Journal of Alloys and Compounds 293–295 (1999) 23–29

Thermal and mechanical properties of zirconium hydride

S. Yamanaka[a,*], K. Yoshioka[a], M. Uno[a], M. Katsura[a], H. Anada[b], T. Matsuda[c], S. Kobayashi[c]

[a]*Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Osaka 565, 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

The physico–chemical properties of zirconium hydride such as mechanical and thermal properties have been studied in the present study. The zirconium hydride specimens in the form of pellets (6 mm $\phi \times 10$ mm l) had the hydrogen contents with 1.5–1.7 H/Zr, which were fabricated directly from zirconium metal in a modified UHV Sieverts apparatus. All the zirconium hydrides prepared in the present study showed CaF_2 type δ ZrH_{2-x}. The lattice parameter slightly increased with the hydrogen content. The thermal expansion coefficients of the zirconium hydrides evaluated from high-temperature X-ray diffraction data were larger than that of zirconium metal and increased with the hydrogen content. The longitudinal and shear sound velocities of the zirconium hydride were slightly different from those of zirconium metal, which enabled us to estimate the elastic properties. The zirconium hydride had higher elastic moduli than zirconium metal and the elastic moduli slightly depended on the hydrogen content. The microhardness of the zirconium hydride was much higher than that of zirconium metal and decreased with increasing hydrogen content. The Debye temperature of the zirconium hydride estimated from the sound velocities was larger than that of pure zirconium metal. The heat capacity was also estimated from the sound velocities and the thermal expansion data.

Keywords: Zirconium hydride; Lattice constant; Thermal expansion coefficient; Elastic modulus; Hardness; Debye temperature; Heat capacity

1. Introduction

Zirconium alloys such as Zircaloy have been widely used as the cladding materials of light water reactors, and hydrogen behavior in the cladding has been watched with keen interest because of high burn up of nuclear fuel in recent years. Problems such as embrittlement of the cladding have stirred interest in the characteristics of zirconium hydride. Zirconium hydride is also of interest as a moderator in nuclear applications.

Therefore, it is important to understand the physico–chemical properties of zirconium hydride such as thermochemical data, mechanical and thermal properties, and transport characteristics. In the present study, the mechanical and thermal properties of zirconium hydride have been studied.

2. Experimental

The zirconium hydride specimen in the form of pellet was directly fabricated from zirconium metal with 99.9% purity in a modified UHV Sieverts apparatus. The hydrogen content of the specimen ranges from 1.5 to 1.7 H/Zr. The hydride specimen consisted of many platelets inside large grains without any microcrack or pore, showing a Widmanstatten characteristic.

The lattice parameters and thermal expansion coefficients were obtained by high-temperature X-ray diffraction analysis. The ultrasonic pulse–echo measurement gave us the sound velocities and elastic moduli. The hardness was also measured. The Debye temperatures and heat capacities were estimated from these results.

3. Results and discussion

It was found from the X-ray diffraction analysis at room temperature that all the zirconium hydrides prepared in the present study showed δ ZrH_{2-x} with a fluorite type structure. Fig. 1 shows the change in the lattice parameter a with the hydrogen content C_H. It is found from this figure that the lattice parameter slightly increases with increasing hydrogen content, according to the following relationship:

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

---

*Corresponding author. Tel.: +81-6-879-7887; fax: +81-6-875-5696.
E-mail address: yamanaka@nucl.eng.osaka-u.ac.jp (S. Yamanaka)

0925-8388/99/$ – see front matter
PII: S0925-8388(99)00389-8

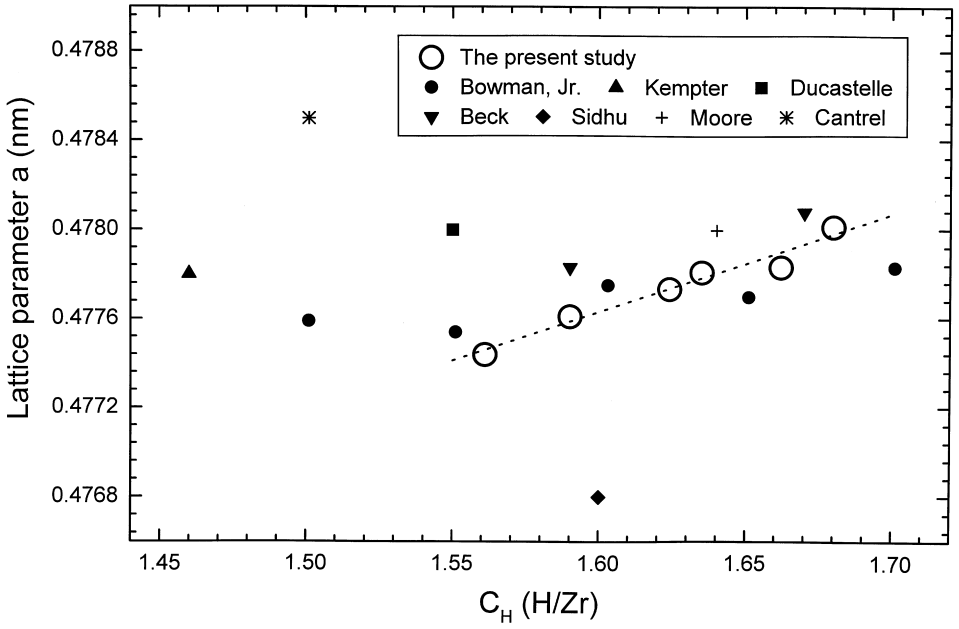

Fig. 1. Change in the lattice parameter *a* of δ ZrH_{2-x} with the hydrogen content C_H.

In this figure, the results obtained in the present study is compared with the reported data [1–8]. Our results are close to the values reported by Bowman [8] and Beck [3]. The densities of the δ hydride were calculated from the lattice parameters. The hydride had much lower density than zirconium metals, but the density of the hydride was almost independent of the hydrogen content.

Average thermal expansion coefficients from 298 to 573 K were estimated from the lattice parameters obtained by high-temperature X-ray diffraction. Fig. 2 indicates that the thermal expansion coefficient α ranges from 2×10^{-5} to 3×10^{-5} for the zirconium hydrides, which is larger than that of α Zr metal. The change in the thermal expansion coefficient with the hydrogen content can be expressed as,

$$\alpha(\mathrm{K}^{-1}) = 5.259\times10^{-6} + 1.330\times10^{-5}\times C_{\mathrm{H}}(\mathrm{H/Zr}).$$

The increase in the atom distance may cause larger

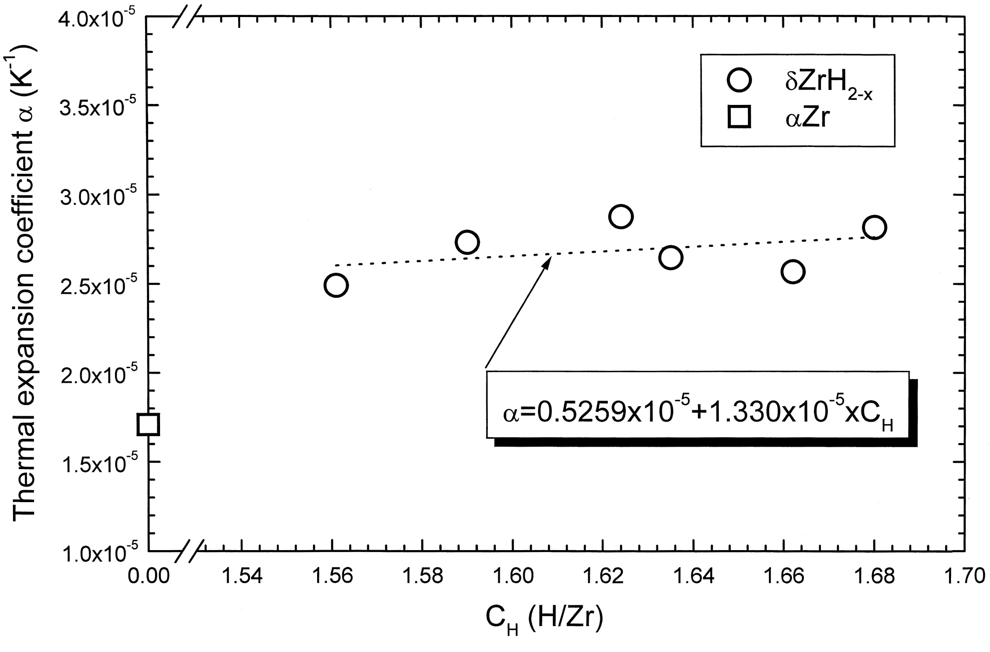

Fig. 2. Change in the thermal expansion coefficient α of δ ZrH_{2-x} with the hydrogen content C_H.

anharmonicity in the potential energy, which brings about larger thermal expansion of hydrides with higher hydrogen contents.

There were marked differences in longitudinal and shear sound velocities at room temperature between zirconium metal and hydrides. From the ratios of the longitudinal sound velocities Vl to shear sound velocities V_s, all the hydride specimens appear to be isotropic. For isotropic media, the shear modulus G, Young's modulus E, bulk modulus K and Poisson's ratio ν can be written in terms of the longitudinal sound velocity V_l and the shear sound velocity V_s by,

$$G = \rho V_s^2$$

$$E = G[(3V_l^2 - 4V_s^2)/(V_l^2 - 4V_s^2)]$$

$$K = \rho(3V_l^2 - 4V_s^2)/3$$

$$\nu = (V_l^2 - 2V_s^2)/(V_l^2 - V_s^2)/2$$

where ρ is the density of the specimen.

Both Young's and shear moduli of δ hydride are larger than those of zirconium metal and slightly decrease with increasing hydrogen content, as shown in Fig. 3. The bulk modulus K showed the same trend as other elastic moduli. The Poisson's ratio of the hydride was estimated to be about 0.32, irrespective of hydrogen content, and no marked difference was observed between zirconium metal and hydride.

The hardness provides the information of the resistance of a material to plastic deformation. The values of microhardness obtained for zirconium hydrides are shown in Fig. 4. The hardness values of the hydrides are higher than that of pure zirconium and decrease with increasing hydrogen content. The variation in microhardness of zirconium hydride with the hydrogen content is written by,

$$H_v(\mathrm{GPa}) = 7.19 - 2.77 \times C_H(\mathrm{H/Zr}).$$

For various materials, the microhardness is known to be associated with Young's modulus. For pure metals, we estimate the relation of hardness H_v with Young's modulus E, as indicated in Fig. 5. For oxide and carbide ceramics, the H_v is also proportional to E, and the values of H_v/E is 0.05 [9], much larger than those for pure metals. As evidenced by this figure, the zirconium hydrides reveals the intermediate characteristics between ceramics and metals. Since other mechanical properties of the zirconium hydride such as fracture strength is important for analyzing the hydrogen embrittlement of the Zircaloy cladding, the study is now in progress.

The Debye temperature Θ_D is related to the longitudinal sound velocity V_l and shear sound velocity V_s as follows:

$$\Theta_D(K) = (h/k)(9N/4\pi V_c)^{1/3}(1/V_l^3 + 2/V_s^3)^{-1/3}$$

where h is the Plank constant, k is the Boltzman constant, N is the number of zirconium atoms in a unit cell, and V_c is the unit cell volume. Fig. 6 indicates the Debye temperatures for the zirconium hydrides obtained in the present study. The Debye temperature Θ_D for the zirconium hydride decreases with increasing hydrogen content C_H. And, it is larger than that of zirconium metal.

The heat capacity C_p for the zirconium hydride can be approximately estimated from the sum of various contributions:

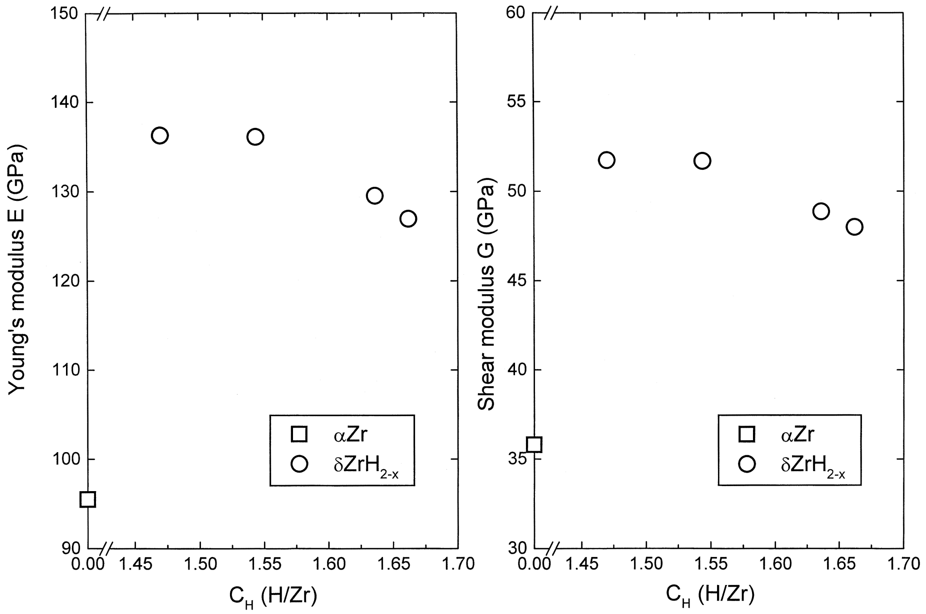

Fig. 3. Change in the Young's modulus E and shear modulus G of δ ZrH_{2-x} with the hydrogen content C_H.

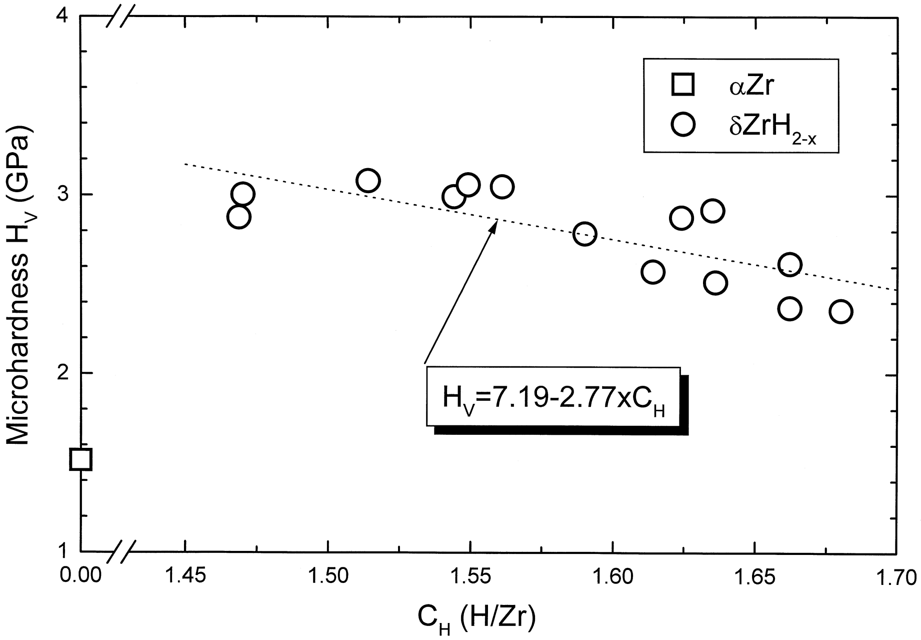

Fig. 4. Change in the microhardness H_v of δ ZrH_{2-x} with the hydrogen content C_H.

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

In this equation, the C_v^{Zr} is the vibrational term for the acoustic mode, the C_d is the dilatational term, the C_{el} is the electronic term, and C_v^H is the vibrational term for the optical mode.

Only zirconium atoms appear to contribute the acoustic mode of the lattice vibration of the zirconium hydride. Using the experimental values of Θ_D obtained in the present study, we can calculate the vibrational term for the acoustic mode using the following equation:

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

where $D(\Theta_D/T)$ is the Debye function, T is the temperature in K, n_{Zr} is the number of zirconium atoms per molecule, and R is the gas constant.

The dilatational term can be estimated from the experimental data of thermal expansion coefficient α, the compressibility $\beta = 1/K$ and the molar volume V_m:

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

Since no information on the electronic heat capacity was

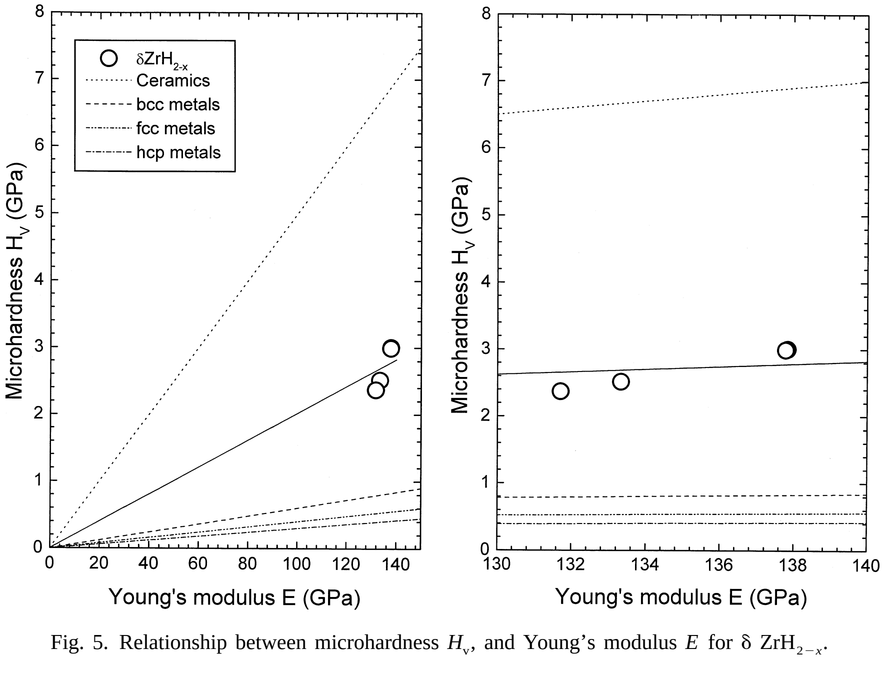

Fig. 5. Relationship between microhardness H_v, and Young's modulus E for δ ZrH_{2-x}.

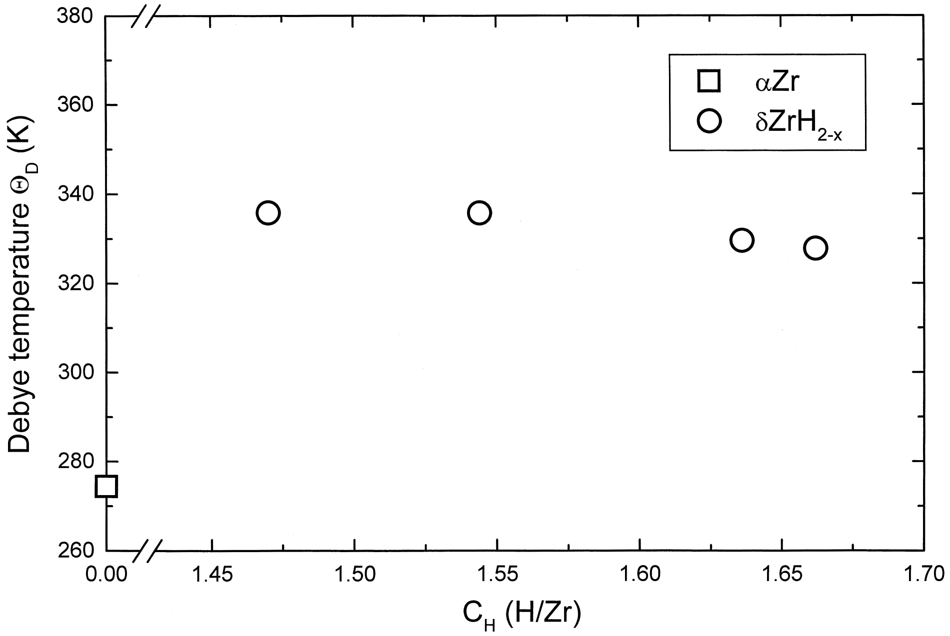

Fig. 6. Change in the Debye temperature Θ_D of δ ZrH_{2-x} with the hydrogen content C_H.

available for δ zirconium hydride, we used the coefficient of electronic heat capacity $\gamma = 4.10 \times 10^{-3}$ J/mol/K^2 reported for ε $ZrH_{2.00}$ [10]. The electronic term C_{el} was estimated by,

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

The vibration of hydrogen mainly contributes to the vibrational term for the optical mode. Assuming that hydrogen behaves as a harmonic oscillator in the zirconium hydride, we estimated the vibrational term for optical mode with this equation. For the calculation, we used the literature value for the vibrational frequency of hydrogen $\nu_H = 3.31 \times 10^{13}$ s^{-1} obtained by neutron scattering measurement for δ $ZrH_{1.5}$ [11]. 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 the zirconium hydride and n_H is the number of hydrogen atoms per molecule.

Fig. 7 shows the temperature dependence of heat capacity C_P, for the zirconium hydride, $ZrH_{1.66}$. As is obvious in this figure, at lower temperatures, the acoustic mode of lattice vibration mainly contributes 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 increases with increasing hydrogen content. The variation of the heat capacity with the hydrogen content and temperature can be given by the empirical equation:

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

In Fig. 8, the heat capacity for δ $ZrH_{1.66}$ estimated in the present study is compared with the experimental data reported in the literature [4,10,12]. The heat capacity of zirconium hydride with the δ phase calculated in the present study is in good agreement with the reported values.

Below room temperature, the heat capacities of zirconium hydride are almost the same as zirconium metal, independent of the crystal structure. This suggests that the heat capacity of hydride is determined by the vibration of zirconium lattice. At higher temperatures, there is marked difference in the heat capacity between hydride and metal. This results from hydrogen vibrational contribution, that is the optical mode of lattice vibration of zirconium hydride.

4. Conclusions

All the zirconium hydrides prepared in the present study showed CaF_2 type δ ZrH_{2-x}. The lattice parameter slightly increased with the hydrogen content. The thermal expansion coefficients of the zirconium hydrides evaluated from high-temperature X-ray diffraction data were larger than that of zirconium metal and increased with the hydrogen content. The longitudinal and shear sound velocities of the zirconium hydride were slightly different from those of zirconium metal, which enabled us to estimate the elastic properties. The zirconium hydride had higher elastic

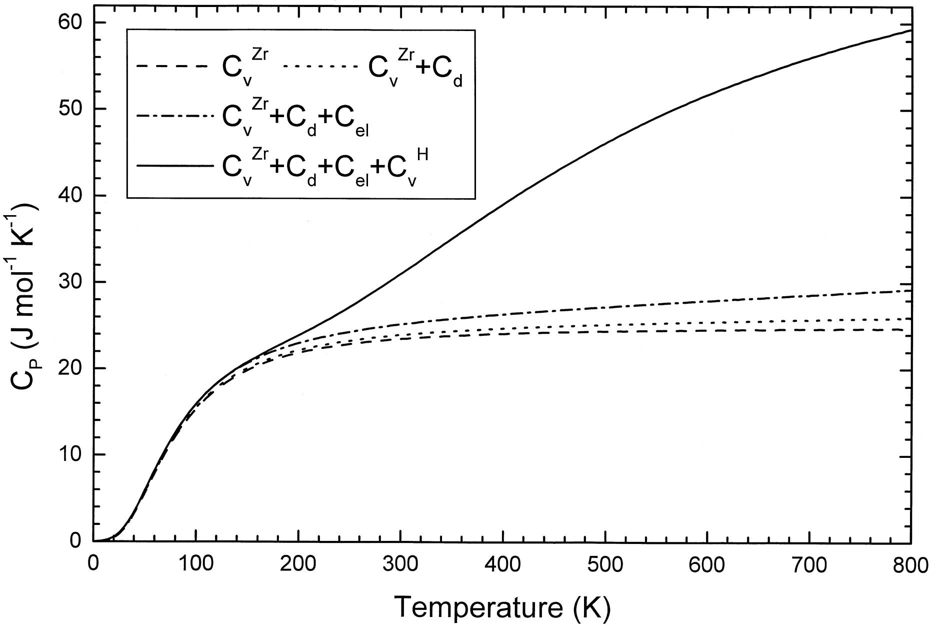

Fig. 7. Temperature dependence of heat capacity C_P, of δ $ZrH_{1.66}$.

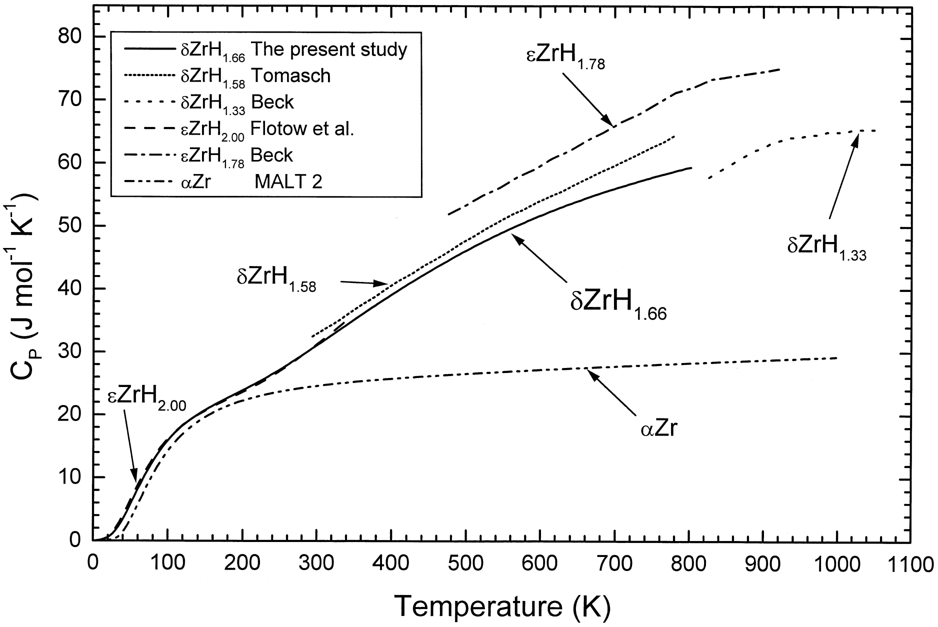

Fig. 8. Temperature dependence of heat capacity C_P of δ ZrH_{2-x}.

moduli than zirconium metal and the elastic moduli slightly depended on the hydrogen content. The microhardness of the zirconium hydride is much higher than that of zirconium metal and decreases with increasing hydrogen content. The Debye temperature of the zirconium hydride estimated from the sound velocities was larger than that of pure zirconium metal. The heat capacity estimated from the sound velocities and the thermal expansion data was in good agreement with the experimental data reported in the literature.

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. Met. Trans. Q 55 (1962) 542.
[4] R.L. Beck, Am. Soc. Met. 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] K. Tanaka, H. Koguchi, T. Mura, Int. J. Eng. Sci. 27 (1989) 11.
[10] H.E. Flotow, D.W. Osborne, J. Chem. Phys. 34 (1961) 1418.
[11] W.L. Whittemore, A.W. McReynolds, Phys. Rev. 113 (1959) 806.
[12] W.J. Tomasch, Phys. Rev. 123 (1961) 510.