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# Formation and crystal structure of $UTi_2D_x$

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**Abstract**

Deuterium absorption properties of U–66.7 at.%Ti alloy and the crystal structure of obtained deuterides $UTi_2D_{4.5}$ and $UTi_2D_{5.2}$ were examined by X-ray and neutron diffraction. Consequently the structure was determined as having C15 cubic structure, in which the 2U-2Ti site at 96(g) in the space group Fd3m and the 1U-3Ti site at 32(e) were occupied by deuterium. Interatomic distances U–D and Ti–D in both sites were nearly equal to those in respective binary deuterides. The results explained the formation of $UTi_2H(D)_x$ from U–Ti alloy with no $UTi_2$-type compound.

*Keywords:* Uranium titanium deuteride; Neutron diffraction; Deuterium site occupancy

## 1. Introduction

It is well known that there exists no compound such as $UTi_2$ in U–Ti binary system. However, in the previous study by the authors [1], U–Ti alloys were hydrogenated to form $UTi_2H_5$, which had C15($MgCu_2$)-type structure as for U and Ti. Here, hydrogen atoms were considered to act an important role in constructing the ternary compound. In this study, ternary deuteride formation from U–66.7 at.%Ti alloy and its crystal structure, especially deuterium distribution, were examined.

## 2. Experimental details

The alloy specimens were prepared by melting the constituent elements in an argon tri-arc furnace. U of 99.95 wt.% purity and Ti of 99.99 wt.% were melted three times being turned upside down at each interval.

Before deuterium absorption, a specimen was outgassed at 973 K in a vacuum until the residual pressure reached $10^{-5}$ Pa. It was held at various temperatures between 773 K and 973 K in deuterium gas at pressures below 0.2 MPa, where amounts of absorbed deuterium were calculated from pressure and volume of the equipment during the experiment and from its mass increase after the experiment.

Crystal structures of the obtained deuterides were studied by X-ray and neutron powder diffractions. The neutron diffractometer, TAS-2, installed in the research reactor, JRR-3, of the Japan Atomic Energy Research Institute was used. The specimen examined was encapsulated in an aluminum container, reflections from which were subtracted from the obtained patterns. Crystal structure was refined by Rietveld's method using the RIETAN system coded by Izumi [2,3].

## 3. Results and discussion

### 3.1. Deuterium absorption properties

As was reported previously, U–Ti alloy absorbed hydrogen to form $UTi_2H_{4.6}$ in the hydrogen of $10^5$ Pa at 873 K. In the deuterium gas of $1\times10^5$ Pa, however, it absorbed no more than 1.6 D atoms per U atom between 823 K and 923 K. When it was held at 923 K in $D_2$ with the initial pressure of $2\times10^5$ Pa, the pressure decreased gradually. About 30 h of reaction formed the $UTi_2D_{5.2\pm0.3}$ in average composition. It was maintained in that condition for 50 h more for homogenization. Then it was cooled to 773 K and turned into $UTi_2D_{5.6\pm0.3}$. It was rapidly cooled down to a room temperature at the same time when the deuterium gas was evacuated in order to prevent it from turning into


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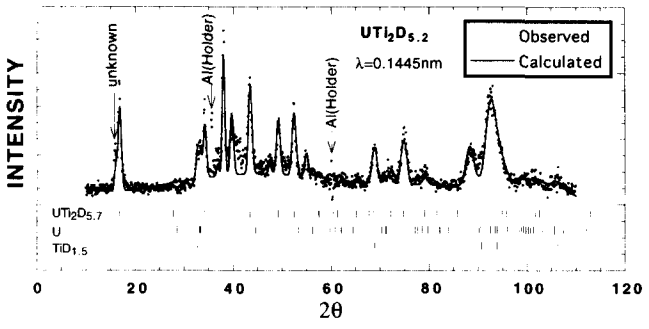


Fig. 1. Observed and calculated neutron diffraction patterns of $UTi_2D_{5.2}$ specimen. Bars below the patterns show peak positions of the phases labelled left.

$UD_3$ and $TiD_2$ with powdering. Another $UTi_2D_5$ specimen had been turned into $UD_3$ and $TiD_2$ by cooling to room temperature in a deuterium gas of $2\times10^5$. Finally the deuterided specimen with average composition of $UTi_2D_{5.2\pm0.1}$ was obtained. Decrease in composition was probably brought on by a slight desorption during the cooling down process. Another specimen was also deuterided until $UTi_2D_{4.8\pm0.3}$ in the vessel and $UTi_2D_{4.5\pm0.1}$ was obtained.

### 3.2. X-ray and neutron diffraction

From X-ray diffraction of the deuterides, the crystal structure of $UTi_2D_{5.2}$ was determined to be of the C15 type as for the metallic atoms. No peak from $TiD_{2-x}$ was observed but some U peaks and one unknown peak were observed. This was very similar to that of $UTi_2H_{5.4}$. From the previous SEM observations of $UTi_2H_{5.4}$ [1], a mole fraction of U and $TiH_x$ phases was estimated as less than 10% in total. The deuteride specimens also seemed to include almost the same fraction of U and $TiD_x$ phases. The unknown peak was considered from a transient state on ternary hydride formation from titanium hydride and uranium as was discussed in Ref. [1].

In the neutron diffraction patterns of both $UTi_2D_{5.2}$ (shown in Fig. 1) and $UTi_2D_{4.5}$, however, $TiD_2$ as well as U was strongly observed owing to the neutron scattering factor of Ti and D comparable to that of U. Two sharp lines labelled as "Al(holder)" are due to the imperfectness of the back ground subtraction. The same unknown peak as in the X-ray patterns was ignored in the calculation because it disturbed the peak of $UTi_2D_x$ just above it.

Three other phases were included in the fitting calculation. Occupancies and coordinates of three kinds of D sites, D(1) at 96(g), D(2) at 32(e) and D(3) at 8(b) in the space group Fd3m were determined together with lattice constants and FWHM parameters and isotropic thermal parameters.

Table 1 and Fig. 1 summarize the determined structural parameters and calculated and observed neutron diffraction patterns of a $UTi_2D_{5.2}$ specimen. Owing to the incompletion of the $UTi_2D_x$ formation, D composition in this phase was not known exactly. For this reason, three deuterium sites occupancies were treated as independent variables in the case of the $UTi_2D_{5.2}$ specimen. Composition of the phase was determined as $UTi_2D(1)_{4.4\pm0.9}D(2)_{1.3\pm0.2}$, where occupancy of D(3) site was judged as none considering its standard deviations. The slight enrichment of deuterium in the phase was consistent with the coexistence of deuterium poor phases as $TiD_{1.5}$ and U phases. In the case of the $UTi_2D_{4.5}$ specimen, however, the same treating gave no reasonable result. Some parameters were fixed as shown in Table 1. For this reason the discussion below will be on only the $UTi_2D_{5.7}$ phase.

Table 1
Results of fitting calculations

| | | | $UTi_2D_{5.2}$ | $UTi_2D_{4.5}$ |
|---|---|---|---|---|
| Agreement factors | | $R_{wp}$ [a] | 0.187 | 0.184 |
| | | $R_f$ [a] | 0.086 | 0.09 |
| Lattice constant, nm | | | 0.848 | 0.845 |
| $D_1$ (96g) | coordinates | x | $0.439\pm0.002$ | $0.440\pm0.002$ |
| | | z | $0.254\pm0.003$ | $0.256\pm0.004$ |
| | occupancy | p1 | $0.363\pm0.073$ | $0.321\pm0.014$ |
| | | D/U | $4.360\pm0.874$ | $3.847\pm0.170$ |
| $D_2$ (32e) | coordinate | x | $0.408\pm0.006$ | $0.397\pm0.010$ |
| | occupancy | p2 | $0.323\pm0.060$ | $0.238\pm0.043$ |
| | | D/U | $1.292\pm0.238$ | $0.953\pm0.170$ |
| $D_3$ (8b) | occupancy | p3 | $0.056\pm0.087$ | Fixed as none |
| | | D/U | $0.056\pm0.087$ | |
| Composition of the phase | | | $UTi_2D_{5.7}$ | $UTi_2D_{4.8}$ (fixed) |

[a] $R_{wp}$ indicates agreement on diffraction profile and $R_f$ on structure factor.

Table 2
Interatomic distances and number of neighbours in parentheses for $UTi_2D_{5.7}$, $\alpha$-$UD_3$, $\beta$-$UD_3$ and $TiD_2$, (nm)

| | $UTi_2D_{5.7}$ | $\alpha$-$UD_3$ | $\beta$-$UD_3$ | $TiD_2$ |
|---|---|---|---|---|
| U-U | 0.367 (4) | 0.360 (8) | $U_1$: 0.370 (12)<br>$U_2$: 0.332 (2)<br>0.370 (4) | |
| U-Ti | 0.352 (12) | | | |
| Ti-Ti | 0.300 (6) | | | 0.312 (4)<br>0.315 (4) |
| U-D | $D_1$: 0.227±3[a] (8.7)<br>$D_2$: 0.232±8 (1.3) | 0.232 (12) | 0.232 (12) | |
| Ti-D | $D_1$: 0.196±2 (4.4)<br>$D_2$: 0.188±6 (1.9) | | | 0.192 (8) |

[a] $\pm n$ gives standard deviations at the last digit.

### 3.3. Interatomic distances

Interatomic distances calculated from the determined atomic distribution are listed in Table 2. It is well known that U–D distance in $UH_3$'s are anomalously long. If the metallic radius of U with coordination number twelve [4], 0.152 nm, is adopted, the radius of D, 0.080 nm, is about twice as large as in that of other metal hydrides or deuterides.

In the compound $UTi_2D_{5.7}$, U–D distances are almost the same as those in $UH_3$'s. Ti–D distances also agreed well with that in $TiD_2$. In forming this C15 $AB_2$ structure, the ratio of A's atomic radius to B's must be near $1.225(=\sqrt{3}\sqrt{2})$; between 1.1 and 1.5 generally. Twelve-coordinated radii of U and Ti atoms; 0.152 and 0.147 nm respectively; are too near to satisfy the condition. U–H(D) and Ti–H(D) distances in each binary hydride, however, are quite different as shown in Table 2. Here an effective radius of M, $r_M^{eff}$, in forming the hydride was defined as

$$r_M^{eff} = d_{M-H} - r_h \quad (1)$$

where $d_{M-H}$ is a M–H distance and $r_h$ is a radius of a hole occupied by H atom. The $r_h$ was assumed as 0.040 nm; an ordinal value in many metal hydrides [5]. Then $r_U^{eff}$ and $r_{Ti}^{eff}$ are 0.187 and 0.156 for the D(1) site and 0.192 and 0.148 for the D(2) site. The radius ratios $r_U^{eff}/r_{Ti}^{eff}$ are 1.2 and 1.3 respectively. They are close to one obtained from M–H distances in binary hydrides; 1.25. These values all satisfy the condition for the C15-type $AB_2$ compound. This explains the formation of $UTi_2H(D)_{5\pm x}$ from the U–Ti alloy with no $UTi_2$ type compound.

A similar case reported in the Th–Zr–D system [6] is also explained. The ratio of the atomic radii using their effective radii is from 1.19 and 1.23 for D(1) and D(2) respectively, whereas the ratio is 1.13 if twelve-coordinated radii are used.

## 4. Conclusions

The U–Ti alloy formed a ternary deuteride as $UTi_2D_{5\pm x}$ with slow absorption of $D_2$ gas of $2\times10^5$ Pa at 923 K. Its crystal structure was determined by X-ray and neutron diffraction as a $MgCu_2$-type Laves phase compound, where deuterium occupying sites were also determined and it revealed U–D and Ti–D distances very similar to those in the respective binary deuterides. It also revealed that the long U–H bond helped to form such a compound on hydrogenation.

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