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Journal of Nuclear Materials 247 (1997) 339–344

journal of nuclear materials

Development of new reactor fuel materials: hydrogenation properties of U–Th–Zr alloys and neutron irradiation effects on their hydrides

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Abstract

Hydrogen absorption properties of four U–Th–Zr alloys with compositions of 2:1:6, 1:1:4, 1:2:6 and 1:4:10 in U:Th:Zr ratio were examined for developing a new U–Th mixed hydride fuel. It was revealed by hydrogen absorption measurement that for all the specimens hydrogen capacities normalized by the sum of Th and Zr contents were similar to or higher than that of the U–ZrH_{2-x} alloy, TRIGA fuel, at temperatures from 773 to 1073 K and under hydrogen pressures from 10^2 to 10^5 Pa. Regarding the microstructure, the alloy hydrides consisted of three phases; α-U, ZrH_{2-x} and $ThZr_2H_{7-x}$, which are finely and homogeneously mixed with each other probably because they were formed from one solid solution phase stable at high temperatures. In the case of Th-rich alloys the α-U was about 1 μm in diameter and dispersed in the bulk of $ThZr_2H_{7-x}$ and ZrH_{2-x}. Such microstructure is quite similar to that of U–ZrH_{2-x} fuel. The hydrides irradiated to 7.4×10^{23} n/m^2 in the reactor showed a high phase stability. © 1997 Elsevier Science B.V.

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1. Introduction

U–Th mixed fuel has been researched mainly on oxides, carbides, molten salts and alloys for many years because of the great advantages in thorium fuel cycle systems such as the abundance of thorium resources, production of less transuranium elements and applicability to thermal breeder reactors. Also, mixed hydrides seem to be useful as such a fuel because both U and Th form stable hydrides. As to the hydride fuel, U–ZrH_{2-x} cermet is well known as the fuel for TRIGA research reactors [1,2]. One of its major and attractive advantages is passive safety. In the cermet, 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}, which behave as isotropic harmonic oscillators, can accelerate neutrons when they are at excited states [2]. With an increase in the temperature of the hydride, the number of such excited hydrogen atoms increases, resulting in the immediate acceleration of neutrons. This phenomenon shifts the neutron energy spectrum to the higher direction, decreases the number of neutrons absorbed in the fuel and consequently reduces the reactivity. It gives a large and prompt negative temperature coefficient of the reactivity because there is practically no delay between hydride heating and fuel heating. Further, the TRIGA-type fuel has several more advantages such as low release of fission products, applicability to a small core, high neutron flux brought by high hydrogen atom concentration as well as low corrosibility in water.

The aim of this research is to develop a U–Th mixed fuel in a hydrogenated form which has the advantages of the TRIGA-type fuel as depicted above, while having the function of converting ^{232}Th to ^{233}U. An ideal material to satisfy this condition would consist of a homogeneous hydride phase containing both U and Th in a wide range of U/Th ratio and keep the homogeneity during the operation of reactor. It seems to be very difficult to develop such an ideal hydride fuel material. In a previous paper by the authors [3], it has been shown that homogenization was disturbed by the formation of a stable Ti–Zr–H ternary hydride phase on hydrogenation. In this study, U–Th–Zr alloys with several different compositions are examined to investigate the morphology of the hydrogenated alloy phases.

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PII S0022-3115(97)00058-5

2. Experimental

2.1. Alloy preparation

U–Th–Zr alloy specimens with four different U:Th:Zr ratios of 2:1:6, 1:1:4, 1:2:6 and 1:4:10 were prepared by melting the constituent elements in a tri-arc melting furnace in argon atmosphere. These compositions were selected to get the (U + Th):Zr ratio to be 1:2 which ensures solid solution formation at high temperatures [4]. The purities of U and Zr were 99.9 wt% each and that of Th was 99.99 wt%. Melting, while turning the molten alloy upside down at each interval, was repeated at least four times for each alloy in order to attain homogeneity.

2.2. Hydrogen absorption–desorption experiments

The hydrogen absorption properties of the prepared alloys were examined at various temperatures from 773 to 1173 K and at various hydrogen pressures from 10^2 to 10^5 Pa using an apparatus shown in Fig. 1. For most specimens, the absorption conditions, hydrogen pressure and temperature, were changed in a following sequence. 1 g of alloy specimen was loaded in a tungsten crucible contained in a quartz vessel, which was heated up to 1173 K in a vacuum of 10^{-5} Pa for outgassing. After closing the valve V1, the reservoir was filled with hydrogen of 30 kPa. Then, the valve was opened to start the reaction of the alloy with hydrogen. The total volume filled with hydrogen gas was about 10^{-3} m^3. The hydrogen pressure was recorded and the amount of absorbed hydrogen was calculated from the pressure decrease. After an equilibrium was attained, the pressure was increased stepwise up to 100 kPa. At a hydrogen pressure of 100 kPa, the temperature was decreased stepwise down to 773 K.

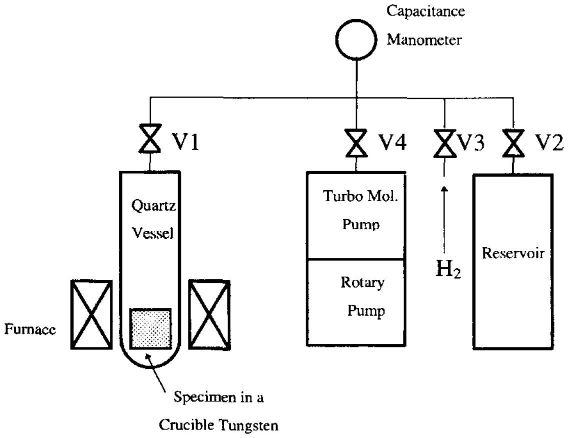

Fig. 1. Schematic diagram of the apparatus used for hydrogen absorption experiments.

2.3. Phase identification

Each specimen to be examined was polished mechanically with sandpaper of grain size #400 to #2000. In order to identify the phase, crystal structures of the starting alloys and the hydrogenated alloys were analyzed with X-ray diffraction technique (XRD), while the microstructure was examined with a scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS).

2.4. Neutron irradiation experiment

Two of the hydrogenated alloys were irradiated to a thermal neutron fluence of 7.4×10^{22}, 2.2×10^{23} and 7.4×10^{23} n/m^2 in the Japan material testing reactor (JMTR) of the Japan Atomic Energy Research Institute. The specimens for irradiation were hydrogenated through the similar history of pressure and temperature as mentioned above, but the final temperature was 1073 K. The change in dimension, weight, microstructure and hardness of the specimens were examined after irradiation.

3. Results and discussion

3.1. Phase identification before hydrogenation

According to the phase diagrams of the U–Th–Zr system in Ref. [4], every specimen forms a ternary solid solution at 1273 K. This phase decomposes to a α-Th–7 at.% Zr phase and β-Th–β-Zr–γ-U solid solution when Th content exceeds ~ 10 at.% at 1188 K. Such a ternary phase in the three Th-rich specimens further decomposes below ~ 880 K into three phases; α-Th with ~ 7 at.% Zr, α-Zr and δ-UZr_{2+x} with ~ 5 at.% Th. In the case of the U-rich specimen only two phases (α-Th and δ-UZr_{2+x}) are formed.

As are shown in Fig. 2, however, the XRD pattern suggested the existence of only two phases, α-Th and δ-UZr_{2+x}, in all of the specimens. The former phase has a slightly larger lattice constant ($a_0 = 0.506$ nm) than pure Th ($a_0 = 0.504$ nm), probably resulting from inclusion of Zr. The latter phase had larger lattice constants ($a_0 = 0.506$ to 0.507 nm and $c_0 = 0.311$ to 0.314 nm) than those of either δ-UZr_{2+x} ($a_0 = 0.503$ nm and $c_0 = 0.308$ nm) or $U_{0.6}Zr_{2.4}$ ($a_0 = 0.5046$ nm and $c_0 = 0.3103$ nm) probably because it contained ~ 5 at.% Th and was rich in Zr.

There can be two interpretations for the fact that an α-Zr phase was not formed. One possibility is that the Th-poor solid solution phase at 1188 K transformed into a Zr-oversaturated δ-UZr_{2+x} phase because of rapid cooling. Another possibility is that the excess zirconium was precipitated as metastable hexagonal ε-Zr phase as suggested by Ref. [4], where X-ray peaks of this phase ($a_0 = 0.5039$ nm and $c_0 = 0.3136$ nm) overlapped with those of the δ-UZr_{2+x} phase.

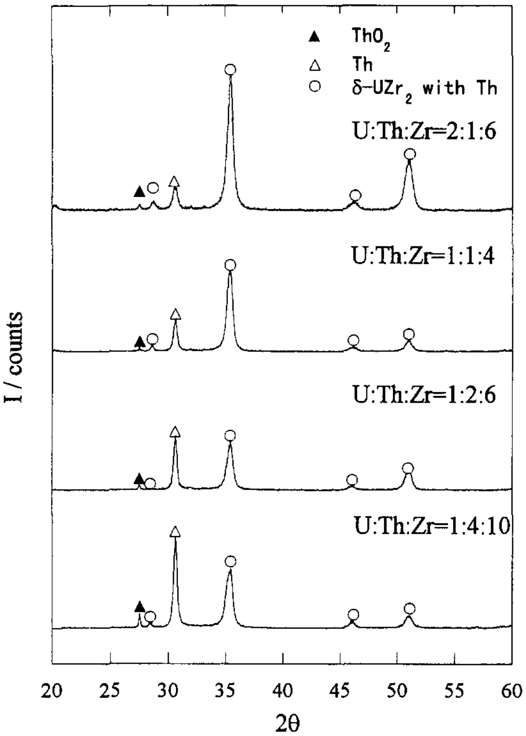

Fig. 2. X-ray diffraction patterns of U–Th–Zr alloy specimens.

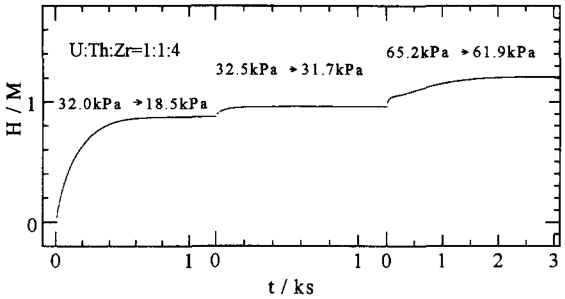

Fig. 4. Hydrogen absorption history of U:Th:Zr = 1:1:4 alloy at 1173 K.

Fig. 3 shows backscattered electron images (BEIs) of the specimens observed with SEM which reflect the average atomic numbers of the phases. Two phases were distinguished, a bulky grey phase and a network-like bright phase. The latter is considered to be an α-Th phase and the former consists dominantly of the δ-UZr_{2+x} phase and also of the ε-Zr phase if any. The compositions of the phases were not identified with EDS because of the fineness of the network morphology. While, the phase diagrams suggest that all the specimens consist of two phases, the α-Th–7 at.% Zr phase and the β-Th–β-Zr–γ-U solid solution, at the temperature to initiate hydrogenation, i.e., 1173 K.


U:Th:Zr=2:1:6
U:Th:Zr=1:1:4
U:Th:Zr=1:2:6
U:Th:Zr=1:4:10

Fig. 3. SEM micrographs (composition images) of U–Th–Zr alloys.

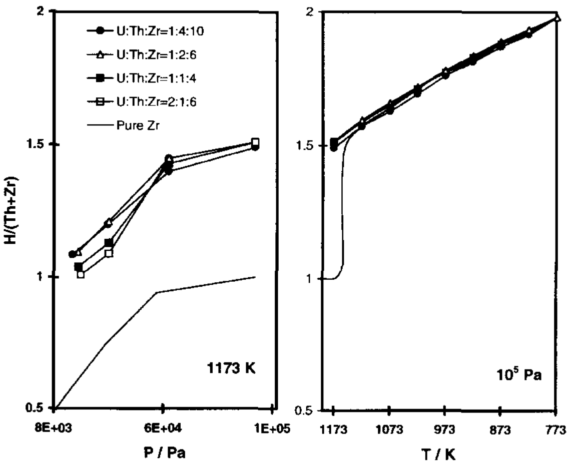

Fig. 5. Equilibrium hydrogen concentrations of U–Th–Zr specimens under various hydrogen pressures at 1173 K and at various temperatures under 10^5 Pa. Those of pure Zr were also shown as a solid line.

3.2. Hydrogen absorption properties

Fig. 4 shows the results of the hydrogen absorption experiment carried out in three serial runs on the 1:1:4 in U:Th:Zr specimen at 1173 K. Initial hydrogen pressures of the three runs were set as 32.0, 32.5 and 65.2 kPa, respectively. All the specimens showed almost the same behavior. The H/(Th + Zr) ratio of each alloy reached about 1 at the first equilibrium, increased by 0.1 at the next and reached about 1.5 at the third. It took about 0.6, 0.2 and 1 to 2 ks for the specimens to achieve equilibrium in the first, second and third runs, respectively. Details of such hydrogenation kinetics were reported elsewhere [5].

The equilibrium hydrogen concentration of the specimens changed as shown in Fig. 5 when the temperature and pressure were changed. It also shows the equilibrium hydrogen concentration of pure Zr calculated from the equilibrium hydrogen pressure-composition isotherms at several temperatures [6], which is almost identical to the present results for U–Zr alloys for less than 1153 K. The equilibrium hydrogen concentrations of all the specimens as normalized by the content of both Th and Zr were observed to show a unique curve. The normalized curves were identical to that of Zr below 1153 K. The hydrogen concentration of the U–Th–Zr specimens, however, is larger than that of Zr in the temperature range above 1153 K (by far larger at 1173 K). Consequently, the ternary alloys can hold more hydrogen than U–Zr alloy at the same temperature. In other words, it can hold a certain amount of hydrogen at a higher temperature than the U–Zr alloy. This fact gives an attractive advantage if it is used as a nuclear fuel.

3.3. Phase identification and microstructure examination of hydrogenated alloys

No specimens disintegrated on hydrogenation. All hydrogenated specimens were obtained in the form of a block. Figs. 6 and 7 show the microstructure and XRD patterns of the hydrogenated alloys, respectively. In the SEM micrographs three phases are observed and the analy-

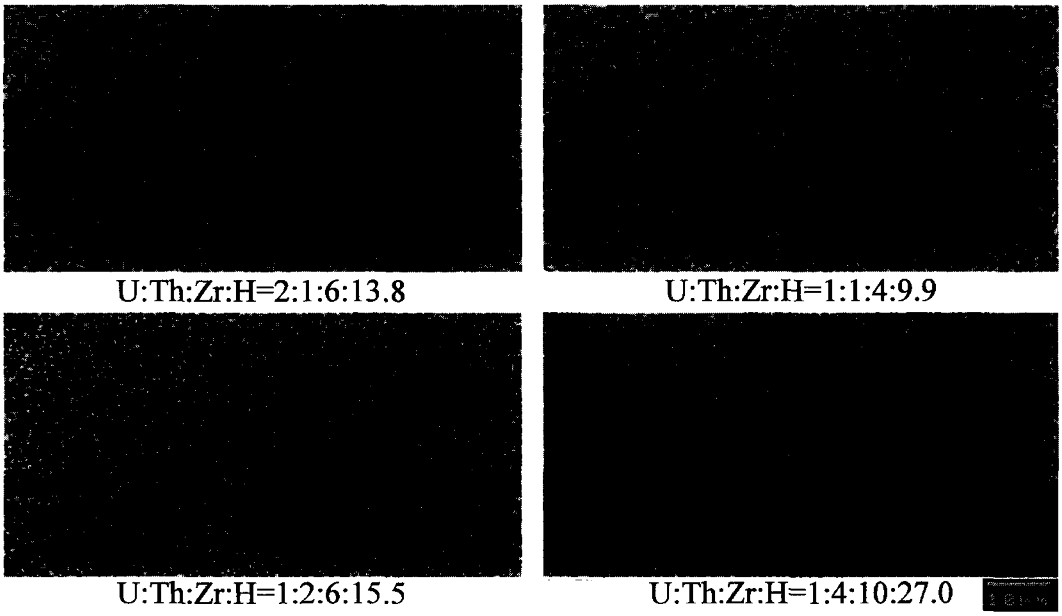
U:Th:Zr:H=2:1:6:13.8
U:Th:Zr:H=1:1:4:9.9
U:Th:Zr:H=1:2:6:15.5
U:Th:Zr:H=1:4:10:27.0

Fig. 6. SEM micrographs (composition images) of U–Th–Zr alloy hydrides.

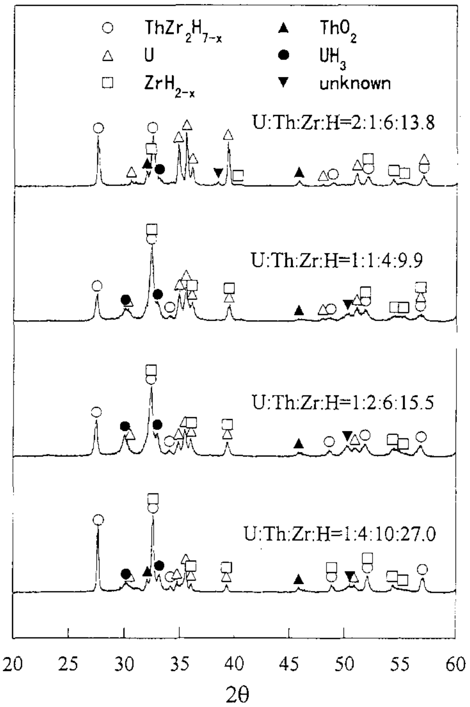

Fig. 7. X-ray diffraction patterns of hydrogenated U–Th–Zr alloys.

sis of the phases with EDS showed that the brightest one, the grey one and the dark one are rich in U, in Th and Zr and in Zr, respectively. Hence these were attributed to the main three phases α-U, $ThZr_2H_{7-x}$ and ZrH_{2-x}, as observed in the XRD patterns. A Th-rich phase of light grey color was also observed sporadically on the surfaces, which may most probably be attributed to ThO_2 as observed weakly in XRD patterns.

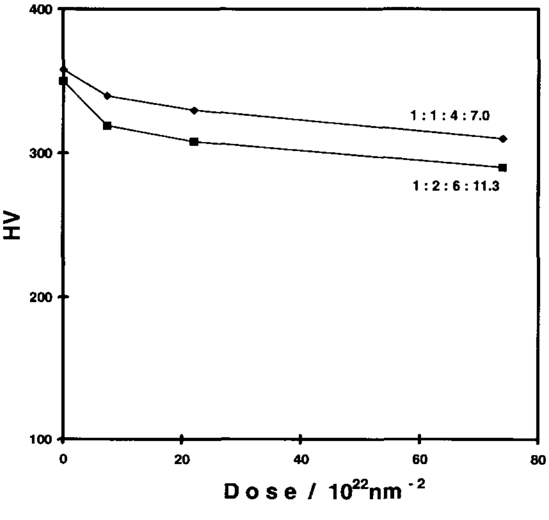

Fig. 8. Vickers microhardness of unirradiated and irradiated U–Th–Zr alloy hydrides with composition of 1:1:4:7.0 and 1:2:6:11.3 in U:Th:H:Zr ratio.

The important feature of the microstructure was that those three phases were very finely mixed with one another. Especially in hydrogenated Th-rich alloys, 1:2:6 and 1:4:10 in U:Th:Zr ratios, α-U phase of grains of about 1 μm in diameter dispersed in the bulk of mixture of two hydrides; $ThZr_2H_{7-x}$ and ZrH_{2-x}. The feature is similar to that of U–ZrH_{2-x} fuel. This fact, combined with the results of the hydrogen capacity measurements mentioned above, suggests that the U–Th–Zr alloys, especially the Th-rich alloy, can be utilized as a substitute for the U–ZrH_{2-x} fuel.

3.4. *Effect of neutron irradiation on the stability of the hydrides*

After neutron irradiation, no significant change was observed in dimension, mass and microstructure of the alloys. The Vickers microhardness decreased only slightly with increasing neutron fluence as shown in Fig. 8. Such a slight effect of neutron irradiation on the mechanical properties would be attributed to its fine microstructure because defects produced in crystals by irradiation are considered to disappear easily at the grain boundaries with a substantially large area. This also supports the fact that the alloys can be attractive as a new fission reactor fuel material.

4. Conclusion

The hydrogen absorption properties as well as the irradiation effect on the mechanical properties of U–Th–Zr alloys of four different compositions were examined to find if there was a possibility for these materials to be used as a new U–Th mixed hydride fuel. For all the specimens, the hydrogen capacities were similar to or higher than that of the TRIGA-type U–ZrH_{2-x} fuel. As for the morphology, the small size of the α-U phase disperses in the bulk mixture of $ThZr_2H_{7-x}$ and ZrH_{2-x} such as in the case of U–ZrH_{2-x}. In addition, a minor effect was observed of neutron irradiation on their microhardness. From these results, it is concluded that U–Th–Zr alloys can be promising as a new U–Th based fission fuel with passive safety possibility.

Acknowledgements

The authors would like to thank the technical staffs of the Oarai Branch, IMR, Tohoku University for their technical supports and Professor Kenji Yamaguchi and Ms Futaba Ono for their valuable discussions and technical supports.

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