Journal of Alloys and Compounds, 187 (1992) 389–399
JALCOM 330

Formation of a nitrogen-rich α-U_2N_{3+x} phase by the reaction of uranium with a stream of ammonia

Masahiro Katsura
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, 565 Yamadaoka 2-1, Suita, Osaka (Japan)

and Hiroyuki Serizawa
Japan Atomic Energy Research Institute, Department of Fuels and Materials Research, 319-11 Tokai-mura, Naka-gun, Ibaraki-ken (Japan)

(Received April 2, 1992; in final form April 13, 1992)

Abstract

The reactions $U + NH_3$(stream) and $U + N_2$(stream) were performed in the temperature range from 400 to 800 °C. The results show that the use of a stream of NH_3 leads to the formation of nitrogen-rich uranium sesquinitrides, which cannot be obtained by the reactions of uranium with N_2 under normal pressures, suggesting that a stream of NH_3 possesses higher nitrogen activity compared with N_2 at 1 atm. The experimental results were analysed on the basis of thermodynamic considerations. It was found that enormously high nitrogen pressures would be required to obtain nitrogen-rich uranium sesquinitride as prepared by the reaction of uranium with a stream of NH_3 if one tried to prepare this material by the reaction of uranium with N_2.

1. Introduction

It is now generally admitted that, in the binary uranium–nitrogen system, there exist four compounds, uranium mononitride (UN), α-uranium sesquinitride (α-U_2N_3), β-uranium sesquinitride (β-U_2N_3) and uranium dinitride (UN_2). The structure of UN is NaCl-type f.c.c. Although both α-U_2N_3 and β-U_2N_3 are termed uranium sesquinitride, they are different compounds: α-U_2N_3 crystallizes in an Mn_2O_3 b.c.c. structure and β-U_2N_3 possesses an La_2O_3-type h.c.p. structure. The structure of UN_2 is CaF_2-type f.c.c. Although α-U_2N_3 and UN_2 are crystallographically dissimilar, α-U_2N_3 may be regarded as a derivation from the fluorite type of structure, by removal of nitrogen atoms from the UN_2 lattice in a regular way, resulting in a distorted CaF_2 structure. This means that there exists a solid solubility between α-U_2N_3 and UN_2, and nitrides in this range may be expressed by a chemical formula α-U_2N_{3+x} ($0 \leqslant x \leqslant 1$). However, as claimed by some workers, the existence of stoichiometric UN_2 still remains in doubt. Even though UN_2 could exist in the U–N system, its preparation would require an enormously high nitrogen pressure.

α-U_2N_{3+x} is usually prepared by the reaction of metallic uranium or UH_3 with N_2 gas at normal pressure. The *P–T–C* (equilibrium nitrogen pres-

0925-8388/92/$5.00

sure–temperature–composition) relationships have been obtained by equilibrating α-U_2N_{3+x} prepared by the reaction between uranium and N_2 with nitrogen gas in the pressure range from 13.3 Pa (10^{-2} Torr) to 100 kPa (760 Torr) by several workers [1–5]. The measured composition of α-U_2N_{3+x} lies between N:U = 1.53 and N:U = 1.70. The N:U ratio of α-U_2N_{3+x} is determined uniquely for given temperature T and nitrogen pressure P_{N_2}. At a fixed temperature, the N:U ratio tends to increase as P_{N_2} is increased. This feature is understood to suggest that nitrogen activity a_N is raised by enhancing P_{N_2} and, as the consequence, the N:U ratio is increased.

Although Rundle *et al.* [6] stated that the formation of UN_2 required high nitrogen pressure (126 atm), Didchenko and Gortsema [7] reported that UN_2 could be easily prepared by passing NH_3 over UH_3 while raising the temperature to 1000 °C. Trzebiatowski and Troc [8] prepared α-U_2N_{3+x} with N:U ratios from 1.5 to 1.86 by various methods. The nitrides of N:U ratios from 1.5 to 1.71 were prepared by treating uranium powder with N_2. However, uranium nitrides of higher nitrogen content up to $UN_{1.86}$ could be obtained solely by the action of ammonia on UH_3. According to Berthold and Delliehausen [9], the reactions of UN or α-U_2N_{3+x} with $N:U < 1.76$ with N_2 or NH_3 at pressures up to 200 atm could lead to the formation of $UN_{1.83}$ (in the case of N_2) or $UN_{1.86}$ (in the case of NH_3). They also reported that a stable uranium nitride $UN_{1.90\pm0.02}$ could be prepared by the reaction of UF_4 with a stream of NH_3.

All the results mentioned above may suggest that the uranium nitrides having N:U ratios above 1.80 can be obtained only by the action of high nitrogen pressure or by use of a stream of NH_3. Katsura [10] has carried out a thermodynamic analysis to elucidate why flowing NH_3 can possess extremely high nitrogen activities and he has shown that the nitrogen activity exhibited by flowing NH_3 may be controlled by $P_{NH_3}/P_{H_2}{}^{3/2}$. He has also carried out some preliminary reaction experiments giving support to the theoretical analysis. Very recently, Katsura [11] has reported in this journal a more detailed thermodynamic study of nitride and hydride formation by the reaction of metals with NH_3 and derived the relation $a_N = (1/K_P)P_{NH_3}/P_{H_2}{}^{3/2}$, where a_N is the activity of nitrogen dissolved in α-U_2N_{3+x} or, equivalently, that exhibited by flowing gas mixture and K_P the equilibrium constant for $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$.

By passing NH_3 through a region held at high temperatures, a state where the dissociation equilibrium $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ is not reached may be produced. However, a fraction of NH_3 inevitably decomposes into N_2 and H_2 by catalytic action of the specimen and the wall of the reaction tube. The extent of dissociation of NH_3 into N_2 and H_2 also depends on the flow rate of a stream of NH_3. Since, at a given temperature, the composition of uranium nitride is determined by the nitrogen activity of the gaseous atmosphere to which the nitride is exposed, it is by all means necessary to know the value of $P_{NH_3}/P_{H_2}{}^{3/2}$, which determines the nitrogen activity of the gaseous phase. Consequently, in dealing thermodynamically with the reaction of uranium with flowing NH_3, the composition of the gaseous phase participating in the reaction must be experimentally determined. This point has received so far totally inadequate consideration in the literature. Those who have prepared nitrogen-rich α-U_2N_{3+x} have not given a clear specification of their experimental conditions, and hence the comparison between the results reported by these researchers may not furnish much information as to the thermodynamics of nitrogen-rich uranium sesquinitride formation. For example, none of these workers have analysed the outlet gas. Therefore, their results cannot be used as a basis for theoretical analyses. In order to know how the composition of α-U_2N_{3+x} prepared by use of a stream of NH_3 depends on the relative amounts of NH_3 and H_2 in the gas stream, analysis of the outlet gas should be carried out.

Although a stream of NH_3 has also been used as a nitriding agent to prepare metal nitrides such as Fe_2N, Fe_4N and MoN, little systematic experimental work has been carried out to study how high nitrogen activity can be provided by flowing NH_3 compared with N_2 under normal pressures. In performing the experiments of the reaction of a metal with a stream of NH_3, the situation is further complicated by the fact that different results may be obtained even under the same conditions of temperature and flow rate unless all the other conditions are the same, including the surface properties and the diameter of the reaction tube, temperature distribution throughout the tube, and the amount and particle sizes of the specimen etc., since the extent of dissociation may also be influenced by all these conditions.

In this work, the reaction of uranium with a stream of NH_3 was carried out in the temperature range from 400 to 800 °C, the composition of the outlet gas being analysed by gas chromatography. Also, for comparison, the reaction of uranium with flowing nitrogen gas (100 kPa $\approx$ 1 atm) was performed in the same temperature range using the same apparatus, since it is felt helpful to have some idea of how the high N:U ratio of α-U_2N_{3+x} can be obtained by the reaction of uranium with a stream of NH_3 compared with that obtained by the reaction of uranium with N_2 at 1 atm carried out in the same apparatus. In this way, the comparison between the reactions $U+NH_3$(stream) and $U+N_2$ becomes possible under the same conditions of temperature, temperature distribution, flow rate, and the geometric construction of the whole system.

It was found from these experiments that the nitrogen content of α-U_2N_{3+x} obtained by the reaction $U+NH_3$ was much higher than that of α-U_2N_{3+x} resulting from the reaction $U+N_2$. These results clearly indicate that the nitrogen activity exhibited by a stream of NH_3 is extremely higher than that of N_2 at 100 kPa (1 atm).

Further, the temperature dependence of the extent of dissociation of NH_3 was examined at a flow rate of 50 ml min^{-1}.

It is also interesting to estimate how high a pressure of N_2 would be required to obtain nitrogen-rich α-U_2N_{3+x} as prepared by the reaction of uranium with a stream of NH_3. For this purpose, the theoretical analysis developed by Katsura [11] was applied to the present experimental results. Also, the thermodynamic quantities for α-U_2N_{3+x} (N:U = 1.54–1.64) given by

Bugl and Bauer [1] were extrapolated to higher N:U ratios and the nitrogen pressures required for obtaining nitrogen-rich α-U_2N_{3+x} were roughly estimated.

2. Experimental details

2.1. *Apparatus and materials*

The experimental apparatus used in this work consists of a vacuum system, a gas supply system, a resistance furnace, and a gas chromatography system. The vacuum system consists of three rotary pumps and an oil diffusion pump, by which the whole system can be evacuated to 1.3×10^{-4} Pa (1×10^{-6} Torr). The gas supply system involves a mercury bubbler and flowmeters. The pressure was measured by means of a mercury manometer. The reaction tube made of quartz was 20 mm in diameter and 450 mm in length. The tube was fitted into the cylindrical resistance furnace.

Temperature was measured by a CA thermocouple placed into the quartz tube, the rear end of which was located as close as possible to the specimen. The temperature was controlled by an on–off type of thermoregulator.

The gas chromatography system consisted of a gas chromatograph (type GC-3BT, Shimazu Co. Ltd., Kyoto, Japan), a gas sampler (type MGS gas sampler, Shimazu Co. Ltd., Kyoto, Japan), and an autorecorder manufactured for the present gas chromatograph. PORAPACK Q (mesh 80–100) was packed in the column. Helium gas with purity of 99.999% was used as the carrier gas.

The gases employed in this work, NH_3 (99.99%), H_2 (99.9995%), and N_2 (99.9995%), were supplied from commercial gas cylinders and were fed into the system through stainless steel capillaries without further purification. A metallic uranium ingot was supplied from Japan Power Reactor and Nuclear Development Corporation. The nominal impurities are listed in Table 1.

TABLE 1

Impurities in the starting uranium metal

Element	Concentration (ppm)	Element	Concentration (ppm)
Ag	< 0.2	Al	4
B	< 0.1	Cd	< 0.2
Co	< 5	Cr	8
Cu	< 3	Fe	7
Mg	< 2	Mn	< 3
Ni	2	Si	5
V	< 10	Zr	< 50
C	< 30	N	7
Li	< 1	K	< 1

2.2. *Procedure*

2.2.1. *Measurement of the extent of dissociation of flowing NH_3*

The extent of dissociation of flowing NH_3 was measured as a function of temperature and flow rate. After the system was evacuated to about 1.3×10^{-4} Pa at room temperature, NH_3 gas was introduced and passed through the reaction tube, in which no uranium metal specimen was placed. The flow rate was kept at 50 ml min^{-1} by the flowmeter. The extent of dissociation of NH_3 into H_2 and N_2 was measured at intervals of several minutes until a constant value of the extent was obtained. The temperature dependence of the extent of dissociation was examined in the temperature range from 300 to 900 °C. Similar measurements were also made in the case where an α-U_2N_{3+x} sample was placed in the centre of the reaction tube.

2.2.2. *Reaction of metallic uranium with a stream of NH_3*

About 0.2 g of a bright metallic uranium chip was leached in 6 N HNO_3 for about 2 h and washed with water and 2-butyl alcohol. Then it was weighed accurately before being brought into the reaction system. A quartz boat containing the thus pre-treated specimen was placed in the centre of the reaction tube and the system was evacuated to about 1.3×10^{-4} Pa at room temperature. Hydrogen gas was admitted into the reaction tube up to about 40 kPa (300 Torr). Uranium metal was converted to the hydride, UH_3, at 235 °C, and temperature was raised to 600 °C to form finely powdered uranium. After evacuation of the system, the sample was cooled to room temperature. Then, NH_3 gas was constantly supplied into the reaction tube at a flow rate of 50 ml min^{-1} and the temperature was increased to the desired value. The reaction experiments were performed in the temperature range from 400 to 800 °C for 5 h. The extent of dissociation was determined by the gas analysis of the outlet gas. The specimen was quenched to room temperature after the system was evacuated by a rotary pump at the experimental temperature. The reactions of uranium powder with a stream of N_2 were also carried out under the same conditions. In order to ascertain the establishment of the equilibrium for the case of the reaction of uranium with N_2, nitrogen gas was passed over a sample of powdered uranium held at 500 °C. The system was closed at intervals of 1 h to make the system a closed system and the pressure change with time was checked. It was found that 4 h was enough to attain equilibrium at 500 °C. From this experimental result, a reaction time of 5 h was selected for all the experiments performed in this work, except for the reaction of $U+N_2$ at 400 °C.

2.2.3. *X-ray analysis and determination of the N:U ratio of α-U_2N_{3+x}*

The X-ray diffraction powder patterns of the reaction products were obtained at room temperature with a diffractometer (Rigaku Denki; Geiger flex rad-rA) using crystal-monochromatized Cu Kα radiation. The reaction product was embedded in an aluminium sample holder with an epoxy resin in order to avoid the oxidation of the specimen during X-ray diffraction.

From the X-ray diffraction patterns obtained, the phases were identified. When the identified phase was α-U_2N_{3+x} only, the lattice parameter of α-U_2N_{3+x} was calculated, and the N:U ratio was determined from the relation between the lattice parameter value and N:U ratio of α-U_2N_{3+x} reported by Tagawa [12].

3. Results and discussion

In order to examine the temperature dependence of the extent of dissociation, NH_3 was passed at a flow rate of 50 ml min^{-1} through the reaction tube in which a temperature distribution was maintained. The extent of dissociation was studied as a function of the highest temperature in the reaction tube in the range from 400 to 900 °C. The results are shown in Fig. 1. In the case where no α-U_2N_{3+x} sample was placed in the reaction tube, no noticeable dissociation was observed up to 700 °C, although the equilibrium degree of dissociation of NH_3 exceeds 99.0% at 400 °C and 99.9% at 700 °C respectively. An appreciable dissociation of NH_3 was first observed at 750 °C and the extent of dissociation becomes about 43% at 900 °C, but these values of the extent of dissociation are much less than the equilibrium degree of dissociation for the corresponding temperatures. Thus, even at a very high temperature such as 900 °C, the dissociation of NH_3 can be suppressed to a great extent. On the contrary, when the α-U_2N_{3+x} sample was placed in the hottest region of the reaction tube, the dissociation occurred even at 400 °C. As can be seen in Fig. 1, the extent of dissociation is much higher at each temperature compared with the case

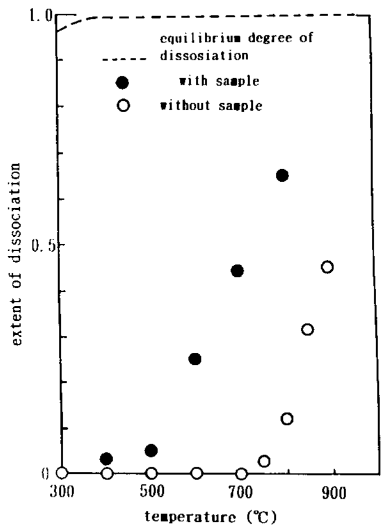

Fig. 1. The extent of dissociation of NH_3 as a function of temperature at a flow rate of 50 ml min^{-1}.

of flowing NH_3 in the reaction tube without any α-U_2N_{3+x} sample in it. The powdered α-U_2N_{3+x} sample may act as a catalyst for the decomposition of NH_3 into N_2 and H_2. Nevertheless, the extent of dissociation is still lower than the equilibrium degree of dissociation. Thus, the suppression of the dissociation of NH_3 may be possible by the use of flowing NH_3 even in the case where the α-U_2N_{3+x} sample is inserted in the hottest zone of the reaction tube in the temperature range examined.

As can be seen from Table 2, where the present experimental results are summarized, the N:U ratio of the α-U_2N_{3+x} phase obtained from the reaction of uranium with a stream of NH_3 is higher than that resulting from the reaction $U+N_2$ if compared at the same temperature, suggesting that the nitrogen activity of a stream of NH_3 is higher than that of N_2 at 100 kPa (1 atm).

Also, as can be seen from the X-ray diffraction pattern, as shown in Fig. 2(a), for the product obtained at 400 °C, the reaction of uranium with flowing NH_3 can provide a homogeneous α-U_2N_{3+x} phase with a high N:U ratio such as 1.83. On the contrary, the X-ray diffraction pattern (Fig. 2(b)) for the product of the reaction $U+N_2$ at 400 °C reveals that it consists of metallic uranium, α-U_2N_{3+x}, and UN, indicating that the reaction $U+N_2$ is not completed within 10 h. These results obtained at 400 °C may suggest that NH_3 is much more favourable as a nitriding agent than N_2. Specifically, when the formation of a metal nitride by use of N_2 at low temperatures is difficult, the use of NH_3 instead of N_2 might provide a method for preparing the nitride.

When NH_3 is being supplied constantly as a stream through a hot zone held at a high temperature where a powdered uranium sample is placed, the nitridation reaction may proceed in parallel with the catalytic decomposition of NH_3 until a steady state is reached where the partial pressures of NH_3,

TABLE 2

Experimental results of the reaction of uranium with flowing NH_3 and those of uranium with N_2; estimated nitrogen activity a_N and estimated P_{N_2} values

Reaction	Temperature (°C)	Time (h)	Lattice parameter (Å)	N:U ratio of formed U_2N_3	a_N	P_{N_2} (atm)
$U+NH_3$	400	5	10.591	1.83	4.3×10^3	1.8×10^7
	500	5	10.615	1.80	1.2×10^4	1.4×10^8
	600	5	10.629	1.76	2.7×10^3	7.3×10^6
	700	5	10.644	1.71	2.0×10^3	4.0×10^6
	800	5	10.651	1.68	1.3×10^3	1.7×10^6
$U+N_2$	400	10	–[a]		1	1
	500	5	10.635	1.74	1	1
	600	5	10.648	1.69	1	1
	700	5	10.663	1.63	1	1
	800	5	10.670	1.60	1	1

[a] $U+U_2N_3+UN$ (the reaction is not completed).

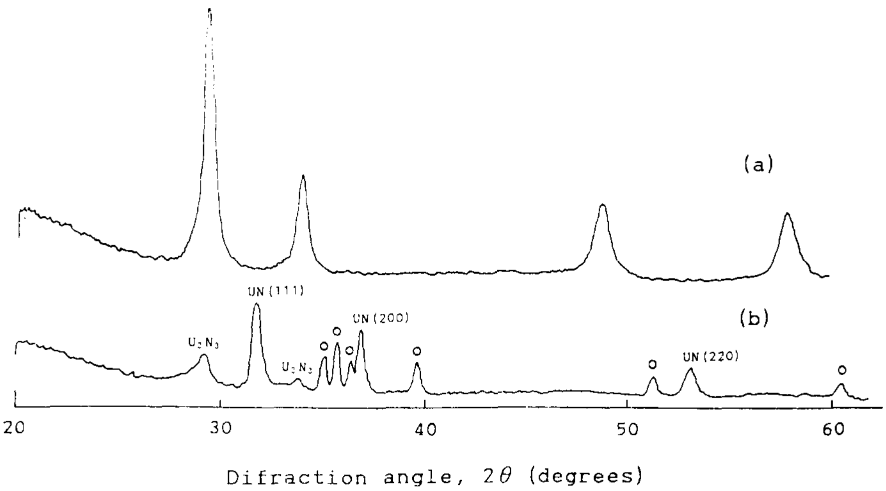

Fig. 2. X-ray diffraction patterns for (a) the product of the reaction of $U+NH_3$ at 400 °C and for (b) the products of the reaction of $U+N_2$ at 400 °C (○, diffraction peaks for uranium).

H_2, and N_2 and the composition of α-U_2N_{3+x} are all uniquely determined. It should be emphasized, however, that the gas phase is constrained to an unstable non-equilibrium state with respect to the dissociation equilibrium $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$ by flowing NH_3. The gas phase contains two kinds of nitriding agents; one is N_2 and the other is NH_3 as a nitrogen-bearing species. The formation of α-U_2N_{3+x} by action of N_2 may be expressed as

$$\tfrac{1}{2}N_2 \longrightarrow N \text{ (in } \alpha\text{-}U_2N_{3+x}) \qquad (1)$$

while the nitride formation by NH_3 may be written as follows:

$$NH_3 \longrightarrow N \text{ (in } \alpha\text{-}U_2N_{3+x}) + \tfrac{3}{2}H_2 \qquad (2)$$

If, in the case of the reaction of uranium with flowing NH_3 at a given temperature, α-U_2N_{3+x} were formed by the action of N_2 present in the flowing gas, the N:U ratio of the formed α-U_2N_{3+x} would be less than that of α-U_2N_{3+x} obtained by the reaction of uranium with a stream of N_2 (1 atm) at the same temperature, since the partial pressure of N_2 in the gas mixture prepared by flowing NH_3 is always lower than 1 atm. However, as clarified by the present experiments, this is not the case. It is, therefore, concluded that, under NH_3 flow, nitrogen-rich α-U_2N_{3+x} is formed according to reaction (2).

Katsura [11] has derived the following equation expressing the nitrogen activity a_N exhibited by flowing NH_3 on the basis of eqn. (2):

$$a_N = \frac{1}{K_p} \frac{P_{NH_3}}{P_{H_2}{}^{3/2}} \qquad (3)$$

where P_{NH_3} and P_{H_2} are partial pressures of NH_3 and H_2 respectively measured in atmospheres. This equation implies that, if higher values of $P_{NH_3}/P_{H_2}{}^{3/2}$

are obtained, then a higher nitrogen activity is attainable. The value of $P_{NH_3}/P_{H_2}{}^{3/2}$ for the gas mixture of NH_3, H_2, and N_2 prepared by flowing NH_3 must be larger than the corresponding value at the dissociation equilibrium since P_{NH_3} is higher than the equilibrium NH_3 partial pressure $P_{NH_3}{}^{eq}$, P_{H_2} is lower than the equilibrium hydrogen partial pressure $P_{H_2}{}^{eq}$, and K_P is a constant at a given temperature. As demonstrated by the present work, it is possible to maintain the extent of dissociation of NH_3 well below the equilibrium degree of dissociation even in the presence of α-U_2N_{3+x} (see Fig. 1). High instabilities of flowing NH_3 may provide high nitrogen activities and the value of $P_{NH_3}/P_{H_2}{}^{3/2}$ may be regarded as a measure of the instability.

The values of a_N calculated using eqn. (3) from the present experimental data at each temperature are also given in Table 2. Apparently, the nitrogen activity of flowing NH_3 is much higher than that of N_2 at 1 atm.

Strictly speaking, the nitriding ability of nitrogen-bearing species must be discussed in terms of nitrogen activity. However, the concept of activity is much less appealing to our sense of perception than that of pressure. In order to assess the order of magnitude of P_{N_2} required for the preparation of nitrogen-rich α-U_2N_{3+x} as obtained by use of a stream of NH_3, a rough estimate was performed using the approximate relation $a_N = P_{N_2}{}^{1/2}$. The estimated nitrogen pressures are also summarized in Table 2. Strictly, the relation $a_N = P_{N_2}{}^{1/2}$ is only valid in the pressure range where N_2 behaves ideally. Nevertheless, the present rough estimation might imply that an enormously high nitrogen pressure of the order of 10^6–10^7 atm would be required if one were to try to prepare nitrogen-rich α-U_2N_{3+x} as prepared by the use of a stream of NH_3. Special stress or importance should not be attached to physical effects such as an extremely high hydrostatic pressure, but the nitriding abilities arising from high P_{N_2} should be emphasized.

Bugl and Bauer [1] calculated the partial molar enthalpy $\overline{\Delta H}$ and partial molar entropy $\overline{\Delta S}$ for the solution of nitrogen in α-U_2N_{3+x} for several values of the N:U ratio on the basis of their own experimental results, which are summarized in Table 3. The solution of nitrogen in α-U_2N_{3+x} can be expressed as follows:

$$U_2N_{3+x} + (\Delta x/2)N_2 \longrightarrow U_2N_{3+x+\Delta x} \qquad (4)$$

This equation expresses that $\Delta x/2$ mol of N_2 dissolves into α-U_2N_{3+x} and α-$U_2N_{3+x+\Delta x}$ forms. At equilibrium, the following relation must hold:

$$\Delta G_f{}^\circ(U_2N_{3+x}) + (\Delta x/2)RT \ln P_{N_2} = \Delta G_f{}^\circ(U_2N_{3+x+\Delta x}) \qquad (5)$$

where $\Delta G_f{}^\circ(U_2N_{3+x})$ and $\Delta G_f{}^\circ(U_2N_{3+x+\Delta x})$ are the standard free energies of formation of α-U_2N_{3+x} and α-$U_2N_{3+x+\Delta x}$ respectively. The relation expressing true equilibrium is obtained by the condition $\Delta x \to 0$. Using Taylor's expansion and retaining only the first-order term in the limit $\Delta x \to 0$, the right-hand term of eqn. (5) may be written as

$$\Delta G_f{}^\circ(U_2N_{3+x+\Delta x}) = \Delta G_f{}^\circ(U_2N_{3+x}) + (\partial\, \Delta G_f{}^\circ(U_2N_{3+x})/\partial x)\, \Delta x \qquad (6)$$

Substitution of eqn. (6) into eqn. (5) gives the following equation:

TABLE 3

Values of the partial molar enthalpy and entropy for solution of nitrogen in α-U_2N_{3+x} reported by Bugl and Bauer [1] and those for α-U_2N_{3+x} with higher N:U ratios estimated by extrapolation

N:U ratio	$\overline{\Delta H}$ (cal (mol N)$^{-1}$)	$\overline{\Delta S}$ (cal (mol N)$^{-1}$K^{-1})
1.54	−28481	−17.977
1.56	−26708	−17.449
1.58	−23669	−15.886
1.60	−21722	−15.355
1.62	−18602	−13.802
1.64	−17334	−14.234
1.68	−12210	−11.903
1.71	−8695	−10.609
1.76	−2838	−8.453
1.80	1847	−6.728
1.83	5362	−5.434

$$\partial\, \Delta G_f^\circ(U_2N_{3+x})/\partial x = \tfrac{1}{2}RT \ln P_{N_2} \tag{7}$$

The left-hand side of eqn. (7) is, by definition, the partial molar free energy $\overline{\Delta G}$ for the solution of nitrogen into U_2N_{3+x}. Thus, one obtains

$$\overline{\Delta G} = \overline{\Delta H} - T\,\overline{\Delta S} = \tfrac{1}{2}RT \ln P_{N_2} \tag{8}$$

Bugl and Bauer [1] gave both $\overline{\Delta H}$ and $\overline{\Delta S}$ as a function of N:U ratio only up to 1.64. In order to estimate the values of these two thermodynamic quantities for nitrogen-rich α-U_2N_{3+x} as obtained by the reaction of uranium with a stream of NH_3, the values of $\overline{\Delta H}$ and $\overline{\Delta S}$ given by these workers have been linearly extrapolated to higher N:U ratios. The estimated values for $\overline{\Delta H}$ and $\overline{\Delta S}$ are shown in Table 3. By substituting these values in eqn. (8) at a given temperature, the nitrogen pressure required for preparing α-U_2N_{3+x} having high N:U ratios by the reaction of uranium with N_2 can be roughly estimated. In the temperature range from 300 to 900 °C, a nitrogen pressure of the order of 10^5–10^6 atm would be needed in order to prepare α-U_2N_{3+x} with an N:U ratio of 1.83. The estimated order of magnitude of P_{N_2} turns out to be in fairly good agreement with that evaluated from a_N values obtained in the present work using the relation $a_N = P_{N_2}{}^{1/2}$, although both of the calculations were based on rough estimations. It is interesting that the use of a stream of NH_3 as a nitriding agent can provide extremely high nitrogen activities which might be attained only by the use of currently available high pressure generators if N_2 were to be employed as a nitriding agent. It is also possible to control the nitrogen activity by regulating the value of $P_{NH_3}/P_{H_2}{}^{3/2}$.

4. Conclusions

The reactions, $U + NH_3$(stream) and $U + N_2$(stream) were performed in the temperature range from 400 to 800 °C. It is found from these experiments that the nitrogen content of α-U_2N_{3+x} formed by the reaction $U+NH_3$ is much higher than that formed by the reaction $U + N_2$, suggesting that extremely high nitrogen activity can be obtained by flowing NH_3. A thermodynamic analysis suggests that a very high nitrogen activity corresponding to a nitrogen pressure of the order of 10^5–10^7 atm can be obtained from flowing NH_3 under a suitable condition. A rough estimation of how high a nitrogen pressure may be required to obtain $UN_{1.83}$ was made on the basis of the experimentally determined P–T–C relationship of α-U_2N_{3+x} (N:U = 1.53–1.64) reported in the literature. The obtained results are in good agreement with the present thermodynamic analysis.

Acknowledgments

The authors wish to thank Mr. H. Takahashi for assistance in carrying out the experimental work and Professor M. Miyake of Osaka University for valuable discussions.

References

1 J. Bugl and A. A. Bauer, in J. T. Waber, P. Chiotti and W. N. Miner (eds.), *Compounds in Nuclear Reactor Technology*, Edwards Bros., Ann Arbor, MI, 1964, p. 215.
2 P. E. Lapat and R. B. Holden, in J. T. Waber, P. Chiotti and W. N. Miner (eds.), *Compounds in Nuclear Reactor Technology*, Edwards Bros., Ann Arbor, MI, 1964, p. 225.
3 H. Tagawa, *J. Nucl. Mater.*, *51* (1974) 78.
4 A. Naoumidis, *Ber. Kernforschungsanlage Jülich*, *472* (1967).
5 F. Müller and H. Ragos, *Thermodynamics of Nuclear Materials*, IAEA, Vienna, 1968, p. 257.
6 T. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, *J. Am. Chem. Soc.*, *70* (1948) 99.
7 R. Didchenko and F. P. Gortsema, *Inorg. Chem.*, *2* (1963) 1079.
8 W. Trzebiatowski and R. Troc, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, *10* (86) (1962) 395.
9 H. J. Berthold and C. Delliehausen, *Angew. Chem.*, *78* (1966) 750.
10 M. Katsura, *Solid State Ionics*, *49* (1991) 225.
11 M. Katsura, *J. Alloys Comp.*, *182* (1992) 91.
12 H. Tagawa, *J. Atom. Energy Soc. Jpn.*, *13* (1971) 267.