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New Ternary Hydride Formation in U-Ti-H System*

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Synopsis

Hydrogen absorption properties of two titanium-rich uranium alloys, UTi_2 and UTi_4 , were studied in order to prepare and identify the recently found ternary hydride. They slowly reacted with hydrogen of the initial pressure of 10^5 Pa at 873K to form the ternary hydride. The hydrogenated specimen mainly consisted of the pursued ternary hydride but contained also U(or UO_2), TiH_x , and some transient phases. X-ray powder diffraction and Electron Probe Micro Analysis proved that it was the UTi_2H_x with the expected $MgCu_2$ structure, though all the X-ray peaks were broad probably because of inhomogeneity. This compound had extremely high resistance to powdering on its formation, which showed high potential utilities for a non-powdering tritium storage system or for other purposes.

I. Introduction

Hydrogen absorption-desorption properties of uranium is suitable for a tritium storage. Uranium easily absorbs hydrogen of 10^5 Pa below 500K to form UH_3 . The desorption pressure of UH_3 is adequately low for holding tritium at a room temperature (lower than 10^{-3} Pa at 298K) and sufficiently high above 700K. Further, in a pressure-concentration isotherm below 700K, a plateau spans nearly whole region of concentration.¹⁾ These are the reason why uranium is dominantly used for tritium storage.

Uranium, however, disintegrates into fine powder on hydrogenation.²⁾ It causes high pyrophoricity³⁾ and high possibility of contamination. The powdering is directly related to the much volume

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expansion on hydrogenation. The holes occupied with hydrogen in UH_3 are by far larger than those of any other binary hydride. The volume expansion ratio on hydrogenation ($\Delta V/V$) is 0.76 and also the largest.

Searching a non-powdering or low-powdering tritium storage material, hydrogen absorption-desorption properties of several uranium compounds and alloys in some binary systems, U-Ti, U-Zr, U-Al, U-Si and U-Fe, have been studied by the authors.⁴⁻⁶⁾ High resistance to powdering or low pyrophoricity was expected for a compound which hydrogenated without forming UH_3 . However, in all the cases, UH_3 was formed as a main phase on hydrogenation. (In only U-Ti system, unusual ternary hydride formation was also observed.⁶⁾ A Ti-rich ternary hydride was observed altogether with UH_3 in the hydrogenated U_2Ti , although there is no binary compound other than U_2Ti . The ternary compound was temporarily identified to be UTi_2H_x of MgCu_2 type structure by the X-ray powder diffraction of some multi-phased specimens where the main phase was U or UH_3 .

In the present paper, hydrogen absorption properties of the Ti-rich alloys —1:2 and 1:4 in U:Ti—were examined to obtain the specimen of a single phase and to identify it accurately.

II. Experimental

The U-Ti specimens were prepared by argon plasma-jet melting. Starting materials (a block of U of 99.8% purity and Ti wire of 99.9% purity) were melted three times by turning the upside down for homogenization. The obtained alloys were used as the specimens without annealing not to promote the grain growth of U_2Ti phase.

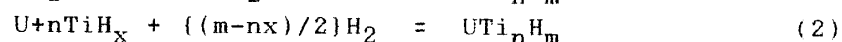
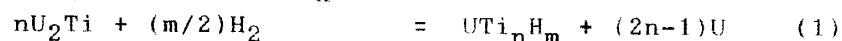
The apparatus used for measurements of hydrogen absorption properties is shown in ref 6). Temperature, pressures and volume was measured to determine hydrogen concentration. Hydrogen absorption of each specimen was examined at various temperatures between 673K and 973K under the initial hydrogen pressure of 10^5Pa . On the hydrogenated specimens, X-ray powder patterns were observed and microscopic phase study was performed by EPMA (Electron Probe Micro-Analyzer).

III. Results and Discussion

1. Hydrogen absorption processes

Because of no annealing, the specimens were initially considered to consist of nonequillibrated three phases; U, Ti and U_2Ti . Here Ti

was expected to be hydrogenated to TiH_x by a rapid reaction. Therefore, the ternary hydride (written as UTi_nH_m below) was probably formed from U_2Ti or from TiH_x and U by the following reactions:



Here, UTi_nH_m cannot be formed above 973K because it shows the decomposition pressure over 10^5Pa at 973K.⁶⁾ On the contrary, below 673K, the formation of UH_3 disturbs the UTi_nH_m formation. These were the reasons why the above-mentioned temperature range was preferred.

The hydrogen absorption properties of the UTi_4 alloy is shown in Fig.1. The specimen rapidly absorbed $3.4\text{H}/\text{UTi}_4$ at the initial temperature; 973K. Though the further absorption was too slow for an exact estimation of its speed, the highest tendency to absorption was observed at 873K during the temperature scanning between 923K and 773K. The reaction was expected slow at the temperatures lower than 773K. Before the scanning, TiH_x was tried to decompose at 1073K, but it ended in failure. Kept at 873K for 4 days, hydrogen was gradually absorbed till the concentration reached $8.7\text{H}/\text{UTi}_4$ and finally $10.5\text{H}/\text{UTi}_4$ was attained. In the temperature range, the maximum hydrogen concentration is $8\text{H}/\text{UTi}_4$ without UTi_nH_m formed, because U can absorb no hydrogen and Ti can absorb $2\text{H}/\text{Ti}$ at most. Therefore, the observed process was considered to be the formation of UTi_nH_m .

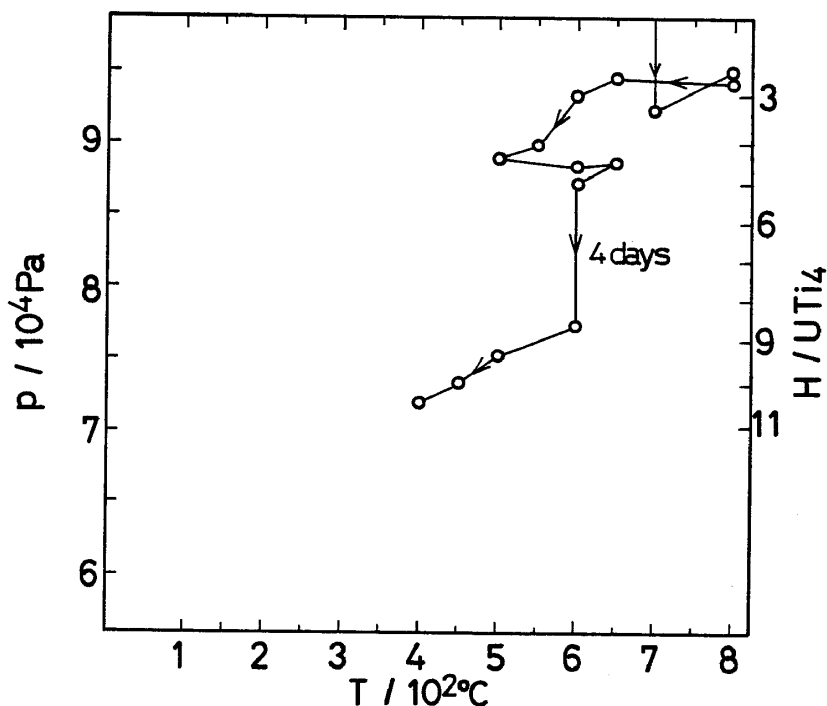


Fig.1 History of the hydrogen absorption by UTi_4 alloy.

Figure 2 shows the absorption process of UTi_2 alloy. It was firstly kept at 873K and gradually absorbed hydrogen after an initial rapid absorption. The absorption for about 60h made equilibrium at the concentration of $4.6H/UTi_2$. By the following cooling down to 673K, much faster absorption was observed and the concentration reached $5.4H/UTi_2$. The change in the pumping speed can be explained as follows: At 873K, UTi_nH_m phase was formed from the other phases through the diffusion of metal and hydrogen atoms, and at 773K and 673K the already formed UTi_nH_m absorbed hydrogen additionally only by hydrogen atom diffusion.

Both alloys showed high resistance to powdering on hydrogenation, and especially UTi_2 was much more resistible than UTi_4 , perhaps depending on the absorption history. The UTi_4 was only cracked but not disintegrated, while almost no crack was observed on the UTi_2 . This resistance will be discussed later.

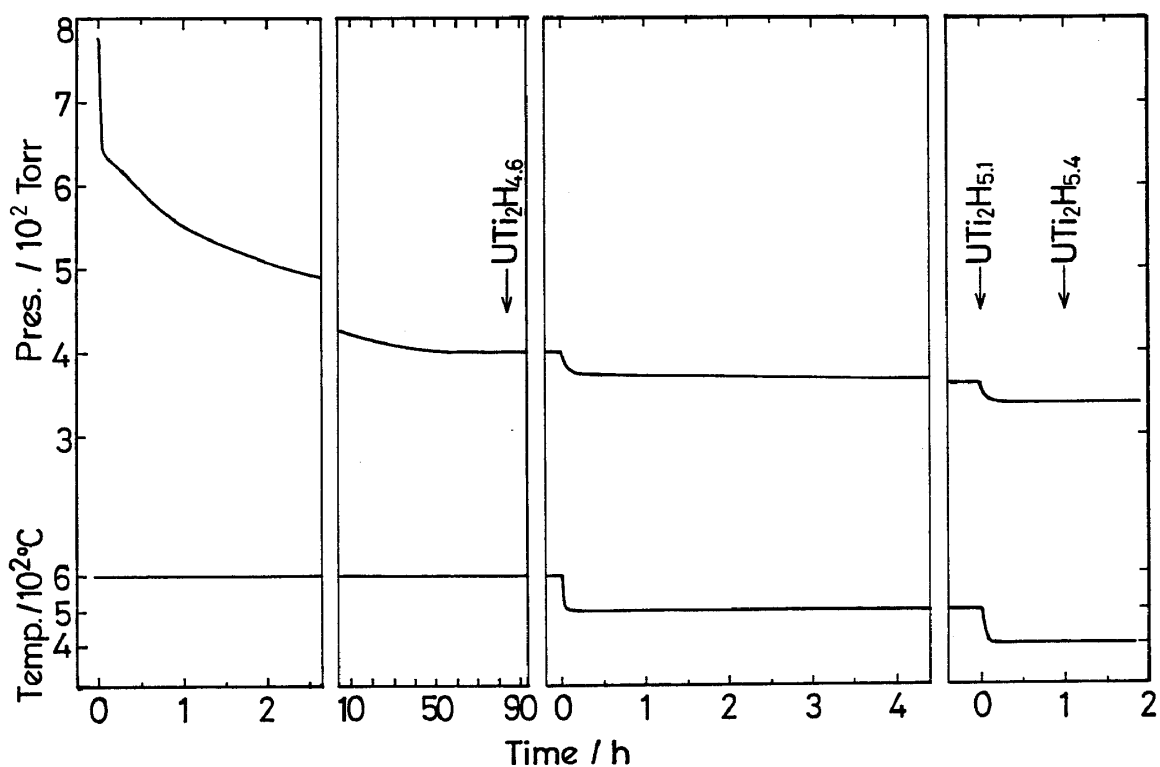


Fig.2 Transitions of pressure and temperature during hydrogen absorption by UTi_2 .

2. Identification of the phases in the hydride

Table 1 shows observed phases in the X-ray diffraction patterns of hydrogenated specimens. The unknown peaks which should be attributed to UTi_nH_m were listed on table 2. Each specimen had the UTi_nH_m phase as a main phase but didn't consist of a single phase. $UTi_2H_{5.4}$ had U phase, $UTi_4H_{10.5}$ had UO_2 and TiH_x phases also. All the peaks were broad so that the FWHMs were about 0.4° . It probably shows a significant deviation in the lattice constants due to the difference in the hydrogen concentration or to the residual distortion. Though it is difficult to distinguish weak peaks because its broadness, the calculated pattern of UTi_2H_m with $MgCu_2$ structure was fitted with all the unknown peaks except one weak peak just below the (111) peak. The unfitted peak will be discussed later.

Figure 3 (a)-(d) show the EPMA images of $UTi_2H_{5.4}$; (a)SEM image(x500), (b)SEM image(x5000), (c)U($M\alpha$) image (x5000) and (d) Ti($K\alpha$) image (x5000). Figure 4 (a) and (b) show the SEM images of $UTi_4H_{10.5}$ ((a)x500 and (b)x5000). Both specimen consisted of three phases of different tones —white, gray and black, though the phase distribution in each specimen was much different from that in the other. The X-ray analysis of $UTi_2H_{5.4}$, which is illustrated also in Fig.3(c) and (d), clarified that the white part is U, gray is UTi_nH_m and black is TiH_x . In the case of $UTi_4H_{10.5}$, the sizes of the phases were too small for the resolution of X-ray analysis. However, the same distinction is considered to be allowed because of the same contrast, and it is reasonable that the black phase(TiH_x) has a larger fraction than in $UTi_2H_{5.4}$.

Table 1 Observed phases in the X-ray diffraction patterns of hydrogenated U-Ti alloys.

Phase	$UTi_2H_{5.4}$	$UTi_4H_{10.4}$
UTi_nH_m	Very Strong	Very Strong
alpha-U	Weak	No
UO_2	No	Very Weak
TiH_x	No	Very Weak

Table 2 Observed X-ray patterns of UTi_nH_m and the calculated pattern for UTi_2H_m of $MgCu_2$ structure.

d/nm	h k l	I(obs)	I(cal)
0.491	1 1 1	37	44
0.301	2 2 0	90	89
0.257	3 1 1	100	100
0.246	2 2 2	4	7
-	4 0 0	-	5
0.195	3 3 1	18	12
0.174	4 2 2	38	35
0.164	3 3 3, 5 1 1	50	29
0.151	4 4 0	21	20
0.144	5 3 1	10	9
-	4 4 2	-	0
0.134	6 2 0	22	15
0.130	5 3 3	18	11
-	6 2 2	-	1
-	4 4 4	-	1
0.119	5 5 1, 7 1 1	3	3
0.114	6 4 2	27	16
0.111	7 3 1, 5 5 3	24	16

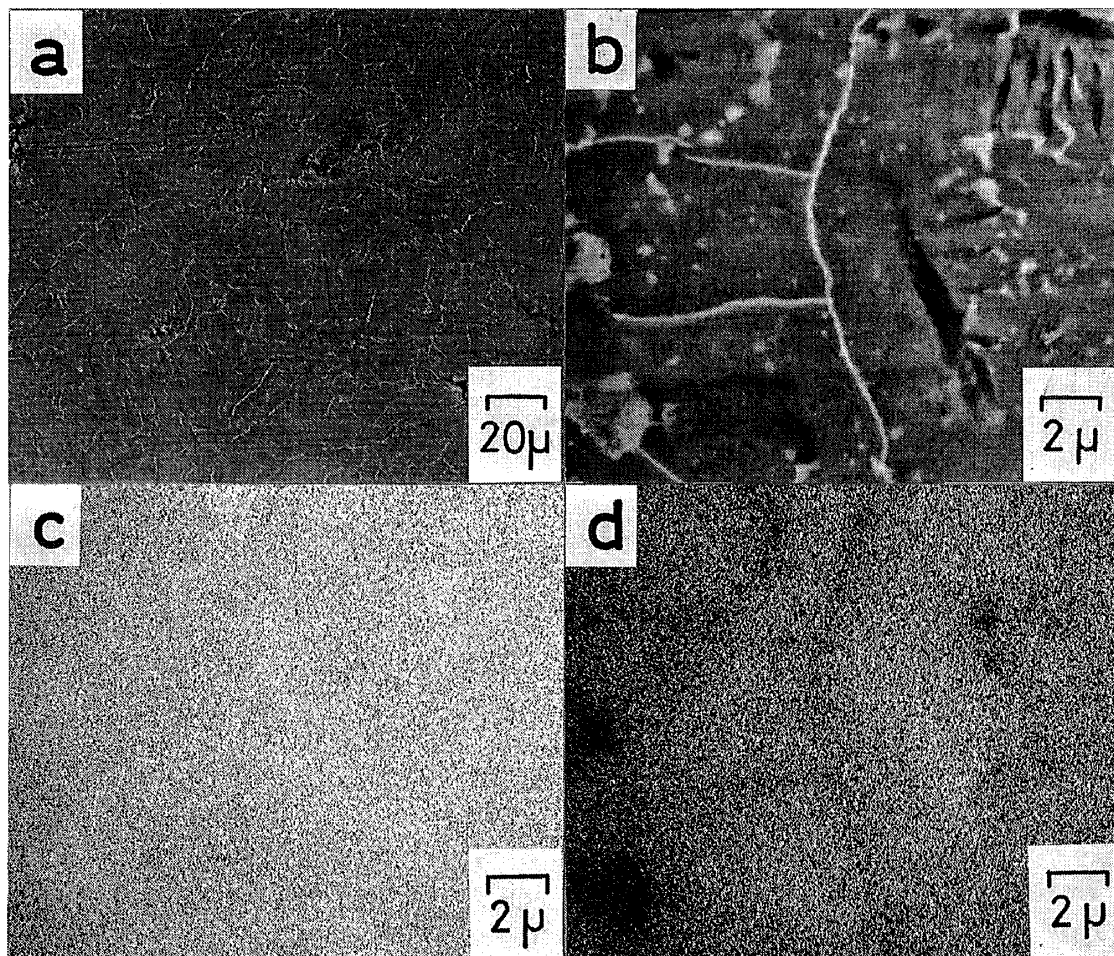


Fig.3 EPMA images of hydrogenated UTi_2 specimen. (a)SEM image (x500), (b)SEM image (x5000) (c)U(M α) image (x5000) and (d) Ti(K α) image (x5000).

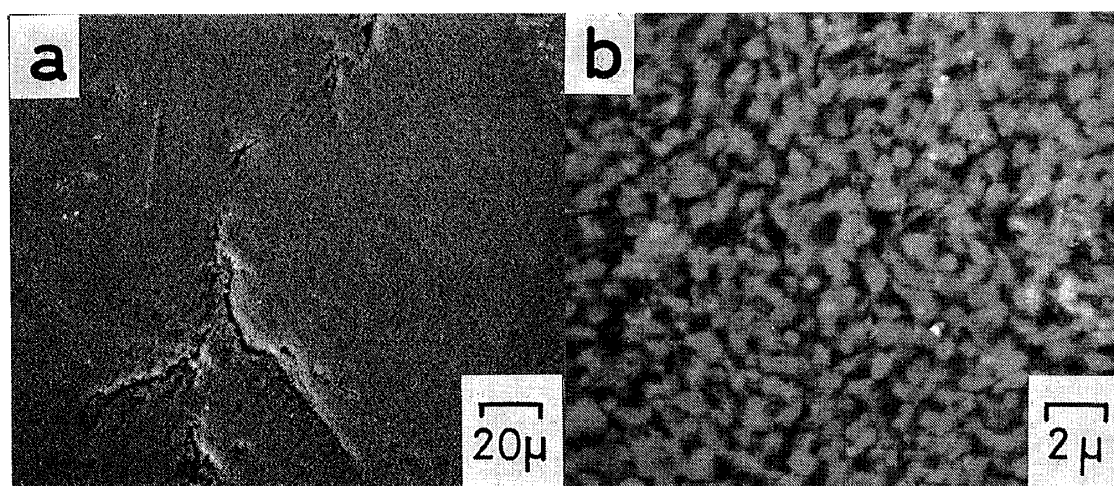


Fig.4 SEM images of hydrogenated UTi_4 specimen, (a) x500 and (b) x5000.

As above, $UTi_2H_{5.4}$ has also TiH_x phase of comparable amount to U, though it could not be observed by X-ray diffraction because Ti has much lower atomic scattering factor for X-ray and the strongest peak of TiH_x can be masked by (310) peak of UTi_2H_m . $UTi_4H_{10.5}$ had TiH_x of comparable amount to that of UTi_nH_m while U is little. From these results of the EPMA and the X-ray powder diffraction, UTi_nH_m is considered to be UTi_2H_m of $MgCu_2$ structure. In the lattice, metal atoms are located at the following sites belonging to the space group $Fd3m$ (No.227):

8U in 8(a) at $1/8\ 1/8\ 1/8; 7/8\ 7/8\ 7/8$.
 16Ti in 16(d) at $1/2\ 1/2\ 1/2; 1/2\ 1/4\ 1/4;$
 $1/4\ 1/2\ 1/4; 1/4\ 1/4\ 1/2$.

3. High resistance to powdering on UTi_2H_m formation

High resistance to powdering observed on the hydrogenation of UTi_2 and UTi_4 is considered to be closely related to the crystal structure of UTi_2H_m . In the structure, Ti atoms make half-filled fcc lattice with a half of the lattice constant (0.426nm). Ti atoms are arranged in a fcc lattice also in δTiH_x , and the lattice constant for $TiH_{1.92}$ is known to be 0.454nm, while that for $TiH_{1.6}$ was 0.442 in this study. Such a similarity enables the smooth phase transformation which can explain the high resistance to powdering.

One possible chain of the smooth transformation was inferred as follows: First, U atoms diffuse into TiH_x lattice and changes places with Ti atoms. Then, the U atoms move to the proper positions in UTi_2H_m absorbing H atoms into their preferred sites. In this case, $Ti_{1-x}U_xH_y$, in which some Ti atoms were changed with U atoms, can be observed as a transient state. In Fig.3(b), if more precisely distinguished, there are five phases of the different tones. The white phase can be divided into two phases—blight one and dark one. And the phase of another kind which is darker than the main gray phase is observed mainly around the black phases. The last phase is probably the $Ti_{1-x}U_xH_y$.

The crystal structure of the $Ti_{1-x}U_xH_y$ cannot be clarified here, but the unindexed X-ray diffraction peak just below the (111) peak of UTi_2H_m is attributable to it. Assuming as an example that U atoms occupy the face centered positions of the cubic of the two-fold lattice constant of TiH_x , the indexed peak is just fitted by the secondly strongest peak, (111), of it, while the strongest peak of (222) is just masked with the (311) peak of UTi_2H_m .

Another effect for the resistance is the low volume expansion at UTi_2H_m at the UTi_2H_m formation. The molar volume of UTi_2H_m was calcu-

lated to be $46.7\text{cm}^3/\text{mol}$ and that of UTi_2 alloy was to be $33.7\text{cm}^3/\text{mol}$ from the elements' molar volume, from which the expansion ratio ($\Delta V/V$) was calculated as 0.39. It is larger than that for TiH_2 formation (0.24) but about half of that for UH_3 (0.76).

Such a high powdering resistance as has never reported on any other uranium compound showed high potential utilities of UTi_2H_m , though the further examination is needed in order to clarify the hydrogenation mechanism. It can be used for a non-powdering tritium storage system if hydrogen pumping speed is improved by, for example, optimizing its shape. It also will be utilizable as a fission reactor fuel, though many other properties of it must be examined hereafter.

IV. Conclusions

UTi_2 and UTi_4 slowly reacted with hydrogen of the initial pressure of 10^5Pa at 873K to form the ternary hydride, UTi_2H_m . The hydrogenated specimens mainly consisted of the pursued ternary hydride. X-ray powder diffraction and Electron Probe Micro Analysis proved that it was the UTi_2H_m with the MgCu_2 structure expectedly, though the specimens were not of a single phase but contained also U (or UO_2), TiH_x , and some transient phases, and all the X-ray peaks were broad probably because of the inhomogeneity. This compound had extremely high resistance to powdering on its formation, which showed high potential use for a non-powdering tritium storage material or for others.

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