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Hydrogen absorption–desorption properties of $UZr_{0.29}$ alloy

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Abstract

Hydrogen absorption–desorption properties of the $UZr_{0.29}$ alloy and uranium metal were investigated in detail at hydrogen pressures as high as to 0.4 MPa and over the temperature range of 300–723 K. Both $UZr_{0.29}$ alloy and uranium metal showed similar hydrogen isotopic effect and hysteresis effect. $UZr_{0.29}$ alloy absorbed hydrogen (deuterium) up to 2.3H (2.18D) atoms per F.U. (formula unit) by only one-step reaction and hence each desorption isotherm had a single plateau over nearly the whole hydrogen composition range. The $UZr_{0.29}$ alloy showed a little lower dissociation pressure than that of pure uranium; however, it exhibited high durability against powdering upon hydrogenation and may have good heat conductivity. The $UZr_{0.29}$ hydride has the potentiality to substitute pure uranium hydride as a material for tritium treatment and storage. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Tritium technology is one of the critically important fields of fusion reactor engineering. In such a field, tritium needs to be purified and storage with high safety measures to keep tritium from being released to the environment. In this sense, a tritium storage bed using metal tritide is rated to be as more suitable than that using either the gaseous or liquid form of tritium. Although many materials can be used as hydrogen storage bed, uranium is the most suitable and prevailing selection for such tritide storage systems. This is because it can easily absorb tritium at ≈0.1 MPa below 500 K to form UT_3, and the tritide exhibits a dissociation pressure lower than 10^{-3} Pa for holding tritium tightly at room temperature and sufficiently high at about 700 K to release tritium easily. Further, the pressure–concentration isotherm below 700 K has only a single plateau, which spans nearly the whole range of concentration of about 0–3 H/U [1].

However, it easily disintegrates into fine powder because of the enormous volume expansion on hydrogenation [2]. The powder is highly pyrophoric [3] and has low heat conductivity, which makes it difficult to control the temperature, and has a high possibility of explosion and contamination.

Therefore, uranium is desired to be improved as to its hydrogen storage property by alloying. Such alloys should have the similar superior hydrogen absorption–desorption properties as uranium, such as high hydrogen absorption capacity, low dissociation pressure at 298 K and sufficiently high at proper temperature, single and wide plateau, and have low powdering tendency as well as low pyrophoricity. So far, the hydrogen absorption–desorption properties of several uranium compounds and alloys, such as U–Al, U–Mo, U–Cr, U–Ti, U_2Ti, U_2Zr, $UZr_{2.3}$, UCo, UNi_2, UNi_5, U_6Ni, U_6Mn, U_3Si, U_6NiPd, UXAl (X ≡ Mn, Co, Ni, Fe) and $U(Al_xNi_{1-x})_2$, have been studied by authors [4–17]. Among these alloys, only U_2Zr, $UZr_{2.3}$ and U_2Ti were reported to show an excellent durability to powdering on hydrogenation [6,

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8,9]. However, there are more than one plateau in these compound systems upon complete hydrogenation, which makes it difficult to assure a constant dissociation pressure over the whole hydrogen concentration range. Here we want to know whether it is possible or not to obtain the aim of a single plateau over the whole hydrogen concentration range and its dissociation characteristics similar to pure UH_3 by lowering the contents of the alloying elements in the U–Zr systems. The $UZr_{0.29}$ alloy was selected in this research; its hydrogen absorption–desorption properties were investigated in detail at hydrogen pressures as high as to 0.4 MPa and at temperatures between 300 and 723 K. The hydrogen absorption–desorption properties of uranium metal with high carbon contents were also studied under the same conditions for comparison.

2. Experimental details

The $UZr_{0.29}$ alloy specimens were prepared from the constituent elements by arc melting in an argon atmosphere using uranium of 99.0% purity and zirconium of ≈99.5% purity. The specimens were annealed under 10^{-5} Pa at 1123 K for 24 h and then quenched in water. About 20 g of each sample were used for the hydrogen absorption–desorption measurements. The element compositions were shown in Table 1. The hydrogenation apparatus employed to examine the hydrogen absorption–desorption properties was shown schematically in Fig. 1. The connecting tubes, reservoir and reactor were made of austenitic stainless steel. The full volume of the charging system was about 280 cm^3, and the volume of the changeable hydriding reactor vessel was approximately 45 cm^3. The high purity hydrogen gas used in the experiments was obtained by the thermal decomposition of $LaNi_5$ hydride.

After the sample had been put into the reactor, the latter was connected to the hydriding system and the sample was outgassed at a temperature of 873 K for several hours to reach a vacuum of about 0.1 Pa. Then the sample was pre-activated under 0.1 MPa of pure hydrogen at the temperature range of 300–873 K, and subjected to several hydriding–dehydriding cycles before the pressure–composition–temperature readings were taken. The absorption isotherm was measured by introducing hydrogen in the reactor in a small decrement till the hydrogen saturated sample was obtained under ≈0.4 MPa hydrogen pressure, while the desorption isotherm was obtained by extracting hydrogen in a small decrement from the hydrogen saturated sample. The sample was outgassed again before each absorption isotherm or after each desorption one was measured. The hydrogen pressure above the sample was read after the equilibrium had been established completely, and the amount of absolute hydrogen concentration was determined according to the amount of hydrogen gas absorbed in or desorbed from the specimens. The isotherms were measured at three temperatures of 623, 673 and 723 K.

The industrial computed tomography (ICT) was used to determine the pulverization of the samples. The ratio of volume change per unit weight after hydrogenation

Table 1
Impurities in the experimental samples, 10^{-6} wppm

Element	C	N	Fe	Mn	Si	Al	Cu	Ni	O
$UZr_{0.29}$	300	44	59	<10	52	31	20	<10	2200
U	560	<20	54	<10	75	50	28	15	–

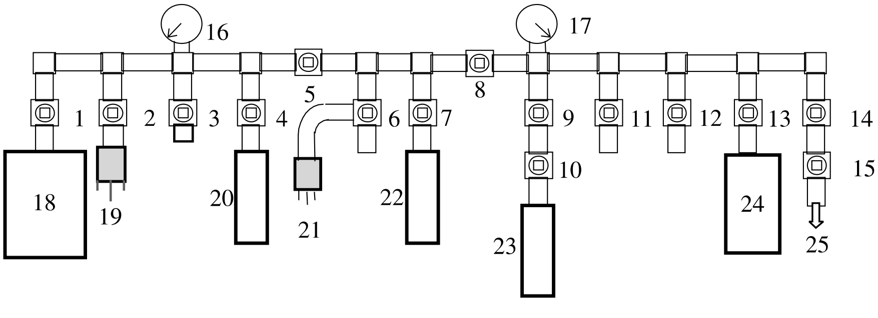


Fig. 1. A schematic diagram of the hydrogen absorption–desorption apparatus: (1)–(15) valve; (16) precise pressure gauge (0-0.4 MPa); (17) precise pressure gauge (0–0.1 MPa); (18) reservoir; (19) condenser manometer; (20) gas recover bed; (21) vacuum pressure sensor; (22) $LaNi_5$ bed; (23) reactor vessel; (24) calibrate vessel; (25) connecting to vacuum system.

was calculated by measuring the height change of the vertical image of the sample. The cross-section photos revealed the powdering characteristics of the samples. The crystal structures and lattice constants of both hydrogenated and de-hydrogenated samples were determined by X-ray powder diffractions.

3. Results and discussion

3.1. Hydrogen/deuterium absorption–desorption isotherms

The pressure–composition isotherms for U-H/D and $UZr_{0.29}$-H/D systems were shown in Figs. 2 and 3. As can be seen from the figures, the compositions corresponding to the maximum hydrogen absorption of each specimen were determined to be $H/M = 2.90$ and $D/M = 2.81$ for U-H/D; $H/M = 2.3$ and $D/M = 2.13$ for $UZr_{0.29}$-H/D, respectively ($M = U$ or $UZr_{0.29}$). The amount of absorbed hydrogen per mole of uranium seemed to be reduced compared to that of pure UH_3 for both specimens. But because the uranium content in the $UZr_{0.29}$ alloy is about 78 at.%. If only the hydrogenation of uranium was measured H/M should be about 2.3 (78% of 3.0), which was equal to the ratio measured in the experiment. This seemed to indicate that the effect of zirconium on hydrogen capacity of the $UZr_{0.29}$ alloy was brought by the fact that some of the uranium atoms in the cubic crystal cell were substituted by zirconium atoms, which might decrease the number of interstitial sites rich in uranium atom and most favorable for hydrogen occupation [18], thus led to the decrease of the hydrogen capacity of the alloy.

In the whole hydrogen composition range of $UZr_{0.29}$-H system, the decomposition characteristics of the hydride are similar to that of pure UH_3. Both have a wide and level desorption–composition–temperature plateau and the hysteresis effect. However, the equilibrium decomposition pressure of the alloy hydride showed a little lower than that of pure UH_3, and the larger hysteresis effect was also observed in the alloy hydride.

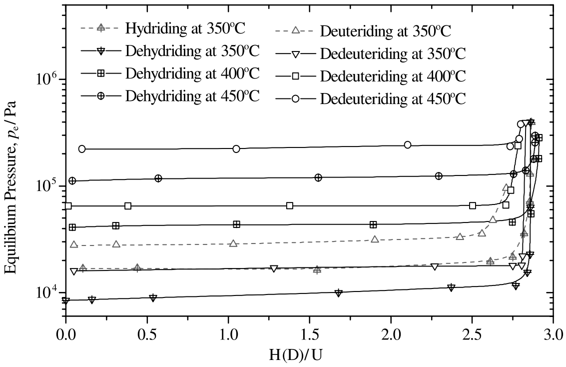


Fig. 2. Hydrogen/deuterium absorption–desorption isotherms of uranium metal at various temperatures.

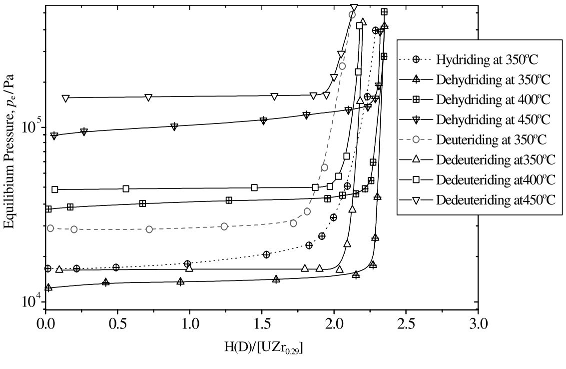


Fig. 3. Hydrogen/deuterium absorption–desorption isotherms of $UZr_{0.29}$ alloy at various temperatures.

3.2. Plateau pressure–temperature relations

Temperature dependence of the measured plateau pressures of desorption in $UZr_{0.29}$ hydride/deuteride and uranium hydride/deuteride were shown in Figs. 4 and 5. Here, open squares and triangles showed the experimental values obtained in this work. The similar relations for hydrides of uranium and uranium–zirconium alloys estimated from the references were also shown for comparison in Figs. 4 and 5. As could be seen from the two figures, the temperature dependence of the plateau pressures obtained in our experiments were found to be a good linear relationship, which could be expressed by the van't Hoff equations.

$$UZr_{0.29}\ \text{hydride}: \log(p_{e,H2}/p_0) = -4118/T + 5.72, \quad (1)$$

$$UZr_{0.29}\ \text{deuteride}: \log(p_{e,D2}/p_0) = -4456/T + 6.32, \quad (2)$$

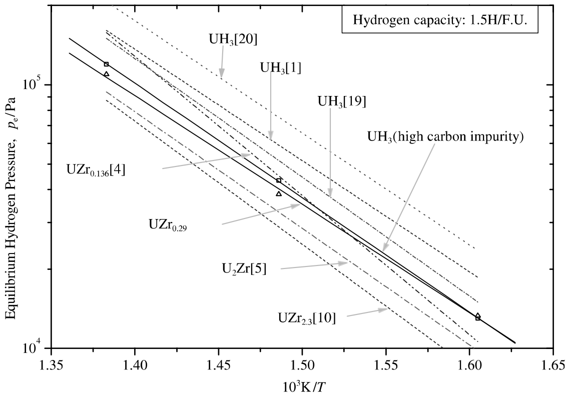


Fig. 4. Temperature dependence of plateau pressures of the U–Zr–H_2 and U–H_2 systems [1,4,5,10,19,20].

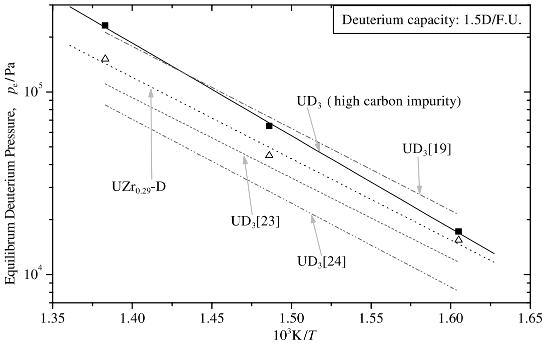


Fig. 5. Temperature dependence of plateau pressures of the U–Zr–D_2 and U–D_2 systems [19,23,24].

$$\text{Uranium hydride}: \log(p_{e,H2}/p_0) = -4343/T + 6.09, \tag{3}$$

$$\text{Uranium deuteride}: \log(p_{e,D2}/p_0) = -5220/T + 7.58, \tag{4}$$

where $p_{e,H2}$ and $p_{e,D2}$ denoted the equilibrium dissociation pressure in Pa over hydride and deuteride, $p_0 = 101,325$ Pa, and T was absolute temperature in K.

From above expressions and other reference data, the thermodynamic variables of the decomposing reactions were deduced and listed in Table 2. As can be seen, the enthalpy change and entropy change of the reaction are −83.2 kJ mol^{-1} H_2, 116.8 J (K mol H_2)$^{-1}$ and −99.9 kJ mol^{-1} D_2, 145.5 J (K mol D_2)$^{-1}$ for UH_3 and UD_3 to decompose, respectively; and −78.9 kJ mol^{-1} H_2, 109.2 J (K mol H_2)$^{-1}$ and −85.3 kJ mol^{-1} D_2, 121.0 J (K mol D_2)$^{-1}$ for $UZr_{0.29}$ hydride and deuteride to decompose, respectively. The set of observed entropy changes almost agree with the standard entropy that is lost by hydrogen as the gas enters into the metal [21]. And the enthalpy values for UH_3 and UD_3 also consist well with the reference, as shown in Table 2.

According to the variables listed in Table 2, desorption pressures at 298 K were calculated by extrapolating the obtained van't Hoff relations and were listed in Table 3. It could be seen from the data that both uranium and uranium–zirconium alloys had normal isotopic effects on hydrogen desorption at high temperatures, which meant that the deuterides had higher decomposition pressure than hydrides at high temperature range. But at lower temperature, hydrogen isotopic effect was reversed, which meant that hydrides had higher dissociation pressure than deuterides. Tanabe et al. [22] also observed such reversing phenomenon of isotopic effect in the research of pure uranium hydride. The critical reverse temperatures for the $UZr_{0.29}$ alloy and uranium specimens were found to be approximately 290 and 316 °C, respectively.

The observed desorption pressures for both $UZr_{0.29}$ alloy and uranium hydrides were slightly lower than that of pure UH_3 at temperature range 623–723 K, as shown in Figs. 4 and 5. This may attribute to the different activity of UH_3 in each specimen. Because both interstitial elements, such as carbon, and substitute elements with larger atomic radius than uranium, such as zirconium, will enlarge the unit cell volume, as well as the hole size of interstitial sites occupied by hydrogen atoms, which will result in more stable hydrides [25]. The larger the zirconium amount added in U–Zr alloy, the bigger the unit cell, thus the more stable the alloy hydrides, as will be discussed in Section 3.4 and also shown in Table 4

Table 2

Thermodynamic variables calculated from the experimental observations and references for some uranium–zirconium–hydrogen/deuterium or uranium–hydrogen/deuterium systems according to the expressions [a]: $\log(p_e/p_0) = -A/T + B$ and $\log(p_e/p_0) = (\Delta H_f^\circ/T + \Delta S_f^\circ)/2.303R$

Specimen	Hydride				Deuteride				Ref.
	A	B	ΔH_f°	ΔS_f°	A	B	ΔH_f°	ΔS_f°	
$UZr_{0.136}$	5280	7.5	−101.1	143.6	–	–	–	–	[4]
$UZr_{0.29}$	4118	5.72	−78.9	109.2	4456	6.32	−85.3	121.0	This work
U_2Zr	4430	6.1	−84.8	116.8	–	–	–	–	[5]
UZr_2	4670	6.4	−89.4	122.5	–	–	–	–	[10]
U	4343	6.09	−83.2	116.8	5220	7.58	−99.9	145.5	This work
U	4500	6.40	−86.2	122.5	4500	6.55	−86.2	125.4	[19]
U	4450	6.32	−85.2	121.0	4500	6.52	−86.2	124.8	[25]
U	4255	6.20	−81.5	118.7	4401	6.13	−84.3	117.4	[26]
U	4480	6.32	−85.8	121.0	–	–	–	–	[27]
U	4410	6.26	−84.4	119.9	–	–	–	–	[28]
U	4225	6.05	−80.9	115.8	–	–	–	–	[24]
U	–	–	–	–	4494	6.30	−86.1	120.6	[29]
U	4366	11.25	−83.6	119.7	4600	6.29	−88.1	120.4	[30]

[a] ΔH°_f – kJ/mol, ΔS°_f – J/K mol, p_e – Pa, T – K, $p_0 = 101,325$ Pa.

Table 3
Desorption pressures in Pa at 298 K for U–Zr and uranium hydrides calculated from the values in Table 2

Specimen	Hydride	Deuteride	Ref.
$UZr_{0.136}$	6.1×10^{-6}	–	[4]
$UZr_{0.29}$	8.0×10^{-4}	2.3×10^{-4}	This work
U_2Zr	1.7×10^{-4}	–	[5]
UZr_2	5.4×10^{-5}	–	[10]
U	3.3×10^{-4}	1.2×10^{-5}	This work
U	2.0×10^{-4}	2.8×10^{-4}	[19]
U	8.3×10^{-4}	3.2×10^{-4}	[26]
U	4.0×10^{-4}	7.1×10^{-5}	[30]

Table 4
Unit cell volume per atom of uranium metal and some uranium–zirconium alloys

Alloy	α-U	$UZr_{0.136}$	$UZr_{0.29}$	$Uzr_{0.5}$	$UZr_{2.3}$
V_a/nm^3 atom^{-1}	0.0207	0.02144	0.02179	0.02254	0.02306

and Fig. 6. Here, the desorption pressures of the $UZr_{0.136}$ hydride at various temperatures were unusual compared with other composition U–Zr hydrides, therefore, the data for this alloy were doubtable.

3.3. Pulverization characteristics of the specimens

Almost all of the uranium alloys easily pulverize upon hydrogenation. However, U–Ti and U–Zr alloys or compounds showed high durability against powdering [5,6,10]. Here the pulverization characteristic of $UZr_{0.29}$ alloy was compared with that of uranium using ICT technology.

Fig. 7 showed the ratios of volume change per unit weight (ΔV_w) after hydrogenation as a function of absorption–desorption cycles. The ratios of volume change per unit weight were calculated by measuring the height change of the vertical CT image of the sample. Fig. 8 showed the cross-section photos of the hydrides in reactors. As can be seen from figures, $UZr_{0.29}$ alloy indeed shows less volume-expanding tendency and high durability against powdering than uranium.

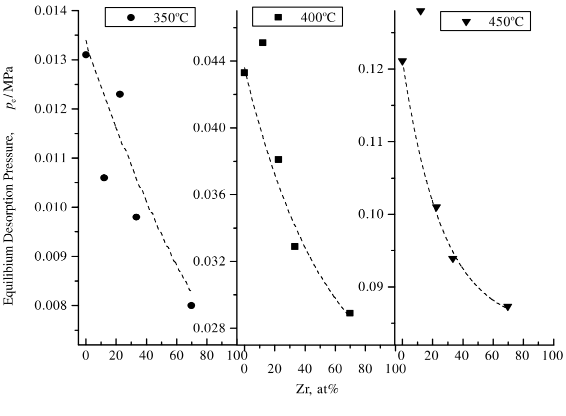


Fig. 6. Hydrogen desorption pressure plotted against zirconium composition in uranium–zirconium alloys.

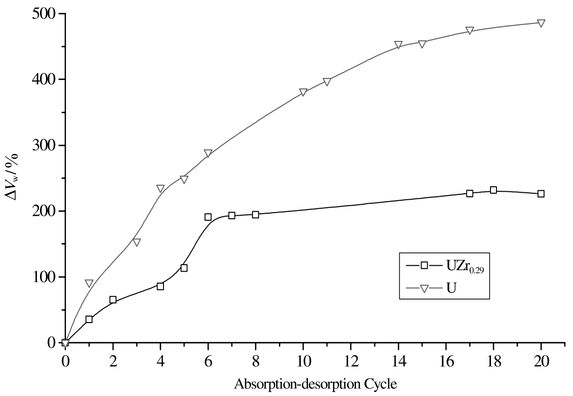
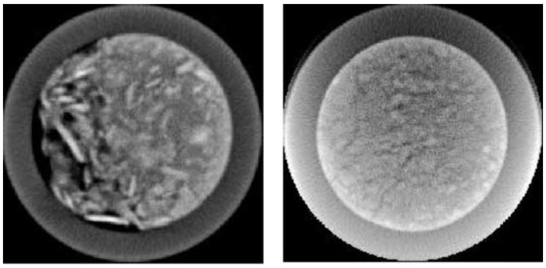


Fig. 7. The ratios of volume change per unit weight after hydrogenation as a function of absorption–desorption cycles.



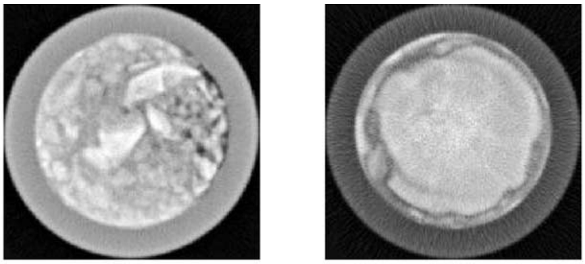
a. $UZr_{0.29}$ b. Uranium metal

Fig. 8. CT image of hydrides after five absorption–desorption cycles for $UZr_{0.29}$ and uranium metal.

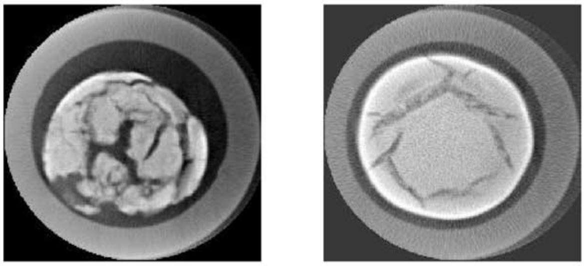
Fig. 9 showed the cross-section photos of the dehydrogenated specimens after twenty cycles of hydrogen absorption–desorption. It can be seen from the images that $UZr_{0.29}$ alloy particles (center in the image) still adhere to the wall of the reactor when the hydride has been decomposed completely. While the uranium particles agglomerate and depart from the wall of the reactor upon complete dehydrogenation. Therefore, it can be inferred that $UZr_{0.29}$ alloy may have higher heat conductivity through the reactor wall than uranium upon hydrogenation.

3.4. X-ray powder diffractions

Figs. 10 and 11 showed the X-ray (Cu K_α) diffraction patterns of the hydride specimens of $UZr_{0.29}H_{2.3}$, $UH_{2.9}$ and the de-hydrogenated powders obtained after complete desorption in vacuum at 873 K. From the X-ray

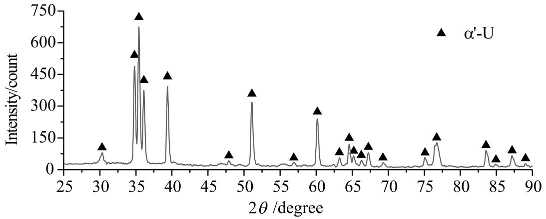


a. Upper part of the $UZr_{0.29}$ alloy sample b. Lower part of the $UZr_{0.29}$ alloy sample

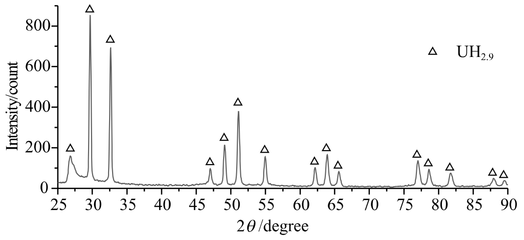


c. Upper part of the uranium metal sample d. Lower part of the uranium metal sample

Fig. 9. CT image of the dehydrogenated specimens after twenty cycles of hydrogen absorption–desorption for $UZr_{0.29}$ and uranium metal.

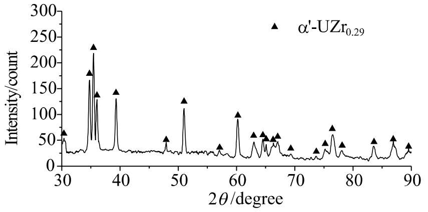


(a) Uranium metal powder sample

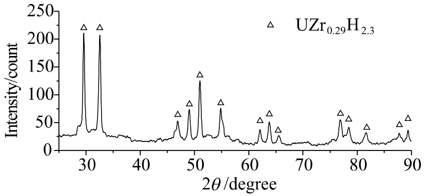


(b) Uranium hydride sample

Fig. 10. X-ray (Cu K_α) diffraction patterns of $UH_{2.9}$ and uranium metal powders obtained after complete desorption of the hydride sample in vacuum at 873 K.



(a) $UZr_{0.29}$ alloy powders



(b) $UZr_{0.29}$ hydride sample

Fig. 11. X-ray (Cu K_α) diffraction patterns of $UZr_{0.29}H_{2.3}$ and $UZr_{0.29}$ alloy powders obtained after complete desorption of the hydride sample in vacuum at 873 K.

patterns of the $UZr_{0.29}H_{2.3}$ and the dehydrogenated alloy, the UH_3 and alpha-uranium phase were identified as the main phases, respectively. No peak from zirconium hydride and zirconium metal were observed.

From the peaks of the UH_3 phase in the X-ray patterns of the hydrides, a cubic (Pm3n) crystal structure was identified with the lattice constants being determined to be 0.661 and 0.667 nm for $UZr_{0.29}H_{2.3}$ and $UH_{2.9}$, respectively. While from the peaks of the alpha-uranium phase, a orthorhombic (Cmcm) structure was identified with lattice constants a_0, b_0 and c_0 of 0.286, 0.600, 0.508 nm and 0.283, 0.569, 0.495 nm for $UZr_{0.29}$ alloy and uranium metal powders, respectively. As could be seen that the unit cell volume of $UZr_{0.29}$ alloy was larger than that of uranium metal, while it was reverse upon hydrogenation, which might be one of the reasons of more stable the uranium–zirconium hydride than uranium hydride as mentioned above in 2.2. The volume expansions were calculated to be ≈66% and 86% upon hydrogenation of $UZr_{0.29}$ alloy and uranium metal, respectively. Therefore, It could also be deduced that the $UZr_{0.29}$ hydride showed higher durability against powdering than pure uranium hydride as mentioned above.

4. Conclusion

Hydrogen absorption–desorption properties of the $UZr_{0.29}$ alloy and uranium metal were investigated in detail at hydrogen pressures as high as to 0.4 MPa and over the temperature range of 300–723 K. Both $UZr_{0.29}$ alloy and uranium metal showed similar hydrogen isotopic effect and hysteresis effect. $UZr_{0.29}$ alloy absorbed hydrogen (deuterium) up to 2.3H (2.18D) atoms per F.U. (formula unit) by only one-step reaction and hence each desorption isotherm had a single plateau over nearly the whole hydrogen composition range. The $UZr_{0.29}$ alloy had a little lower dissociation pressure than that of pure uranium, however, it showed high durability against powdering upon hydrogenation and may have good heat conductivity. From the properties mentioned above, the $UZr_{0.29}$ hydride has the potentiality to substitute pure uranium hydride as a material for tritium treatment and storage.

Acknowledgements

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