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The formation of uranium sesquinitride by reactions of U or UH_3 with a N_2–H_2 mixture

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Abstract

The reaction of massive uranium with a mixture of N_2 and H_2 ($N_2/H_2=1:3$), and that of UH_3 with a mixture of N_2 and H_2, have been carried out at 300°C. It was found that although the reaction of U with N_2 does not proceed at 300°C, the use of a mixture of N_2 and H_2 leads to the formation of uranium sesquinitride at this temperature. Furthermore, NH_3 is formed by the above two reactions at 300°C. © 1998 Elsevier Science S.A.

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1. Introduction

α-U_2N_{3+x} crystallizes in a Mn_2O_3 b.c.c. structure and the lattice parameter a_0 decreases continuously as the atomic ratio N/U of α-U_2N_{3+x} is increased [1,2]. The atomic ratio N/U of the nitrides prepared by the reaction of U with N_2 at $\leq$1 bar and above 600°C never exceeds 1.70. Many experimental results suggest that the nitrogen-rich α-U_2N_{3+x} phase (N/U$\geq$1.80), which cannot be obtained by the reaction of U with N_2 under normal pressures, can be prepared by use of a stream of NH_3 at temperatures of $\geq$600°C [3–7]. According to Katsura and Serizawa [7], it is possible to prepare α-U_2N_{3+x} with a N/U ratio >1.8 by the reaction of massive U with static NH_3 at 250 and 300°C, temperatures at which α-U_2N_{3+x} will never be formed within ordinary reaction periods by the reaction of U with N_2 at 10^2 kPa (1 bar). Rundle et al. [8] reported in 1951 that the reaction of uranium hydride with nitrogen gave a product of approximate composition $UN_{1.75}$ and that the reaction required for completion 10 to 12 h at 250°C and 1 to 2 h at 350°C. Tagawa [9] also studied the nitrogenation of UH_3 with N_2 using thermogravimetry. The weight gain started at about 160°C and accelerated above 240°C. Fujino and Tagawa [10] prepared UH_3 at 200–250°C and then added N_2 up to 46.7–53.3 kPa (350–400 Torr). The hydride was readily converted to the uranium nitride with a N/U ratio of about 1.7.

These results lead to the recognition that the presence of hydrogen, either in the form of H_2 or NH_3 in the gas phase or in the form of UH_3 in the solid phase, may play an important role in the formation of α-U_2N_{3+x}. In preparing some metal nitrides, a mixture of N_2 and H_2 is often used, instead of N_2, as a nitriding agent and in some cases the addition of H_2 into the gas phase is indispensable for nitride formation. However, the role of hydrogen is not yet well understood. Thermodynamics tells us that the ultimate position of the equilibrium in a chemical system does not depend upon the reaction path. By use of a suitable catalyst for NH_3 decomposition, the equilibrium $NH_3 \rightleftarrows (1/2)N_2 + (3/2)H_2$ may be reached from the NH_3 side. This equilibrium must also be reached from a mixture of N_2 and H_2 from a thermodynamic equilibrium point of view. Thus, both NH_3 and gaseous mixtures of N_2 and H_2 may be regarded as being in an unstable state with respect to the above equilibrium. Therefore, it would be expected that mixtures of N_2 and H_2 may have more effective nitriding and hydriding abilities than N_2 alone or H_2 alone due to their thermodynamic instability, as in the case of a stream of NH_3 [11].

To gain insight into the role of hydrogen in α-U_2N_{3+x} formation, the reaction of a U chip with a mixture of N_2 and H_2 ($N_2/H_2=1:3$) and the reaction of UH_3 with a N_2–H_2 mixture were performed at 300°C.

2. Experimental details

The experimental apparatus used in this work consisted

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of a resistance furnace, a vacuum system, a gas supply system, a capacitance manometer, and a gas chromatography system. A quartz tube (30 mm in diameter and 750 mm in length) was placed in the cylindrical resistance furnace. This furnace comprised upper and lower halves, which were connected to each other by hinges in such a way that the upper half could be opened for occasional visual observation of the specimen.

In the case of the reaction of a U chip with a N_2–H_2 mixture, a quartz boat containing about 0.15 g of a bright U chip pretreated as described in a previous paper [7] was placed in the reaction tube and the system was evacuated to 1.33×10^{-5} Pa at room temperature. Nitrogen gas was first admitted into the reaction system up to $P_{N_2} = 22.7$ kPa and then H_2 gas was introduced to $P_{H_2} = 68.0$ kPa. The temperature was raised quickly to 300°C. Then, the total pressure, P_{total}, and the partial pressures of N_2, H_2, and NH_3, P_{N_2}, P_{H_2}, and P_{NH_3}, were measured as functions of temperature. During the run, visual observations of the sample appearance was made at intervals. The reaction time was 190 h.

For the reaction of UH_3 with a N_2–H_2 mixture, UH_3 was prepared by the reaction of a U chip with H_2 at 225°C. Hydrogen gas was introduced up to 65.3 kPa into the reaction tube, in the center of which about 0.15 g of UH_3 was placed. Then, N_2 was admitted to $P_{N_2} = 22.7$ kPa. The following operation and measurements were similar to the case of the reaction of the U chip with the N_2–H_2 mixture.

The phases were identified from the X-ray diffraction powder patterns of the reaction products at room temperature.

3. Results and discussions

In addition to the above two experiments, the reaction between finely pulverized U and N_2 ($P_{N_2} = 25.0$ kPa) was also examined at 300°C. The nitrogen pressure, P_{N_2}, remained constant over the reaction period (67 h), suggesting that no reaction occurred between U and N_2. The time variations of P_{total}, P_{N_2}, P_{H_2}, and P_{NH_3} for the reaction of the U chip with the N_2–H_2 mixture at 300°C are shown in Fig. 1. (For clarity, the scale of the P_{NH_3} variation is different, and indicated on the right-hand side.) During the initial hours (about 5 h) P_{N_2} dropped sharply and P_{H_2} decreased slowly. Visual observation of the specimen disclosed that the luster of the U chip diminished immediately after the beginning of the run and, at the same time, its surface became blackish. The U chip continued to be pulverized during this initial stage until appreciable change in the sample appearance was no longer observed. The X-ray diffraction pattern of the solid phase after the run revealed only the presence of α-U_2N_{3+x} (see Fig. 2a). This result is remarkable in that nitriding, which does not proceed at all in a N_2 only atmosphere, occurs readily if H_2 is added. It should be emphasized that the uranium specimen in the reaction $U+(N_2+3H_2)$ was not powder but massive uranium, which is expected to have much less surface area and consequently to be less chemically

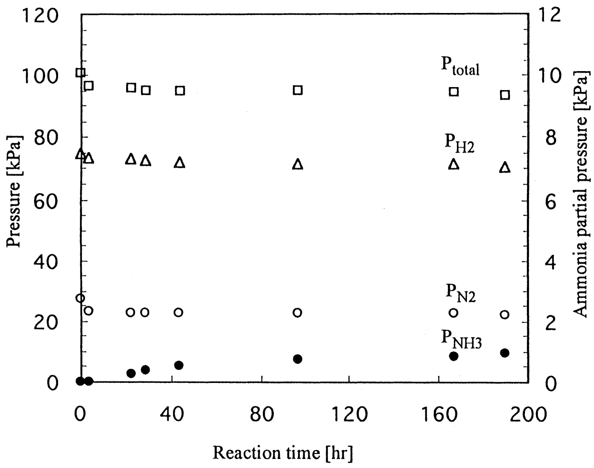

Fig. 1. Variation of P_{total}, P_{N_2}, P_{H_2}, and P_{NH_3} with time during the reaction $U+(N_2+3H_2)$ in a closed system at 300°C.

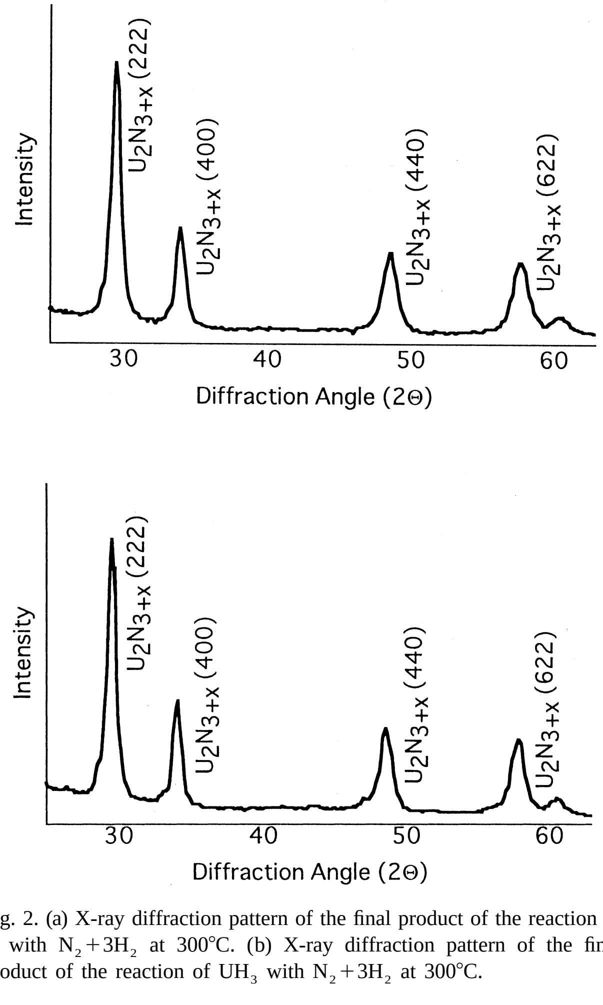

Fig. 2. (a) X-ray diffraction pattern of the final product of the reaction of U with N_2+3H_2 at 300°C. (b) X-ray diffraction pattern of the final product of the reaction of UH_3 with N_2+3H_2 at 300°C.

reactive than powdered uranium. For α-U_2N_{3+x} to be formed by the reaction of U with nitrogen gas, N_2 molecules must be adsorbed and dissociated on the surface of the uranium sample and then the dissociated N atoms must migrate in the bulk phase. But this reaction does not occur at 300°C, probably because N_2 physically adsorbed on a U surface cannot be dissociated. However, α-U_2N_{3+x} is easily formed by the addition of H_2 to N_2. This suggests that the presence of H_2 results in a rather drastic disruption of the bonding in an adsorbed N_2 molecule. In this work, nitrogen gas was first admitted prior to H_2 introduction. Thus, the surface of the uranium specimen may have been covered by N_2 molecules before the H_2 gas was introduced. (Physical adsorption is generally attained more rapidly than chemisorption and it is reversible.) Presumably, chemisorbed hydrogen atoms on the uranium might attract strongly adsorbed N_2 molecules so that the disruption of N_2 could result. The thus formed N atoms on the surface might continue to migrate into the U metal and eventually α-U_2N_{3+x} might be formed. It may also be possible that α-U_2N_{3+x} is formed by the reaction of UH_3, once formed, with N_2.

Judging from the fact that NH_3 appeared after a rather long time, the reaction of nitrogen-rich α-U_2N_{3+x} with H_2 led to ammonia synthesis. The α-U_2N_{3+x} formed was so rich in nitrogen that the nitrogen activity of the nitride was extremely high. In other words, N atoms dissolved in α-U_2N_{3+x} are in such a thermodynamically unstable state that they can easily combine with hydrogen atoms chemisorbed on the surface of these nitrides to form NH_3.

The variations of P_{total}, P_{N_2}, P_{H_2}, and P_{NH_3} are shown in Fig. 3. The overall feature is almost the same as that of the reaction of the U chip with the N_2–H_2 mixture, except that P_{H_2} first increased and then dropped at the initial stage of the run. The reaction product was α-U_2N_{3+x}, as shown in Fig. 2b. Consequently, the initial increase in P_{H_2} and decrease in P_{N_2} may result from the formation of α-U_2N_{3+x} by the reaction $2UH_3+(3+x/2)N_2=U_2N_{3+x}+3H_2$. For α-$U_2N_{3+x}$ to be formed in the present situation, the N≡N bond must be broken. Presumably this may occur by interaction of adsorbed N_2 on the surface of UH_3 with hydrogen atoms in this hydride, since the disruption of N_2 can never be expected to occur in the gas phase. The resulting N atoms might continue to migrate in the bulk UH_3 phase by ejecting H as H_2 and eventually α-U_2N_{3+x} is formed. Tagawa [9] reacted UH_3 with N_2 at 9.87, 19.7 and 39.5 kPa (75, 150 and 300 Torr) in the absence of H_2 and found that the reaction began at about 160°C and accelerated above 240°C. In this case, H_2 must have accumulated in the gas phase since the system pressure was much lower than the equilibrium hydrogen pressure over UH_3. Therefore, the presence of hydrogen must always be taken into account even when no H_2 is present initially. The present results and those of Tagawa suggest that the presence of hydrogen is a prerequisite for the formation of α-U_2N_{3+x} since the $U+N_2$ reaction at 300°C never leads to the formation of α-U_2N_{3+x}. As for the reaction $U+(3H_2+N_2)$, NH_3 is formed after 20 h in the case of the UH_3+N_2 reaction. Tagawa did not report the formation of NH_3 [9].

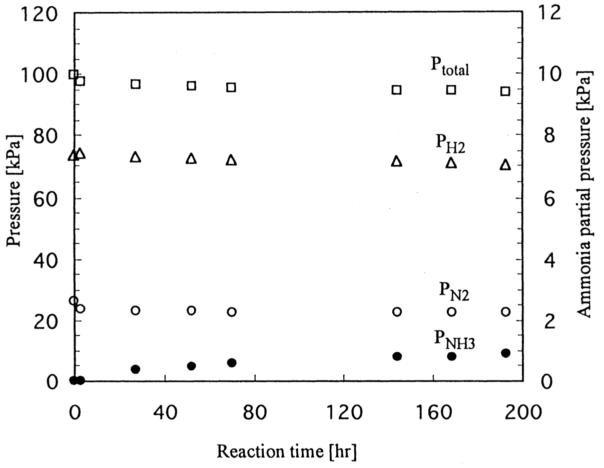

Fig. 3. Variation of P_{total}, P_{N_2}, P_{H_2}, and P_{NH_3} with time during the reaction $UH_3+(N_2+3H_2)$ in a closed system at 300°C.

Apart from the reaction mechanisms for the formation of α-U_2N_{3+x}, a mixture of N_2 and H_2 must be regarded as being thermodynamically unstable with respect to the equilibrium $(1/2)N_2+(3/2)H_2 \rightleftarrows NH_3$. When N_2 gas only is present in the gas phase at a specified temperature and pressure, no change can be expected and the system is thermodynamically stable. However, if H_2 is added to the system, the situation is quite different in that the gas phase is no longer stable from a thermodynamic point of view because the reaction $(1/2)N_2+(3/2)H_2 \rightleftarrows NH_3$ must proceed to the right. The thermodynamic instability brought about by the addition of H_2 to N_2 will make the nitrogen activity of the phase much higher than that of N_2 alone, which, in turn, leads to the formation of α-U_2N_{3+x}.

The present experimental results show that the partial pressure of NH_3 in the last stage of the run reaches about 1 kPa, which is about half the equilibrium partial pressure of NH_3 under the present experimental conditions. This indicate that α-U_2N_{3+x} acts as an effective catalyst for NH_3 synthesis.

Although uranium and some uranium compounds are known as good catalysts for NH_3 synthesis, none of them has been used industrially because iron-based catalysts were developed and employed in the Haber–Bosch process. Since the introduction of this process the industrial production of NH_3 has remained basically unchanged.

4. Concluding remarks

(1) When metallic uranium is employed as the starting material, the reaction of U with a N_2+H_2 mixture is the best way to obtain α-U_2N_{3+x}. This reaction may occur at

low temperatures such as 300°C and this gaseous mixture can be handled more easily than NH_3.

(2) Ammonia has been synthesized by the reaction of U with a N_2+H_2 mixture at 300°C under normal pressure. Thus, uranium may act as an excellent catalyst for NH_3 synthesis.

(3) The thermodynamic instability of the gaseous mixture of N_2 and H_2 with respect to the equilibrium $(1/2)N_2+(3/2)H_2 \rightleftarrows NH_3$ may play a key role in the formation of α-U_2N_{3+x} by the reaction $U+(N_2+3H_2)$.

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