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Preparation, analysis and irradiation of hydrided U–Th–Zr alloy samples for a new fuel

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Abstract

To get the properties of U–Th–Zr–H alloys, which are needed to utilize them for nuclear fuels, changes in the dimensions and weights of the alloys on hydrogenation and in microstructure and hardness on neutron irradiation to 7.4×10^{23} n/m^2 were examined. The hydrogenated alloys show high apparent densities and high durability for the irradiation, which promotes the utilization of the alloys for a new type of nuclear fuel. © 1998 Elsevier Science S.A.

Keywords: Uranium–thorium–zirconium alloy; Hydrogenation; Volume expansion; Density; Neutron irradiation; Nuclear fuel

1. Introduction

U–Th mixed fuel has been researched mainly on oxides, carbides, molten salts and alloys for many years, to utilize the abundant thorium resource for breeder reactors. Previous studies by us have showed that U–Th–Zr alloy hydrides are also candidate materials for a mixed fuel [1,2]. The alloys showed apparently no disintegration on hydrogenation and absorbed more hydrogen at 10^5 Pa H_2 and 1173 K than Zr, which is actually used as a fueled moderator for TRIGA reactors in the form of U–ZrH_{2-x}. The standard TRIGA fuel contains 8.5–12 wt.% U as a fine metallic dispersion in a ZrH_{2-x} matrix (x is typically 0.4). Such a microstructure is responsible for its inherent safety, the most attractive feature of the fuel [3,4]. U–Th–Zr–H fuels are also expected to have such properties by having a similar microstructure; metallic U particles are finely dispersed in the hydrides, $ThZr_2H_{7-x}$ and ZrH_{2-x}. Recently the concept of MA-burning hydride fuel has been proposed by Yamawaki et al. [5] and the U–Th–Zr–H alloys are gaining attention. However, most of the properties of U–Th–Zr–H alloys are still unknown. In this paper, changes in the dimensions, apparent density, microhardness and microstructure on hydrogenation and/or neutron irradiation are reported.

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2. Experimental

2.1. Sample preparation

Three U–Th–Zr alloys with U:Th:Zr atomic ratios of 1:1:4, 1:2:6 and 1:4:10 and one U–Zr alloy with a U:Zr ratio of 1:10 were prepared by melting constituent elements in an argon-arc furnace. Purities of the U and Zr were 99.9 wt.% and that of Th was 99.99 wt.%. In order to attain homogeneity, melting was repeated at least four times; at each step, the molten alloy was turned over. The alloy buttons were cut into rectangular parallelepiped blocks. Typical dimensions of a block were $5\times5\times6$ mm^3 and its weight was 1 g. The dimensions and weight of the blocks were monitored on hydrogenation and on neutron irradiation.

Various hydrogenating conditions of the alloys were tested and the most suitable sequence from the previous studies was chosen. The final condition was a hydrogen pressure of 100 kPa and a temperature of 1073 K for all alloys. Hydrogen concentrations in the alloys were calculated from the weight gain on hydrogenation (Table 1).

2.2. Neutron irradiation

Neutron irradiation to 7.4×10^{22}, 2.2×10^{23} and 7.4×10^{23} n/m^2 (for thermal components) were performed in Japan Material Testing Reactor in JAERI, Oarai. The

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Table 1
Compositions of hydrogenated alloy specimens

U–Th–Zr ratio	Absorbed H per U–Th–Zr unit	at.%			
		U	Th	Zr	H
1:1:4	7.2	7.6	7.6	30.3	54.5
1:2:6	11.4	4.9	9.8	29.4	55.9
1:4:10	19.4	2.9	11.6	29.1	56.4
1:0:10	11.2	4.5	–	45	50.5

nominal neutron flux at the specimen position was 5.3×10^{16} and 8.6×10^{17} n/m^2/s for the fast ($E>1.0$ MeV) and the thermal component, respectively. The specimens were held in quartz tubes filled with 100 kPa He and the tubes were mounted into the irradiation capsules, which was made of aluminum.

2.3. Micro-hardness measurement and microstructure observation

Each specimen to be examined was polished mechanically by SiC papers of #400 to #2000. Vickers microhardness was measured by applying a load of 200 g. The microstructure was observed using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Changes in weight, dimensions and apparent density on hydrogenation

Table 2 shows changes in dimensions of the alloys on hydrogenation, where dL/L (%) is the averaged expansion of the block length, dV/V (%) is volume expansion and dV/dw (cm^3/g) is the ratio of volume increase per weight increase (i.e. hydrogen absorption). The expansion ratios increase monotonously with increasing Th content in the alloys. The phases should be $ThZr_2H_x$, ZrH_y and U in the U–Th–Zr–H alloys [2]. For these alloys, the H content increases linearly with increasing Th content following the equation,

Table 2
Changes in dimensions and weight on hydrogenation

U–Th–Zr–H	H/Th+Zr	Changes on hydrogenation		
		dL/L (%)	dV/V (%)	dV/dw (cm^3 g^{-1})
1:1:4:7.2	1.44	4.0	12.6	1.6
1:2:6:11.4	1.43	4.5	14.2	1.8
1:4:10:19.4	1.39	5.3	16.6	2.1
1:0:10:11.2	1.11	3.1	9.7	1.4

Table 3
Theoretical densities of several concerned phases and theoretical expansion on hydrogenation

Phase	ρ (g cm^{-3})	dV/V (%)	dV/dH (cm^3 g^{-1})
U	19.05	–	–
Zr	6.51	–	–
Th–5 at.% Zr	11.54	–	–
ZrH	5.84	12.7	1.79
$ZrH_{1.6}$	5.65	17.3	1.52
$ThZr_2H_{3.6}$	7.51	16.4	2.17
$ThZr_2H_{4.8}$	7.36	19.1	1.90

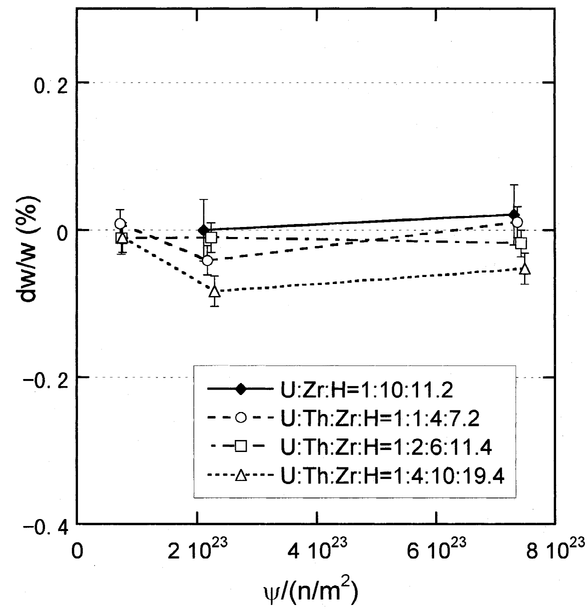

Fig. 1. Changes in weight of the U–Th–Zr–H and U–Zr–H alloy specimens with neutron irradiation dose.

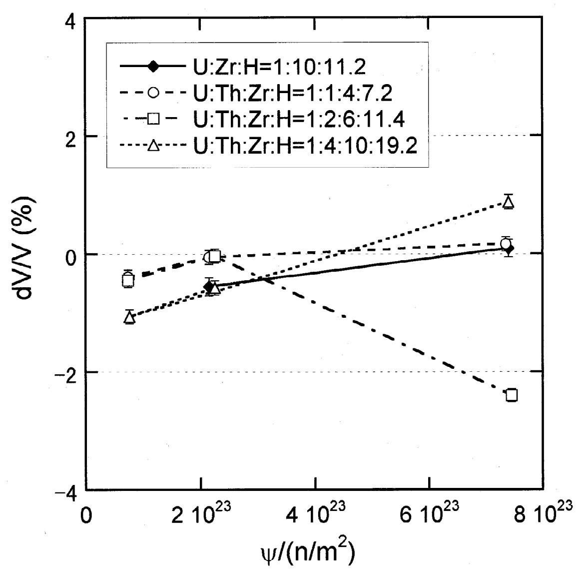

Fig. 2. Changes in the dimensions of U–Th–Zr–H and U–Zr–H alloy specimens with neutron irradiation dose.

Table 4
Apparent and theoretical densities of hydrogenated alloys

U–Th–Zr–H	Apparent density, ρ (g cm^{-3})			Theoretical density of the hydrogenated, ρ (g cm^{-3})
	Before hydrogenation	After hydrogenation		
1:1:4:7.2	9.0	8.08	97.4% TD	8.29
1:2:6:11.4	8.8	7.80	97.6% TD	7.99
1:4:10:19.4	8.7	7.53	97.0% TD	7.77
1:0:10:11.2	7.1	6.56	99.5% TD	6.59

$$H/U = 3.2 + 4.06Th/U, \quad (1)$$

which suggests that the hydrides are $ThZr_2H_{4.06}$ and $ZrH_{1.6}$. Theoretical densities of $ThZr_2H_x$ and ZrH_y were calculated from X-ray diffraction data of the hydrides or deuterides given in refs. [6,7] and theoretical expansion on their formation was estimated. The results listed in Table 3 show expansion per unit hydrogen uptake by Th–Zr alloys to be much higher than that by Zr. This explains the tendency shown in Table 2 well.

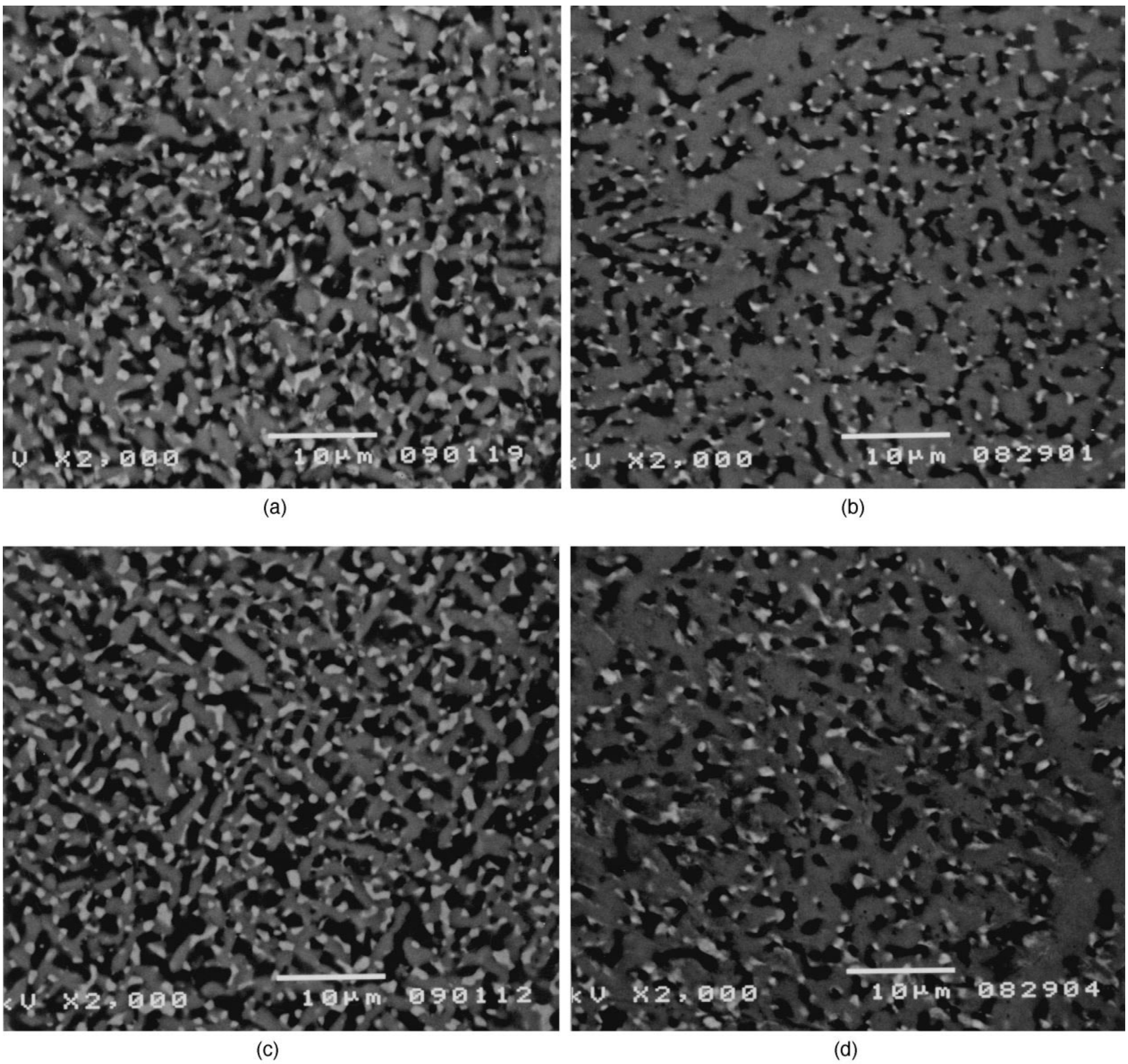

Fig. 3. Microstructure of two U–Th–Zr–H alloys after two neutron irradiation doses. (Back-scattered electron images by SEM. White: U; Gray: $ThZr_2H_x$; Black: ZrH_y) (a) 1:1:4:7.2 alloy, 7.4×10^{22} n/m^2, (b) 1:4:10:19.4 alloy, 7.4×10^{22} n/m^2, (c) 1:1:4:7.2 alloy, 7.4×10^{23} n/m^2, (d) 1:4:10:19.4 alloy, 7.4×10^{23} n/m^2.

Table 4 shows apparent densities of the alloys together with theoretical values that are calculated assuming the alloys are mixtures of the phases mentioned above. In the case of the U–Zr–H alloy, the apparent density was almost the same as the theoretical value. Those of the U–Th–Zr–H alloys were slightly lower, about 97% TD, probably due to the integral atomic-scale gap volume over the large grain boundary area between $ThZr_2H_x$ and ZrH_y. However, the densities are quite high considering that no pressure was applied on the specimens during or after hydrogenation. The low crack formation illustrated by this result is one of the most attractive properties of the alloys from the viewpoint of fabrication, thermal conductivity and fission gas retention if they are used as fuels.

3.2. Effect of neutron irradiation on dimensions, densities, microstructure and micro-hardness

Figs. 1 and 2 show changes in weight and volume after neutron irradiation. There is almost no change in weight. The volume changed slightly more than expected from the rather constant weight, although the change still remains small. With the exception of the alloy with the ratio 1:2:6, the specimens at first shrank slightly and then swelled. However, it should be noted that the change is quite small.

The microstructure of the alloys showed no significant change. Fig. 3 represents back scattered electron images of the U–Th–Zr–H alloys after neutron irradiation and shows the distribution of the phases. There are still two phases that are finely dispersed in a principal phase and the microsturucture seems to be only slightly affected by the irradiation dose in Figs. 3b and d.

Fig. 4 shows the variation of the Vickers micro-hardness with the neutron dose. The hardness measured for U–Th–Zr–H alloys as well as the U–Zr–H alloy decreased slightly with increasing neutron dose, except for U–Th–Zr–H = 1:4:10:19.4 at low irradiation. No hardening was observed on 1:1:4 and 1:2:6 alloys, although it should be caused by accumulation of defects in the matrix. In the alloys, especially the 1:1:4:7.2 alloy (see Figs. 3a and c), each phase is quite small (about 1 μm^2) and there are about 400 grains under an indent, if roughly estimated, which means that the strength of the grain boundaries has the greatest importance on the mechanical properties of the alloys. However, in the 1:4:10:19.4 alloy the $ThZr_2H_x$ phase forms the bulk, and its mechanical properties have greater importance than that of the boundaries. Hence, the change in hardening shown in Fig. 4 is interpreted by two effects of neutron irradiation on the mechanical properties; one is hardening of the hydride matrix and the other is weakening of the grain boundaries. The former effect is important at the beginning of irradiation only for the 1:4:10:19.4 alloy and the latter is more important in all other cases.

Regardless of the hardening/softening mechanism, it

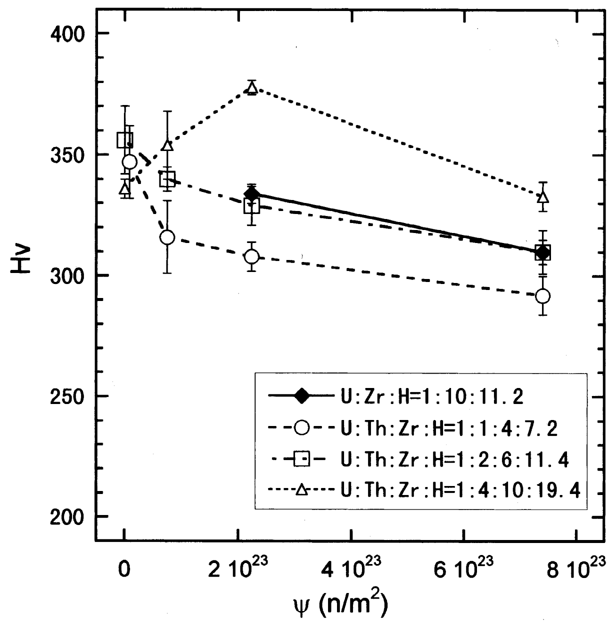

Fig. 4. Changes in Vickers micro-hardness of U–Th–Zr–H and U–Zr–H alloy specimens with neutron irradiation dose. Each dot represents an average of five measurements while the error bar shows a standard deviation.

can be stated that a 16% decrease, at most, in hardness under the irradiation is quite an attractive feature of the alloys for utilizing them as nuclear fuels.

4. Conclusion

Changes in dimensions and weight of the U–Th–Zr alloys on hydrogenation and in microstructure and hardness on neutron irradiation were examined. The hydrogenated alloys showed high apparent densities and high durability of microstructure and hardness against the neutron irradiation, which promotes the utilization of the alloys for a new type of nuclear fuel.

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