

# Preparation of $\text{UH}_3$ by the reaction of U with $\text{NH}_3$ or with a mixture of $\text{H}_2$ and $\text{N}_2$

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## Abstract

To examine how a high nitrogen activity and high hydrogen activity can be obtained by keeping the extent of dissociation of  $\text{NH}_3$  below its dissociation equilibrium, reactions of U with static  $\text{NH}_3$  were carried out at 250 °C. The formation of N-rich  $\text{U}_2\text{N}_{3+x}$  and that of  $\text{UH}_3$  are discussed from a thermodynamic point of view. The experimental results suggest, however, that the formation of  $\text{UH}_3$  must be ascribed to a much lower activation energy for its formation.

## 1. Introduction

There are reports on the formation of  $\text{U}_2\text{N}_{3+x}$  ( $0 \leq x \leq 1$ ) by the reaction of U or  $\text{UH}_3$  with static  $\text{NH}_3$  [1–3]. Tagawa [1] found that the reaction between  $\text{UH}_3$  and static  $\text{NH}_3$  begins at 150 °C, and becomes rapid above 350 °C, while Alire and McCrary [2] prepared  $\text{U}_2\text{N}_{3+x}$  by the reaction of powdered U with  $\text{ND}_3$ . Katsura and Serizawa [3] ascribed the formation of  $\alpha\text{-U}_2\text{N}_{3+x}$  by the reaction of U with static  $\text{NH}_3$  at 250 and 300 °C to an enormously high nitrogen activity  $a_{\text{N}}$  of the gas phase, arising from the suppression of the dissociation of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$  well below its equilibrium dissociation. However, a small amount of  $\text{UH}_3$  was present in the final reaction products, together with  $\text{U}_2\text{N}_{3+x}$ .

By keeping the extent of dissociation of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$  below the equilibrium dissociation degree at the temperature in question, gaseous mixtures of  $\text{N}_2$ ,  $\text{H}_2$  and unstable  $\text{NH}_3$  can be prepared [4]. These mixtures possess high nitrogen and hydrogen activities ( $a_{\text{N}}$  and  $a_{\text{H}}$ ).

In dealing with the reactions of metals with  $\text{NH}_3$  at low temperatures, the hydriding ability of unstable  $\text{NH}_3$  must be taken into account. To examine the role of the hydriding ability of  $\text{NH}_3$  in reactions between metals and  $\text{NH}_3$ , the reactions between U chips and static  $\text{NH}_3$ , and those of U powder with  $\text{NH}_3$  were carried out at 250 °C. In addition, the reaction of U with an  $\text{N}_2 + \text{H}_2$  mixture was carried out at 100 °C.

## 2. Experimental details

The apparatus and materials used in this work were essentially the same as those used in the previous work [3, 5]. U chips or powdered U was exposed to  $\text{NH}_3$  at 250 °C. The total pressure  $P_{\text{total}}$  and the partial pressures of  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$  ( $P_{\text{NH}_3}$ ,  $P_{\text{N}_2}$ , and  $P_{\text{H}_2}$ ) were measured as functions of the reaction time. Powdered U was treated in a gaseous mixture of  $\text{N}_2 + \text{H}_2$  at 100 °C for 122 h. X-ray diffraction analysis of the solid products was carried out using a diffractometer.

## 3. Results and discussion

Figure 1(a) shows the variations in  $P_{\text{total}}$ ,  $P_{\text{NH}_3}$ ,  $P_{\text{H}_2}$  and  $P_{\text{N}_2}$  with time, during the reaction of massive U (2.57 g) with  $\text{NH}_3$  (run 1).  $P_{\text{NH}_3}$  continues to decrease and  $P_{\text{H}_2}$  continues to increase until a stationary state is reached, where the gas phase consists practically of only  $\text{H}_2$  and any appreciable change in  $P_{\text{H}_2}$  is not observable, suggesting that practically all the  $\text{NH}_3$  initially admitted into the system has been consumed. (Gradual decreases in  $P_{\text{H}_2}$  and  $P_{\text{total}}$  may be attributable to the samplings made at intervals for the gas analysis.)

The results of the reaction of powdered U (0.27 g) with  $\text{NH}_3$  (run 2) are shown in Fig. 1(b). These pressure variation curves show similar tendencies to those in Fig. 1(a); namely,  $P_{\text{NH}_3}$  decreases and  $P_{\text{H}_2}$  increases, and a stationary state is eventually reached. However,

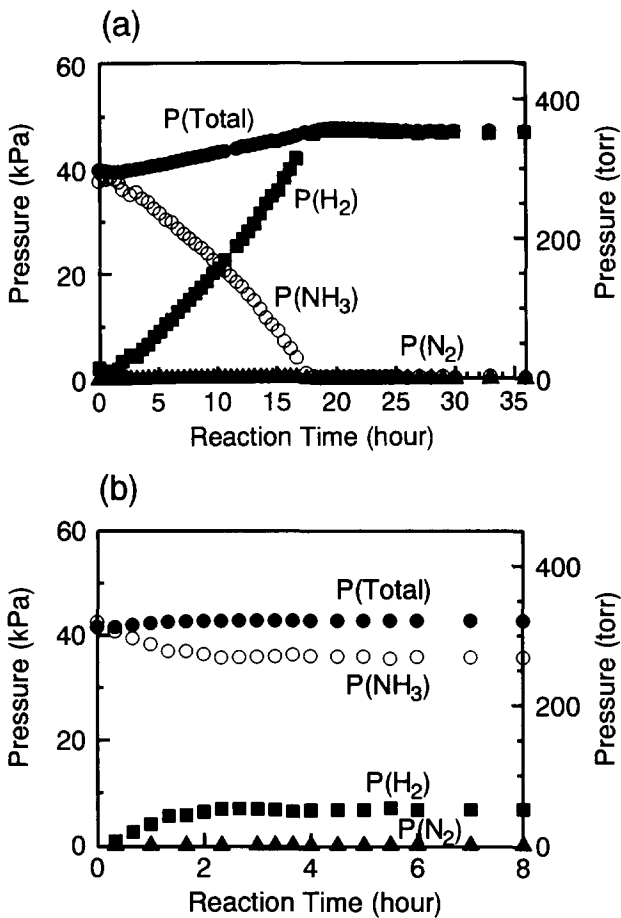


Fig. 1. Variations in  $P_{\text{total}}$ ,  $P_{\text{NH}_3}$ ,  $P_{\text{H}_2}$  and  $P_{\text{N}_2}$  with time; (a) during the reaction of massive U with  $\text{NH}_3$  at 250 °C, and (b) those during the reaction of powdered U with  $\text{NH}_3$  at 250 °C.

the result of run 2 (Fig. 1(b)) differs from that of run 1 (Fig. 1(a)), in that a large amount of  $\text{NH}_3$  still remains in the system, presumably as a result of the smaller amount of U used in run 2 than that in run 1. The results shown in Fig. 1(b) also suggest that, at 250 °C,  $\text{U}_2\text{N}_{3+x}$  does not function as an effective catalyst for  $\text{NH}_3$  decomposition.

X-ray diffraction patterns for the final solid products are shown in Figs. 2(a) and 2(b). (The N:U ratio of  $\text{U}_2\text{N}_{3+x}$ , calculated from the lattice parameter of the product from run 1, is about 1.70 and that for run 2 is about 1.80). Although  $\text{U}_2\text{N}_{3+x}$  is the major phase, a considerable amount of  $\text{UH}_3$  is also present. (In the case of the reaction of massive U with  $\text{NH}_3$ , peaks corresponding to UN can be observed.)

The nitrogen activity  $a_{\text{N}}$  and hydrogen activity  $a_{\text{H}}$  of gaseous mixtures of unstable  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{N}_2$  are given respectively by

$$a_{\text{N}} = (1/K_{\text{P}})(P_{\text{NH}_3}/P_{\text{H}_2}^{3/2}) \quad (1)$$

$$a_{\text{H}} = \{(1/K_{\text{P}})(P_{\text{NH}_3}/P_{\text{N}_2}^{1/2})\}^{1/3} \quad (2)$$

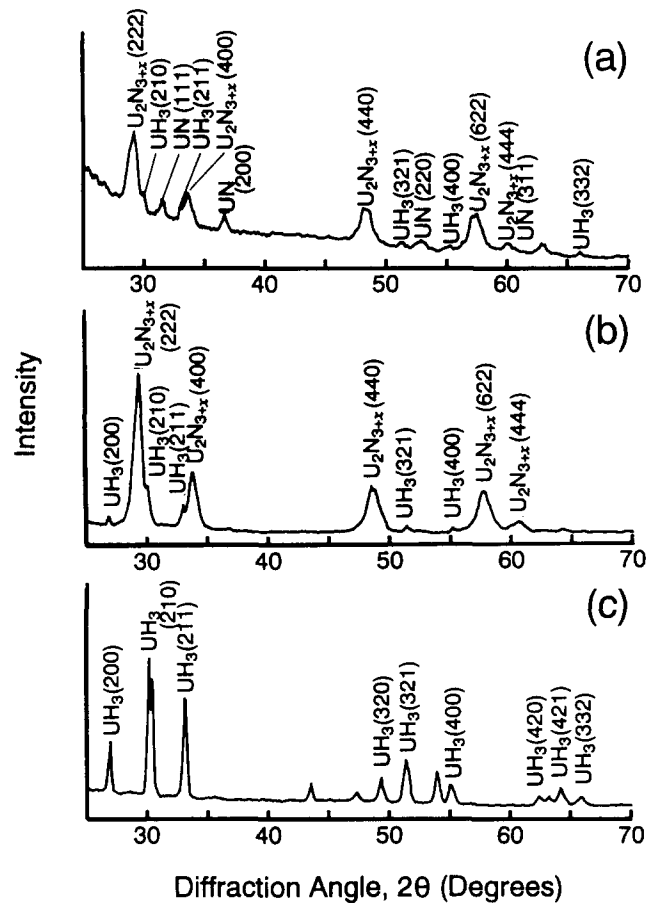
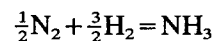


Fig. 2. X-ray diffraction patterns for the products of the reactions of (a) U (ingot) and  $\text{NH}_3$  at 250 °C, (b) U (powder) and  $\text{NH}_3$  at 250 °C, and (c) U (powder) and  $\text{N}_2/\text{H}_2$  (=1/3) at 100 °C.

where  $K_{\text{P}}$  is the equilibrium constant for



and the respective partial pressures are expressed in atmospheric units [4].

The values for  $a_{\text{N}}$  and  $a_{\text{H}}$  of the gas phase, calculated from the data given in Fig. 1 using eqns. (1) and (2), are given as functions of time for the two reactions above (see Fig. 3). In either case, extremely high  $a_{\text{N}}$  values (of the order of magnitude  $10^3$ ) are realized in the early stage of the run, and  $a_{\text{N}}$  continues to decrease rapidly until a constant  $a_{\text{N}}$  value is obtained. In the case of run 1,  $a_{\text{N}}$  drops to low values ( $7\text{--}8 \times 10^{-2}$ ) in the final stage, which correspond to  $P_{\text{N}_2} = 0.005\text{--}0.0064$  bar. In contrast, the  $a_{\text{N}}$  value remains at the order of  $10^2$  in the later stage of run 2 ( $P_{\text{N}_2} = 10^4$  bar).

The existence of UN, together with  $\text{U}_2\text{N}_{3+x}$  in run 1 might be attributable to an  $a_{\text{N}}$  value much smaller than that in run 2. The higher  $a_{\text{N}}$  value in run 2 may be responsible for the higher N:U ratio of  $\alpha\text{-U}_2\text{N}_{3+x}$  (N:U  $\approx 1.80$  was estimated for  $\alpha\text{-U}_2\text{N}_{3+x}$ , obtained in

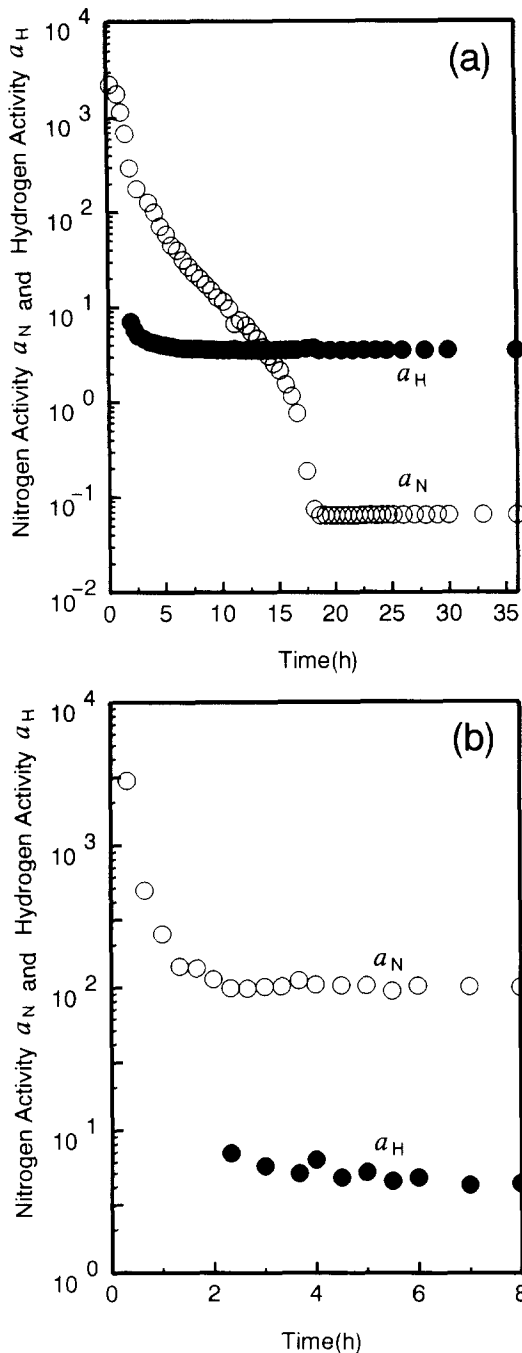
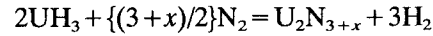


Fig. 3. Variations of nitrogen activity  $a_N$  and hydrogen activity  $a_H$  with time, (a) during the reaction of massive U with  $\text{NH}_3$  at  $250^\circ\text{C}$ , and (b) during the reaction of powdered U with  $\text{NH}_3$  at  $250^\circ\text{C}$ .

run 2). However, the  $a_H$  values obtained in the final stage of runs 1 and 2 do not differ substantially, ranging from 4 to 6, which corresponds to  $P_{\text{H}_2} = 15\text{--}35$  bar. It

is also likely that a high  $a_H$  value is obtained in the early stage of the runs. Since the  $P_{\text{N}_2}$  values in this stage are small, the estimation of  $\alpha_H$  from the data has not been performed.

The free energy change for



calculated using the literature thermodynamic data for  $\text{U}_2\text{N}_{3+x}$  and  $\text{UH}_3$  [6], suggests that, from a thermodynamic viewpoint,  $\text{UH}_3$  must have been converted to  $\text{U}_2\text{N}_{3+x}$  in the gas phase examined in run 2. Thus, the presence of  $\text{UH}_3$  in the products may suggest that the activation energy for  $2\text{UH}_3 + \{(3+x)/2\}\text{N}_2 = \text{U}_2\text{N}_{3+x} + 3\text{H}_2$  is very high at low temperatures ( $250^\circ\text{C}$  or less).

To examine how easily  $\text{UH}_3$  is formed compared with  $\alpha\text{-U}_2\text{N}_{3+x}$ , the reaction of U powder and an  $\text{H}_2 + \text{N}_2$  mixture ( $P_{\text{H}_2} = 68$  kPa,  $P_{\text{N}_2} = 23$  kPa; reaction time, 122 h) was performed at  $100^\circ\text{C}$ . The free energy change for  $2\text{UH}_3 + \{(3+x)/2\}\text{N}_2 = \text{U}_2\text{N}_{3+x} + 3\text{H}_2$  under this condition amounts to about  $-560$  kJ mol $^{-1}$ , suggesting that  $\text{U}_2\text{N}_{3+x}$  is much more stable than  $\text{UH}_3$ . As can be seen from the X-ray diffraction data for the product (Fig. 2(c)),  $\text{UH}_3$  was formed, indicating that  $\text{UH}_3$  can be formed at a temperature as low as  $100^\circ\text{C}$ .

#### 4. Concluding remarks

Variations in the  $a_N$  and  $a_H$  values with time are calculated using the  $P_{\text{NH}_3}$ ,  $P_{\text{H}_2}$  and  $P_{\text{N}_2}$  data obtained during the reaction of U with  $\text{NH}_3$  at  $250^\circ\text{C}$ . Under suitable experimental conditions, high nitrogen activities of the order of  $10^3$  can be realized by using  $\text{NH}_3$ : the gas phase also possesses high hydrogen activities. Although the reaction of  $\text{U} + \text{NH}_3$  leads to the formation of  $\alpha\text{-U}_2\text{N}_{3+x}$  at temperatures as low as  $250^\circ\text{C}$ , owing to very high  $a_N$  values,  $\text{UH}_3$  is also formed. The formation of  $\text{UH}_3$  must be attributed to a very low activation energy for the reaction  $\text{U} + \frac{3}{2}\text{H}_2 = \text{UH}_3$ .

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