Thermodynamics of nitrogen-rich uranium sesquinitride formation by reaction of uranium monocarbide with ammonia

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Abstract

According to our thermodynamic analysis, the flowing NH_3 possesses high nitrogen and hydrogen activities due to its instability with respect to the dissociation equilibrium, $NH_3 \rightleftarrows (1/2)N_2 + (3/2)H_2$. As the extent of dissociation of NH_3 into N_2 and H_2, α, is lower, nitrogen and hydrogen activities exhibited by unstable gaseous mixture of NH_3, N_2 and H_2 become higher. The reaction experiments of UC with a stream of NH_3 at 600, 700, 800 and 900°C were performed at two different values of α. Some runs employed 1 g UC as the starting material and the others used 2 g UC. At each of these four temperatures two runs were performed under the same experimental conditions except for the difference of the amount of used UC. The experimental results that the extent of dissociation, α, is larger in the case of using 2 g UC than in the case of using 1 g UC may suggest that the extent of NH_3 dissociation is greatly influenced by the amount of UC as the starting material. It was found that the gaseous phase consisting of NH_3, N_2 and H_2 with lower α yields U_2N_{3+x} with higher N/U ratio at a given temperature. These experimental results are consistent with our thermodynamic analysis. © 1998 Elsevier Science S.A.

Keywords: Uranium sesquinitride; Uranium monocarbide; Ammonia; Extent of dissociation

1. Introduction

The non-stoichiometric uranium sesquinitride, α-U_2N_{3+x}, was prepared by the reaction of uranium with N_2 to obtain the P–T–C (equilibrium N_2 pressure–temperature–composition) relationship by Bugl and Bauer [1], Tagawa [2], Lapat and Holden [3] and Müller and Ragos [4]. The N/U ratio of α-U_2N_{3+x} ranged from 1.5 to 1.7. Price and Warren [5] and Trzebiatowski and Troc [6] prepared nitrogen-rich α-U_2N_{3+x} (N/U$\geq$1.80) by the reaction of uranium with flowing NH_3. These results suggest that the reaction of uranium with flowing NH_3 yields nitrogen-rich α-U_2N_{3+x}, which cannot be obtained by the reaction of N_2 under normal pressure.

Katsura [7] has carried out a thermodynamic analysis to explain why flowing NH_3 can possess extremely high nitrogen activity and has 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 U_2N_{3+x} or, equivalently, that exhibited by flowing gas mixture and K_p is the equilibrium constant for $1/2N_2 + 3/2H_2 = NH_3$. According to the analysis, flowing NH_3 possesses high nitrogen and hydrogen activities due to its instability with respect to the dissociation equilibrium. That is, the lower the dissociation of NH_3 into N_2 and H_2 becomes, the higher their activities become.

In our laboratory, the reactions of various metals such as U, Fe, Mo and some transition elements with flowing NH_3 were performed to test our theoretical analysis. In this work, the reaction experiments of UC (1 or 2 g) with a stream of NH_3 (100 or 200 ml min^{-1}) in the temperature range from 600 to 900°C were carried out. Also the reaction of UC with flowing N_2 was carried out.

2. Experimental

2.1. Materials

Chemical analysis for UC powder sample used in this work shows; 95.00 wt % U, 4.80 wt % combined carbon and 0.03 wt % free carbon. Reactant gases, NH_3

(99.9998%) and N_2 (99.9998%) were supplied from commercial gas cylinders.

2.2. Apparatus

The experimental apparatus employed in this work consisted of a vacuum system, a reaction system, a gas supply system, a pressure measurement system and a gas analysis system.

The vacuum system comprised two rotary pumps and an oil diffusion pump, by which the overall system can be evacuated up to the order of 10^{-6} Pa. Quartz reaction tube of 30 mm in outer diameter and 750 mm in length was placed in the centre of cylindrical resistance furnace. The temperature of specimen was measured by a C.A. thermocouple mounted close to the specimen on the outer surface of the reaction tube. The temperature control of the furnace was made by using an on–off type thermo-regulator automatically. In the gas supply system, NH_3 and N_2 were fed into the reaction tube through stainless steel capillaries from the commercial gas cylinders without any further purification. An Hg bubbler and flow-meters were also included. The pressure of the whole system was measured by means of the capacitance manometer within the range from 10 to 10^5 Pa. The gas analysis system consisted of a gas sampler with two sampling loops, a gas chromatograph (Type GC-8APT, Shimadzu and Co., Ltd.) and an integrator (Type C-R6A, Shimadzu and Co., Ltd.). Helium gas with nominal purity 99.999% was used as a carrier gas. The outlet gas from the reaction tube was analyzed by a gas chromatograph and the determination of the partial pressures of NH_3 and N_2 in the reaction system was carried out.

2.3. Procedure

A quartz boat containing UC powder was placed in the centre of the reaction tube. After the system was evacuated to the order of 10^{-5} Pa at room temperature, the temperature was raised up to 900°C. For degassing, the specimen was kept at this temperature for 14 h while maintaining the system below 10^{-4} Pa and then the temperature was changed to the desired one. The reaction experiments were performed in the temperature range from 600 to 900°C. Then ammonia gas or nitrogen gas was supplied constantly as a stream at the flow rate of 100 ml min^{-1} or 200 ml min^{-1} for the predetermined periods. In the reaction with NH_3, during each run, the total pressure of the system, P_{Total} was measured with the capacitance manometer and the partial pressures of NH_3 and N_2, P_{NH_3} and P_{N_2}, in the outlet gas were determined by the gas chromatograph measurement and that of H_2, P_{H_2}, was calculated by the relation $P_{Total} = P_{NH_3} + P_{N_2} + P_{H_2}$. In the case of that with N_2, P_{N_2} was determined by the capacitance manometer.

After each run, the reaction product was divided into two portions. One was leached in 10 M HNO_3 solution held at 100°C for about 10 h to dissolve U_2N_{3+x} and solutions were filtered off through a glass-filter to check whether indissoluble residue (free carbon) was present. The other was subjected to X-ray analysis. The reaction product was embedded in an aluminum sample holder with an epoxy resin in order to avoid the oxidation of the specimen during the analysis. From the obtained X-ray diffraction pattern, U_2N_{3+x} phase was identified and the lattice parameter of U_2N_{3+x} was calculated. Using this lattice parameter, the N/U atom ratio was determined from the relation between the lattice parameter value and the N/U ratio of U_2N_{3+x}.

3. Results and discussion

When NH_3 is supplied constantly as a stream into a high temperature region, where a powdered UC sample is placed, the nitridation reaction may proceed according to the following equation.

$$2UC + (3+x)NH_3 = U_2N_{3+x} + 2C + \frac{9+3x}{2}H_2 \qquad (1)$$
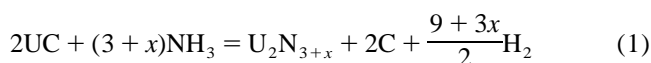
In general, NH_3 is unstable at elevated temperatures studied in this work, 600–900°C, at which almost all NH_3 molecules, more than 99.9%, should dissociate on the basis of thermodynamics.

$$NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2 \qquad (2)$$

However, as is pointed out by many researchers including the present authors, this dissociation can be considerably suppressed by flowing the gas containing NH_3. In other words, the flowing gas is regarded as in an unstable state not in a thermodynamic equilibrium but merely in a thermal equilibrium. This instability is established as a balance of the dissociation, nitridation, and continuous supply of NH_3. This balance should be sensitive to temperature, the flow rate, reactivity of the solid surface and its area on which the dissociation occurs. A nitride phase obtained in this reaction is regarded as in a chemical equilibrium with the unstable gas mixture as expressed by the following equation.

$$NH_3 = N(\text{in } U_2N_{3+x}) + \frac{3}{2}H_2 \qquad (3)$$
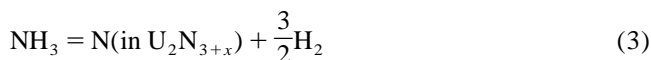
The N/U ratio obtained in the present reaction is, therefore, reasonably expected to depend on the surface area, temperature, the flow rate, etc., some of which are controllable but the others are not.

Katsura [7] has derived the following equation expressing equation of the nitrogen activity, a_N, given by the unstable gaseous mixture of NH_3, N_2 and H_2 on the basis of Eq. (3);

$$a_{\mathrm{N}} = \frac{1}{K_{\mathrm{p}}} \frac{P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}^{3/2}}$$

where K_{p} is the equilibrium constant for NH_3 formation, a function of temperature alone. The values of $P_{\mathrm{NH_3}}$ and $P_{\mathrm{H_2}}$ are expressed in atmospheres. It should be noted that N_2 makes no contribution to a_{N} in this nitriding reaction.

The experimental results obtained in the reaction of UC with flowing NH_3 or with flowing N_2 are given in Table 1. As seen there, the N/U ratio for U_2N_{3+x} phases obtained with flowing NH_3 exceeds 1.74 and increases with decreasing temperature in the examined range, while those with flowing N_2 are lower than 1.70 in the same temperature range. These results may suggest that a_{N} of the unstable gas mixture of NH_3, N_2 and H_2 is higher than that of N_2 of 1 atm, since the gas phase with a high nitrogen activity corresponds to a high N/U ratio.

The reaction experiments of UC with flowing NH_3 at 600, 700, 800 and 900°C have been performed at two values of α, extent of dissociation of NH_3, for each temperature. Runs 1, 3, 5 and 7 employed 1 g of UC as the starting material and runs 2, 4, 6 and 8 did 2 g. Except for the difference in the amounts of UC, these runs have been performed under the same experimental conditions. This difference in the UC amounts leads to that in the surface areas. It was found that the value of α measured with 2 g of UC was larger than that with 1 g UC, suggesting that the surface area in the starting material significantly influences the extent of dissociation of NH_3. In order to investigate the effect of the flow rate on the nitrogen activity, a trial with NH_3 (200 ml min^{-1}) was also performed (run 9). This run 9 with a higher flow rate gave rise to a lower α of 0.86, which is smaller than 0.90 found in run 8 with a lower flow rate of 100 ml min^{-1}. Note that N/U = 1.80 yielded in this run 9 is higher than N/U = 1.74 in run 8. To summarize the effect of α on these resultant

N/U ratios, the lower the α is observed, the higher the N/U is obtained.

It has been also reported that the unstable gaseous mixture of NH_3, N_2 and H_2 has a high hydriding ability, and the hydrogen activity given in the hydriding reaction, a_{H} is derived as the following equation [7].

$$a_{\mathrm{H}} = \frac{1}{K_{\mathrm{p}}} \frac{P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}^{1/2}} \tag{5}$$

According to Eq. (1), the present reaction should liberate free carbon. In fact, the reaction products at 600, 700 and 800°C (runs 1–6) consisted of U_2N_{3+x} and free carbon, while that at 900°C only U_2N_{3+x} and no free carbon. Muromura and Tagawa [8,9], who studied the preparation of UN by the carbothermic reduction, stated that free carbon could not be removed by use of H_2 at 1200°C and much higher temperatures would be required. In the present experiments, when NH_3 passes over UC held at 900°C, U_2N_{3+x} is first formed by NH_3 as a nitriding agent and liberates free carbon; subsequently the free carbon reacts with NH_3 as a hydriding agent to form CH_4, resulting in the removal of the free carbon. The present results indicated that the free carbon was removed by the flowing NH_3 serving as a hydriding agent much more effective than 1 atm H_2 gas. Such hydriding ability of the flowing NH_3 has not been explicitly reported so far.

4. Conclusions

The formation of U_2N_{3+x} by the reaction of UC with flowing NH_3 in the temperature range 600–900°C has been discussed. By flowing NH_3 through a high temperature region at a sufficient speed, the dissociation to the equilibrium can be suppressed to a great extent. In other words, if the duration time of NH_3 in the high temperature region is

Table 1
Experimental results of the reaction of UC with flowing NH_3 and with N_2

Run	Reaction gas	Amount of UC(g)	Reaction temp. (°C)	α	a_{N}	a_{H}	Free carbon	U_2N_{3+x} Lattice const. (nm)	N/U
1	NH_3	1	600	0.47	742.5	9.7	Present	1.0591	1.83
2	100 ml min^{-1}	2		0.51	618.0	9.3	Present	1.0621	1.78
3		1	700	0.64	711.7	10.6	Present	1.0590	1.83
4		2		0.79	318.4	8.7	Present	1.0620	1.78
5		1	800	0.63	1375.5	13.1	Present	1.0600	1.82
6		2		0.80	555.3	10.5	Present	1.0632	1.74
7		1	900	0.69	1766.7	14.7	Absent	1.0602	1.82
8		2		0.90	401.6	9.8	Absent	1.0632	1.74
9	NH_3 200 ml min^{-1}	2		0.86	611.1	9.0	Absent	1.0610	1.80
10	N_2	1	600		1		Present	1.0649	1.69
11	100 ml min^{-1}	1	700		1		Present	1.0657	1.66
12		1	900		1		Present	1.0659	1.65

short enough, an unstable gaseous mixture consisting of NH_3, N_2 and H_2 can be constantly supplied to the hot region. When UC is placed in this hot region, the reaction of UC with the unstable gaseous mixture may proceed until U_2N_{3+x} and free carbon are formed. The nitrogen activity of the formed U_2N_{3+x} must be equal to that of the gaseous phase. Thus, the nitrogen activity of U_2N_{3+x} and, as a consequence, the N/U ratio of U_2N_{3+x}, are raised by enhancing that of the flowing gaseous mixture. The results obtained in the present work may give clearly an experimental support to these thermodynamic considerations. Moreover, the fact that CH_4 is formed as a result of the reaction of the carbon precipitated from the reaction UC with flowing NH_3 may be an experimental evidence to the suggestion that NH_3 is an effective hydriding agent.

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