

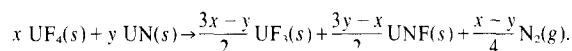
THE REACTION OF URANIUM TETRAFLUORIDE WITH URANIUM MONONITRIDE

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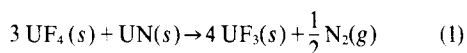
Abstract—The reaction of UF_4 with UN at 950°C yields UF_3 or UNF depending on the mixing ratio; the product is UF_3 for the UF_4 :UN ratio of 3:1, and UNF for 1:3. The reaction is generally expressed as



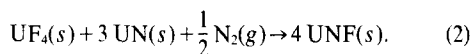
The free energy change for the formation of UF_3 is discussed on the basis of the experimental results.

INTRODUCTION

IN THE course of studies of the high-temperature reactions with uranium nitride, it was found that UF_4 was readily converted to UF_3 or UNF. The typical reactions are represented by the equations:



and



In the present paper, the reaction of UF_4 with UN has been investigated, with the different mixing ratios of starting materials in a nitrogen atmosphere or in a vacuum at temperatures below 1000°C.

EXPERIMENTAL

Materials

UF_4 was provided from Sumitomo Metal and Mining Co., with the composition: UF_4 , >99.0%; UO_2F_2 , 0.8%; and UO_2 , 0.05%.

UN, prepared by arc-melting of uranium metal in a nitrogen atmosphere, was provided from Mitsubishi Metal Co. The composition is as follows: total U, 94.73%; nitrogen 5.53%; and oxygen, 0.01%; the N/U atom ratio is 1.00.

Procedure

Both the compounds were ground in a dry box filled with high-purity argon gas and were mixed at different mole ratios (UF_4 :UN = 3:1, 1:1 and 1:3) and compacted at 3 ton/cm² into cylindrical pellets, 7 mm in diameter and 5 mm in height. The resulting pellets of about 2 gm, placed in a nickel crucible, were heated in a quartz tube. The reactions were carried out in a closed system of an atmosphere of nitrogen or of a vacuum. The volume of the reaction system, consisting of the quartz tube, a liquid nitrogen trap, an oil manometer and a mercury manometer, was about 400 ml. The temperature was raised at the rate of 3°C/min.

Analysis

The fluorine was separated as hydrogen fluoride by pyrohydrolysis at 850°C for 20 min. Its content was determined photometrically using lanthanum-alizarine complexone[1]. The uranium content was determined as U_3O_8 from the residual oxide of pyrohydrolysis. The amount of nitrogen was determined photometrically with thymol[2].

RESULTS

The conditions of experiments and the results are given in Table 1.

Reactions in mole ratio UF_4 :UN = 3:1

The reaction *in vacuo* was followed with the pressure change in nitrogen evolved with time. The reaction took place at about 700°C, became rapid at temperatures above 840°C, and terminated before the temperature attained 900°C. The nitrogen pressures at temperatures between 1103 and 1148K are given by the equation:

$$\log p_{\text{N}_2}(\text{atm}) = 39.57 - 4.695 \times 10^4/T. \quad (3)$$

X-ray diffraction pattern showed that the product was the single phase of UF_3 . The pattern of UF_3 was consistent with that of the ASTM file[3]. The reaction therefore is expressed as Eqn (1).

On the inside surface of the quartz tube slightly above the crucible, grayish-brown film was formed. This compound was found to be UO_2 by chemical and X-ray analyses. It is probably produced by the reaction of the evaporated UF_4 with the quartz tube. The reaction product $\text{SiF}_4(g)$ was trapped by the liquid nitrogen, so that the nitrogen pressure in the system was not affected by it.

When heated in 1 atm nitrogen to 950°C, the mixture was also converted to UF_3 . The formation of a UO_2 film was not observed.

Reaction in mole ratio UF_4 :UN = 1:1

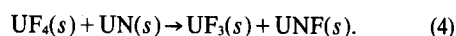
In the reaction *in vacuo*, nitrogen was not evolved by heating up to 950°C. Gray-brown film was deposited on

Table 1. The reaction of UF₄ with UN

Experimental conditions				Products				
Mixing ratio (mole) UF ₄ :UN	p _{N₂} (atm)	Max. temp.* (°C)	Retention time (min)	X-ray analysis	U	Chemical analysis (wt%) N F U:N:F		
3:1	0	900	20	UF ₃	80.70	0.10	20.32	1.00:0.02:3.15
3:1	1	950	10	UF ₃	80.11	0.04	20.20	1.00:0.01:3.16
1:1	0	900	30	UF ₃ , UNF	83.69	2.56	12.63	1.92:1.00:3.64
1:1	1	950	0	UF ₃ , UNF	83.76	2.66	11.83	1.85:1.00:3.28
1:3	0	950	0	UF ₃ , UNF, UN	86.87	3.86	9.20	1.33:1.00:1.76
1:3	1	950	20	UNF	86.86	4.73	5.87	1.08:1.00:0.92

*The heating rate was 3°C/min.

the inner wall of the quartz tube, similarly to the case of the reaction (UF₄:UN = 3:1) *in vacuo*. The product was a mixture of UF₃ and UNF. The compound UNF was identified by X-ray diffraction to have a tetragonal structure with lattice parameters of $a_0 = 5.61 \text{ \AA}$ and $c_0 = 5.71 \text{ \AA}$; its pattern was consistent with that reported by Yoshihara *et al.*[4]. The reaction thus proceeds as



When heated in a nitrogen atmosphere, the product also consisted of UF₃ and UNF. There was no change in the nitrogen pressure before and after heating. The formation of UO₂ was hardly observed on the wall of the tube.

Reaction in mole ratio UF₄:UN = 1:3

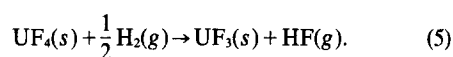
In the reaction *in vacuo*, no evolution of nitrogen was observed. A gray-brown film of UO₂ was also found on the inner wall of the tube. X-ray diffraction showed the product to be a mixture of UF₃, UNF and UN. It is considered that the reaction occurs in equimolar ratio of UF₄ and UN as shown in Eqn (4), and UN remains as the unreacted starting material.

When heated in a nitrogen atmosphere, the reaction could be followed by the pressure change. The reaction occurred above 740°C and was terminated at about 900°C. The product was only UNF; U₂N₃ was not formed. The reaction is given as Eqn (2). The gain in weight during the heating process is in agreement with Eqn (2). The formation of UO₂ on the inner wall of the quartz tube was not observed.

DISCUSSION

UF₃ can not be prepared directly by the reaction of uranium with fluorine. The attempts to synthesize UF₃ have been reviewed by Katz and Rabinowitch[5]. Two successful methods are described:

(A) UF₄ is reduced with purified hydrogen at 1000°C. The reaction proceeds according to

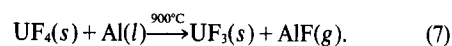


(B) UF₄ is reduced with finely divided uranium metal at

1050°C:

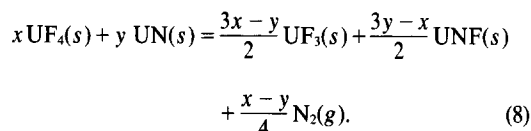


Subsequently, another method was reported by Runnals[6]:



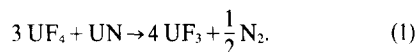
In these reactions, UF₄ is partially reduced by hydrogen, uranium or aluminium. The reaction (1), observed in the present work, is considered a modification of Eqn (6); UN acts as the reducing agent.

Uranium nitride-fluoride UNF was found by Yoshihara *et al.*[4] as an intermediate in the nitride formation from UF₄ using the reducing agent Si. Before that, Juza *et al.*[7-9] prepared the similar compounds UNX (X = Cl, Br and I) by the reactions: $\text{UX}_4(s) + 3 \text{UN}(s) + \frac{1}{2} \text{N}_2(g) \rightarrow 4 \text{UNX}(s)$; and $\text{UX}_4(s) + \text{NH}_3(g) \rightarrow \text{UNX}(s) + 3 \text{HX}(g)$. In the present experiments, however, UNF is readily formed in the reaction of UF₄ with UN at the UF₄/UN mole ratio smaller than three. When an equimolar mixture of UF₄ and UN is heated, the product is then the equimolar mixture of UF₃ and UNF, regardless of the presence of nitrogen. In the case of UF₄:UN = 1:3, UNF is obtained as the single phase. Therefore, the reaction of UF₄ with UN can be generally described as



By using the free energies for the formation of UF₃ and UF₄[10], it cannot be shown thermochemically that the reaction of UF₄ with UN yields UF₃ even at temperatures as high as 1000°C. Actually, however, the reaction takes place at temperatures above 700°C *in vacuo*, and proceeds at a sufficient velocity at temperatures between 800 and 900°C. Therefore, the thermochemical data for UF₃ and UF₄ should be reexamined.

The reaction (1) is composed of two equations (a) and (b):



The nitrogen pressures in Eqn(1) around 1120K were already given as Eqn (3). Using this equation, the temperature where the nitrogen pressure becomes 1 atm is taken to be 913°C. This temperature agrees well with the result that the reaction in the mole ratio $\text{UF}_4:\text{UN} = 3:1$ yields only UF_3 at 950°C even at 1 atm nitrogen. Assuming that the reaction system is in equilibrium and the activities of UF_3 and UF_4 are unity, the Gibbs free energy change of the reaction (1) is shown as

$$\Delta G_T^\circ = 107.4 - 90.5(T/1000) \text{ (kcal/mole, 1100–1150K)}, \quad (9)$$

and the value at 1100K becomes $\Delta G_{1100}^\circ(1) = 7.9$ kcal/mole. The reaction (a) is the decomposition of UN. Its free energy change at 1100K evaluated from the data in the literature is $\Delta G_{1100}^\circ(\text{a}) = 49.4$ kcal/mole[11]. The free energy change of the reaction (b), obtained from Eqn (1) and (a), is thus $\Delta G_{1100}^\circ(\text{b}) = -41.5$ kcal/mole. On the other hand, the free energies for the formation of UF_3 and UF_4 at 1100K estimated by Rand and Kubaschewski[10] are -285.0 and -376.1 kcal/mole, respectively, so that the

free energy change in Eqn (b) is $\Delta G_{1100}^\circ(\text{b}) = -11.9$ kcal/mole. The difference in $\Delta G_{1100}^\circ(\text{b})$ values between the present result and Rand and Kubaschewski's result [10] is about 30 kcal/mole. If calculation is based on the free energy for the formation of UF_4 , the value for UF_3 , obtained from the present results, is $\Delta G_{1100}^\circ = -292.5$ kcal/mole; which is in agreement with that determined by Long and Blankenship[12]. $\Delta G_{1100}^\circ = -295 \pm 5$ kcal/mole.

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