

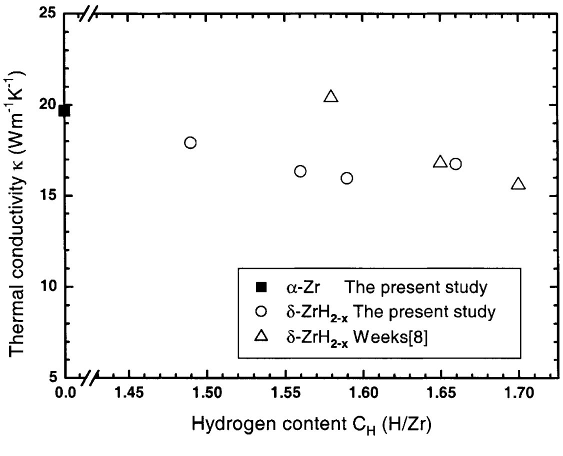

Fig. 6. Change in the thermal conductivity κ of δ-ZrH_{2-x} at room temperature with the hydrogen content C_H.

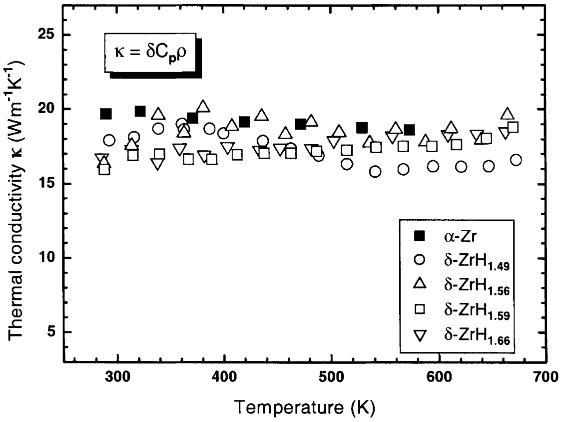

Fig. 7. Temperature dependence of the thermal conductivity κ of δ-ZrH_{2-x}.

than pure zirconium metal. The thermal conductivity of zirconium hydride obtained in the present study agrees reasonably well with the reported data [9]. The thermal conductivity of δ-zirconium hydride with hydrogen content of 1.45–1.65 H/Zr shows a nearly constant value of 16–18 W/m K at room temperature.

The temperature dependence of the thermal conductivity of zirconium hydride is indicated in Fig. 7. The figure shows that the thermal conductivity is not markedly affected by the temperature, and that the thermal conductivity is slightly lower for the zirconium hydride than for zirconium metal.

4. Summary

The zirconium hydride specimens with hydrogen content of 1.45–1.70 H/Zr fabricated directly from zirconium metal formed in the CaF_2-type δ-ZrH_{2-x} phase. In the temperature range from 350 to 700 K, the measurement of the heat capacity of the zirconium hydride was performed with a DSC, and the results obtained in the present study agreed with the literature data. The values of heat capacity estimated from the sound velocities and the thermal expansion coefficient were consistent with the experimental data. The heat capacity of zirconium hydride appears to be mainly determined by vibrational contributions. The empirical equation expressing the temperature and hydrogen content dependence of the heat capacity was obtained for the δ-zirconium hydride.

The thermal diffusivity of zirconium hydride was examined by the laser flash method at temperatures from 300 to 700 K. The thermal diffusivity decreased with increasing temperature and was almost independent of the hydrogen content. The thermal conductivity of δ-zirconium hydride was calculated from thermal diffusivity, heat capacity and density and was slightly lower than for pure zirconium metal. The temperature dependence of the heat capacity of the zirconium hydride was found to be small.

Acknowledgements

The present study has been performed under the auspices of the Japan Atomic Energy Research Institute.

References

[1] C.P. Kempter, R.O. Elliott, K.A. Schneider Jr., J. Chem. Phys. 33 (1960) 837.
[2] F. Ducastelle, R. Caudron, P. Costa, J. Phys. 31 (1970) 57.
[3] R.L. Beck, Am. Soc. Metall. Trans. Q 55 (1962) 542.
[4] R.L. Beck, Am. Soc. Metall. Trans. Q 55 (1962) 556.
[5] S.S. Sidhu, N.S.S. Murthy, F.P. Campos, D.D. Zauberis, Adv. Chem. Ser. 39 (1963) 87.
[6] K.E. Moore, W.A. Young, J. Nucl. Mater. 27 (1968) 316.
[7] J.S. Cantrell, R.C. Bowman Jr., D.B. Sullenger, J. Phys. Chem. 88 (1984) 918.
[8] R.C. Bowman Jr., B.D. Craft, J.S. Cantrell, E.L. Venturini, Phys. Rev. B 31 (1985) 5604.
[9] E. Zuzek, J.P. Abriata, A. San-Martin, F.D. Manchester, in: F.D. Manchester (Ed.), Phase Diagrams of Binary Hydrogen Alloys, ASM, Metals Park, OH, 2000, p. 309.
[10] S. Yamanaka, K. Yoshioka, M. Uno, M. Katsur, H. Anada, T. Matsuda, S. Kobayashi, J. Alloys Compounds 293–295 (1999) 23.
[11] M. Aou, T. Yoneoka, Y. Takahashi, in: Proceedings of the 13th Japan Symposium on Thermophysical Properties, 1992, p. 237.
[12] Japan Thermal Measurement Society, Thermodynamics data base for personal computer MALT 2.
[13] W.J. Tomasch, Phys. Rev. 123 (1961) 510.
[14] C.C. Weeks, M.M. Nakata, C.A. Smith, in: Proceedings of the Seventh Conference on Thermal Conductivity, 1967.
[15] H.E. Flotow, D.W. Osborne, J. Chem. Phys. 34 (1961) 1418.
[16] W.L. Whittemore, A.W. McReynolds, Phys. Rev. 113 (1959) 806.
[17] M. Murabayashi, S. Tanaka, Y. Takahashi, J. Nucl. Sci. Technol. 12 (1975) 661.
[18] Y. Takahashi, M. Yamawaki, K. Yamamoto, J. Nucl. Mater. 154 (1988) 141.