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Hydrogen desorption properties of hydrogenated U–Th–Zr alloys

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Abstract

Hydrogen desorption properties of hydrogenated U–Th–Zr alloys of varied compositions were investigated using a hydrogen absorption–desorption experimental system, TG-DTA and DSC analyzers. Isothermal desorption at 900°C of elemental ratio U:Th:Zr:H = 1:1:4:9.5 exhibited that there were two distinct plateau regions identified as $ZrH_{1.4}$–ZrH and $ThZr_2H_{7-x}$–$ThZr_2$ systems. TG-DTA and DSC measurements under the temperature range from room temperature to 1000°C have shown that there were three endothermic peaks identified as dehydrogenation reactions of ZrH_{2-x}–ZrH and $ThZr_2H_{7-x}$. The DTA curve identified the first peak area as the $ZrH_{1.4}$–ZrH system, while the DSC curves identified that the second peak is the decomposition of ZrH and the third peak is the decomposition of $ThZr_2H_{7-x}$. It was also shown that both ZrH_{2-x} and $ThZr_2H_{7-x}$ are more stable in the alloy than the pure ones. Measured enthalpy changes during decomposition of the hydrogenated U–Th–Zr alloy are similar to the theoretical calculation. Oxidation during measurement of the U:Th:Zr:H = 2:1:6:13.1 resulted in a different measured enthalpy change and calculation. Isothermal decomposition of the U:Th:Zr:H = 1:1:4:9.5 without any disintegration indicates stability of the alloy against powdering on hydriding–dehydriding cycles. Stability of the samples at high temperature similar to that of U–$ZrH_{1.6}$ for TRIGA fuel can be maintained after the first decomposition. © 1997 Elsevier Science B.V.

1. Introduction

For utilizing abundant thorium resources, U–Th mixed fuel has been researched for many years especially in such chemical forms as oxide, carbides, molten salts and alloys. The hydride form seems useful as a mixed fuel because both Th and U form stable hydrides, and also, in a TRIGA reactor, the use of U–ZrH_{2-x} has shown to reduce the probability of reactivity accidents. The latter is attributable to the prompt negative temperature coefficient of reactivity. In this cermet fuel, fine particles of metallic uranium are dispersed in the bulk of ZrH_{2-x} (x is typically 0.4) which plays an important role in safety. Hydrogen atoms in ZrH_{2-x} that behave as an isotropic harmonic oscillator can accelerate neutrons as well as moderate them when it is in an excited state. Heating the hydride increases the number of excited hydrogen atoms and thus the probability for the neutrons to be accelerated. It reduces the reactivity immediately.

Previous work by the authors showed that hydrides of U–Th–Zr alloys can be candidate materials for U–Th mixed hydride fuel [1,2]. The microstructures of the alloy hydrides were very fine and the α-U phase was dispersed in the bulk of the $ThZr_2H_{7-x}$ and ZrH_{2-x} phases similar to TRIGA reactor fuel where the U phase is finely dispersed in the ZrH_{2-x} bulk. They would show an inherent safety if hydrogen atoms act not only as a moderator but also as an accelerator of neutron. For this it is at least necessary that the hydride phases can hold hydrogen tight at elevated temperatures. Such hydrogen holding or desorption properties of these materials, however, are not well known.

In this paper, hydrogen desorption properties of the hydrogenated U–Th–Zr alloys were studied in order to

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clarify the stability of hydride phases in the alloys at the high temperature region.

Both TG-DTA and DSC measurements were conducted on the alloy hydrides to evaluate the phase transition temperature of the alloys while X-ray diffraction was used to identify the phases in the specimens.

2. Experimental details

U–Th–Zr alloys, with the constituent ratio of U:Th:Zr = 2:1:6, 1:1:4, 1:2:6 and 1:4:10 were prepared by arc melting in an argon atmosphere. Each alloy was melted five times and turned up side down periodically, in order to make it homogeneous. The initial phases of the alloys were identified by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) in which the major phases were identified as U–Zr and Th. Hydrogenation of the samples was carried out using a Sieverts system at a temperature from 900°C down to 500°C under various hydrogen pressures below 10^5 Pa. The quantity of hydrogen absorbed by each sample was controlled by and calculated from the pressure changes in the system. The final compositional ratios of the obtained hydrides were U:Th:Zr:H = 2:1:6:13.1, 1:1:4:9.5, 1:1:4:9.9, 1:2:6:15.5, 1:4:10:27 and 1:0:10:15, respectively.

An isothermal desorption experiment was conducted at 900°C for the sample with the composition ratio of U:Th:Zr:H = 1:1:4:9.5 by decreasing the pressure stepwise after each decomposition equilibrium was attained.

The thermal gravimeter-differential thermal analysis (TG-DTA) and differential scanning calorimeter (DSC) experiments of the samples were carried out on about 20–60 mg of the powdered samples in an argon atmosphere (99.9995%) with a heating rate of 20°C/min. Before and after TG-DTA and DSC experiments all samples were examined by X-ray diffraction.

3. Results and discussion

3.1. Isothermal decomposition

Fig. 1 presents the desorption isotherm of the U:Th:Zr:H = 1:1:4:9.5 specimen at 900°C, compared with that of pure $ThZr_2H_{7-x}$ at 910°C [3] and at 900°C and the predicted isotherm for the two immiscible phases of $ThZr_2H_{3.9}$ and $2ZrH_{1.4}$ at 900°C (equal to U-free Th:Zr:H = 1:4:6.7). The predicted isotherm was constructed from those of $ThZr_2H_{7-x}$ and $ZrH_{1.4}$ at 900°C [4].

Similar to the predicted one, the experimental curve exhibited a small plateau at a pressure of 9×10^4 Pa. The plateau width is in good agreement although the experimental isotherm has a significantly lower plateau pressure. Bartscher et al. [3] has proven that the stability of C15 type $ThZr_2H_{7-x}$ depends on its preparation history. The stable bcc solid solution at high temperature can be cooled without disproportion if H/M is maintained at 1.3 or greater. In the case of the Zr–H system, Beck [4] has found that, at 900°C and a pressure of 1.23×10^5 Pa, zirconium hydride is in the equilibrium state of the ZrH–$ZrH_{1.4}$ system. Therefore, under this operating condition the only suggestion of the plateau equilibrium is the ZrH–$ZrH_{1.4}$ system. The presence of zirconium hydride is due mainly to excessive Zr in the alloy. After the small plateau, the experimental curve shows a wide slanted plateau, at $x = 5.7 - 0.5$ in Fig. 1, which is wider and lower than that of the predicted isotherm. It contributed much to a higher hydrogen capacity. At 10^5 Pa and 900°C, the hydrogen content in the predicted curve is about 5.3 while that of the present work is 6.7. The high hydrogen capacity of the sample is an attractive result and can be attributed to the fact that by alloying the stability of ZrH_x and $ThZr_2H_{7-x}$ phases is shifted higher. As shown in Fig. 1, the plateau pressure for ZrH–$ZrH_{1.4}$ of the sample,

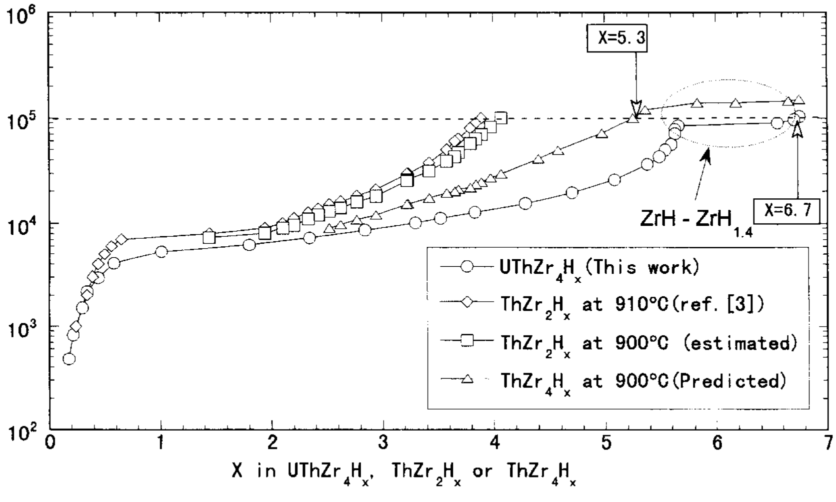

Fig. 1. Isothermal desorption at 900°C of $UThZr_4H_x$, $ThZr_2H_x$ and predicted $ThZr_4H_x$.

9×10^4 Pa, is lower than the predicted plateau, 1.23×10^5 Pa, and the final pressure plateau of the $ThZr_2H_x$ is also lower than that of Ref. [3]. Although it has not yet been proven, the phase stabilization seems to be brought about by excess zirconium.

Visual examination of the sample showed that there was no disintegration of the decomposed sample, which indicates the integrity of the alloy against powdering in a hydriding–dehydriding process.

3.2. Thermal analysis

Fig. 2 shows the TG-DTA curves of the 1:2:6:15.5 specimen heated under argon. Decomposition started at about 343°C and finished at about 843°C and three endothermic peaks are clearly observed in DTA curve. The XRD result on the sample U:Th:Zr:H = 1:2:6:15.5 before thermal analysis, as presented in Fig. 3a, exhibited that before dehydrogenation the sample consisted of three phases which were identified as α-U, $ThZr_2H_{7-x}$ and ZrH_{2-x}. The XRD result on the sample 1:2:6:15.5 after thermal analysis, as presented in Fig. 3b, exhibited that it consisted of α-U, α-Th, ThO_2, Zr and δ-UZr_{2+x} and no Th–Zr system was identified. The oxide compound after thermal analysis is due mainly to the presence of oxygen as an impurity in the argon. The TG curve of the sample shows that after the end of the third decomposition temperature, the TG equilibrium curve bent slightly upward due to oxidation. By also taking the P–c–T diagram of the alloy 1:1:4 into account, the decomposition at a lower temperature can be explained as follows. Under argon atmosphere, the hydrogen concentration in the gas phase can be relatively zero which may make it easier for hydrogen in the sample to start to decompose. Under such low pressure, ZrH_{2-x} will release hydrogen to form a stable hydride of lower hydrogen capacity. Since the less stable hydride comes from ZrH–$ZrH_{1.4}$ [4], this compound will decompose before the other two compounds. In addition, at 10^5 Pa and 900°C there is no plateau region for the $ThZr_2H_{7-x}$ [3]. Consequently, the peak at 418°C was identified as a peak transition temperature of the $ZrH_{1.4}$–ZrH system.

Above 670°C, the TG curve bent sharply and ended at 843°C. The second and third peaks can not be identified clearly, although we can suggest here that they could be caused by the decomposition temperature of the $ThZr_2H_{7-x}$–$ThZr_2H_x$ and ZrH–Zr systems. The DSC curves will identify these peaks.

In the Th–Zr and U–Zr phase diagrams, the Th–Zr solid solution phase can only exist above 908°C and the stable U–Zr solid solution can be formed instead [5]. Hence, it is inferred that on dehydrogenation $ThZr_2H_{7-x}$ decomposes into its elements and at the end of decomposition zirconium will react with uranium in the sample to

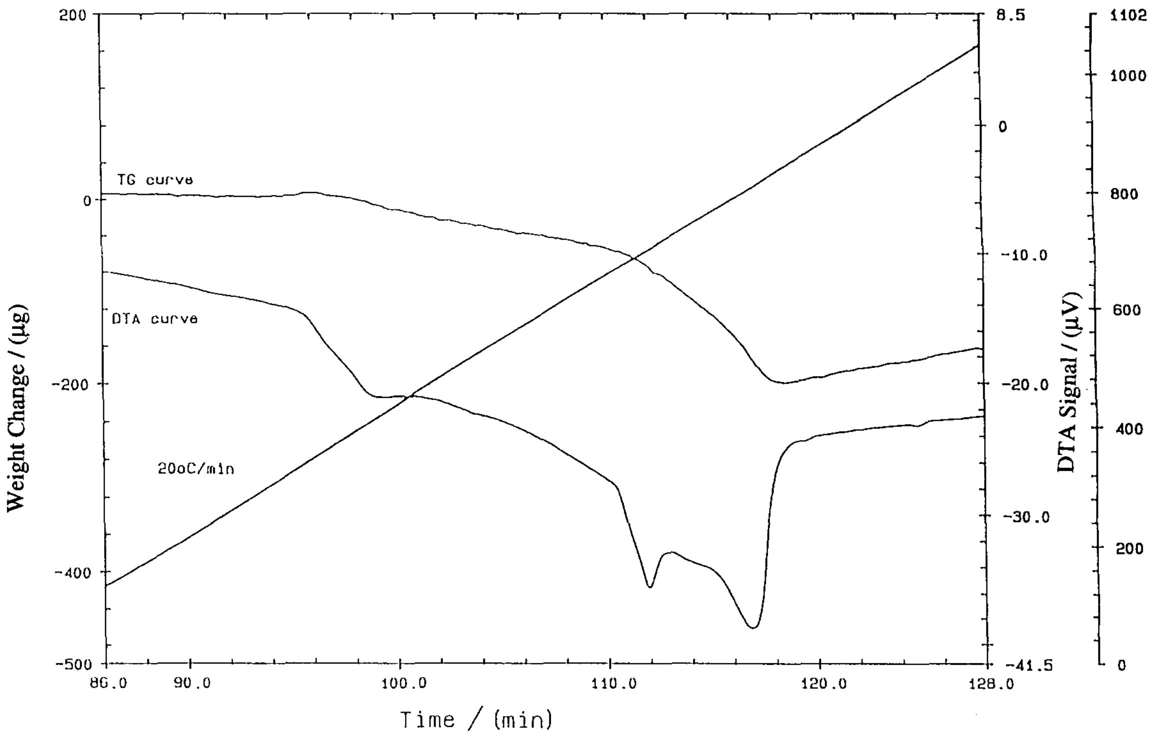

Fig. 2. TG-DTA curve of U:Th:Zr:H = 1:2:6:15.5.

form a stable U–Zr solid solution, which would turn into δ-UZr_2 when it was cooled to below 606°C.

Fig. 4 presents the DSC curves for all the samples, U:Th:Zr:H = 2:1:6:13.1, 1:1:4:9.9, 1:2:6:15.5 and 1:4:10:27. Similar to that in Fig. 2, the curves in Fig. 4 have broad peaks at the beginning of decomposition identified as the $ZrH_{1.4}$–ZrH system. From the curves, it is shown that at a higher uranium content (22.2 at.% U), curve 1, there is also a small peak, at about 728°C, while no peak at the temperature of 807 ± 2°C was observed. On reducing the uranium content, curve 2 (16.7 at.% U), the 728°C peak became smaller and the peak at a temperature of 807 ± 2°C started to grow. This 728°C peak cannot be identified clearly. On continuous reduction of the uranium

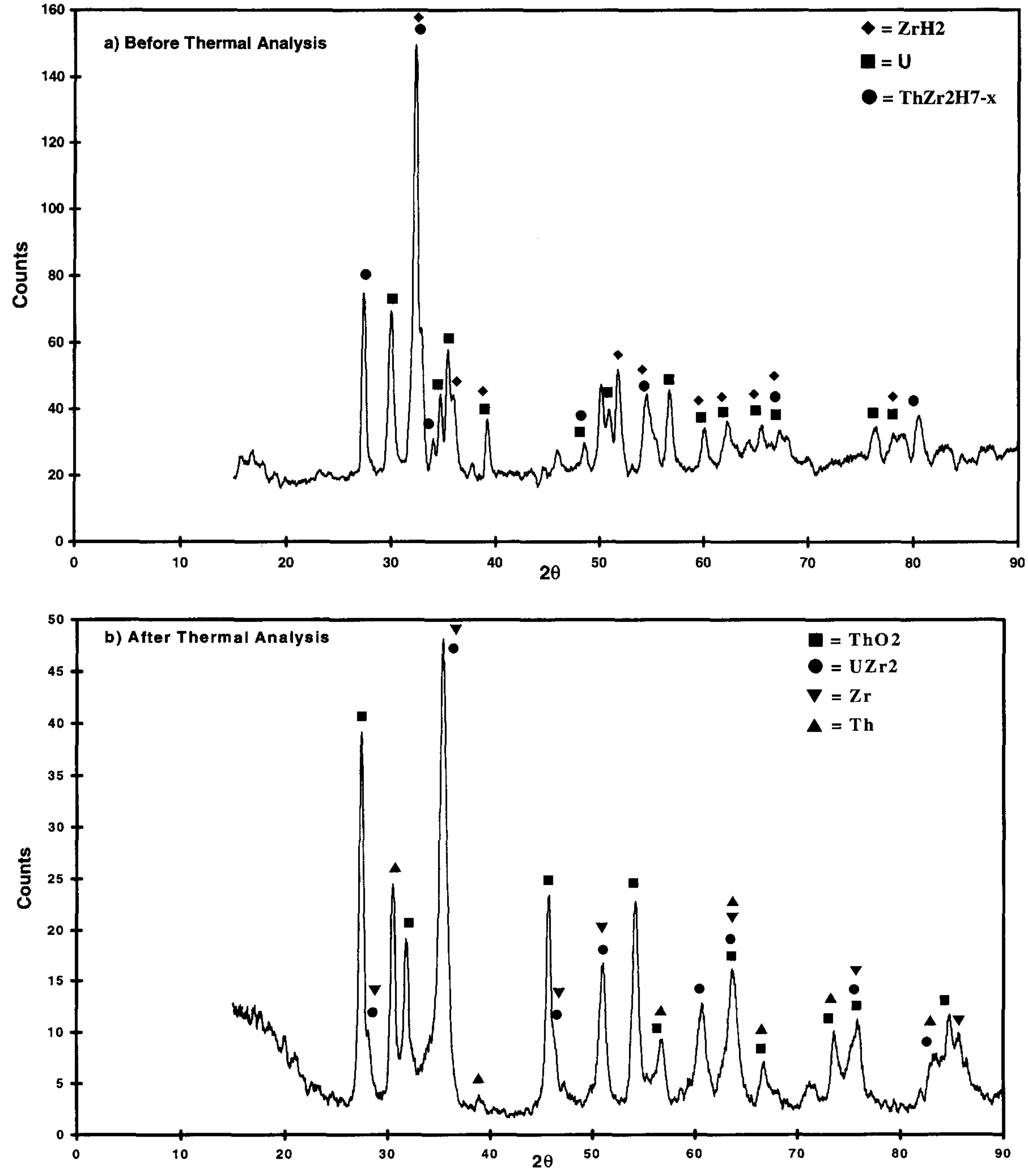

Fig. 3. X-ray diffraction patterns of U:Th:Zr:H = 1:2:6:15.5 before (a) and after (b) thermal analysis.

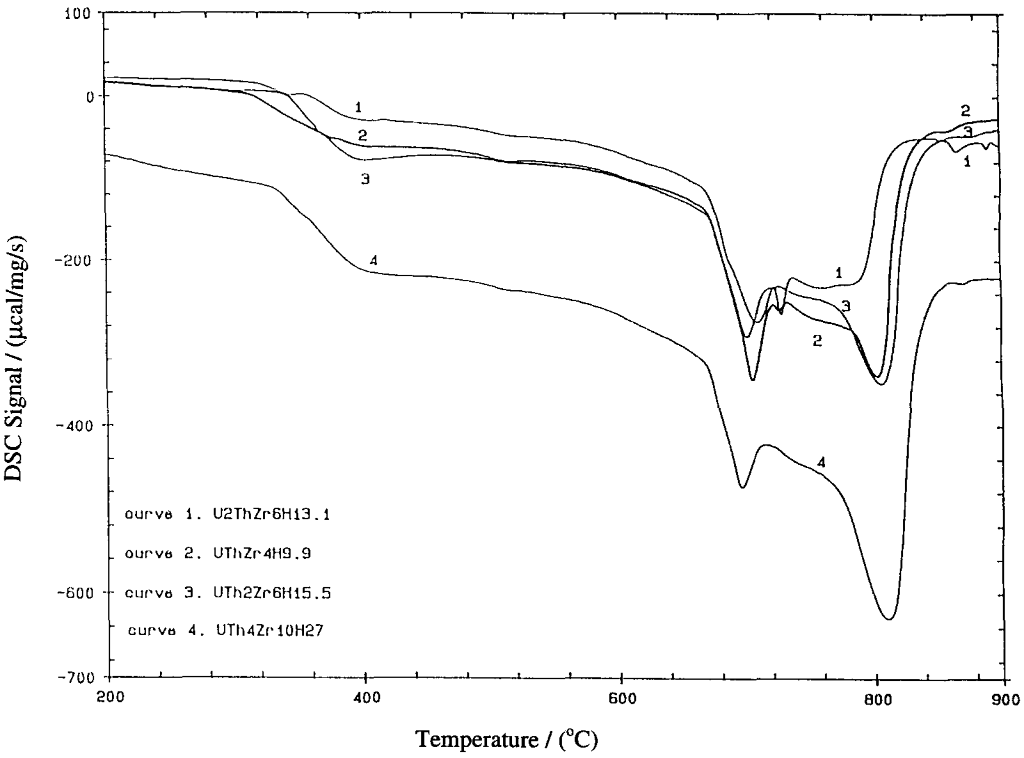

Fig. 4. DSC curves of U:Th:Zr:H = 2:1:6:13.1, 1:1:4:9.9, 1:2:6:15.5 and 1:4:10:27.

content to 11.1 and 6.7 at.% U (equal to increasing the thorium content), the 728°C peak disappears and the peak at 807 ± 2°C grows, as can be seen in the curves 3 and 4, meanwhile the peaks at 705 ± 2°C remain relatively constant. These facts indicate that the peaks at 807 ± 2°C are of the $ThZr_2H_{7-x}$ compound and, consequently, the peaks at 705 ± 2°C are of the ZrH_{2-x} compound. In addition to the curves, the growth of the peaks results from the different concentration of each metal in the samples.

Figs. 2 and 4 exhibited that the decomposition temperatures of the samples started at a relatively low temperature, while the phases of ZrH_{2-x} and $ThZr_2H_{7-x}$ showed a higher stability than each pure hydride as can be seen in the pressure equilibrium in Fig. 1. Considering the TRIGA fuel, the total volume of the gap between the fuel pellet and the stainless steel cladding is very narrow and the maximum volumetric fuel growth, $\Delta V/V$, is low [6]. Hence, when the U–Th–Zr alloy is used as fuel, the first decomposition temperature of the sample (decomposition of $ZrH_{1.4}$–ZrH) will increase the total pressure in the fuel clad gap so that a condition similar to Fig. 1 would be attained and stability of the sample can be maintained.

3.3. Enthalpy changes

Enthalpy changes associated with the decomposition of $ThZr2H_{7-x}$–$ThZr_2$ and ZrH_{2-x}–Zr systems were evaluated from the areas under the peaks of the DCS curves. Table 1 tabulates the enthalpy changes of all samples, by assuming that the hydrides in the samples compose of $ThZr2H_6$ and ZrH_{2-x} compounds. Referring to Table 1 and Fig. 4, there is no major difference in the character of transition among the U–Th–Zr–H samples and the difference in DSC peak temperature results mostly from the different concentrations of the metal constituents. Except for U:Th:Zr = 2:1:6 and 1:1:4, the enthalpy changes of the samples are equal to the theoretical calculation. As can be seen in Fig. 4, the third peak of curves 1 and 2 are

Table 1
Enthalpy changes of hydrogenated U–Th–Zr alloys

Composition U:Th:Zr:H	Enthalpy changes (kcal/mol alloy)	
	measured	calculated
$U_2ThZr_6H_{13.1}$	147.08	237.16
$UThZr_4H_{9.9}$	168.81	174.76
$UTh_2Zr_6H_{15.5}$	265.67	265.67
$UTh_4Zr_{10}H_{27}$	453.36	453.34
$ThZr_2H_6$	–	−98.71 [a]
ZrH_2	39.15	−39.0 [b]

[a] From Ref. [3].
[b] From Ref. [7].

relatively smaller than curves 3 and 4 due to oxidation before the dehydrogenation is completed, as shown in Fig. 2.

4. Conclusions

Isothermal desorption at 900°C of the alloy with elemental ratio U:Th:Zr:H = 1:1:4:9.5 exhibited that there were two distinct plateau regions identified as the $ZrH_{1.4}$–ZrH and $ThZr_2H_{7-x}$–$ThZr_2$ systems. The pressure plateaus of the hydride compounds in the sample are lower than those of pure compounds and the hydrogen capacity in the $ThZr_2H_{7-x}$ is higher than the pure one.

The DTA and DSC decomposition curves of U–Th–Zr–H compounds under argon exhibit three endothermic peaks identified as the decomposition of ZrH_{2-x} and $ThZr_2H_{7-x}$. The DTA curve indicated that the first peak is the decomposition temperature of $ZrH_{1.4}$–ZrH system, while the DSC curves indicated that the second peaks, at a temperature of 705 ± 2°C, are the decomposition temperatures of ZrH, and the third peaks, at a temperature of 807 ± 2°C, are the decomposition temperatures of $ThZr_2H_{7-x}$. Decomposition of the samples under argon exhibited the decomposition into its constituents and was followed by the reaction of zirconium with uranium to form stable U–Zr solid solution.

Isothermal decomposition of the $UThZr_4H_{9.5}$ compound without any disintegration indicates the stability of the alloy against powdering in hydriding–dehydriding cycles.

The high stability of the samples showed that they can be promoted as a new fuel material.

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