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Study of the formation of α-U_2N_{3+x} using unstable ammonia – reaction sequence and control of nitrogen activity

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Abstract

The formation of α-U_2N_{3+x} by the reactions between U and NH_3 or a gas mixture of NH_3 and H_2 was examined at 300 °C. It was found that there were two routes for the reaction process. One route was the direct formation of α-U_2N_{3+x} by the reaction of U and NH_3; the other included the formation of UH_3. Although the UH_3 formed in this way was finally converted to α-U_2N_{3+x}, the reaction rate was very slow compared with the rates of nitride and hydride formation. It was presumed that the conversion of UH_3 to α-U_2N_{3+x} was the rate-determining step in the series of reactions. It was also confirmed that the nitrogen content of α-U_2N_{3+x} varied when the composition of the reactant gas mixture was changed. This result implies that the nitrogen activity of the unstable gas mixture is dependent on the composition.

Keywords: Unstable ammonia; Nitrogen activity; Hydride formations

1. Introduction

A metal nitride is commonly prepared by reaction of the metal with N_2 gas. For Fe_4N, Mo_2N, MoN, and nitrogen-rich α-U_2N_{3+x} for example, it is difficult to produce the nitride by this reaction. In such cases unstable NH_3 is employed instead of N_2 gas. The use of unstable NH_3 brings about a considerable reduction in the reaction time. In addition, the metal nitride can be produced at a relatively low temperature by employing the unstable NH_3 gas as a nitriding agent. Briefly, the difference between these two nitriding agents, NH_3 and N_2, can be described as follows: (i) NH_3 gas acts not only as a nitriding agent but also as a hydriding agent; (ii) the unstable NH_3 leads to a high nitrogen activity compared with N_2 gas at normal pressure. These distinctions might affect the kinetic merits of using NH_3 gas as described above. Recently, Katsura [1] studied the reaction between metal and NH_3 from a thermodynamic point of view and suggested that the activities of nitrogen and hydrogen of the gas phase (denoted a_N and a_H respectively) were dependent on the degree of dissociation of NH_3. He derived the relations $a_N = A(T)P_{HN3}/P_{H2}^{3/2}$ and $a_{HJ} = [A(T)P_{NH3}/P_{N2}^{3/2}]^{1/3}$, where $A(T)$ is the reciprocal of the equilibrium constant of NH_3 dissociation, and P_{NH3}, P_{H2} and P_{N2} are the partial pressures of NH_3, H_2 and N_2 respectively. These relationships imply that we can arbitrarily select or change the activities of nitrogen or hydrogen of the reactant gas at constant temperature by changing P_{NH3}, P_{H2} and P_{N2}. So far, however, no experimental study of this point has been reported.

The formation of uranium sesquinitride has been examined by several workers [2–17]. It is known that there are three nitrides in the U–N system. UN (NaCl-type structure), α-U_2N_3 (Mn_2O_3-type structure) and β-U_2N_3 (La_2O_3-type structure). Among these nitrides, α-U_2N_3 exists in a wide range of composition by dissolving nitrogen in the N vacant site, so its formula is denoted α-U_2N_{3+x}. Masaki *et al.* [8] suggested that the crystal structure was modified from b.c.c. to f.c.c. in the vicinity of the composition $[N]/[U] = 1.75$, hinting at the existence of another nitride, U_4N_7 (CaF_2-type structure). However, our recent study [7] indicated that a nitrogen-rich α-U_2N_{3+x} phase ($1.75 < [N]/[U]$) had an Mn_2O_3-type structure like the nitrogen-poor α-U_2N_{3+x} phase ($[N]/[U] < 1.75$).

The nitrogen-poor α-U_2N_{3+x} can be prepared by the reaction of UH_3 or U-metal powder with N_2 at atmospheric pressure. The composition of the product varies with the reaction temperature and the partial pressure of N_2 gas. The *C–P–T* (composi-

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tion–pressure–temperature) relationships of the nitrogen-poor phase have been derived by equilibration of the product with N_2 gas over the temperature range 500–1000 °C in the pressure range up to 100 kPa [2,9–12,18]. The composition of the samples prepared in this way was measured as [N]/[U] = 1.50–1.75 [2,9–2,18]. Rundle *et al.* [2] stated that a high nitrogen pressure (more than 100 atm) should be required for the formation of nitrogen-rich α-U_2N_{3+x}.

However, it has been reported that α-U_2N_{3+x} with an N-to-U ratio of more than 1.75 can be prepared by the reaction employing NH_3 [13–17]. Trzebiatowski and Troc [13] prepared α-U_3N_{3+x} with a high nitrogen content up to [N]/[U] = 1.86 by the reaction of UH_3 and NH_3. Alire and McCrary [14] reported that α-U_2N_{3+x} could be prepared at 265–385 °C by the reaction between U and ND_3. Tagawa [16] studied the formation of the nitride using thermogravimetry and found that UH_3 could react with static NH_3 at 150 °C and the reaction rate became faster above 350 °C. These results indicate that uranium sesquinitride might be formed at 300 °C or less by the reaction of U with NH_3. In a previous study, Katsura and Serizawa [15] reported in this journal that α-U_2N_{3+x} with a high nitrogen content could be prepared at 250 and 300 °C by the reaction between U-metal and static NH_3. They discussed the role of unstable NH_3 in the nitride or hydride formation from a thermodynamic point of view. They concluded that the equilibrium nitrogen solubility of the nitride increased owing to the increase in the nitrogen activity of the gas phase which was in equilibrium with the solid phase [15].

In this study, we looked at two interesting aspects of the reaction. One is the sequence of the reaction between unstable NH_3 and U-metal. As mentioned above, NH_3 has the possibility to act as a hydriding agent. Thus, there must be at least two routes for nitride formation; one is a direct reaction between NH_3 and U-metal, and the other is the conversion of hydride to nitride. The reaction process was studied by X-ray diffraction (XRD) and composition analysis of the gas phase in the reaction system. The rate-determining step in the series of reactions is discussed. The other aspect is how to control the nitrogen activity in the reaction system. We shed light on the effect of variation in the partial pressure of H_2 of the reactant gas on the composition of the product.

2. Experimental details

2.1. Apparatus

The experimental arrangement shown in Fig. 1 consisted of a reaction system, a gas mixing system, a vacuum system and a gas analysis system. The reaction system contained a resistance furnace that comprised upper and lower halves. The upper portion of the furnace could be opened when the reaction was finished for effective cooling of the sample. The total pressure in the reaction system was measured by a capacitance manometer and an ionization gage. The gas mixing system involved a gas static mixer and a resistance furnace. The vacuum system had a turbomolecular pump and a rotary pump, by which the reaction system could be evacuated to 4×10^{-5} Pa. The inlet and outlet gases of the reaction system could be introduced to the gas analysis system, which was composed of a gaschromatograph with an automatic gas sampler and a digital integrator (Shimazu Co. Ltd., Kyoto, Japan).

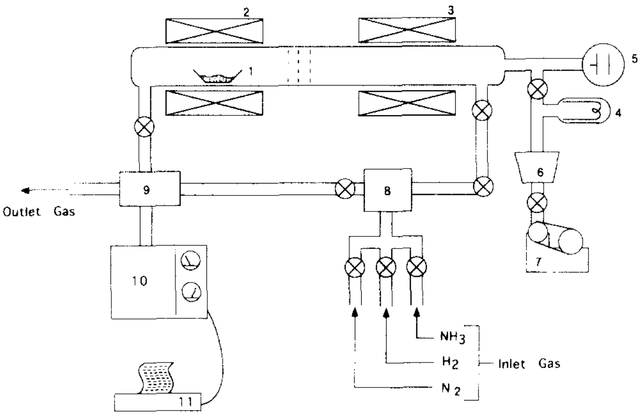

Fig. 1. Schematic diagram of the experimental arrangement: 1, sample; 2, 3, furnace; 4, ionization gage; 5, capacitance manometer; 6, turbomolecular pump; 7, rotary pump; 8, static gas mixer; 9, gas sampler; 10, gaschromatography; 11, digital integrator.

2.2. Procedures

2.2.1. Reaction of U-metal with ammonia

The uranium metal was freed from surface oxide by nitric acid treatment before use. After flushing the reaction tube with nitrogen, the boat carrying a sample that weighed about 0.5 g was pushed into the furnace. Heat treatment with hydrogen, which was purified by flowing through a liquid nitrogen trap, converted the metal chip to finely divided UH_3 powder. The UH_3 was decomposed again into U-metal by heating up to 600 °C. After the reaction system was evacuated, NH_3 gas was introduced and passed over the sample. The metal sample was converted to α-U_2N_{3+x} at 300 °C. During the reaction, the outlet gas was sampled intermittently and analyzed by the gaschromatograph. The partial pressures of NH_3, H_2 and N_2 gases were measured as a function of time. At the end of the heat treatment, the reaction system was evacuated again, and the sample was cooled quickly to room temperature. To clarify the reaction process, the products sampled in the course of the reaction were analyzed by XRD.

2.2.2. *Reaction of uranium hydride with gas mixture of ammonia and hydrogen*

The starting material UH_3 was prepared in situ by the reaction of U-metal and H_2 as described above. A stream of NH_3 and H_2 gas mixture was used as the reactant gas in this experiment. The gases were mixed with a gaseous blender and passed into the hot zone heated to 900 °C to confirm miscibility. The composition of the inlet gas mixture was checked by a gaschromatograph just before the experiment began and after it finished. The reaction was carried out at a constant temperature of 300 °C using gas mixtures of various compositions. The outlet gas was analyzed by the same method as described above to confirm the end of the reaction. The heat treatment was continued at least for 4 h after the variation in each partial pressure was diminished.

2.2.3. *X-ray diffraction study*

The α-U_2N_{3+x} samples prepared in this way were treated in a glove box with a high purity Ar atmosphere. The samples for XRD were prepared in the same way as described in Ref. [7]. The α-U_2N_{3+x} embedded in epoxy resin was analyzed using Cu Kα radiation monochromated by the (002) plane of graphite at room temperature. The diffraction pattern was analyzed using the Rietveld analysis program RIETAN described by Izumi [19], and the lattice parameter was evaluated. The [N]/[U] ratio was determined from the lattice parameters using the composition–lattice parameter relationship summarized in Ref. [7].

3. Results and discussion

3.1. *Reaction process*

When NH_3 gas is employed as a nitriding agent, the process of nitride formation is somewhat different from that using N_2 gas, because there is a possibility of NH_3 acting as a hydriding agent. Thus two types of reaction,

$$NH_3 \longrightarrow \text{N(in nitride)} + \tfrac{3}{2}H_2 \quad (1)$$

and

$$NH_3 \longrightarrow \text{3H(in hydride)} + \tfrac{1}{2}N_2 \quad (2)$$

might take place. In addition to these reactions, the unstable NH_3 gas tends to decompose into N_2 and H_2 gases as follows,

$$NH_3 \longrightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \quad (3)$$

The rate of dissociation expressed by Eq. (3), however, is very slow at low temperature, and the decomposition of NH_3 can be depressed effectively if NH_3 gas is used as a stream. Katsura and Serizawa [15] carried out the reaction between a U-metal chip and static NH_3 in a closed system at 300 °C and discussed the formation of nitride and hydride. However, the reaction process that occurred in the closed system was complicated because the reaction products, H_2 and N_2 gases, remained in the reaction system, causing the composition of the gas phase to change continuously during the reaction. Therefore, the activities of nitrogen and hydrogen of the gas phase varied dramatically with time [1,15]. This complexity in the analysis of the reaction process can be circumvented by using the flowing method, where pure NH_3 gas is always supplied to the sample, and the gases produced by the reaction are successfully removed from the reaction system.

To examine the reaction process at low temperature, powdered U-metal was reacted with a stream of NH_3 gas at 300 °C. Prior to the experiment with a sample, the degree of NH_3 dissociation on the inner wall surface of the reaction tube was examined. The boat without a metal sample was loaded into the reaction tube, and pure NH_3 gas was introduced into the reaction system at a flow rate of 100 $cm^3\ min^{-1}$. The outlet gas from the reaction system was sampled and the composition was analyzed by the gaschromatograph. In this run, however, no N_2 or H_2 due to the dissociation of NH_3 was observed in the outlet gas. Thus it was confirmed that any H_2 and N_2 gases observed in the reaction experiment were attributable only to the interaction between the inlet gas and the sample.

The results of the gas analysis recorded during the reaction experiment are shown in Fig. 2, where P_{NH3}, P_{H2} and P_{N2} of the outlet gas are given as a function of the reaction time. As can be seen in the figure, the reaction process can be divided into three steps, (A),

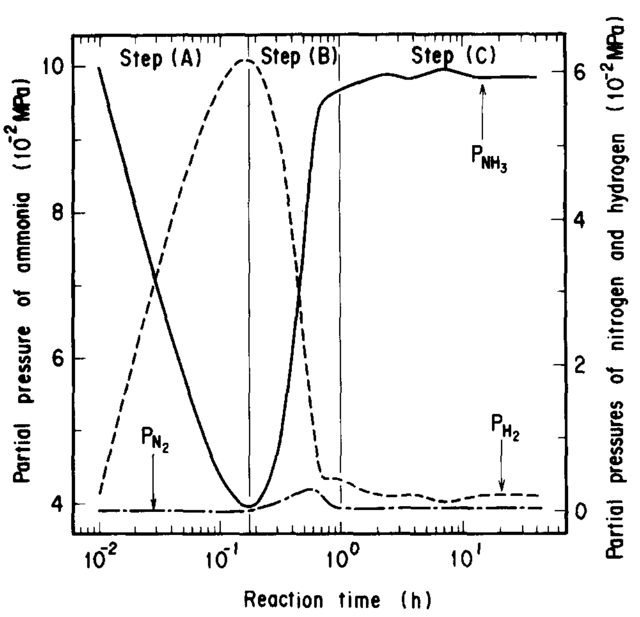

Fig. 2. Variations in P_{NH3}, P_{H2} and P_{N2} with time in the reaction between U and NH_3: —— P_{NH3}, - - - P_{H2}, —·— P_{N2}.

(B) and (C). The variation in the product with time, which was analyzed by XRD, is summarized in Table 1. The reaction process can be estimated from these results.

In the initial part of the reaction, step (A), the partial pressures of NH_3 and H_2 in the gas phase varied simultaneously; P_{NH3} dropped and P_{H2} increased rapidly. However, the partial pressure of N_2 was very low, indicating that the formation of uranium nitride expressed by Eq. (1) might have occurred primarily. The product obtained in this step consisted of U-metal, α-U_2N_{3+x} and a small amount of UH_3. In step (B), a temporary increase in P_{N2} was clearly observed in addition to the variations in P_{NH3} and P_{H2}. Although the increase in P_{N2} seemed to show the formation of UH_3, the XRD peak intensity of UH_3, given in Table 1, was less intense compared with that observed in the former step, which indicated a decrease in the amount of UH_3. Thus, N_2 gas detected in this step should arise from the dissociation of NH_3. In step (C), the UH_3 detected in steps (A) and (B) was completely converted to U_2N_{3+x}. Then the variation in the curves of each partial-pressure leveled off and a plateau appeared in the curve, indicating that no reactions between the solid and the gas phase progressed thereafter. As can be seen in the figure, small amounts of N_2 and H_2 gases were constantly detected during step (C). These gases are considered to derive from the dissociation of NH_3 on the surface of the specimen, because the partial pressure ratio between these gases, P_{N2}/P_{H2} is about 1/3.

The reaction sequence of nitride formation is summarized in Fig. 3, where steps (A), (B) and (C) are equivalent to those shown in Fig. 2. There may be two reaction flows for the formation of α-U_2N_{3+x}. In step (A), the formation of UH_3 was observed simultaneously along with that of α-U_2N_{3+x}. These reactions are designated reactions (β) and (α) respectively in the figure. In addition to these reactions, reaction (γ), which was distinctly observed in steps (B) and (C) might also be occurring. However, if reaction (γ) took precedence over the other reactions (α) and (β), the formation of UH_3 shown in Table 1 should not be observed. Therefore, the reaction of UH_3 with NH_3 is considered not to be the principal process of nitride formation in this step; reaction (γ) proceeds slowly following reaction (β). In steps (B) and (C) where no metallic U remains, it might be deduced that the conversion of hydride to nitride is the main reaction, which implies that nitride formation by the reaction between hydride and NH_3 is the rate-determining step in the reaction process. Katsura and Serizawa [15] previously reported that the rate of the reaction between UH_3 and NH_3 is slow and more than 20 h is required to complete the reaction. However, the reaction rate was considerably faster in the present experiment, and the reaction proceeded easily. This difference might be due to the difference in particle size of the solid specimen, which was an important factor in the discussion of the reaction rate.

In all steps, the dissociation equilibrium of NH_3 was not attained, meaning that the gas phase was in an unstable state. The uranium sesquinitride observed in each step was nitrogen rich α-U_2N_{3+x} which cannot be produced by the reaction using N_2 gas at normal pressure. Although the reaction temperature was relatively low, the reaction between the solid and gas phases proceeded rapidly; the product at the last step consisted only of α-U_2N_{3+x}. It should be noted that the reaction between U-metal and N_2 gas is not appreciable at 300 °C, even if the reaction time is extended to 1 or 2 weeks [15]. This fact indicates that the reaction rate can be accelerated by using an unstable nitriding agent that shows high nitrogen activity.

3.2. *Effect of hydrogen gas on nitride formation*

As described above, the gas phase in the reaction system was thermodynamically in an unstable state with respect to the decomposition of NH_3, which is the most important and interesting factor in this study. Katsura [1] has mentioned the high nitrogen activity that arose from the thermodynamic instability of NH_3. He showed that the nitrogen activity a_N for the unstable gas mixture of NH_3, H_2 and N_2 can be evaluated from the following equation,

$$a_N = P_{NH3}/K_P P_{H2}^{3/2} \tag{4}$$

Table 1
Characterization of the samples prepared by the reaction of U metal with NH_3

Temperature (°C)	Reactant gas	Reaction time (h)	XRD intensity of products		
			U	UH_3	U_2N_{3+x}
300	NH_3	0.13	+ + +	+ + +	+ + + + +
300	NH_3	0.5	–	+ +	+ + + + +
300	NH_3	1.0	–	+	+ + + + +
300	NH_3	48	–	–	+ + + + +

+ very weak; + + weak; + + + medium; + + + + + strong.

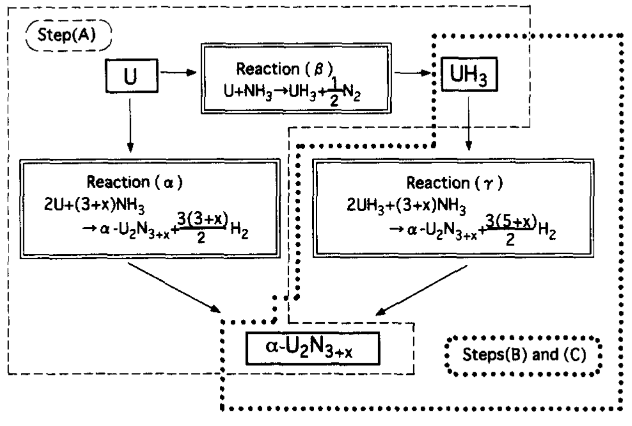

Fig. 3. Reaction sequence of nitride formation.

where K_P is the equilibrium constant of the dissociation of NH_3. a_N is a function only of P_{NH3}, P_{H2} and the temperature. It is interesting that a_N does not depend on the partial pressure of N_2 gas, even though this gas coexists in the reactant gas phase. It should be emphasized that Eq. (4) suggests the possibility of regulation of the nitrogen activity by changing P_{NH3} and P_{H2} at an arbitrary temperature and pressure. In order to confirm how P_{H2} affects the nitrogen activity of the gas phase, the reactions at 300 °C were carried out again using a gas mixture of NH_3 and H_2 gases. In this experiment, UH_3 was selected as the starting material instead of metallic U.

The effect of P_{H2} on the reaction was examined by varying the composition of the inlet gas. The experimental conditions and the results of XRD measurement of the product in each run are given in Table 2. All of the products were entirely α-U_2N_{3+x}. The changes in P_{NH3}, P_{H2} and P_{N2} with reaction time recorded in RUN-(1) are given in Fig. 4 as a typical result. In the figure, the pressure variation curves are divided into two regions, (D) and (E). The decrease in P_{NH3} and the increase in P_{H2} in step (D) show the conversion of UH_3 to α-U_2N_{3+x} by reaction (γ) in Fig. 3. As can be seen in Fig. 4, the reaction was completely finished within about 400 min. In step (E), a stationary state was attained between the solid phase and the gas phase. The calculated nitrogen activity a_N in the last step (E) is also given in Table 2 together with the [N]/[U] atomic ratio estimated from the lattice parameter [7]. It was confirmed that the nitrogen content of α-U_2N_{3+x} increased with increasing a_N. As already mentioned, reactions between the solid phase and the gas phase do not proceed in step (E). Therefore, the nitrogen activity of the gas phase a_N in Table 2 should be exactly equal to that in the solid phase. Although there are no available data to compare with the results in the present study, the activity of nitrogen in α-U_2N_{3+x} unquestionably increases with increasing nitrogen content when the temperature is held constant. Thus, this result shows that the nitrogen activity of the NH_3–H_2 gas mixture depends on the composition of the gas phase and decreases with increasing partial pressure of H_2 gas.

It should be emphasized that our results suggest another interesting possibility of obtaining hitherto unknown thermodynamic information on the metallic nitride. Thus far, some thermodynamic data on α-U_2N_{3+x} phase have been reported. They are, however, limited to phases with low nitrogen content ([N]/[U] < 1.70) in a relatively high temperature range (500 °C < T) [2,9–12,18]. As can be seen from our results, use of the unstable gas phase enables us to accelerate the formation of α-U_2N_{3+x} even at the low temperature of 300 °C, where the nitriding reaction using N_2 gas does not proceed. If a_N of the gas phase could be successfully controlled, which is the case in the present study, we would be able to prepare C–P–T relationships at such low temperatures using the relation $a_N = P_{N2}^{1/2}$. The C–P curve at 300 °C evaluated in this way is given in Fig. 5.

4. Conclusions

The formation of α-U_2N_{3+x} by the reaction of U with unstable NH_3 was studied from the standpoint of the reaction process and the instability of the gas phase.

NH_3 gas acted as both a hydriding and a nitriding agent at 300 °C. It was confirmed that there were two

Table 2
Results of reaction between UH_3 and NH_3–H_2 gas mixture

Experiment	Temperature (°C)	Partial pressure (kPa)		Γ_N [a]	Activity of nitrogen a_N	Lattice constant (nm)	[N]/[U] ratio
		P_{NH3}	P_{H2}				
RUN-(1)	300	9.20	97.5	9.62×10^{-2}	1.30	1.0624	1.79(0)
RUN-(2)	300	30.3	74.0	4.79×10^{-1}	6.48	1.0610	1.81(5)
RUN-(3)	300	56.0	50.7	1.56	21.2	1.0600	1.83(5)
RUN-(4)	300	68.9	36.3	3.18	43.0	1.0592	1.84(5)

[a] Γ_N is $P_{NH3}/P_{H2}^{3/2}$ in atmospheric units.

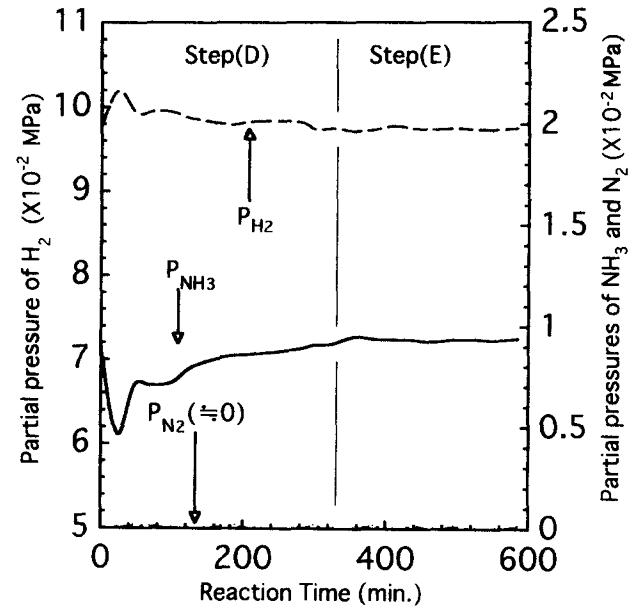

Fig. 4. Variations in P_{NH3}, P_{H2} and P_{N2} with time in the reaction between UH_3 and gas mixture of NH_3 and H_2: —— P_{NH3}, – – – P_{H2}, – · – P_{N2}.

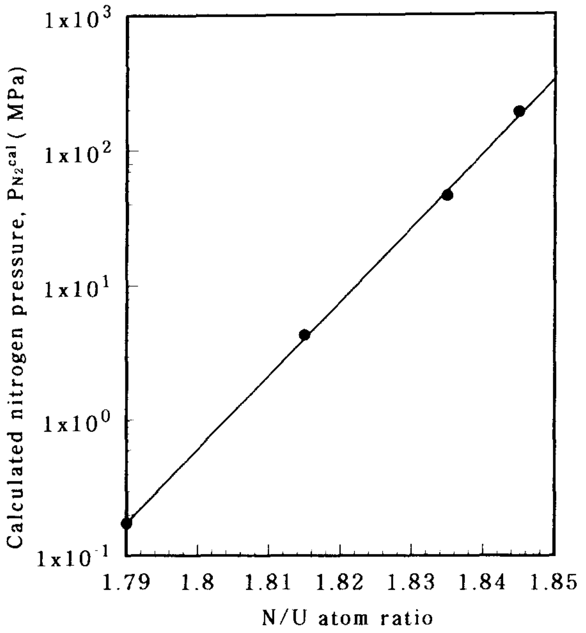

Fig. 5. Composition–pressure curve of α-U_2N_{3+x} at 300 °C.

routes in the process of nitride formation. One route was the direct reaction between NH_3 and U-metal to form α-Uj_2N_{3+x}. The other was the formation of UH_3 and conversion to α-U_2N_{3+x}. In the series of reactions, the formation of α-U_2N_{3+x} and UH_3 proceeded almost simultaneously, whereas the rate of the reaction between UH_3 and NH_3 was slow compared with the other two reactions. This result indicates that the conversion of UH_3 to nitride was the rate-determining step in the reaction process.

The reaction between UH_3 and a gas mixture of NH_3 and H_2 was examined. It was found that the nitrogen content of α-U_2N_{3+x} varied with the partial pressure of H_2, which meant that the nitrogen activity in the gas phase depended on its composition, as pointed out by theoretical consideration. The results in the present study also suggested that the nitrogen activity could be regulated successfully by controlling the composition of the inlet gas. This is a useful and interesting aspect of nitride formation using an unstable gas phase.

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