

Crystal structure of hydride and deuteride of UNiAl

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Abstract

The hydrogen and deuterium absorption behaviour of UNiAl was examined at hydrogen isotope pressures below 10^5 Pa and temperatures up to 973 K. Under these conditions UNiAl absorbed hydrogen and deuterium up to UNiAlH_{0.8} and UNiAlD_{0.7} respectively. Neutron powder diffraction of UNiAlD_{0.7} revealed that each D atom occupies a 3U–2Ni site formed by three U atoms and two Ni atoms. It is at the centre of a triangle of U atoms which two 3U–1Ni-type tetrahedral sites share. This occupation slightly changed the arrangement of metal atoms to enlarge the 3U triangle. Changes in X-ray diffraction pattern suggested the further movement of metallic atoms to form UNiAlH_{2.7}.

1. Introduction

The hydrogen absorption properties of UNiAl have been investigated by Drulis *et al.* [1] and Jacob *et al.* [2]. It forms UNiAlH_{2.7}, the crystal structure of which is similar to that of UNiAl. No other uranium compound which absorbs hydrogen while maintaining its crystal structure is known. Nevertheless, neither the metal atom distribution nor the hydrogen occupation site has been clarified yet. In this paper the detailed crystal structures of the hydride and deuteride of UNiAl at low hydrogen content were investigated, focusing on the deuterium occupation site.

2. Experimental details

2.1. Preparation of specimens

The UNiAl specimen was prepared by melting the constituent pure metals directly in an argon plasma jet furnace three times, followed by annealing at 1223 K in a vacuum of 10^{-5} Pa for 72 h. The purities of U, Ni and Al were over 99.8%, 99.9% and 99.9% respectively. The obtained specimen was identified to be UNiAl by X-ray diffraction. After outgassing in a vacuum of 10^{-5} Pa at 973 K, it was cooled to room temperature in 50 K steps under a hydrogen or deuterium gas pressure of 10^5 Pa.

2.2. Crystal structure analysis

The neutron powder diffraction pattern of the obtained deuteride was examined in order to determine the distribution of atoms. The diffractometer CTNS installed in the research reactor JRR-2 of JAERI (Japan Atomic Energy Research Institute) was used. The pattern of the quartz glass container was first subtracted from the observed pattern. The resultant pattern was fitted to a calculated pattern by means of the Rietveld method [3]. The software package RIETAN coded by Izumi [4] was used for this calculation. The structure of the other specimens was examined by X-ray diffraction with a Cu target.

3. Results and discussion

3.1. Crystal structure of deuterides

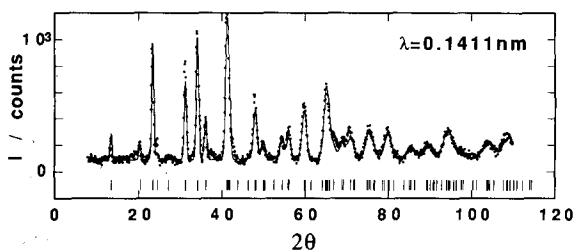
The UNiAl specimen absorbed hydrogen and deuterium only below 323 K at a pressure of 10^5 Pa and UNiAlH_{0.8} and UNiAlD_{0.7} respectively were formed. The observed neutron diffraction pattern of UNiAlD_{0.7} is shown by dots in Fig. 1. The peaks were indexed on the same hexagonal structure as that of UNiAl. The lattice constants a and c were 0.6962 and 0.3992 nm respectively. Those of UNiAl before hydrogenation were 0.6732 and 0.4036 nm respectively. The lattice was 3.4% elongated along the a axis and 1.1% contracted along the c axis.

TABLE 1. Determined atomic distribution in UNiAlD_{0.7} (standard deviations in parentheses)

Atom	Number of positions and Wyckoff notation	Fractional coordinate			Occupancy
		x	y	z	
U	3(g)	0.592 (0.004)	0	$\frac{1}{2}$	1
Ni(1)	1(b)	0	0	$\frac{1}{2}$	1
Ni(2)	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	0	1
Al	3(f)	0.239 (0.009)	0	0	1
D	4(h)	$\frac{1}{3}$	$\frac{2}{3}$	0.488 (0.262)	$\frac{1}{2}$

TABLE 2. Interatomic distances (nanometres) in UNiAlD_{0.7}

U	-4U	0.365	-1Ni	0.284	-2Al	0.317	-5D	0.211
			-4Ni	0.290	-4Al	0.318		
Ni(1)	-3U	0.284			-6Al	0.260		
Ni(2)	-6U	0.290			-3Al	0.271	-4D	0.195
Al	-2U	0.317	-2Ni	0.271	-2Al	0.288		
	-4U	0.318						
D	-3U	0.211	-1Ni	0.195				
			-1Ni	0.204				

Fig. 1. Neutron diffraction patterns of UNiAlD_{0.7}; dots, observed pattern; solid curve, calculated pattern; vertical bars, peak positions.

In the Rietveld analysis the following interstitial sites in the space group *P62m* (No. 189) were taken into account: 3U-2Ni site at 4(*h*) ($\frac{1}{3}$ $\frac{2}{3}$ 0.452), 3U-1Ni site at 2(*d*) ($\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$), 3U-1Al site at 3(*g*) (0.29 0 $\frac{1}{3}$), 2U-1Ni-2Al site at 6(*k*) (0.303 0.064 $\frac{1}{2}$), 2U-1Ni-1Al site at 12(*l*) (0.462 0.182 0.290), 2U-1Ni-1Al site at 6(*j*) (0.521 0.033 0), 2U-2Al site at 3(*f*) (0.671 0 0). The best fit was achieved when only the 4(*h*) site was occupied. The determined atomic distribution is given in Table 1 and the calculated diffraction pattern for this structure is shown by the solid curve in Fig. 1. Here the fractional coordinate *z* of D has such a large standard deviation that the position extends over the two 4(*h*) sites sharing the 3U triangle. It was concluded that the D atom vibrates in the 3U-2Ni site made of two 3U-1Ni sites.

Interatomic distances for the determined structure are listed in Table 2. Owing to increases both in the fractional coordinate *x* of U compared with that in UNiAl (0.574 ± 0.004 nm) and in the lattice constant

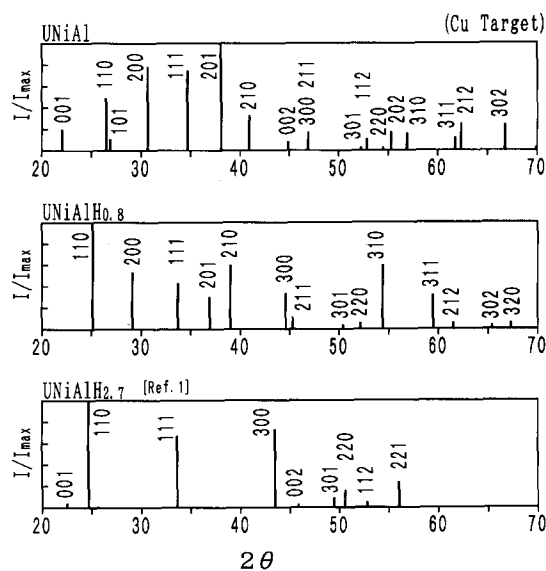


Fig. 2. X-ray diffraction patterns of UNiAl and its hydrides.

a, the U-U distance lengthened by 5.1% from 0.3475 to 0.3652 nm. The U-D distance was 0.211 nm for the centre of the fitted position, but 0.237 nm at the longest within the range of the deviation. It was very close to that in UD₃, 0.232 nm [5].

3.2. Crystal structure of hydrides

X-ray diffraction patterns of the specimen at various stages of hydrogen absorption are shown in Fig. 2. Here the pattern of UNiAlH_{2.7} is taken from ref. 1. The lattice constants of UNiAlH_{0.8} were calculated to be

$a=0.697$ nm and $c=0.399$ nm. The lattice changed similarly to that for UNiAlD_{0.7} formation, *i.e.* elongated along the a axis and shortened along the c axis compared with UNiAl.

Besides the changes in lattice constants, noticeable changes in the peak intensities were also observed. The number of peaks in the X-ray pattern decreased with increasing hydrogen concentration. The 001 and 002 reflections disappeared upon hydrogenation from UNiAl to UNiAlH_{0.8}, while upon further hydrogenation to UNiAlH_{2.7} the 200 and 201 peaks also vanished. Figure 3 shows the dependence of the calculated X-ray peak intensities on the U atom position (coordinate x). A shift in the U atom position as in UNiAlD_{0.7} formation can explain only the trend of changes; further studies to explain the whole pattern are currently in progress. As shown in Fig. 4, however, the disappearance

of the peaks upon formation of UNiAlH_{2.7} can be fully explained by moving U atoms further to $(\frac{2}{3} 0 \frac{1}{2})$, Al to $(\frac{1}{3} 0 0)$ and also Ni(1) to $(0 0 0)$. Such a deformation in the atomic arrangement makes the shape of 3U–1Al more favourable for D or H occupation and also creates a new 3U–1Ni (1) site. It also explains well the high hydrogen capacity of 2.7H/UNiAl.

4. Conclusions

UNiAl absorbed 0.8H and 0.7D per formula unit under a gas pressure of 10⁵ Pa only below 323 K. Neutron diffraction of UNiAlD_{0.7} revealed that each D atom occupies a 3U–2Ni site. U atoms changed their fractional coordinates to enlarge the 3U triangle and the U–D distance became close to that of UD₃. Significant changes in X-ray diffraction intensities upon hydride formation suggested further changes in atomic distribution.

Acknowledgments

We would like to thank Dr. Takanori Nagasaki and Dr. Hideo Ohno for valuable discussions and technical support with the neutron diffraction. We are grateful for the support from the Department of Research Reactor and the Department of Physics of JAERI.

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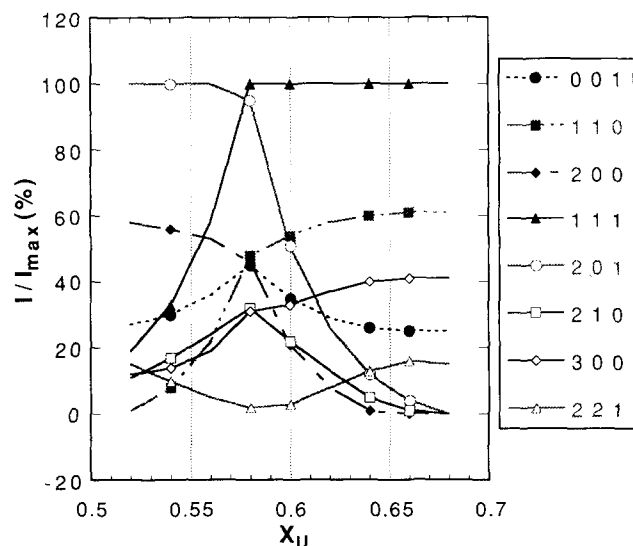


Fig. 3. Dependence of major X-ray peak intensities of UNiAlH_x on position of U atom.

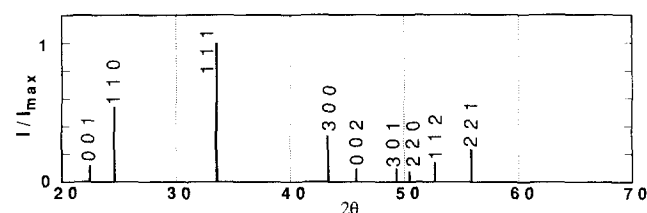


Fig. 4. Calculated X-ray pattern of UNiAlH_{2.7} with assumed structure of U at $(\frac{2}{3} 0 \frac{1}{2})$, Al at $(\frac{1}{3} 0 0)$ and Ni (1) at $(0 0 0)$.