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Journal of Alloys and Compounds 330–332 (2002) 99–104

Journal of ALLOYS AND COMPOUNDS

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Characteristics of zirconium hydride and deuteride

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Abstract

The electrical and thermal properties of zirconium hydride and deuteride have been measured. The lattice parameter of δZrD_{2-x} was smaller than that of δZrH_{2-x}, and the deuteride had higher elastic moduli than the hydride. The electrical and thermal conductivities of δZrH_{2-x} were slightly different from pure Zr metal. The electronic structure of the zirconium hydride was found from XPS measurements to differ from those in the pure Zr metal, and there was a peak due to the Zr–H bond at 6.4 eV below Fermi energy in the XPS spectra. The density of states was estimated by a molecular orbital calculation, and the agreement between the XPS valence band measurements and the calculations was quite satisfactory. Some of the mechanical and thermal properties of zirconium hydride and deuteride were interpreted in terms of the results of the molecular orbital calculation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium hydride; Zirconium deuteride; Isotope effect; Lattice constant; XPS; Molecular orbital method; Elastic modulus; Hardness; Heat capacity; Electrical resistivity; Thermal conductivity

1. Introduction

Zirconium alloys such as Zircaloy and Zr–Nb are widely used as nuclear materials in fission reactors such as LWRs and CANDUs. The characteristics of zirconium hydride and deuteride are required to understand the mechanism of hydrogen embrittlement of the cladding and the pressure tube.

Therefore, the mechanical properties of zirconium hydride and deuteride have been examined in our previous study [1,2]. The electrical and thermal properties of zirconium hydride have been measured in the present study. To understand the effects of composition content and isotope on the characteristics of zirconium hydride, the electronic structure of zirconium hydride was also estimated by X-ray photoelectron spectroscopy (XPS) and molecular orbital calculation.

2. Experimental

The zirconium hydride and deuteride specimens were directly prepared from zirconium metal with 99.9% purity in a modified Sieverts apparatus. The hydrogen isotope content of the specimen ranges from 1.45 to 1.70 Q/Zr atomic ratio (Q=H or D).

The lattice parameters and thermal expansion coefficients were obtained by high-temperature X-ray diffraction analysis. The sound velocities and elastic moduli were measured by an ultrasonic pulse–echo method. The details of these measurements were described elsewhere [1].

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a QUANTUM 2000 (PHYSICAL ELECTRONICS). The surface of the hydride specimen was sputtered with Ar ion for 15 min in a vacuum below 10^{-6} Pa. Two energy regions, the valence band (the binding energy ranges from Fermi energy to 40 eV) and Zr 3d level (the binding energy ranges from 175 to 190 eV), were scanned concurrently (the scanning step was 0.125 eV). The background was removed from the obtained spectrum by employing a Shirley type function.

The electrical resistivity of zirconium hydride in the temperature range of room temperature to 700 K was measured by a standard four-probe method using a 2010 MULTIMETER supplied by KEITHLEY. The thermal diffusivity measurement was made for the zirconium hydride at the temperatures between room temperature and 700 K by means of a laser flash apparatus (TC-7000,

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PII: S0925-8388(01)01448-7

ULVAC). The thermal conductivity was estimated from the thermal diffusivity, the heat capacity and the density.

3. Results and discussion

3.1. Crystallographic properties

All the zirconium hydrides and deuterides prepared in the present study showed a δ single phase with a fluorite type structure. Fig. 1 shows the lattice parameters of zirconium hydride and deuteride with various compositions, together with the reported data [3–6]. From this figure, the lattice parameter of the zirconium deuteride is found to be markedly smaller than that of the hydride and slightly increases with the deuterium content.

The vibrational frequency of deuterium in δZrD_{2-x} is lower than that of hydrogen in δZrH_{2-x}, which can be expressed by the relationship: $\nu_D = \nu_H / 2^{1/2}$. Under the anharmonic Zr–Q interatomic potential, the lower vibrational frequency of deuterium appears to cause smaller mean distance of Zr–D than Zr–H. The isotope effect on the lattice parameter appears to result from the difference in the mean interatomic distance of Zr–Q between hydride and deuteride. This trend has been observed for other hydrides and deuterides such as the 4th group metals and the lanthanides.

3.2. Electronic structure

The XPS spectra of zirconium metal and hydrides are shown in Figs. 2 and 3. Fig. 2 indicates that in the spectrum of the zirconium metal, the Zr 4d peak appears at about 1 eV below the Fermi energy E_F and that in the spectrum of the hydride, the Zr–H bonding peak appears at 6.4 eV below E_F. The height of the Zr 4d peak decreases and that of the Zr–H bonding peak increases with increasing hydrogen content, as shown in this figure. The Zr 4d peak of the hydride is smaller than that of the zirconium metal. It is found from Figs. 2 and 3 that a chemical shift is observed between the zirconium metal and hydride. The peak positions of the hydride show lower energy than those of the metal. The differences are about 0.8 eV for Zr 4p and about 0.4 eV for Zr 3d, respectively. Veal et al. [7] have reported the XPS spectrum for $ZrH_{1.65}$ and observed a strong peak appearing at 7 eV below the Fermi level. The results obtained in the present study are in good agreement with the XPS spectrum measured by Veal et al.

The density of states of zirconium hydride and metal was calculated by a molecular orbital method (DV-X α). The DV-X α cluster method is based on the Hartree–Fock–Slater approximation, and the detailed explanation of this method is given in the literature [8]. Comparison of calculated density of states with X-ray photoelectron spectra of zirconium metal and hydrides are shown in Fig. 4. As is obvious in this figure, the density of states of zirconium hydride obtained by the molecular orbital calculation is consistent with the XPS spectra. The peak for the Zr–H bond is found from the calculation to be generated in the vicinity of −6.5 eV and to increase in

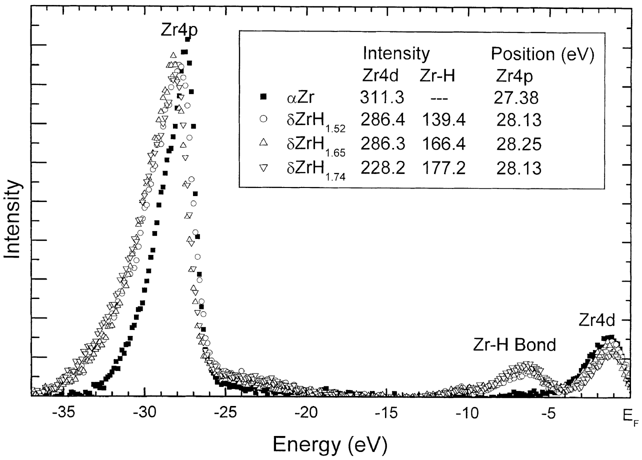

Fig. 2. XPS spectra of the valence band and Zr 4p level for zirconium metal and hydride.

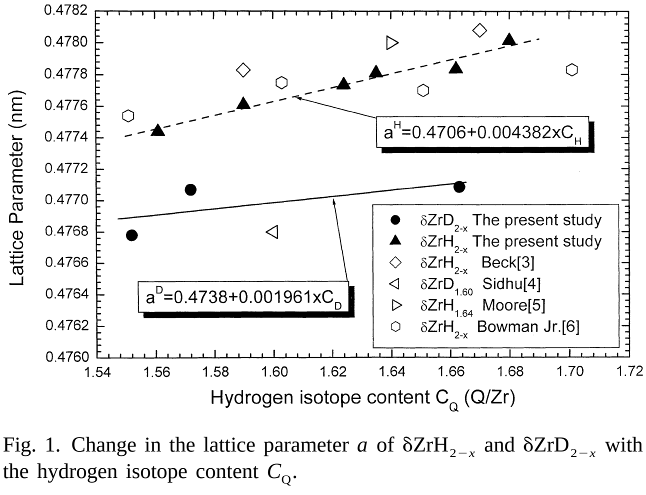

Fig. 1. Change in the lattice parameter *a* of δZrH_{2-x} and δZrD_{2-x} with the hydrogen isotope content C_Q.

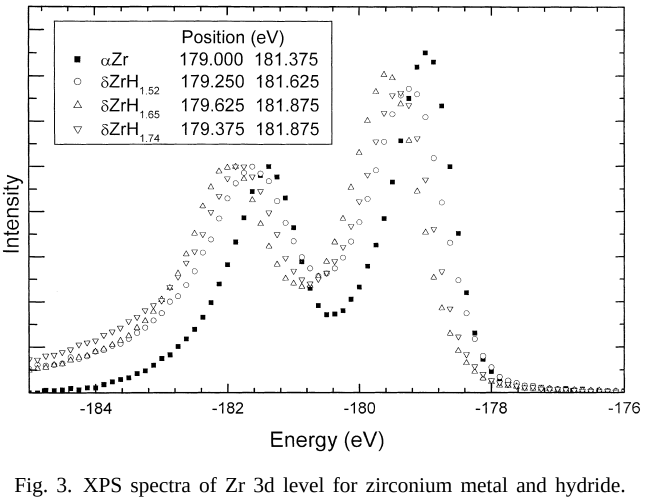

Fig. 3. XPS spectra of Zr 3d level for zirconium metal and hydride.

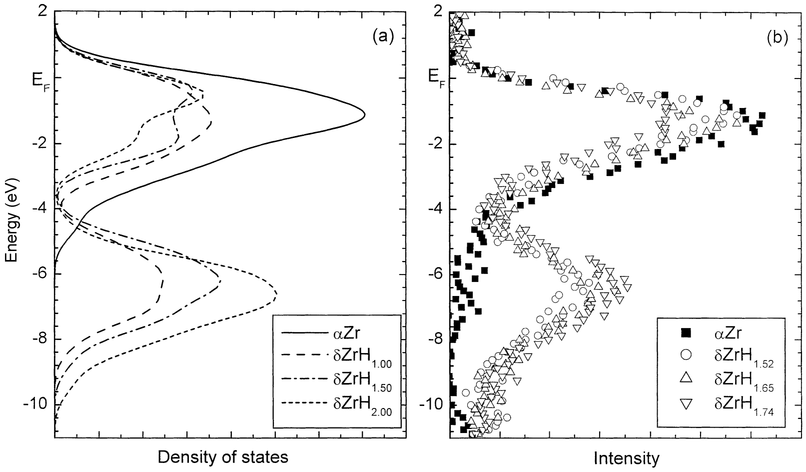

Fig. 4. Comparison of the calculated density of states and the valence band XPS spectra for zirconium metal and hydride. (a) Calculated by the DV-X α method; (b) measured by the XPS.

magnitude with increasing hydrogen content. The shoulder in the vicinity of −2 eV for Zr 4d electrons, which take part in a metallic bond in a 4d transition element, is reduced with the hydrogen content. By donating Zr 4d electrons to the Zr–H bond, the bond between Zr atoms in the zirconium hydride is weaker than that in pure zirconium metal.

The bond order which is the overlap population of the electrons between atoms can be estimated by the DV-X α calculation and is a measure of the strength of the covalent bond between atoms. The changes in the bond orders of Zr–Zr bond and Zr–H bond in zirconium hydrides with the hydrogen content are shown in Fig. 5. Though the bond order of Zr–Zr bond decreases with increasing the hydrogen content, the change in that of Zr–H bond is not strongly influenced by the hydrogen content.

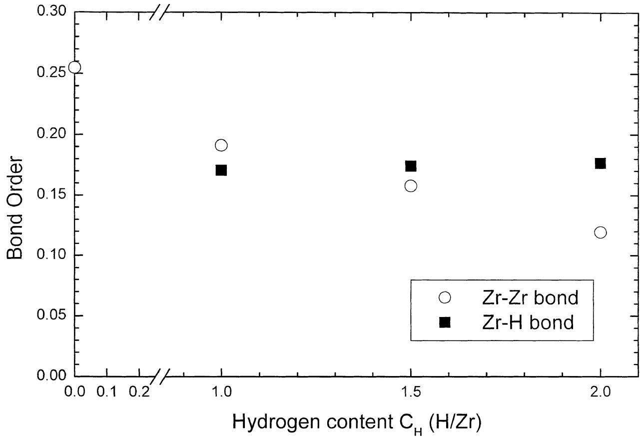

Fig. 5. Change in the bond order of zirconium hydride with the hydrogen content.

3.3. Mechanical properties

Longitudinal and shear sound velocities at room temperature differ from the hydrides to the deuterides, as shown in Table 1. This table also indicates that both Young's and shear moduli are larger for the deuteride than for the hydride and slightly decrease with increasing hydrogen isotope content.

Since the Zr–Zr bond is reinforced with some Zr–H bonds, the elastic moduli of the zirconium hydride are larger than those of pure metal. While the Zr–Zr bond decreases with the hydrogen content, Zr–H bond hardly changes with the hydrogen content. This suggests that the elastic moduli of the hydride slightly decrease with increasing hydrogen content. Since the electronic structure of the deuteride appears to be similar to that of the hydride, the electronic state of deuterium is almost the same as that of hydrogen. Therefore, the interatomic potential in the deuteride may be the same as that in the hydride. Since the interatomic distance between Zr and D atoms is smaller than that between Zr and H atoms at a given composition, the elastic constant for the Zr–D is larger than that for the Zr–H. This implies that the elastic moduli of the deuteride are larger than those of the hydride.

Table 1 also shows that the microhardness value decreases with increasing hydrogen isotope content for both zirconium hydride and deuteride and there also exists the isotope effect on the microhardness.

3.4. Electrical and thermal properties

The electrical conductivity of zirconium metal and hydride is shown in Fig. 6, indicating that the hydride has lower conductivity than pure metal and is almost independent of the hydrogen content. Bickel and Berlincourt [9] have studied the electrical properties of zirconium

Table 1
Characteristics of zirconium hydride and deuteride

	Hydrogen content	Lattice parameter		Density ρ (kg/m^3)	Mechanical properties from Ref. [1]					Thermal properties from Ref. [1]		Sound velocity	
	C_Q (Q/Zr)	a (nm)	c (nm)		E (GPa)	G (GPa)	β (GPa^{-1})	ν	H_V (GPa)	θ_D (K)	α (K^{-1})	V_l (m/s)	V_s (m/s)
αZr	0	0.3232	0.5147	6.507×10^3	95.49	35.80	1.045×10^{-2}	0.334	1.52	274.4	1.710×10^{-5}	4700	2348
δZrH_{2-x}	1.47	0.4771	–	5.671×10^3	137.8	52.33	7.970×10^{-3}	0.317	3.00	335.9	2.481×10^{-5}	5868	3038
	1.54	0.4774	–	5.664×10^3	137.8	52.33	7.997×10^{-3}	0.316	2.99	335.8	2.580×10^{-5}	5865	3040
	1.64	0.4778	–	5.655×10^3	133.3	50.31	7.868×10^{-3}	0.325	2.52	329.6	2.702×10^{-5}	5860	2983
	1.66	0.4779	–	5.653×10^3	131.7	49.80	8.095×10^{-3}	0.322	2.37	327.8	2.737×10^{-5}	5797	2968
δZrD_{2-x}	1.55	0.4768	–	5.686×10^3	158.2	63.26	9.478×10^{-3}	0.250	3.21	366.0	2.033×10^{-5}	5779	3335
	1.57	0.4771	–	5.677×10^3	157.2	61.98	8.862×10^{-3}	0.268	3.05	363.1	2.381×10^{-5}	5868	3304
	1.66	0.4771	–	5.682×10^3	150.7	59.57	9.362×10^{-3}	0.265	3.01	355.6	2.674×10^{-5}	5725	3238

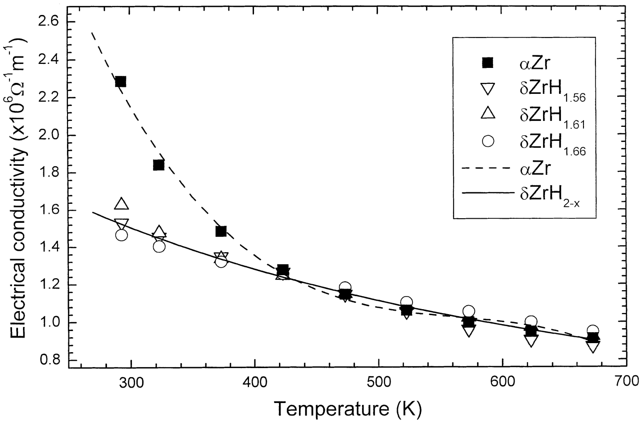

Fig. 6. Temperature dependence of the electrical conductivity for zirconium metal and hydride.

hydride and deuteride at temperatures between 1.1 and 410 K. The electrical conductivity obtained in the present study ranged from 0.8 to $1.6\times10^{-6}\ \Omega^{-1}\ \mathrm{m}^{-1}$ and agreed with the values reported by Bickel and Berlincourt. The difference in the electrical conductivity between the metal and hydride may be associated with reduction in the number of free electrons as a carrier, and some free electrons are spent on Zr–H bond. Since the electric conductivity is also closely related to the carrier carrier, the experimental and theoretical evidence of mobility of the carrier is required for a detailed explanation of electrical conductivity of zirconium hydride.

As shown in Table 1, the average thermal expansion coefficients of zirconium hydride and deuteride estimated from the high-temperature X-ray diffraction range from 2×10^{-5} to $3\times10^{-5}\ \mathrm{K}^{-1}$. The thermal expansion coefficients increased with the hydrogen or deuterium contents. The thermal expansion of zirconium hydride and deuteride appears to be related to anharmonicity of the interatomic potential of Zr–Zr bond. As the hydrogen content increases, the Zr–Zr distance increases and the Zr–Zr bond becomes weaker. The anharmonicity of the Zr–Zr potential in the zirconium hydride increases with the hydrogen content, resulting in an increase in the thermal expansion coefficient.

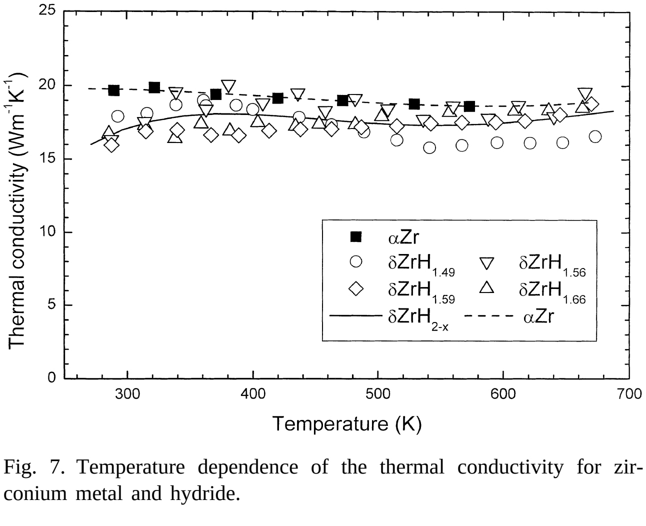

Fig. 7. Temperature dependence of the thermal conductivity for zirconium metal and hydride.

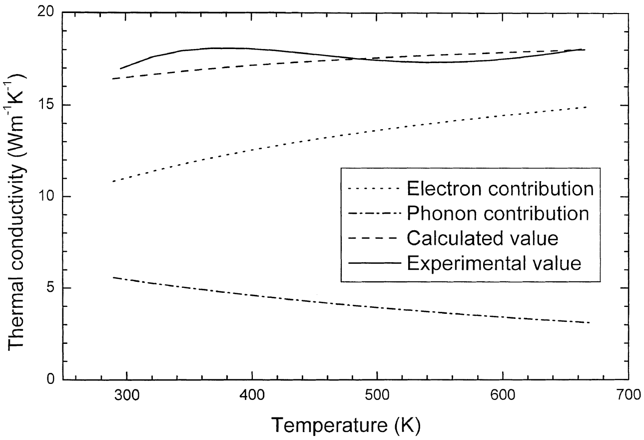

Fig. 8. Electron and phonon contributions to thermal conductivity of zirconium hydride.

Fig. 7 reveals the thermal conductivity of zirconium metal and hydride obtained in the present study. As is obvious from this figure, the thermal conductivity of the hydride is slightly lower than that of the metal and not strongly affected by the hydrogen content or temperature.

The thermal conductivity of zirconium hydride can be written by the sum of contributions of electron and phonon. The contribution of electron to the thermal conductivity κ^{e} was estimated from Wiedemann–Franz relationship expressed as, $\kappa^{e}=L\sigma T$, where T is the temperature, σ is the electrical conductivity and L is the Lorentz constant. On the assumption that the value of $L=2.44\times10^{-8}\ \mathrm{W}\Omega\ \mathrm{K}^{-2}$ for the free-electron gas model can be applied to the zirconium hydride, the electronic contribution to the thermal conductivity was estimated using the experimental values of the electrical conductivity of zirconium hydride. As shown in Fig. 8, the electronic contribution to the thermal conductivity of zirconium hydride is larger than that of the phonons. The electronic contribution for zirconium hydride is smaller than that for pure zirconium metal.

4. Conclusions

The lattice parameter of zirconium hydride was larger than that of zirconium deuteride. The isotope effect on the lattice parameter may be caused by the difference in the vibrational frequency between hydrogen and deuterium.

The electronic structure of zirconium hydride was obviously different from that of pure zirconium metal. There was the peak for Zr–H bond at 6.4 eV below Fermi energy in the XPS spectra of zirconium hydride. With increasing hydrogen content in the hydride, the peak height for the Zr–H bond increased and the peak height for the Zr

4d electrons decreased. The state of electrons calculated by the molecular orbital method was consistent with the results for the XPS measurement.

The elastic moduli of zirconium hydride and deuteride were higher than that of pure zirconium metal and decreased with increasing the hydrogen isotope content. The deuteride has higher elastic moduli than the hydride. The microhardness of zirconium hydride slightly decreased with increasing the hydrogen content and was higher than that of pure zirconium metal. The deuteride had slightly higher microhardness than the hydride.

The electrical resistivity of zirconium hydride was slightly higher than that of zirconium metal and almost independent of the hydrogen content. The thermal conductivity of zirconium hydride was slightly lower than that of zirconium metal and there was no marked change in the thermal conductivity of the hydride with the hydrogen content and temperature. The electron contribution to the thermal conductivity of zirconium hydride was found to be dominant, rather than the phonon.

Acknowledgements

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

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