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A NEW COMPOUND—UNF

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Abstract—A new compound UNF has been prepared by the reaction of UF_4 with silicon and nitrogen. The crystal structure of UNF has been determined to be tetragonal with dimensions of $a = 5{\cdot}612 \pm 0{\cdot}001$ Å, $b = 5{\cdot}712 \pm 0{\cdot}001$ Å. This compound is converted to U_2N_3 in nitrogen atmosphere, and also converted to UN in argon atmosphere at elevated temperatures. This compound is not stable in air even at room temperature due to its oxidation.

INTRODUCTION

No COMPOUND has been known in the U—N—F system. A uranium compound containing both nitrogen and fluorine has been found as an intermediate compound in the preparation of U_2N_3 by the reaction of UF_4 with silicon and nitrogen[1]. Silicon was preferable as the reducing agent for UF_4, since the sublimation point of SiF_4 is -95°C. The equation of this reaction is as follows:

$$4UF_4 + 4Si + 3N_2 \rightarrow 2U_2N_3 + 4SiF_4 \qquad (1)$$

The reaction proceeds as follows; $UF_4 \rightarrow UF_3 \rightarrow$ An unknown uranium compound containing both nitrogen and fluorine $\rightarrow U_2N_3$.

In this report, this unknown compound has been identified as UNF by the chemical and X-ray analyses, and some properties of this substance are also reported.

EXPERIMENTAL

Materials. The silicon powder (99·9 per cent pure) was procured commercially. UF_4 was supplied by Power Reactor and Nuclear Fuel Development Corporation, with the following analytical quality: Ag: <0·2 ppm, Al: <10 ppm, B: <0·1 ppm, Cd: <0·2 ppm, Co: <5 ppm, Cr: 9 ppm, Cu: <3 ppm, Fe: 22 ppm, Mg: <2 ppm, Mn: 3 ppm, Ni: 28 ppm, Si: <10 ppm, V: <10 ppm, Zn: <50 ppm, H_2O: <0·9 per cent. The nitrogen gas in a cylinder was purchased and purified by passing through silicagel, activated copper kept at 180°C and magnesium perchlorate.

Procedure. The experiments were carried out by simply heating the mixed powder of UF_4 and silicon in the nitrogen stream (200 cc/min).

The apparatus was composed of a vacuum line, a purification system for the nitrogen gas and a sintered alumina reaction tube. The duration of the reaction was precisely controlled by a magnetic sliding device, which was able to move the reaction boat from the reaction part to the colder part of the reaction tube and was operated from outside of the tube.

Analysis. The contents of uranium, nitrogen and fluorine in the products were determined by chemical analyses, which was carried out as follows: The uranium content was determined by Ce^{+4} titration[2]. The fluorine content was determined by the pyrolysis method[3]. The nitrogen content

1. K. Yoshihara, M. Kanno and T. Mukaibo, *J. nucl. Sci. Technol.* **5**, 643 (1968).
2. C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, p. 75. McGraw-Hill, New York (1950).
3. H. Hashitani and H. Muto, *Japan Analyst* **14**, 1114 (1965).

was determined by Kriege method[4]; uranium compound was fused with NaOH at 700°C and the ammonia liberated was absorbed and estimated by titration.

RESULTS AND DISCUSSION

Preparation of UNF

UF_4 and Si were mixed by two ways; one mixture had a stoichiometric composition according to Equation (1), and another mixture had a composition of which Si content was $\frac{3}{4}$ of the stoichiometric amount. These mixtures were heated in nitrogen atmosphere at 900°C, which was determined by preliminary experiments.

The contents of uranium and nitrogen in the products were determined by chemical analyses. In Fig. 1 N/U ratio calculated from the chemical analyses is shown as a function of the reaction time. N/U ratio of the reaction with Si content of $\frac{3}{4}$ of the stoichiometric composition reached almost unity after 3 hr of the reaction time, and the reaction did not proceed further thereafter, while the reaction with the stoichiometric composition of Si proceeded gradually even after the N/U ratio exceeded unity in 2 hr.

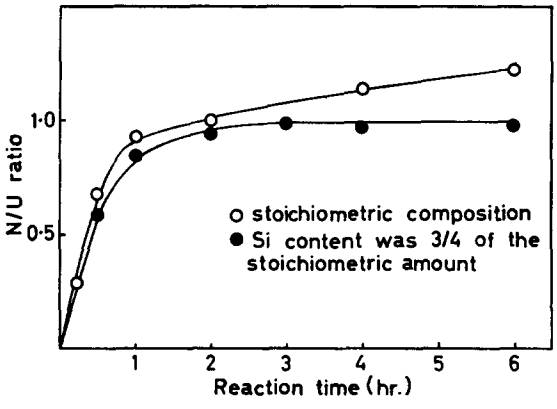

Fig. 1. Change of N/U ratio during the reaction.

When N/U ratio of the product was unity, its X-ray pattern did not agree with any other known patterns. When N/U ratio of the product was over unity, its X-ray pattern showed both the phase of b.c.c. U_2N_3 and the same unknown phase, and when N/U ratio was below unity, its X-ray pattern showed both the phase of UF_3 and the same unknown phase.

From these results it is possible to deduce that the product of which N/U ratio was unity was a certain definite unknown compound.

Identification of UNF

This unknown compound prepared by the reaction with Si in the amount of $\frac{3}{4}$ of the stoichiometric composition according to Equation (1) was analysed for uranium, nitrogen and fluorine as follows; uranium; 87·1%, nitrogen; 5·0%, fluorine; 6·9%. From these results, the chemical composition of this material was

4. K. Tada, *et al.*, *Toshiba Rev.* **22**, 1339 (1967).

calculated as $UN_{0.98}F_{0.99}$, which was nearly equal to the formula UNF. Therefore, it was supposed that UNF was prepared by the reaction according to the following equation:

$$4UF_4 + 3Si + 2N_2 \rightarrow 4UNF + 3SiF_4 \quad (2)$$

This reaction proceeded as follows; $UF_4 \rightarrow UF_3 \rightarrow UNF$.

This substance was also prepared at 1000°C by using Al as the reducing agent instead of Si, although it was difficult to prepare pure UNF. The higher temperature was necessary for this reaction than that for the case using Si, since AlF_3 is not so volatile as SiF_4.

The X-ray diffraction pattern of UNF is shown in Table 1. The lines of the diagram have been indexed on the basis of a simple tetragonal unit cell with dimensions;

$$a = 5{\cdot}612 \pm 0{\cdot}001 \text{ Å}$$
$$c = 5{\cdot}712 \pm 0{\cdot}001 \text{ Å}$$

The axial ratio of 1·018 indicates that this crystal structure was almost cubic.

The density measured pycnometrically, was 9·80 g cm^{-3} indicating that there were four molecules of UNF per unit cell. The calculated value was 10·01 g cm^{-3}.

Table 1. X-ray diffraction data of UNF (CuK_α).
$a = 5{\cdot}612 \pm 0{\cdot}001$ Å $c = 5{\cdot}712 \pm 0{\cdot}001$ Å

hkl	d(Å)	I/I_0
0 0 1	5·717	8
1 1 1	3·255	100
0 0 2	2·856	15
2 0 0	2·799	49
2 0 1	2·515	9
1 1 2	2·318	29
2 0 2	2·001	55
2 2 0	1·984	40
0 0 3	1·906	9
2 2 1	1·874	6
1 1 3	1·717	18
1 3 1	1·694	80
2 2 2	1·630	18
2 0 3	1·576	22
1 3 2	1·507	22

Properties of UNF

Physical appearance. The prepared UNF was a black fine powder.

Solubility. UNF reacted readily with solutions of nitric acid but was not attacked by sulfuric acid or hydrochloric acid.

Behavior at elevated temperatures. UNF was converted gradually to U_2N_3 in nitrogen atmosphere above about 1100°C. This reaction rate was so low that

even after 6 hr at 1100°C the major phase was UNF and the minor phase was U_2N_3. UNF with Si in the amount enough to convert all fluorine to SiF_4 was converted to U_2N_3 when heated in nitrogen atmosphere. However, this reaction looked to proceed faster than that without enough Si, since after 6 hr at 1100°C almost all peaks of the X-ray pattern of the product were assigned to U_2N_3.

UNF was converted gradually to UN in argon atmosphere above about 1100°C. This reaction rate was so low that after 2 hr at 1100°C, the major phase was still UNF and the minor phase was UN. UNF was also converted to UN by heating with Si in argon atmosphere, but this reaction proceeded faster, and after 2 hr at 1100°C, almost all peaks of the X-ray patterns were assigned to UN.

UNF has a tendency to loose fluorine at elevated temperatures, and this tendency increases if a reducing agent is present.

Oxidation behavior. UNF changed gradually in air at room temperature due to its oxidation, and this reaction was accelerated in the dry oxygen stream at 90°C. The oxidized product, however, was not identified since its X-ray pattern did not agree with any other known patterns.

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