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Diffraction Study on the Nonstoichiometric α - U_2N_{3+x} Phase

H. Serizawa, K. Fukuda, Y. Ishii, S. Funahashi

**Japan Atomic Energy Research Institute, Tokai-mura, Naka-Gun,
Ibaraki-Ken, 319-11 Japan**

and

M. Katsura

**Osaka University, Department of Nuclear Engineering, Faculty of
Engineering, Yamadaoka 2-1, Suita, Osaka, 565 Japan**

Abstract

X-ray and neutron diffraction studies were performed on nonstoichiometric α - U_2N_{3+x} having a composition range $1.68 < N/U < 1.84$. It was confirmed that the crystal structure of α - U_2N_{3+x} in this composition range was distorted Mn_2O_3 -type. Structure parameters of U and N atoms were determined. The results showed that positions of U atoms varied continuously with nitrogen content. No evidence of the modification from bcc to fcc could be obtained. Interatomic distances of U-U and U-N were determined. The position parameter of N atoms showed that N atoms were slightly deviated from the tetrahedral site.

1. Introduction

In U-N system, there are two sesquinitrides, which are named as β - U_2N_3 and α - U_2N_3 . The crystal structure of β - U_2N_3 formed at temperatures higher than 800 °C is hexagonal with La_2O_3 -type structure. The other sesquinitride, α - U_2N_3 , is indexed as body-centered cubic with Mn_2O_3 -type structure, and exhibits a wide range of composition by dissolving nitrogen in N vacant site, so that its formula is denoted as α - U_2N_{3+x} . Although the other nitride, U_4N_7 , with CaF_2 -type structure was reported [1], the existence is still in question. It is well known that the lattice constant and X-ray diffraction pattern of α - U_2N_{3+x} vary with its composition. These variations seem to indicate some phase transition which may occur with dissolving nitrogen in the α - U_2N_{3+x} phase.

Several works on the phase transition have been reported, in which two predictions were proposed on it so far. Rundle et al. [2] and Anselin [3] analyzed α - U_2N_{3+x} phase by X-ray diffraction (XRD) in the composition range, $1.435 < N/U < 1.75$, and suggested that the crystal structure of α - U_2N_{3+x} should be modified continuously from α - U_2N_{3+x} with Mn_2O_3 -type bcc

structure toward CaF_2 -type fcc structure with increasing the nitrogen content. On the other hand, Tobisch and Hase [4], and Masaki et al. [1] reported that such a phase transition could not be found. In order to clarify the phase transition, on which there are contradictory predictions, it is necessary to perform the crystallographic study on nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ phase ($\text{N/U} > 1.75$). We have, therefore, undertaken X-ray and neutron powder diffraction studies on $\alpha\text{-U}_2\text{N}_{3+x}$ with a wide composition range. The diffraction data were refined by means of RIETAN-program [5] to obtain variations of position parameters and occupation factors of U and N atoms. we also calculated interatomic distances (U-U and U-N) which would provide the useful information for the thermodynamic property of the phase.

2. Experimental

All samples of $\alpha\text{-U}_2\text{N}_{3+x}$ were prepared from high-purity uranium metal. The metal was converted to UH_3 powder through a heat treatment with hydrogen, which was purified by flowing through a liquid nitrogen trap. The nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ ($\text{N/U} > 1.75$) was prepared by the reaction of UH_3 and a gas mixture of ammonia, hydrogen and nitrogen at 400°C . The composition of the product could be controlled by changing the mixing ratio of the three gases. The products were then quickly cooled and stored in vacuum, since $\alpha\text{-U}_2\text{N}_{3+x}$ obtained in this way is easily oxidized in the air. The nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ ($\text{N/U} < 1.75$) were obtained by heat treatments of UH_3 at 800°C and 1000°C in dried nitrogen atmosphere of 1 atm for 72 hours. The samples for X-ray and neutron diffraction analyses were prepared in a glove-box with a high-purity argon atmosphere (oxygen concentration < 10 ppm). The chemical analyses were carried out on three samples with high nitrogen content. The nitrogen content of the sample was determined by a modified Kjeldahl method developed by Handa et al. [6]. The oxygen contained as impurity in the sample was determined by an inert gas fusion-coulometry [7].

Results of the chemical analyses are presented in Table 1 together with corresponding lattice constants. The XRD patterns showed that the samples were composed of a single phase. Although oxygen detected by the chemical analysis should exist as UO_2 , no trace of the phase was recognized by the XRD analysis. We, therefore, disregarded the presence of oxygen in the following discussions.

The XRD analyses were made at room temperature using a diffractometer (rotating anode X-ray tube type, RU-200B, Rigaku Co. Ltd.) with CuK_α radiation monochromated by (002) plane of graphite. The measurements on the samples were conducted with stepwise scanning from 15° to 125° at intervals of 0.05° for a duration of 7 seconds.

The neutron diffraction patterns were taken with a neutron wave length of 0.18225 nm at room temperature by the High Resolution Powder Diffractometer (HRPD) installed in the

Table 1 Results of chemical analysis of $\alpha\text{-U}_2\text{N}_{3+x}$

Sample name	Nitrogen (wt%)	Oxygen (wt%)	N/U ratio	Lattice constant (nm)
SAMPLE-1	9.77±0.06	0.2±0.1	1.83	1.0594
SAMPLE-2	9.77±0.04		1.83	1.0600
SAMPLE-3	9.69±0.05		1.82	1.0596

3. Results and Discussion

3.1 Relationship between nitrogen content and lattice constant

The composition dependence of the lattice constant was reported previously by other workers [2, 3, 8-15]. The relationship between the lattice constant and N/U atomic ratio for $\alpha\text{-U}_2\text{N}_{3+x}$ is plotted in Fig. 1, where a dotted line and a solid line were reported by Tagawa and Masaki [10], and GMELIN handbook [15], respectively. The solid line in the figure suggest the continuous phase transition from bcc to fcc. While, an existence of discrepancy and slope change of the dotted line at N/U=1.75 implies the discrete transformation from $\alpha\text{-U}_2\text{N}_{3+x}$ with Mn_2O_3 -type structure to U_4N_7 with CaF_2 -type structure at the composition [10].

The data of the chemical analysis and XRD obtained in the present work are consistent with those expressed by the solid line. As described above, this result suggests the phase transition should occur continuously.

3.2 Information on displacements of U atoms in the unit cell

Typical XRD patterns of both of nitrogen-rich and -poor $\alpha\text{-U}_2\text{N}_{3+x}$ obtained in the present study were given in Fig.2. Weak peaks are reflections being characteristic of a bixbyte-type (bcc) lattice, which corresponds to Mn_2O_3 -type structure. It should be noted that the intensity of each weak reflection which can be seen in the pattern of nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ decreased in the pattern of nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$, but those peaks did not disappear completely. This is one of the evidence that the crystal structure of nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ is still keeping bcc structure in space group Ia3 which is the same as that of nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$.

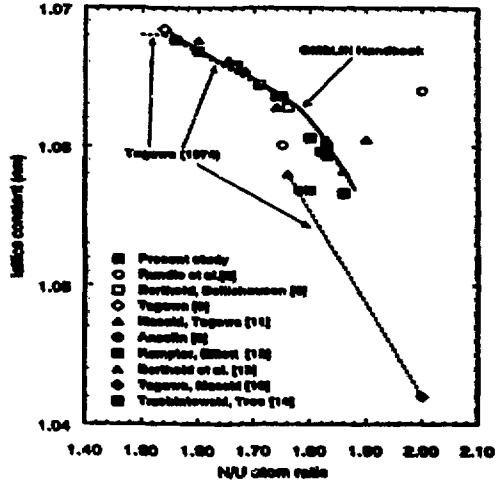


Fig. 1 Variations of lattice constant of $\alpha\text{-U}_2\text{N}_{3+x}$ as a function of the composition

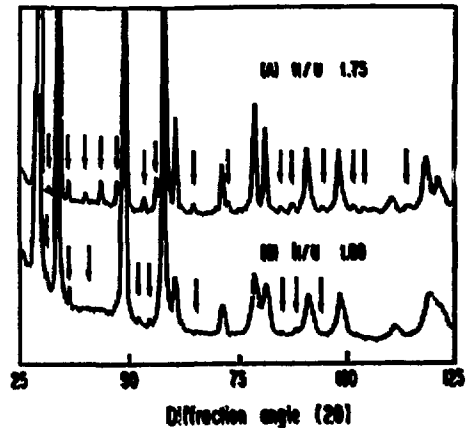


Fig. 2 Typical X-ray diffraction patterns of $\alpha\text{-U}_2\text{N}_{3+x}$ obtained in this study

Consequently, it may be concluded to consider that phase transition which was suggested by Masaki et al.[1] would not occur in $\alpha\text{-U}_2\text{N}_{3+x}$ phase. XRD patterns were refined with the RIETAN-program by a FACOM large scale computer[5]. The discrepancy index, R_p (structure factor R -factor), which was defined as

$$R_p = \frac{\sum_k |\sqrt{I_k('o')} - \sqrt{I_k('c')}|}{\sum_k \sqrt{I_k('o')}} \quad (1)$$

for the refinements, for each refinement was less than 6, where $I_k('o')$ is the integrated intensity evaluated from a summation of contributions of k -th peak to net observed intensities, and $I_k('c')$ denotes the integrated intensity calculated from refined structure parameters.

$\alpha\text{-U}_2\text{N}_{3+x}$ contains 32 U atoms in its unit cell, where U atoms occupy 8(b) and 24(d) sites in space group $Ia\bar{3}$ [16]; we designate U atoms at 8(b) and 24(d) sites as U(1) and U(2), respectively.

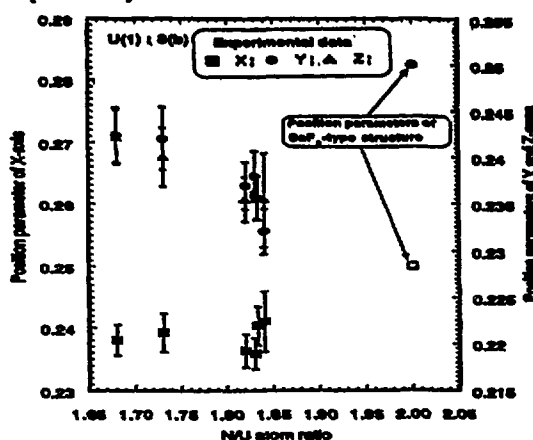


Fig. 3 Variations of position parameters of U(1) (U atoms at 8(b) site)

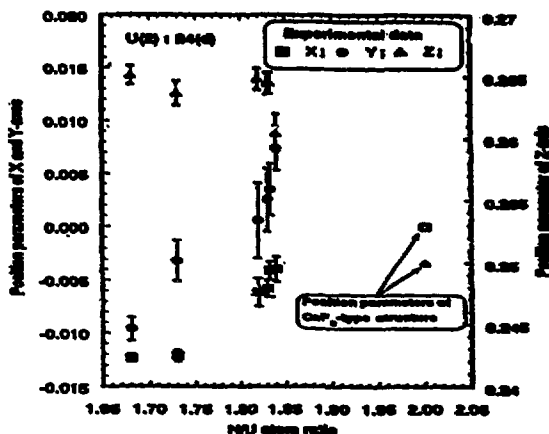


Fig. 4 Variations of position parameters of U(2) (U atoms at 24(d) site)

The atomic scattering factor of N atom for X-ray was negligibly small, so that the effect of N atom on the position parameters of U atoms could be neglected.

Variations of the position parameters of U(1) and U(2) with increasing nitrogen content are given in Figs. 3 and 4, respectively. The composition for each specimen in the Figs. 3 and 4 was estimated with the lattice constant by referring the solid line in Fig. 1. A marked tendency was observed as follows; in the lower nitride region ($N/U < 1.75$), the position parameters of U(1) and U(2) did not vary steeply with increasing nitrogen content. Figures 3 and 4 indicate that U(1) and U(2) shift toward $\langle 0, -1, -1 \rangle$ and $\langle 1, 1, -1 \rangle$, respectively. Figure 3 shows that displacement of U(1) along X-axis is small compared with those along Y and Z-axes. Figure 4 shows that U(2) shifts with composition change, and traverse $(c, 1, 0)$ plane in the vicinity of the composition $N/U = 1.82$. The displacement of U(2) along the X-axis was also recognized, but that along Z-axis was scarcely changed. When the crystal structure of

$\alpha\text{-U}_2\text{N}_{3+x}$ is modified from bcc to fcc with increasing nitrogen content, the position parameters of U(1) and U(2) should approach those expressed by open symbols in Figs. 3 and 4. However, in these figures, the variations of the position parameters did not show such tendency.

Using the numerical values of the lattice constant and the position parameters, we calculated the interatomic distance between U(1) and U(2). Variation of the interatomic distance is given as a function of the composition in Fig. 5. The interatomic distance decreases rapidly with increasing nitrogen content. The dotted line in the figure denotes the calculated distances on the assumption that the displacement of U atoms is neglected even if the nitrogen content changes. The difference between the experimental data and the calculated line indicates that the displacement of U atoms in the unit cell cannot be neglected to elucidate the interatomic distances.

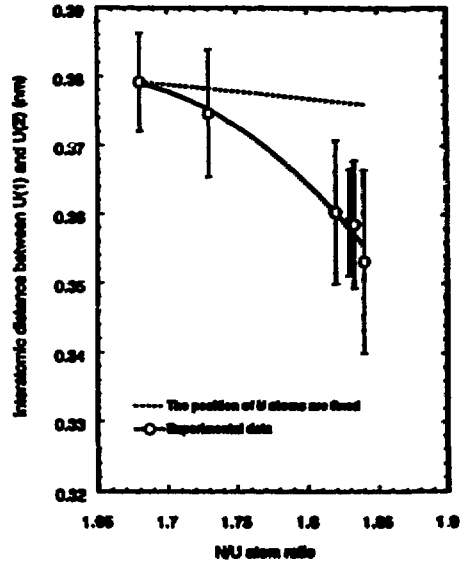


Fig. 5 Composition dependence of interatomic distance between U(1) and U(2)

3.3 Information on nitrogen dissolved in the unit cell

The neutron diffraction analysis reveals the positions of N atoms dissolved in $\alpha\text{-U}_2\text{N}_{3+x}$. Some information on the position parameters and occupation factors of N atoms for nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ were provided by Tobisch and Hase [4], and Masaki and Tagawa [11]. The N atoms in nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ occupy at 16(c) and 48(e) in the space group Ia3; we denote N atoms in the positions of 16(c) and 48(e) as N(1) and N(2), respectively. The neutron diffraction patterns obtained in the present study are shown in Fig. 6. These patterns were also refined by using RIETAN program. The R_F values for the refinement of the diffraction patterns of the samples with the composition, $N/U=1.82$ and 1.73 were 5.36 and 6.17 , respectively. The position parameters of U atoms which had been determined in the XRD study were used in this refinement. The position parameters and occupation factors of N atoms

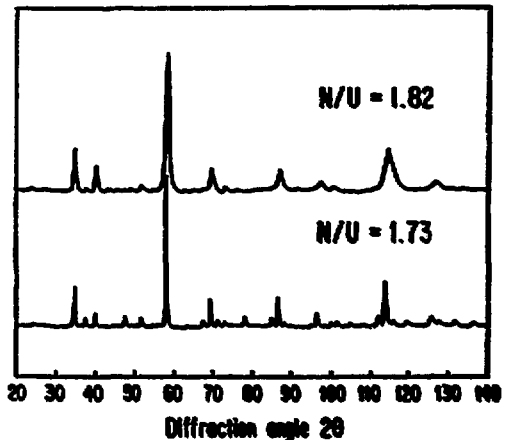


Fig. 6 Neutron diffraction patterns of nitrogen-rich and poor $\alpha\text{-U}_2\text{N}_{3+x}$

obtained in the present study are summarized in Table 2 together with the previous results. N/U atom ratio in the table was estimated from the lattice constant. The occupation factors of N atoms in nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ ($N/U=1.73$) agree well with those of the previous works [4, 11]. The composition dependence of the occupation factor at 16(c) site listed in Table 2 shows that the factor increases with the composition. Therefore, it is evident that excess N atoms occupy the position of 16(c) predominantly. Although the presence of empty sites in a small part of the position 48(e) was suggested in nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$, the occupation factor was larger than that at 16(c) site. The difference in the occupation factors would express an inequivalence between these two positions, 16(c) and 48(e) sites. If nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ was CaF_2 -type structure, these two positions were to be equivalent. Then, this result also means that nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ should be crystallized as $\text{M}_{1.2}\text{O}_3$ -type structure.

Table 2 Position parameters and occupation factors of N atoms in $\alpha\text{-U}_2\text{N}_{3+x}$

N/U	Position	Fractional coordinate			Occupation factor
		X	Y	Z	
1.55-1.67*	16(c)	0.173-0.013	0.173-0.013	0.173-0.013	—
	48(e)	0.173-0.011	0.173-0.011	0.173-0.011	1.00
1.74-1.83*	16(c)	0.173-0.009	0.173-0.009	0.173-0.009	—
	48(e)	0.173-0.002	0.173-0.002	0.173-0.001	1.00
1.87**	16(c)	—	—	—	0.20
	48(e)	—	—	—	1.00
1.87**	16(c)	—	—	—	0.31
	48(e)	—	—	—	1.00
1.87**	16(c)	—	—	—	0.37
	48(e)	—	—	—	1.00
1.73**	16(c)	—	—	—	0.43
	48(e)	—	—	—	1.00
1.73	16(c)	0.121	0.125	0.002	0.60-0.62
	48(e)	0.176	0.177	0.132	0.39-0.42
1.82	16(c)	0.126	0.129	0.107	0.61-0.62
	48(e)	0.173	0.174	0.177	0.39-0.42

* Data of this work
 ** Data of Ref. [11]

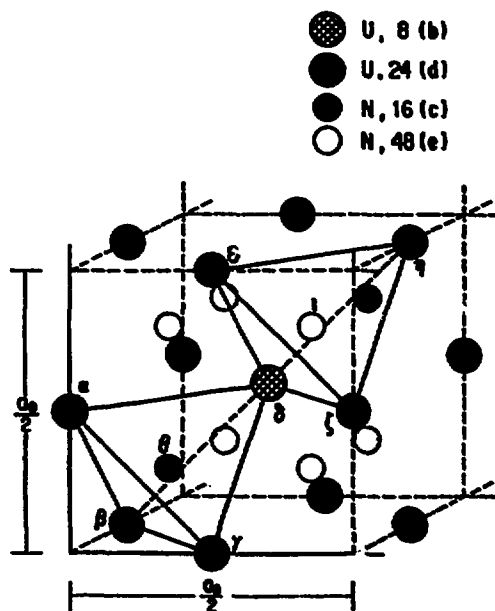


Fig. 7 Arrangement of U and N atoms in bixbyte-type structure

A part of the unit cell of $\alpha\text{-U}_2\text{N}_{3+x}$ is drawn in Fig. 7. Both of N(1) and N(2) have the four nearest neighboring U atoms. The interatomic distances between U atom and N atom in $\alpha\text{-U}_2\text{N}_{3+x}$ are summarized in Table 3. Symbols in the second and third columns in the table correspond to atoms appearing in Fig. 7. The mean error was about 0.003 nm. As seen in Table 3, in nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$, the interatomic distances between N atom and three U atoms (γ, β, δ for N(1) and ζ, η, δ for N(2)) among neighboring four U atoms were nearly the same, and the distance between the N atoms and the rest of neighboring U atom was larger than above three values, meaning that the positions of N atoms deviate from the tetrahedral site. The interatomic distances between N atom and U atom in the

composition range from N/U=1.73 to 1.82 did not depend on the composition.

Table 3 Interatomic distance between U atom and N atom

5. Summary

1) U atoms in $\alpha\text{-U}_2\text{N}_{3+x}$ displaced continuously with increasing nitrogen content. The pronounced displacement was observed in nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ phase. However, any modifications, such as the formation of other nitrides (UN_2 or U_4N_7), were not observed. A specimen in nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$ phase examined in the present study was crystallized Mn_2O_3 -type structure which is the same as that of nitrogen-poor $\alpha\text{-U}_2\text{N}_{3+x}$ phase.

2) The interatomic distance between U(1) and U(2) decreased steeply with increasing nitrogen content.

3) The position of excess nitrogen dissolved in $\alpha\text{-U}_2\text{N}_{3+x}$ phase was confirmed. The excess nitrogen atoms were located predominantly at the position 16(c). In nitrogen-rich $\alpha\text{-U}_2\text{N}_{3+x}$, the presence of the empty site in the position 48(e) was suggested.

4) The position of N atoms in $\alpha\text{-U}_2\text{N}_{3+x}$ were shifted from their tetrahedral site.

N/U ratio	N atom	U atom	Distance (Å)	Average (Å)
1.73	0 (14C)	a	0.209	0.218
		β	0.211	
		γ	0.217	
		δ	0.216	
	1 (14D)	e	0.226	0.234
		ζ	0.228	
		η	0.221	
		θ	0.220	
1.82	0 (14C)	a	0.201	0.214
		β	0.208	
		γ	0.208	
		δ	0.210	
	1 (14D)	e	0.234	0.234
		ζ	0.227	
		η	0.224	
		θ	0.220	

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