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Hydrogen absorption properties of U–Th–Ti–Zr alloys

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Abstract

The hydrogen absorption properties of U–Th–Ti–Zr alloys were investigated for the purpose of developing a new hydride nuclear fuel. The alloy specimens consisted of two phases before hydrogenation, namely a Th phase and a U–Ti–Zr phase. The phases in the hydrogenated alloys depended strongly on their history. Upon hydrogenation at low hydrogen pressure above 1073 K, the $ThZr_2H_6$ phase grew fairly well but not enough owing to the formation of the stable ternary hydride in the Ti–Zr–H system. This also disturbed the formation of UTi_2H_5. Although a homogeneous phase was consequently not achieved, hydrides without disintegration were obtained.

1. Introduction

U–Th mixed fuel has been researched for many years, especially as oxides, carbides and molten salt alloys. Because both Th and U form stable hydrides, they also seemed useful for a mixed fuel. In the TRIGA reactor [1] the use of U–ZrH_x has been shown to reduce the probability of a reactivity accident, called a prompt negative temperature coefficient of reactivity. Further, it was found by the authors [2] that U–Ti alloy forms monolithic UTi_2H_5, which has the same crystal structure as $ThZr_2H_6$. In this study the hydrogen absorption properties of several alloys in the UTi_2–$ThZr_2$ system were examined in order to develop a new reactor fuel.

2. Experimental details

2.1. Alloy preparation

An alloy specimen with a UTi_2:$ThZr_2$ molar composition of 1:1 (written as $UThTi_2Zr_2$ hereinafter) was prepared by melting the constituent elements in an argon arc furnace. Melting was done five times, with the melt being turned upside down during each interval. Th-rich specimens $UTi_2(ThZr_2)_x$ ($x = 1.9$ and 4.8) were also prepared by melting the $UThTi_2Zr_2$ alloy together with $ThZr_2$ alloy. The initial phases in the $UThTi_2Zr_2$ alloy were identified by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). It consisted of two phases, namely a U–Ti–Zr solid solution and a Th phase containing a little dissolved Zr.

2.2. Hydrogen absorption–desorption experiments

The hydrogen absorption properties of the prepared alloys were examined at various temperatures between 723 and 1173 K and at various hydrogen pressures below 10^5 Pa. The hydrogen concentrations of the specimens were calculated from the pressure change in an apparatus of known volume and also from the mass change after the experiments. The desorption properties were examined at 1073 K for the $UThTi_2Zr_2$ specimen. X-ray diffraction (XRD), SEM and EDS techniques were used to examine the phases in the specimens.

3. Results and discussion

3.1. Hydrogen absorption properties and phases in hydrides

The amount of hydrogen absorbed by the $UThTi_2Zr_2$ specimen under various equilibrium conditions is plotted in Fig. 1. Also shown is the temperature dependence of the equilibrium pressure in related M–H systems, where a line labelled MH_x–MH_y denotes the pressure of the plateau extending between MH_x and MH_y and a line labelled MH_x indicates the equilibrium pressure of MH_x outside any plateau region.

These results show that the hydrogen concentration in a specimen depended strongly on the history of pressure and temperature conditions of the specimen. Figure 2 shows the X-ray diffraction patterns of several $UThTi_2Zr_2$ specimens. The $ThZr_2H_{7+x}$ phase grew most in run 3, where the temperature was the highest of

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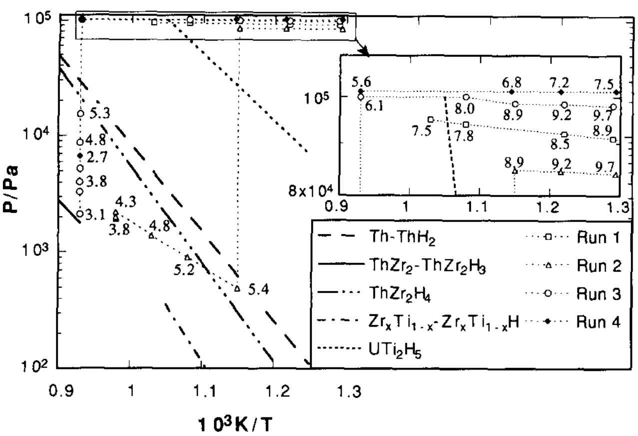

Fig. 1. Hydrogen concentration in $UThTi_2Zr_2$ alloy at various pressures and temperatures, together with temperature dependence of equilibrium pressure of related M–H systems [3–5].

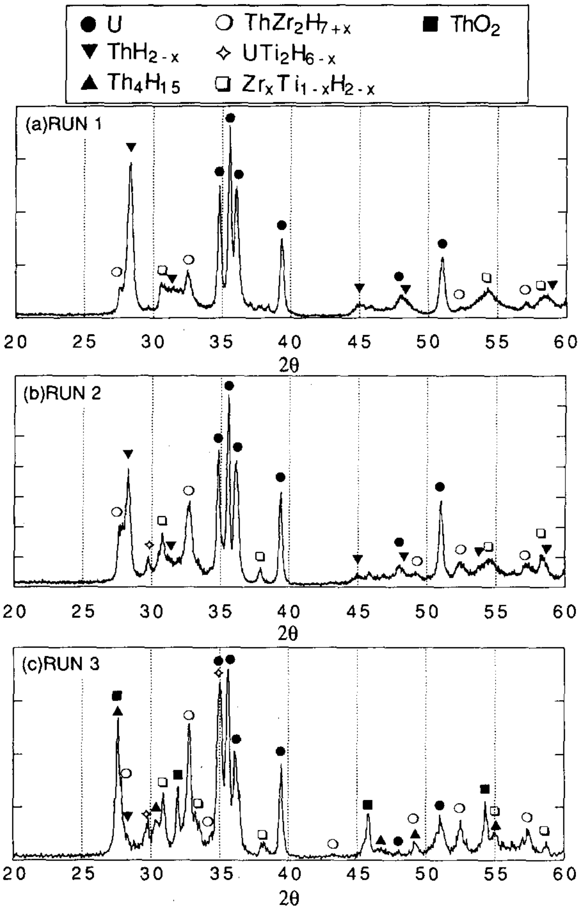

Fig. 2. X-Ray diffraction patterns of hydrogenated $UThTi_2Zr_2$ alloys with various histories.

the three runs. As shown in Fig. 1, hydrogen pressures were kept below the plateau pressure of ZrTi–$ZrTiH_2$ till the H content reached $UThTi_2Zr_2H_{3.8}$ and further kept below the plateau pressure of ZrH–$ZrH_{1.4}$ or Th–ThH_2 till the H content reached $UThTi_2Zr_2H_5$ in both runs 2 and 3. Under these conditions the $ThZr_2H_5$ phase could grow. Furthermore, significant growth of that phase required a temperature higher than 1073 K, because Th and Zr existed in different phases before hydrogenation.

A higher temperature of 1173 K was adopted for hydrogenation of the $ThZr_2$-rich alloys $UTi_2(ThZr_2)_{1.9}$ and $UTi_2(ThZr_2)_{4.8}$. For these alloys the H/M ratios were 1.3 and 1.6 respectively at 10^5 Pa and 1073 K and 1.7 in both alloys at 10^5 Pa and 773 K. Figure 3 shows the XRD patterns of polished surfaces of specimens of (a) $UThTi_2Zr_2H_{9.7}$, (b) $UTi_2(ThZr_2)_{1.9}H_{14.4}$ and (c) $UTi_2(ThZr_2)_{4.8}H_{30.3}$. The fraction of $ThZr_2H_7$ phase increased with increasing Th and Zr content. However, other phases such as U, Th_4H_{15} and Zr–Ti–H were always observed. The ThO_2 phase seemed to be formed from ThH_2 upon polishing.

The phases were also confirmed by SEM and EDS as shown in Fig. 4. The fraction of the bulky grey phase $ThZr_2H_7$ increased with increasing Th and Zr content. However, the bright U phase, the dark Zr–Ti–H phase and the Th_4H_{15} and ThO_2 phases, which are slightly lighter than the bulk, never vanished. On the contrary,

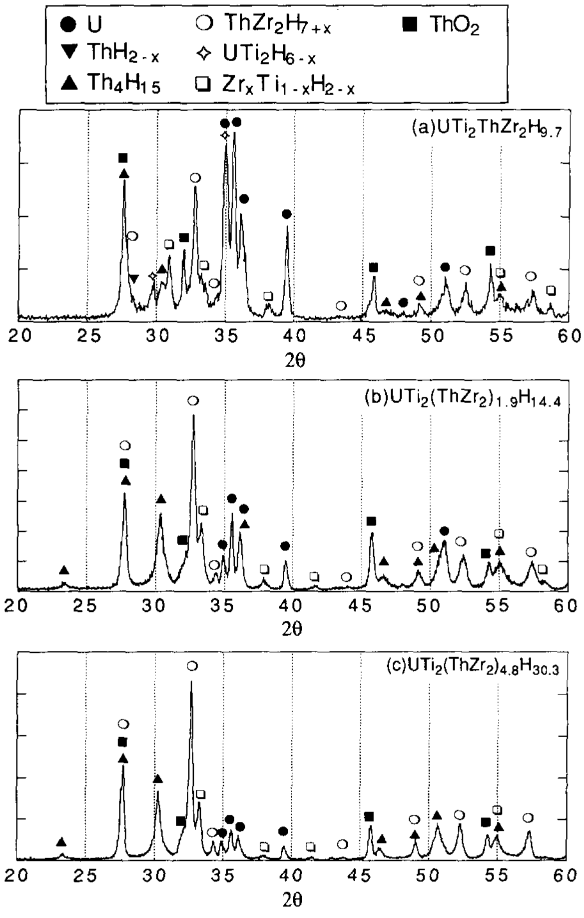

Fig. 3. X-Ray diffraction patterns of hydrogenated U–Th–Ti–Zr alloys with various compositions: (a) $UTi_2ThZr_2H_{9.7}$; (b) $UTi_2(ThZr_2)_{1.9}H_{14.4}$; (c) $UTi_2(ThZr_2)_{4.8}H_{30.3}$.

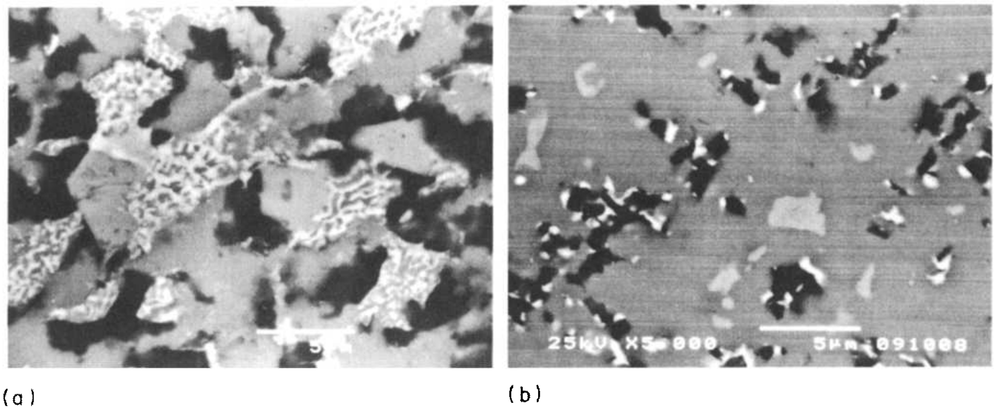

Fig. 4. Backscattered electron images of hydrogenated U–Th–Ti–Zr alloys observed by SEM: (a) $UThTi_2Zr_2H_{9.7}$; (b) $UTi_2(ThZr_2)_{4.8}H_{30.3}$.

the increase in Th and Zr content made formation of the UTi_2H_5 phase more difficult. $UThTi_2Zr_2H_{9.7}$ contained a small fraction of the grey UTi_2H_5 phase intercalated into the U phase as shown in Fig. 4(a). $UTi_2(ThZr_2)_{4.8}H_{30.3}$ shown in Fig. 4(b) has no UTi_2H_5 phase, since all the Ti was probably bound tightly in the Ti–Zr–H ternary hydride phase.

3.2. Isothermal desorption experiment

Figure 5 shows the desorption pressure–composition isotherm of the 1:1 specimen obtained at 1073 K. There are clearly four distinct plateau regions. Each plateau indicates that two solid phases are involved in the desorption equilibrium. Comparing with the plateau pressure data compiled in Fig. 2 and ref. 6 and considering the phases observed using XRD and SEM, the plateaux can be attributed to the equilibrium reactions $ThZr_2$–$ThZr_2H_3$, Zr_xTi_{1-x}–$Zr_xTi_{1-x}H$, $Zr_xTi_{1-x}H$–$Zr_xTi_{1-x}H_{1.5}$ and Th–ThH_2 from the lowest to the highest respectively. The highest plateau was slightly higher than that for pure ThH_2. X-Ray diffraction showed that the crystal lattices of ThH_{2-x} and Th_4H_{15} were slightly larger than those of the pure ones. These facts suggest that Ti or Zr was probably dissolved in the phase.

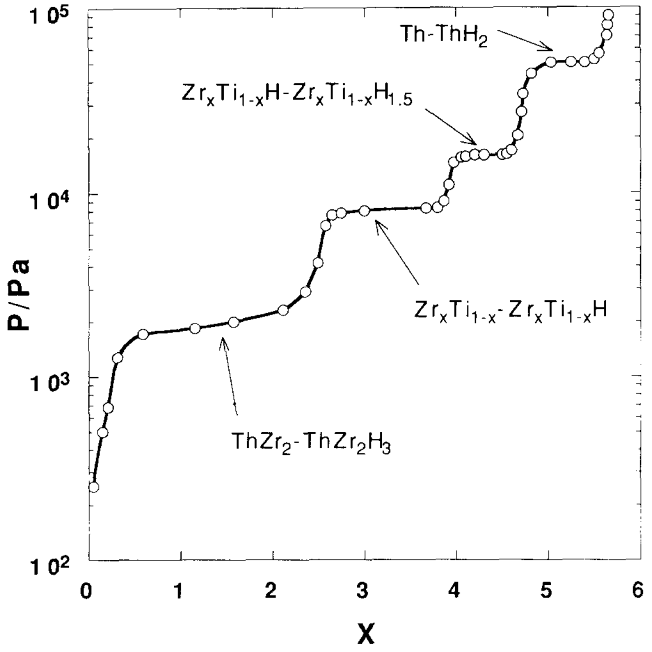

Fig. 5. Desorption isotherm of $UThTi_2Zr_2H_x$ at 1073 K.

From the obtained properties the $UThTi_2Zr_2$ alloy can accommodate 0.93H/M at 1073 K at a hydrogen pressure of 10^5 Pa, whereas for U–ZrH_x fuel 1.6H/Zr can be held in the hydride. This low capacity is due to the presence of U and Ti which show a high hydrogen desorption pressure. As described above, increasing the $ThZr_2/UTi_2$ ratio made the H/M ratio at 1073 K competitive with that of U–ZrH_x alloy, since Ti inhibited homogenization rather than promoting it. Further, the alloy never disintegrated during hydrogenation. Therefore, by decreasing Ti, it will be a good material for mixed hydride fuel.

4. Conclusions

The hydrogen absorption and desorption properties of three kinds of U–Th–Ti–Zr alloys were examined. The $ThZr_2H_7$ phase grew well when the alloy was held at a temperature 1073 K under a sufficiently low hydrogen pressure that neither ThH_2 nor ZrH_2 could be formed in it. However, owing to the easy formation of Zr–Ti–H phase, a homogeneous hydride was not obtained. Nevertheless, the absence of disintegration and the rather low hydrogen desorption pressure showed that it can be used as a nuclear fuel.

Acknowledgments

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