Journal of Nuclear Materials 389 (2009) 170–172

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Fabrication and mechanical characterization of zirconium and gadolinium hydrides

Yuki Kitano [a], Ken Kurosaki [a,*], Masato Ito [a], Hiroaki Muta [a], Masayoshi Uno [a], Kenji Konashi [b], Shinsuke Yamanaka [a]

[a] Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita Osaka 565-0871, Japan
[b] Institute for Materials Research, Tohoku University, 2145-2, Narita, Oarai-machi, Ibaraki 311-1313, Japan

A B S T R A C T

We prepared three kinds of metal hydrides: Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys (Zr:Gd = 10:1, 8:1, 6:1), and characterized their mechanical properties. It was confirmed that the hydrides of Zr–Gd alloys were composed of Zr hydrides and Gd hydrides mixtures. We evaluated the Vickers hardness and the Young's modulus of the hydrides. We succeeded in proposing empirical equations describing the density, Vickers hardness, and Young's modulus of the hydrides of Zr–Gd alloys, as functions of the hydrogen content and the Gd content.

1. Introduction

Zr and Gd absorb hydrogen, and therefore they form metal hydrides with attractive functions for use as nuclear core materials. For example, Zr hydrides have been used as a neutron reflection material in fast reactors. Although, Gd hydrides are unstable and easily decomposed, by combining them with Zr hydrides they could be stably retained. If we develop such Zr–Gd mixed hydrides, they would be a new functional material such as a burnable poison in fast reactors leading to decreasing the initial reactivity and consequently to improving the safety and economic efficiency. Although, from a practical perspective, it is necessary to understand the physical and chemical properties of the hydrides, these properties have been scarcely reported.

The purpose of this study is to fabricate Zr hydrides and Gd hydrides and to evaluate the mechanical properties. Moreover, we also fabricate and characterize the hydrides of Zr–Gd alloys to compare the results with those of Zr hydrides and Gd hydrides.

2. Experiment

In this study, we prepared three kinds of metal hydrides: Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys.

Zr hydrides and Gd hydrides were fabricated directly from various shapes of polycrystalline metals (Ø10 × 5 mm, 10 × 10 × 1 mm and 5 × 5 × 15 mm) with 99.9 wt% purity. Firstly, the metals were introduced in the Sieverts' apparatus. After evacuating in the apparatus below the pressure of 8×10^{-6} Pa, the metals in the reaction chamber were heated up to 1073 K with the rate of temperature increase of ~200 K/h and kept at that temperature for 24 h for degassing. Then, appropriate amounts of pure hydrogen gas (7 N) was passed through a liquefied nitrogen tarp and hold in the reserve tank, followed by slowly introduced over several days to the reaction chamber which was kept at 1073 K. After introducing total amounts of the hydrogen gas in the reserve tank, the temperature of the reaction chamber fell to room temperature very slowly with the rate of temperature decrease of ~20 K/h in order to prevent sample's pulverization.

The starting materials for the hydrides of Zr–Gd alloys (Zr:Gd = 10:1, 8:1, 6:1) were Zr and Gd metals with 99.9 wt% purity. Firstly, ingots of Zr–Gd alloys were made by an arc-melting from the appropriate quantities of the constituent elements under an argon atmosphere. The obtained ingots were cut into various shapes for characterizations. Hydrogenation was carried out through the same method with those for the Zr hydrides and the Gd hydrides.

To examine the sample purity and determine the lattice parameter, the X-ray diffraction (XRD) data were collected on a diffractometer on RINT2000 (Rigaku) with Cu Kα radiation in air at room temperature. The sample microstructure was observed by using a scanning electron microscope (SEM). The chemical composition of the experimental samples was determined using an energy-dispersive X-ray (EDX) analysis in vacuum at room temperature.

The Vickers hardness was measured using a Vickers hardness tester (MHT-1, Matsuzawa Co. Ltd.) in air at room temperature under the maximum load of 9800 mN and the loading time of 10 s. The measurements were repeated more than 10 × for each sample, and the average value was calculated from the data obtained.

The longitudinal and shear sound velocities were measured by an ultrasonic pulse-echo method (Nihon Matech Echometer 1062) in air at room temperature. The experimental samples were bonded to a 5 MHz longitudinal or shear sound wave echogenic

* Corresponding author. Tel.: +81 6 6879 7905; fax: +81 6 6879 7889.
E-mail address: kurosaki@see.eng.osaka-u.ac.jp (K. Kurosaki).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.01.024

transducer. From the sound velocities, the Young's modulus was evaluated.

3. Results

Fig. 1 shows the XRD patterns of the hydrides of Zr–Gd alloys (Zr:Gd = 6:1), together with the literature data of Zr hydrides and Gd hydrides [1]. The phase states of the hydrides of Zr–Gd alloys for all compositions determined from the XRD patterns are summarized in Table 1. The hydrides of Zr–Gd alloys with low hydrogen contents (~1.5–1.6 H/*M*, where *M* = Zr + Gd) had γZrH and δZrH_x phases. On the other hand, the hydrides of Zr–Gd alloys with high hydrogen contents (~1.8–1.9 H/*M*) had εZrH phase. The existing of γZrH implies that there is a sort of interaction between Zr and Gd in the samples, because γZrH does not exist in the same hydrogen content region in the Zr–H binary system. δGdH_x phase was observed in all the samples (H/*M* = 1.52–1.93). The lattice parameter of δGdH_x was almost constant independent of the sample compositions. From these results, it can be concluded that, in the hydrides of Zr–Gd alloys, the H/Gd ratio was always constant whereas the H/Zr ratio changed in accordance with the hydrogen content of the hydrides of Zr–Gd alloys.

Fig. 2 shows the SEM photographs and EDX mapping images of the surface area of the hydride of Zr–Gd alloy (Zr:Gd = 10:1, H/*M* = 1.93). In the low magnification figures (left ones), a specific microstructure was observed, in which grains and grain boundaries were composed of Zr hydride and Gd hydride, respectively. The grain size was several dozens of micro-meters. On the other hand, in the high magnification figures (right ones), it can be confirmed that a small amount of Gd hydrides existed in the Zr hydride grains. Nevertheless, the XRD and SEM/EDX analysis revealed that the hydrides of Zr–Gd alloy were not solid solutions but mixtures of Zr hydrides and Gd hydrides. Completely the same morphology was observed in the starting Zr–Gd alloys, in which Zr grain was surrounded by Gd, in other words, Gd exists in the grain boundaries. Therefore, it can be said that the morphology of hydrides depends on the morphology of starting Zr–Gd alloys.

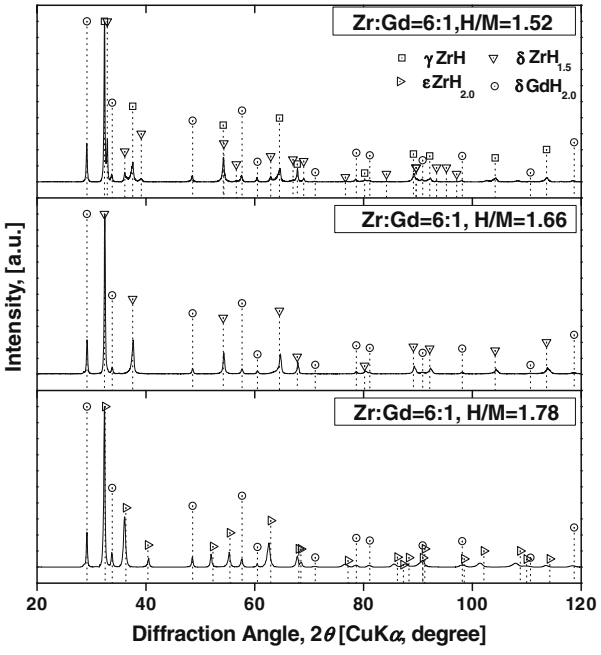

Fig. 1. XRD patterns of the hydrides of Zr–Gd alloys (Zr:Gd = 6:1, H/*M* = 1.52, 1.66, and 1.78), together with the literature data of Zr hydrides and Gd hydrides.

Table 1
Phase states in the hydrides of Zr–Gd alloys.

Zr:Gd	Hydrogen content (H/(Zr + Gd))	Phase states	
6:1	1.52	$\gamma ZrH + \delta ZrH_x$	$+ \delta GdH_x$
	1.61	$\gamma ZrH + \delta ZrH_x$	$+ \delta GdH_x$
	1.66	δZrH_x	$+ \delta GdH_x$
	1.78	εZrH_x	$+ \delta GdH_x$
	1.90	εZrH_x	$+ \delta GdH_x$
8:1	1.52	$\gamma ZrH + \delta ZrH_x$	$+ \delta GdH_x$
	1.57	$\gamma ZrH + \delta ZrH_x$	$+ \delta GdH_x$
	1.60	δZrH_x	$+ \delta GdH_x$
	1.79	εZrH_x	$+ \delta GdH_x$
	1.93	εZrH_x	$+ \delta GdH_x$
10:1	1.58	$\gamma ZrH + \delta ZrH_x$	$+ \delta GdH_x$
	1.75	δZrH_x	$+ \varepsilon ZrH_x + \delta GdH_x$
	1.93	εZrH_x	$+ \delta GdH_x$

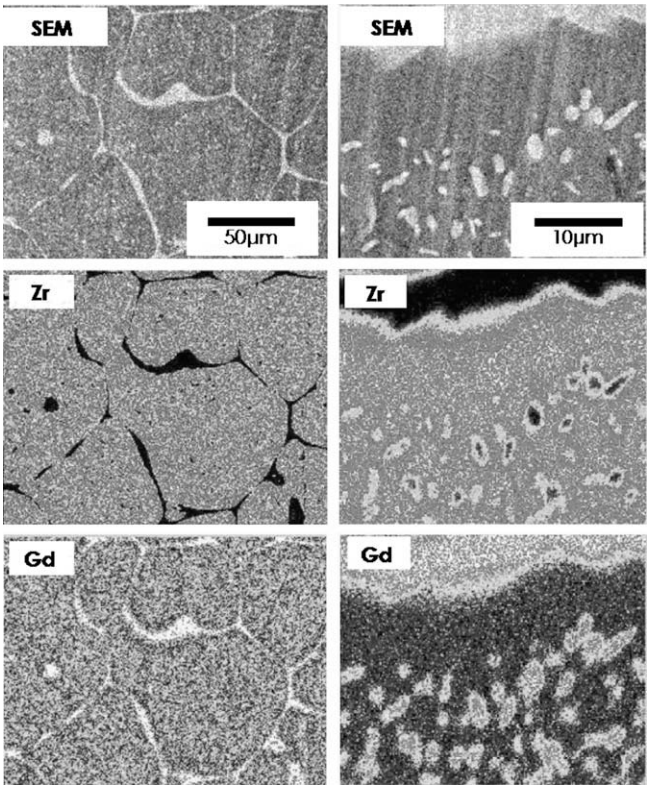

Fig. 2. SEM photographs and EDX mapping images of the hydride of Zr–Gd alloy (Zr:Gd = 10:1, H/*M* = 1.93).

Fig. 3 shows the bulk density of the hydrides of Zr–Gd alloys calculated from the weight and dimensions of the samples, together with literature data of Zr hydrides [2,3]. The density of the hydrides of Zr–Gd alloys was larger than that of Zr hydrides and decreased slightly with increasing the hydrogen content. At the same H/*M* ratio, high Gd content led to large density.

Fig. 4 shows the room temperature values of the Vickers hardness of Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys, together with the literature data of pure Zr and Zr hydrides [2,4]. The Vickers hardness values of the hydrides of Zr–Gd alloys were nearly equal to those of Zr hydrides, and they were almost the same in different Gd contents. In the low hydrogen content regions (H/*M* = 1.47–1.66), the Vickers hardness of the hydrides of Zr–Gd alloys was similar independent of the hydrogen content, whereas

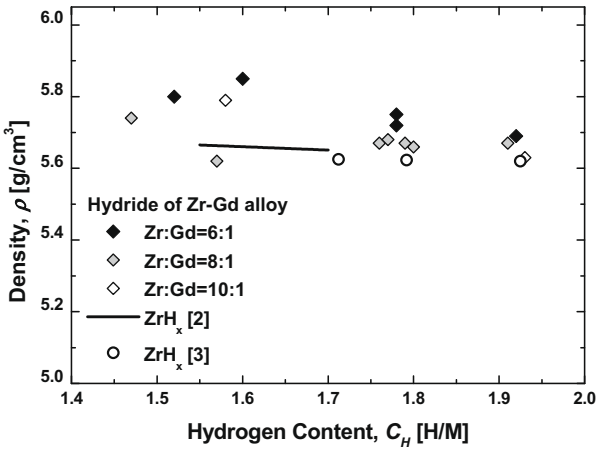

Fig. 3. Bulk densities of the hydrides of Zr–Gd alloys as a function of the hydrogen content ($C_H = H/M$), together with literature data of Zr hydrides.

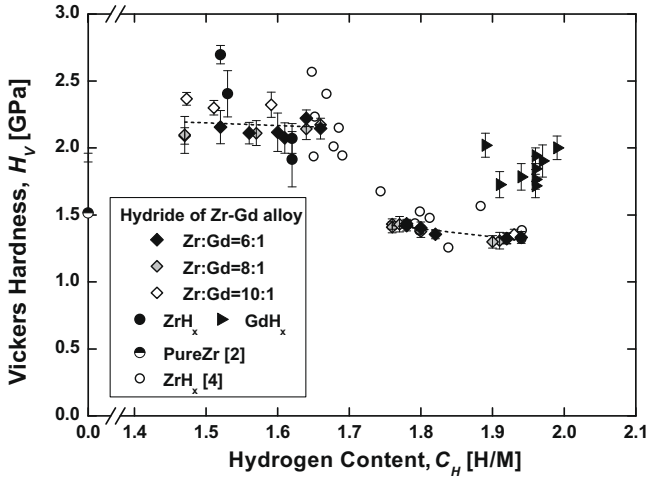

Fig. 4. Vickers hardness of Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys as a function of the hydrogen content ($C_H = H/M$), together with literature data of pure Zr and Zr hydrides.

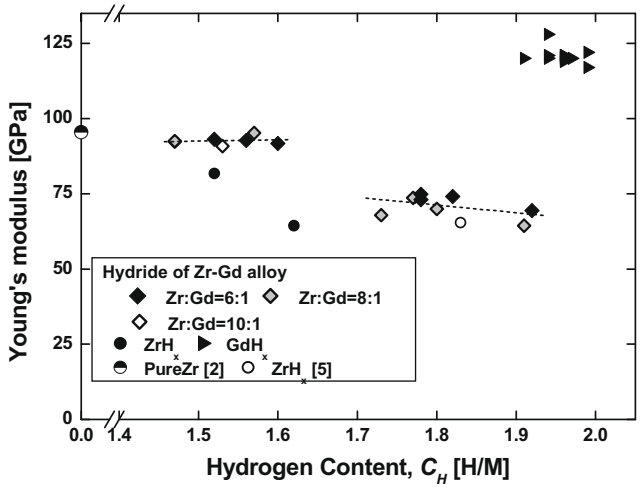

Fig. 5. Young's modulus of Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys as a function of the hydrogen content ($C_H = H/M$), together with literature data of pure Zr and Zr hydrides.

in the high hydrogen content regions ($H/M = 1.76$–1.94) it decreased slightly with increasing the hydrogen content. The hardness of Gd hydrides was higher than those of Zr hydrides and the hydrides of Zr–Gd alloys.

Fig. 5 shows the room temperature values of the Young's modulus of Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys, together with the literature data of pure Zr and Zr hydrides [2,5]. The hydrides of Zr–Gd alloys exhibited the similar Young's modulus in the investigated Gd contents, and the values existed in an intermediate region between those of Zr hydrides and Gd hydrides. As in the case of the hardness, the Young's modulus of the hydrides of Zr–Gd alloys was almost constant independent of the hydrogen content in the low hydrogen content regions ($H/M = 1.47$–1.60), whereas it decreased slightly with increasing the hydrogen content in the high hydrogen content regions ($H/M = 1.73$–1.92). In addition, Gd hydrides exhibited the highest Young's modulus among three kinds of hydrides investigated in this study.

4. Summary

We fabricated Zr hydrides, Gd hydrides, and the hydrides of Zr–Gd alloys (Zr:Gd = 10:1, 8:1, 6:1) and measured their mechanical properties. From the XRD and SEM/EDX analysis, we revealed that the hydrides of Zr–Gd alloys were micro-scale mixtures of Zr hydrides and Gd hydrides. We obtained the following empirical equations describing the density, Vickers hardness, and Young's modulus of the hydrides of Zr–Gd alloys, as functions of the hydrogen content, ($C_H = H/M$) and the Gd content, x (Gd/Zr):

$$\rho(\mathrm{g/cm^3}) = 5.56 + 4.21x + (0.0306 - 2.01x)C_H \quad (C_H = 1.45\text{–}1.95,\ x = 0\text{–}0.166) \tag{1}$$

$$H_V(\mathrm{GPa}) = 2.48 - 0.197 \times C_H \quad (C_H = 1.47\text{–}1.66,\ \text{independent of } x) \tag{2}$$

$$H_V(\mathrm{GPa}) = 2.50 - 0.610 \times C_H \quad (C_H = 1.76\text{–}1.94,\ \text{independent of } x) \tag{3}$$

$$E(\mathrm{GPa}) = 86.6 + 3.97 \times C_H \quad (C_H = 1.47\text{–}1.60,\ \text{independent of } x) \tag{4}$$

$$E(\mathrm{GPa}) = 118 - 25.8 \times C_H \quad (C_H = 1.73\text{–}1.92,\ \text{independent of } x) \tag{5}$$

These data would be useful in designing the fast reactors that was equipped with the hydrides of Zr–Gd alloys as a burnable poison.

Acknowledgments

Present study includes the result of 'Development Study of Fast Reactor Core with Hydride Neutron Absorber' entrusted to Tohoku University by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

References

[1] JCPDS 34-0690 (ZrH), JCPDS 71-4972 ($ZrH_{1.5}$), JCPDS 70-3771 ($ZrH_{2.0}$), JCPDS 71-4524 ($GdH_{2.0}$).
[2] S. Yamanaka, K. Yoshioka, M. Uno, M. Katsura, H. Anada, T. Matsuda, S. Kobayashi, J. Alloys Compd. 293–295 (1999) 23.
[3] W.M. Mueller, J.P. Blackledge, G.G. Libowitz, Metal Hydrides, Academic, New York, 1968.
[4] R.L. Beck, Trans. Am. Soc. Metals 55 (1962) 542.
[5] X. Jiujun, S.Q. Shi, J. Nucl. Mater. 327 (2004) 165.