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Thermal properties of hydride fuel 45% U–$ZrH_{1.6}$

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Abstract

Hydride fuel of 45% U–$ZrH_{1.6}$ was fabricated and the measurement of its thermal properties was carried out. The thermal conductivity of 45% U–$ZrH_{1.6}$ in the range of room temperature −773 K was evaluated to be about three times higher than that of UO_2 and nearly independent of temperature. Such a high thermal conductivity is favorable when this material is used as nuclear fuel. The pressure–composition–temperature (P–C–T) characteristics of UZr alloy hydrogen system were different from that of pure Zr. A plateau of the hydrogen pressure was found for H concentration (relative to the Zr concentration) between 0.2 and 0.6 for all temperature below 1173 K. This plateau region was attributed to UZr hydride formation from the UZr alloy. Over the plateau region in H concentration from 1.0 to 1.4, the equilibrium hydrogen pressure was a little higher than that of pure Zr, which was attributed to the reduced activity of Zr in UZr alloy. The activity of Zr calculated from the equilibrium hydrogen pressure was 0.90 at 1073 K, and 0.83 at 973 K.

1. Introduction

Hydride fuel of U–$ZrH_{1.6}$ has been proven to be useful as a fuel for TRIGA reactors over the world for years. The use of U–$ZrH_{1.6}$ has been shown to reduce the probability of reactivity accidents [1]. Hydrogen atoms in $ZrH_{1.6}$ can accelerate neutrons as well as moderate them when the hydrogen is in an excited state [1]. Recently, Greenspan [2] proposed to use hydride fuel instead of water channel/rod for boiling water reactors (BWRs) as moderated fuel, and Yamawaki [3] developed U–Th–Zr hydride fuel as a highly promising target for burning minor actinides (MA). The thermochemical and thermophysical properties of U–$ZrH_{1.6}$ have been measured extensively in TRIGA reactor-related research, but data for hydride fuel with higher uranium addition is quite scarce. It is the aim of the present study to fabricate and measure thermal properties of uranium hydride fuel of concentration 45 wt% U–55 wt% $ZrH_{1.6}$ (abbreviated 45% U–$ZrH_{1.6}$).

2. Experimental

A UZr alloy, with the weight ratio of U:Zr = 45:55, was prepared using an arc melting method in an argon atmosphere. The alloy was melted five times and turned upside down periodically, in order to homogenize it. The initial phases of the alloy were identified with scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) according to which the alloy was confirmed to be highly homogeneous. Hydrogenation of the alloy was carried out using a Sieverts system at a temperature of 1173 K under various hydrogen pressures below 10^5 Pa. The quantity of absorbed hydrogen in the alloy was calculated from the pressure changes of the system and the alloy mass changes before and after hydrogenation. The final composition was evaluated as 45% U–$ZrH_{1.6}$. The obtained hydride was examined with SEM–EDS. The thermal conductivity was evaluated, which was calculated using a common equation as follows:

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$$k = \alpha c_p \rho, \quad (1)$$

where k (W m^{-1} K^{-1}) is the thermal conductivity, α (m^2 s^{-1}) the thermal diffusivity, c_p (J g^{-1} K^{-1}) the heat capacity, and ρ (g m^{-3}) is the density of the specimen. The thermal diffusivity was measured by the laser flash measurement from room temperature to 1273 K. The specimen was kept in high vacuum during the laser flash measurements. The heat capacity was measured by differential scanning calorimetry (DSC) from 373 to 773 K in an argon atmosphere, and the density was from the liquid immersion method combined with thermal expansion measurement. Also, an isothermal hydrogen absorption–emission measurement was conducted for UZr alloy at various temperatures.

3. Results and discussion

3.1. Hydriding of UZr alloy

The hydride sample had a metallic color, almost as same as before hydrogenation. Under specific preparation conditions during hydrogenation, cracking in the hydride sample was avoided. Fig. 1 shows an SEM micrograph of 45% U–$ZrH_{1.6}$. Mainly, two phases were observed and the analyses of the phases with EDS and X-ray diffraction showed that the white and the grey ones, rich in U and Zr, respectively, were attributed to α-U and $ZrH_{1.6}$ phases, respectively. The important feature of the microstructure was that these two phases were very finely mixed with each other. The material can be described as α-U phase grains of about 1 μm diameter dispersed in $ZrH_{1.6}$ hydride.

3.2. Specific heat capacity

Specific heat capacity was measured by DSC. Fig. 2 shows the specific heat of 45% U–Zr and 45% U–$ZrH_{1.6}$. According to Simnad [1,4], the specific heat of hydrides

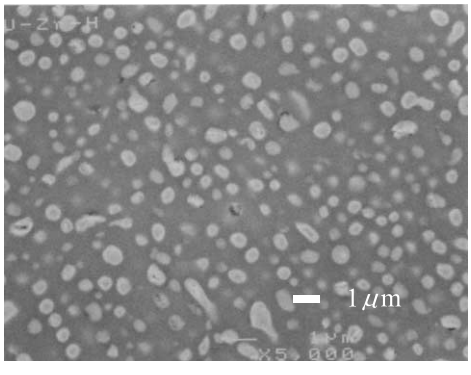

Fig. 1. SEM image of hydrogenated 45% U–$ZrH_{1.6}$.

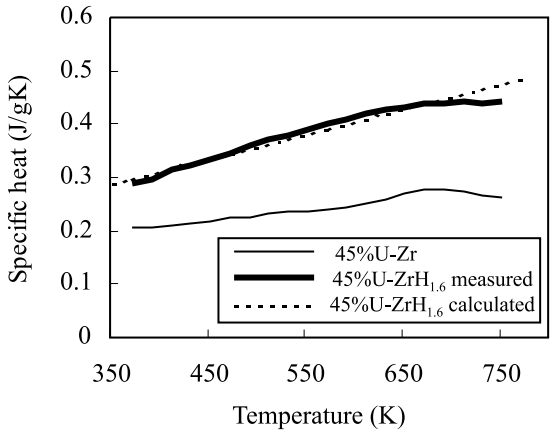

Fig. 2. Specific heat curves for 45% U–Zr alloy and 45% U–$ZrH_{1.6}$.

can be expressed as a sum of the specific heat of each phase, weighted by its mass fraction:

$$c_{p(U-ZrH)} = W_U c_{p(U)} + W_{ZrH} c_{p(ZrH)}. \quad (2)$$

The present result shown in the figure was in good agreement with calculated values using the reported values for the specific heats of U and ZrH [4].

3.3. Thermal diffusivity and thermal conductivity

Fig. 3 shows the thermal diffusivity of 45% U–Zr and 45% U–$ZrH_{1.6}$. The thermal diffusivity for 45% U–Zr increases with increasing temperature. In temperature range 673–873 K there is a large increment due to the transition of δ-UZr to U–Zr solid solution at 873 K [5]. On the other hand, the thermal diffusivity of hydrogenated specimen of 45% U–$ZrH_{1.6}$ decreased slightly with increasing temperature to around 873 K. Then, the

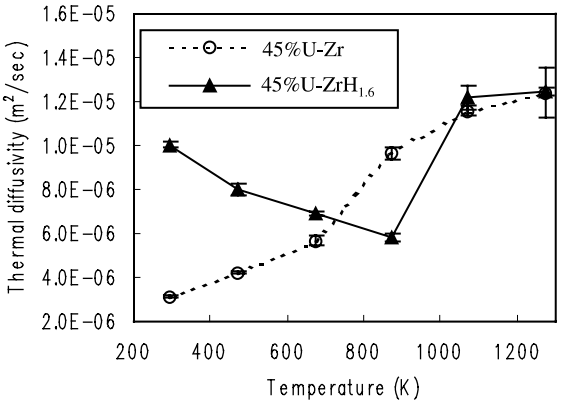

Fig. 3. Thermal diffusivity of 45% U–Zr alloy and 45% U–$ZrH_{1.6}$.

thermal diffusivity of the hydrogenated specimen increased to 1073 K. This increase of thermal diffusivity resulted from de-hydrogenation of the specimen. It should be noted that during the laser flash measurements the specimen was kept in high vacuum. After hydrogen emission was nearly completed at 1073 K, the thermal diffusivity became almost constant at a value close to that of the unhydrogenated alloy specimen. Fig. 4 shows the thermal conductivity of these samples from room temperature to 773 K. The thermal conductivity of 45% U–$ZrH_{1.6}$ was almost independent of temperature, because the thermal diffusivity decreased with increasing temperature, while the specific heat increased with increasing temperature. The thermal conductivity of hydrogenated sample was about three times higher than that of UO_2. Such a high thermal conductivity is very favorable for its application to BWRs. Also, this value was almost the same as the reported value of ZrH (δ phase) [6,7]. Therefore, the addition of U had little influence on the thermal conductivity of hydride fuel.

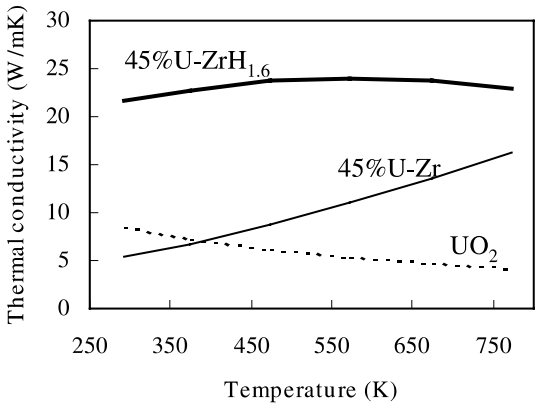

Fig. 4. Thermal conductivity of 45% U–Zr alloy and 45% U–$ZrH_{1.6}$.

3.4. Isothermal hydrogen absorption–emission properties

Fig. 5 shows pressure–composition–temperature (P–C–T) diagram of H–45% U–Zr. There were two plateau regions (Plateau 1 and Plateau 2 in Fig. 5). Plateau 1 is slanted and the other Plateau 2 is narrow and quite horizontal. According to the Zr–H phase diagram [8], there is no plateau in the region of H concentration from 0.2 to 0.6 (here, and henceforth, 'H concentration' means the ratio (H/Zr) of the number of H atoms to the number of Zr atoms) at 1173 K, whereas our data indicate that there is. This plateau region 1 is attributed to the formation of UZr hydride from UZr alloy. On the other hand, H concentration (H/Zr) in Plateau 2 was almost the same as that of $\beta + \delta$ phase region given in the Zr–H phase diagram [8]. The equilibrium hydrogen pressure over UZr alloy was a little higher than that over pure Zr. The hydriding reaction in Zr is expressed as follows [9]:

$$\mathrm{Zr} + \frac{\delta}{2}\mathrm{H_2} \leftrightarrow \mathrm{ZrH_\delta}, \tag{3}$$

where ZrH_δ refers to the Zr hydride (δ phase). The equilibrium constant can be obtained as follows:

$$K = \frac{\alpha_{\mathrm{ZrH_\delta}}}{\alpha_{\mathrm{Zr}} f_{\mathrm{H_2}}^{\delta/2}}, \tag{4}$$

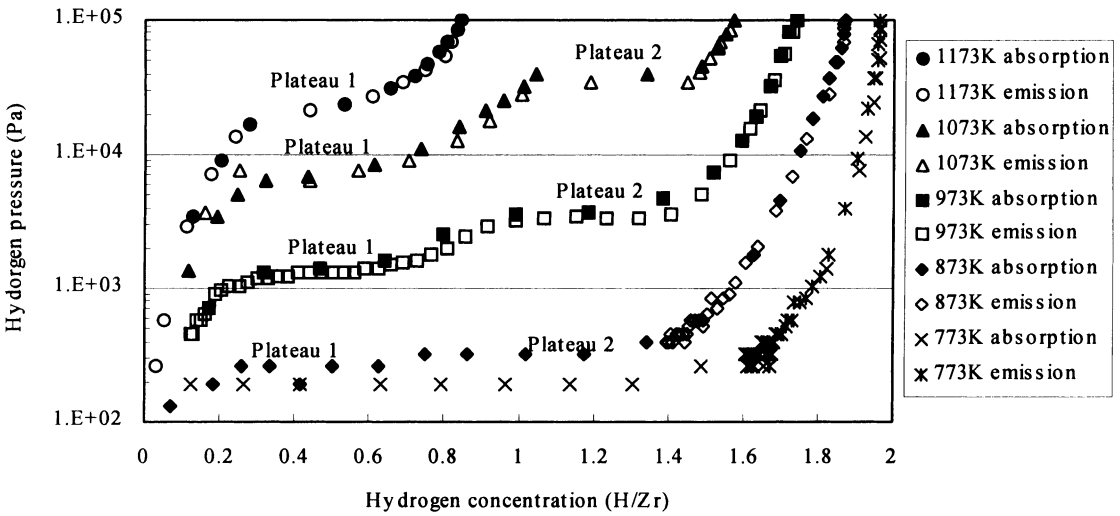

Fig. 5. P–C–T diagram of H–45% U–Zr.

$$f_{H_2}^{\delta/2} = \frac{\alpha_{ZrH_\delta}}{\alpha_{Zr} K}, \quad (5)$$

where α is the activity and f_{H2} is the fugacity. When the hydrogen pressure is low, the fugacity is equal to the hydrogen pressure. So, from Eq. (5), for low hydrogen pressure, the hydrogen pressure can be expressed as

$$P_{H_2}^{\delta/2} = \frac{\alpha_{ZrH_\delta}}{\alpha_{Zr} K}. \quad (6)$$

The hydrogen pressure thus depends on the activities. In case of pure Zr, the activities of Zr and ZrH_δ are nearly equal to 1. However in case of UZr alloy, the activity of Zr in UZr alloy is smaller than 1 [10]. Consequently, from Eq. (6), the hydrogen pressure over UZr is somewhat higher than that over pure Zr. The calculated activities of Zr from these equilibrium hydrogen pressures at 1073 and 973 K are 0.90 and 0.83, respectively. These values are larger than the reported value (0.7) at 1100 K [11]. The reported value of α_{Zr} was evaluated for Zr in UZr alloy, while, in this case, the activity of Zr relates with hydrogen-loaded UZr alloy (β phase). Therefore, the observed deviation of the activity of Zr from the reported value can be attributed to the effect of hydrogen in hydrogen solid solution.

4. Conclusion

Uranium–zirconium hydride 45% U–$ZrH_{1.6}$ was fabricated and its thermal properties were measured. The thermal conductivity of 45% U–$ZrH_{1.6}$ was found to be about three times higher than that of UO_2 and was nearly independent of temperature. Such a high thermal conductivity is very favorable for nuclear fuels. The P–C–T properties of the UZr alloy were different from that of pure Zr. There was found a plateau in H concentration (H/Zr) form 0.2 to 0.6 at 1173 K and below. This plateau region was attributed to UZr hydride formation from UZr alloy. The equilibrium hydrogen pressure was a little higher than that of pure Zr due to the reduced activity of Zr in UZr alloy. The activity of Zr calculated from the equilibrium hydrogen pressure was 0.90 and 0.83 at 1073 K and at 973 K, respectively.

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