Journal of Alloys and Compounds, 213/214 (1994) 444–446
JALCOM 4035

Preparation of nitrogen-rich α-uranium sesquinitride

Masanobu Miyake, Masayuki Hirota, Shinichiro Matsuyama and Masahiro Katsura
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565 (Japan)

Abstract

Reactions of massive U with static NH_3 were carried out at 300 and 350 °C. The variations in the partial pressures of NH_3, N_2 and H_2 with time were investigated. The experimental results are discussed in terms of the nitrogen activity of the gas phase.

1. Introduction

Recently, Katsura and coworkers [1–3] have prepared N-rich α-U_2N_{3+x} with N:U ratios of 1.80 or more by treating U with unstable NH_3 which had an extremely high nitrogen activity a_N. They claimed that the practically attainable N:U ratio for α-U_2N_{3+x} may be about 1.90. They also suggested that the slope of the P_{N_2}–N:U isotherm becomes steeper with decreasing temperature, and that N-rich α-U_2N_{3+x} can be in equilibrium with N_2 at 100 kPa or less, from a thermodynamical point of view. To examine these points, reactions of U with NH_3 were performed at 300 and 350 °C in a closed system. The reaction processes are discussed in terms of a_N.

2. Experimental details

The experimental apparatus used in this work consisted of a resistance furnace, a vacuum system, a capacitance manometer and a gas chromatograph system. The nominal impurities of the U ingot were given in a previous paper [4]. NH_3 (99.998%) was supplied from a commercial gas cylinder into the reaction system, through a stainless steel capillary without further purification. A quartz boat containing metallic U (about 2.4 g) was placed in the center of the reaction tube and the system was evacuated to 4×10^{-6} Pa at room temperature. Then, NH_3 gas was admitted into the tube up to a desired pressure. After raising the temperature to 300 or 350 °C, the total pressure P_{total}, P_{N_2}, and P_{NH_3} and P_{N_2} were measured as functions of time. P_{H_2} was calculated by the relationship $P_{H_2}=P_{total}-P_{NH_3}-P_{N_2}$, since P_{NH_3} could be much more accurately determined by the gas chromatograph measurement than could P_{H_2}. The N:U ratio of α-U_2N_{3+x} was determined from the relationship between the lattice parameter value and the N:U ratio [5].

3. Results and discussion

As often claimed, NH_3 is considered to be kinetically favorable as a nitriding agent compared with N_2. Two points should be noted: (i) the reaction period necessary to produce a nitride is reduced, and (ii) the nitride formation occurs at relatively low temperatures compared with the case where N_2 gas is used. These kinetic effects brought about by the use of NH_3 are regarded as resulting from the high instability of NH_3.

When NH_3 gas is introduced into a quartz vessel up to a desired pressure less than 100 kPa and the system is kept at a temperature of 350 °C or less, the decomposition of NH_3 can be suppressed almost completely, and unstable NH_3 molecules can exist in the gas phase over a long period of time. Under these conditions, if a given amount of U metal is placed in the vessel, NH_3 is continuously consumed and H_2 is continuously accumulated in the system, owing to the formation of α-U_2N_{3+x} according to

$$2U+(3+x)NH_3=U_2N_{3+x}+(9+3x/2)H_2$$

The experimental results of the reaction of U chip with static NH_3 carried out at 300 and 350 °C are given in Figs. 1 and 2, respectively, where the variations in P_{total}, P_{NH_3}, P_{H_2}, and P_{N_2} with time are shown graphically. The pressure variation curves can be roughly divided into three regions, as shown in Figs. 1 and 2. In regions I and II, P_{total} and P_{H_2} increase rapidly with time, while P_{NH_3} decreases rapidly. Although a slow increase in P_{N_2} is observed in region I, P_{N_2} is kept almost constant,

0925-8388/94/$07.00
SSDI 0925-8388(94)04035-3

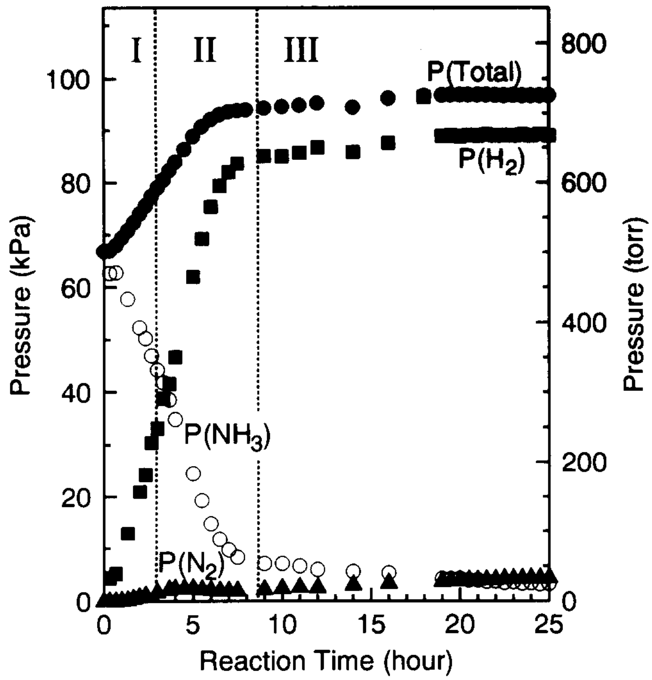

Fig. 1. Variations in P_{total}, P_{NH_3}, P_{H_2} and P_{N_2} with time during the reaction of massive U with static NH_3 at 300 °C.

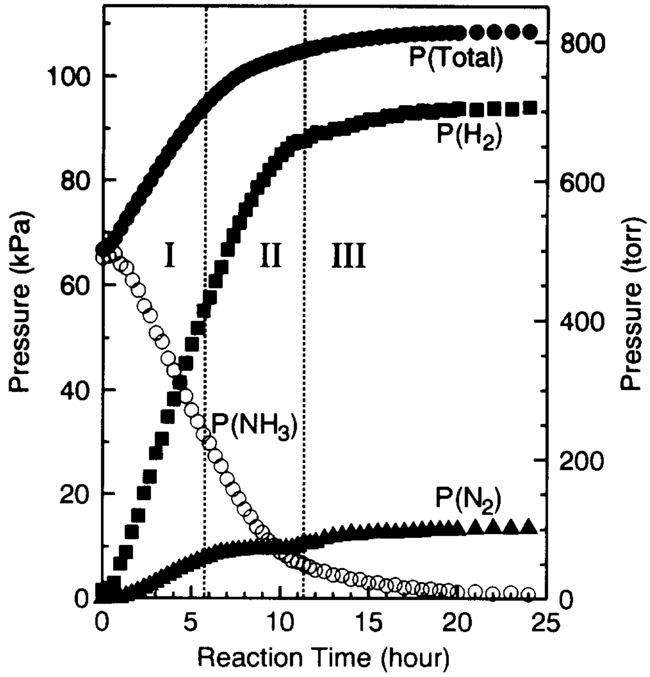

Fig. 2. Variations in P_{total}, P_{NH_3}, P_{H_2} and P_{N_2} with time during the reactions of massive U with static NH_3 at 350 °C.

at least within the experimental errors. In region III, both P_{H_2} and P_{N_2} continue to increase slowly, and P_{NH_3} continues to decrease gradually.

Katsura [6] has demonstrated that, even for the unstable mixtures of NH_3, H_2 and N_2, the relationship $a_N = (1/K_P)(P_{NH_3}/P_{H_2}{}^{3/2})$ is valid, where K_P is the equilibrium constant for

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$$

and P_{NH_3} and P_{H_2} are expressed in atmospheric units. Using this equation and the results in Figs. 1 and 2, the value of a_N can be calculated as a function of time, as shown graphically in Fig. 3. Extremely high a_N values of the order of 10^3–10^4 were obtained in the early stage of each run ($a_N = 1$ corresponds to $P_{N_2} = 100$ kPa). When a metallic U specimen is brought into contact with NH_3, the following three reactions are possible:

$$2U + (3+x)NH_3(g) = U_2N_{3+x} + \tfrac{3}{2}(3+x)H_2 \tag{1}$$

$$U + NH_3(g) = UH_3 + \tfrac{1}{2}N_2(g) \tag{2}$$

$$NH_3(g) = \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \tag{3}$$

The decrease in P_{NH_3} and increase in P_{H_2} observed in regions I and II may be ascribed to the formation of α-U_2N_{3+x} by reaction (1). It is known that the reaction of massive U with N_2 at such low temperatures as 300 °C proceeds only to a negligible extent or not at all during a reaction period of 1–2 weeks. Finely powdered U prepared by the thermal decomposition of powdered UH_3 was exposed to N_2 with a pressure of 25 kPa (190 Torr) at 300 °C for 65 h in the same apparatus used for the reaction of U and static NH_3. No pressure change was observed during the run, and

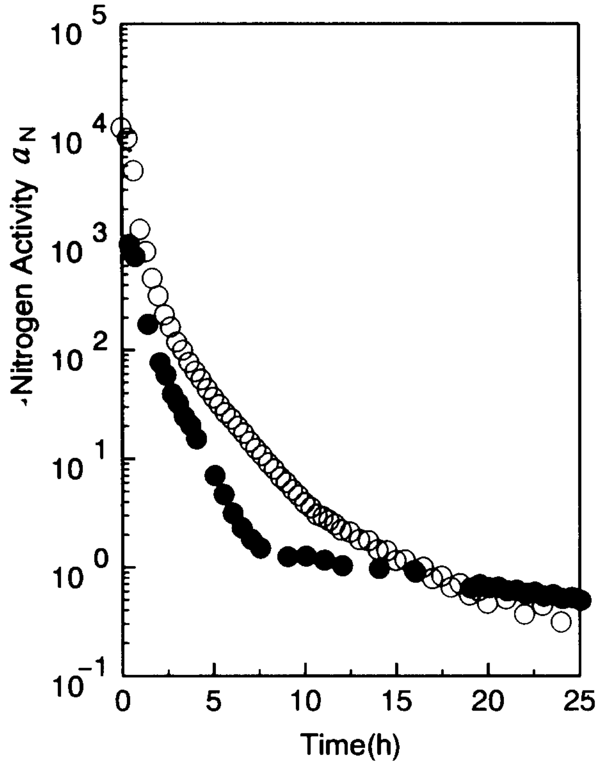

Fig. 3. Nitrogen activity a_N as a function of reaction time during the reaction of massive U with static NH_3 at 300 °C (●; evaluated from the data in Fig. 1) and at 350 °C (○; evaluated from the data in Fig. 2).

TABLE 1. Experimental conditions and N:U ratio of α-U_2N_{3+x}

Temperature (°C)	Time (h)	Pressures (kPa) at the beginning of the run			Pressures (kPa) at the end of the run			N:U ratio of α-U_2N_{3+x}
		P_{NH_3}	P_{H_2}	P_{N_2}	P_{NH_3}	P_{H_2}	P_{N_2}	
300	69	66.7	0	0	3.3	89.0	4.5	1.80–1.83
350	24	66.7	0	0	0.8	94.2	13.7	1.80–1.83

X-ray diffraction of the solid sample revealed only the existence of U. This result, which indicates that even the reaction of powdered U with N_2 does not proceed to any appreciable extent at 300 °C, contrasts sharply with the reaction of massive U with static NH_3 at 300 or 350 °C, which results in the formation of α-U_2N_{3+x}. The fact that the conversion of massive U to α-U_2N_{3+x} at such a low temperature as 300 or 350 °C by the action of NH_3 must be ascribed to an extremely high nitrogen activity a_N realized in the early stage of the run, which arises from the high instability of NH_3.

The gradual increases in P_{H_2} and P_{N_2} and slow decrease in P_{NH_3} may be attributed to the dissociation of NH_3 into N_2 and H_2, suggesting that U_2N_{3+x} can act as a catalyst for NH_3 decomposition. The decomposition proceeds more rapidly at 350 °C than at 300 °C. (How rapidly NH_3 decomposition proceeds depends on the amount of α-U_2N_{3+x} and, as a consequence, on the amount of U sample initially loaded.) Although why the plateaus (region II) appear cannot be explained well at present, it may be possible that N_2 is evolved from N-rich α-U_2N_{3+x} and this cancels the increase in P_{N_2}, according to reaction (3).

The N:U ratios of α-U_2N_{3+x} obtained at 300 and 350 °C in the present work range from 1.80 to 1.83 (see Table 1), although a_N in the gas phase in the final stage of the run is less than unity. This result suggests that α-U_2N_{3+x} with N:U$\geqslant$1.80 may be in equilibrium with N_2 at 100 kPa or less, and that the slope of the P_{N_2}–N:U ratio isotherm at 300 or 350 °C may be very steep.

4. Concluding remarks

From the time variations in P_{NH_3}, P_{H_2} and P_{N_2} during the reactions of massive U with static NH_3 at 300 and 350 °C, the nitrogen activity a_N was evaluated as a function of time. When U metal is exposed to NH_3, a large nitriding driving force prevails between the gas phase and the metal, resulting in a rapid nitriding reaction, even at such low temperatures as 300 and 350 °C. As the reaction proceeds, a_N continuously decreases until it is less than unity. In this state, α-U_2N_{3+x} may be regarded as being in equilibrium with the gas phase, with a_N less than unity.

References

1 M. Katsura, M. Miyake and H. Serizawa, *J. Alloys Comp.*, *193* (1993) 101.
2 T. Urabe, K. Takahashi, M. Katsura and M. Miyake, *J. Alloys Comp.*, *193* (1993) 122.
3 M. Katsura and H. Serizawa, *J. Alloys Comp.*, *196* (1993) 191.
4 M. Katsura and H. Serizawa, *J. Alloys Comp.*, *187* (1992) 389.
5 H. Tagawa, *J. Atom. Energy Soc.*, *13* (1971) 267.
6 M. Katsura, *J. Alloys Comp.*, *182* (1992) 91.