BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1158—1161 (1973)

Formation of Uranium Nitride by the Reaction of Uranium Hydride with Nitrogen and Ammonia

Hiroaki Tagawa
Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11

(Received June 23, 1972)

The hydrogenation of uranium metal and the nitrogenation of uranium and its hydride with either nitrogen or ammonia have been studied using thermogravimetry. The reactions were examined at different pressures of hydrogen, nitrogen, and ammonia. The reaction of uranium with hydrogen takes place at 200°C and proceeds quickly above 210°C. The conversion curve depends greatly on the hydrogen pressure. In the reaction of the hydride with nitrogen, the weight gain occurs at about 160°C and becomes fast above 240°C. The reaction is shown to proceed in two steps: the formation of the mononitride and that of the sesquinitride. The reaction between uranium hydride and ammonia begins at 150°C and becomes rapid above 300°C. The reaction proceeds monotonously, and no step is observed. The nitrogenation behavior of uranium hydride with ammonia is found to be quite different from that in reaction with nitrogen.

The phases in the uranium–nitrogen system were first characterized by Rundle *et al.*[1]: NaCl-type face-centered cubic UN, Mn_2O_3-type body-centered cubic U_2N_3, and CaF_2-type face-centered cubic UN_2. Another nitride was found by Mallett and Gerds[2] and by Vaughan,[3] and was indexed as La_2O_3-type hexagonal close-packed U_2N_3. The bcc and hcp U_2N_3 are designated as the α- and β-U_2N_3, respectively. The α-U_2N_3 phase exhibits a wide range of composition, and ordinarily contains more nitrogen than is represented by its chemical formula; *i. e.*, $UN_{1.54}$-$UN_{1.75}$. α-U_2N_3 is transformed into β-U_2N_3 above 800 °C near the decomposition pressure of the α phase. Uranium nitride, prepared at temperatures below 1300 °C in a nitrogen atmosphere, is usually the α phase. The composition depends on the fabrication conditions–the temperature and the nitrogen pressure. Uranium mononitride is obtained by decomposing α-U_2N_3 at 1500—1600 °C *in vacuo*.

Uranium nitride is prepared by the following methods:

1) $U+N_2$[2,4–7]
2) UH_3+N_2[4,8]
3) $U+NH_3$[4,9]
4) UO_2+C+N_2[8,10,11]
5) UCl_4+NH_3[12]
6) UX_4+Me+N_2(X=F, Cl; Me=Si Al)[13,14]

Methods (1) and (2) are commonly used for preparing the pure material, but the reaction process is not known well in detail. Method (4) is useful for producing the

---

[1] R. E. Rundle, N. C. Baenzieger, A. S. Wilson, and R. A. McDonald, *J. Amer. Chem. Soc.*, **70**, 99 (1948).

[2] M. W. Mallett and A. F. Gerds, *J. Electrochem. Soc.*, **102**, 292 (1955).

[3] D. A. Vaughan, *J. Metals*, **8**, 78 (1956).

[4] R. E. Rundle, N. C. Baenzieger, A. S. Newton, A. H. Daane, T. A. Butler, I. B. Johns, W. Tucker, and P. Figard, USAEC Report TID-5290, Book 1 (1958) p. 53.

[5] C. Moreau and J. Philippot, *C. R. Acad. Sci. Paris*, **253**, 1100 (1961).

[6] Y. Sasa and T. Atoda, *J. Amer. Ceram. Soc.*, **53**, 102 (1970).

[7] R. Benz and W. B. Hutchinson, *J. Nucl. Mater.*, **36**, 135 (1970).

[8] K. M. Taylor, C. A. Lenie, P. A. Smudski, L. N. Hailey, and T. J. Keaty, USAEC Report ORO-248 (1959).

[9] R. E. Alire and J. H. McCrary, *J. Chem. Phys.*, **45**, 3958 (1966).

[10] K. R. Hyde, D. A. Landsman, J. B. Morris, W. E. Seddon, and H. J. C. Tulloch, UKAEA Report AERE-R 4650 (1965).

[11] J. R. McLaren, R. J. Dicker, J. D. L. Harrison, and L. E. Russell, UKAEA Report AERE-R 5710 (1968).

[12] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Dover Pub. Inc., New York (1951).

[13] T. Mitamura, M. Kanno, and T. Mukaibo, *J. Nucl. Sci. Tech.*, **5**, 60 (1968).

[14] K. Yoshihara, M. Kanno, and T. Mukaibo, *ibid.*, **5**, 643 (1968).

nitride on an industrial scale. All the reactions except (4) produce the sesquinitride. The composition of α-U_2N_3 produced varies with the fabrication methods and the annealing conditions. This report describes a study of the behavior of the hydrogenation of uranium metal and of the nitrogenation of uranium and its hydride in thermogravimetry. Although TG does not give precise data on the kinetics, the use of TG will yield some valuable information on the kinetics of these reactions and on the preparations of hydride and nitride of uranium

Experimental

Apparatus and Procedures. The experimental apparatus for heating uranium metal or its hydride in either hydrogen, nitrogen, or ammonia was very similar to that described in an earlier paper reporting on the measurement of the equilibrium nitrogen pressure over a UN and U_2N_3 mixture.[15] It consisted of a Cahn RH-type automatic electrobalance, used as a thermobalance, a Kanthal resistance furnace, a pressure measurement system, a gas supply system, and vacuum pumps. The volume of the reaction system, including the balance chamber and mercury manometer, was 5550 ml. The reaction behavior was examined in a closed system in an atmosphere of hydrogen, nitrogen, or ammonia.

The balance was adjusted so as to have a maximum weight change of 500 mg and a sensitivity of 0.01 mg. A quartz crucible, 25 mm in height and 18 mm in outer diameter, was hung from the balance, and then a quartz tube of 30 mm in outer diameter was connected to the vessel containing the balance. After the connection, the system was evacuated to 5×10^{-6} mmHg or below.

The temperature of the specimen was measured by means of a Pt/Pt+13%Rh thermocouple placed close to the crucible inside the reaction tube. Most of the experiments were made by the thermogravimetric method, with a heating rate of 2 °C/min.

Materials. Pure uranium metal, in the form of chips 0.5 mm thick, 5 mm wide, the 7 mm long, was washed successively with 1 : 1 HNO_3, distilled water, and acetone. About 1 g of the bright metal thus prepared was quickly weighed; it was then placed in the quartz crucible and converted into the hydride and the nitride *in situ.*

High-purity nitrogen was further purified by passing it over a copper gauze heated at 520 °C, and then through a liquid nitrogen trap. The hydrogen was purified by passage through palladium asbestos heated at 300 °C and through a liquid nitrogen trap. The ammonia was solidified in a liquid nitrogen trap, and was then gasified after evacuating the trap.

Results and Discussion

Formation of Uranium Hydride. The bright uranium metal was placed in the quartz crucible, which was hung from one end of the balance arm. The reaction chamber was evacuated, and then hydrogen was admitted into the system. The hydrogen pressures applied were 75, 100, 150, and 300 mmHg. The temperature was raised at a rate of 2 °C/min. Some typical results are shown in Fig. 1. As seen in the figure, the temperature at which the hydrogenation begins depends on the hydrogen pressure. The temperatures are 200, 210, 220, and 260 °C at the hydrogen pressures of 300, 150, 100, and 75 mmHg, respectively. As the initial hydrogen pressure is lowered, the rate of the reaction becomes smaller. After the reaction terminated, the pressure of the hydrogen consumed was found to decrease by 20 mmHg from the initial level. At the hydrogen pressure of 100 mmHg or less, the hydrogenation did not terminate: the conversion into UH_3 was 87% at 100 mmHg and 20% at 75 mmHg. In these cases, the hydride once formed conversely decomposed into uranium and hydrogen above 350 °C before the hydrogenation was complete. The composition of the hydride was $UH_{3.00}$ at room temperature and $UH_{2.97}$ at temperatures between 200 and 400 °C. The values were in agreement with those obtained by equilibration.[12,16] The product was a fine black powder.

The reaction between uranium and hydrogen was found to occur at temperatures exceeding 200 °C, but the initiation temperature and the rate of the reaction were affected by the surface conditions, the shape of the metal-powder, the film or block, and the heating rate, as well as by the hydrogen pressure. When the oxide layer on metal surface was not completely removed, or when the surface was slightly oxidized, the temperature at which the hydrogenation began became obviously higher than that on the clean surface.

In the reactions at the hydrogen pressures of 100 and 75 mmHg, a plateau on the conversion curve appeared, as seen in Fig. 1. The formation of the hydride did not proceed any further beyond a certain temperature, resulting in a pseudo-equilibrium state. Its temperature was 325 °C at the hydrogen pressures of both 100 and 75 mmHg. Spedding *et al.*[17] and Albrecht and Mallett[18] have reported that the reaction

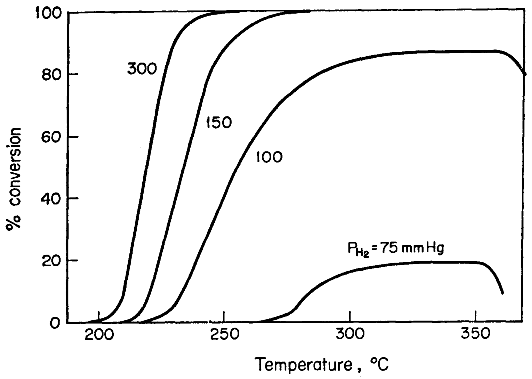

Fig. 1. Thermograms for the hydrogenation of uranium metal in hydrogen of various pressures in mmHg: a heating rate, 2 °C/min.

---

[15] H. Tagawa, *J. Nucl. Mater.*, **41**, 313 (1971).

[16] G. G. Libowitz, "Metal Hydrides," ed. by W. M. Mueller, J. P. Blackedge, and G. G. Libowitz, Academic Press, New York (1968), p. 490.

[17] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. H. Daane, *Nucleonics*, **4**, 4 (Jan. 1949).

[18] W. M. Albrecht and M. W. Mallett, *J. Electrochem. Soc.*, **103**, 404 (1956).

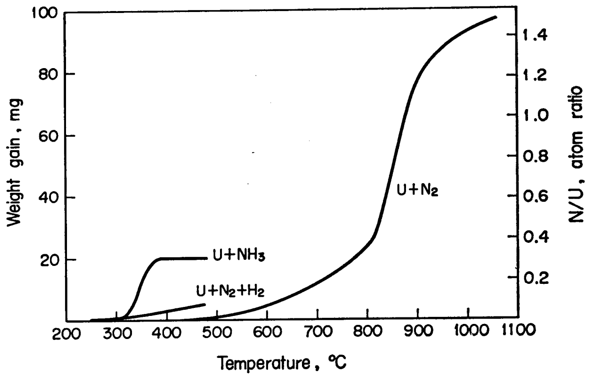

Fig. 2. Thermograms for the reactions of uranium metal with nitrogen and ammonia: the weight of uranium metal, 1.110 g; p_{N_2}, p_{NH_3}=300 mmHg; p_{H_2}=150 mmHg; a heating rate, 2 °C/min.

rate is a function of the p-p_0 value, i. e., C$(p$-$p_0)^{5/2}$ and k$(p$-$p_0)/p_0$, respectively, where p is the system pressure, p_0, the dissociation pressure of uranium hydride, and C and k, constants. In the present experiment, the p-p_0 values at 325 °C were 29 and 19 mmHg at the initial hydrogen pressures of 100 and 75 mmHg, respectively. The hydrogenation did not actually proceed before the value became zero.

Reaction between Uranium Metal and Nitrogen. As in the hydrogenation, 1 g of chips was heated in a nitrogen atmosphere at 300 mmHg up to 1000 °C. The results for the heating rate of 2 °C/min are shown in Fig. 2. The curve shows that the reaction begins at about 400 °C and that the weight changes rapidly in the temperature range between 800 and 900 °C. The temperature range with the maximum velocity did not vary, even if the heating rate was changed. Mallett and Gerds[2)] found, in the reaction of uranium rods with nitrogen, that the Arrhenius plot of the reaction rate was made from two slopes below and above the temperature band of 750—775 °C and that the activation energy changed from 25.5 kcal/mol below 750 °C to 15.1 kcal/mol above 775 °C, where the reaction rate obeyed the parabolic law. If their results are plotted as the relation between the reaction rate and the temperature, the curve is similar to that in Fig. 2. The nitride formed on the metal surface was in the form of a film below 800 °C and coarse powder above 800 °C. The rapid increase in the reaction vleocity in the upper temperature region must be based on the formation of highly porous reaction layers, accompanied by spalled powders.

From the fact that the hydrogenation of uranium metal proceeds at a lower temperature than the nitrogenation of uranium with nitrogen, the nitride formation in the presence of hydrogen may be expected to occur more readily than in the absence of hydrogen. The reaction was examined in a mixture of hydrogen of 150 mmHg and nitrogen of 300 mmHg. The results are also shown in Fig. 2. The nitride formation proceeded slightly more rapidly, but it was not like the case for the hydrogenation in Fig. 1. The surface of the metal was covered with a grayish nitride film, and no powder such as that observed in the hydrogenation appeared. The hydrogenation of the metal, followed by the nitrogenation of the hydride, was scarcely found to occur; thus, the growing of the nitride film on the surface was inferred to be rather predominant over the hydrogenation.

When ammonia of 300 mmHg was used, the reaction began at about 250 °C, but the reaction was terminated at 380 °C, before it was complete. These results are also shown in Fig. 2. As in the case of the mixture of nitrogen and hydrogen, the metal surface was coated with a nitride film, and there existed a small amount of a fine black powder spalled at the bottom of the crucible.

Reaction between Uranium Hydride and Nitrogen. Uranium hydride was prepared in a crucible at about 280°C in a hydrogen atmosphere of 200 mmHg. The nitrogenation behavior was examined by varying the pressures of nitrogen and hydrogen. Figure 3 shows the reaction of uranium hydride with nitrogen of 75, 150, and 300 mmHg in the absence of hydrogen. The reaction began at about 160°C and became rapid above 240°C. In the case of each pressure, the slope of the curve appeared to vary sharply at about 290°C at a composition a little below $UN_{1 \cdot 0}$. The temperature at the bend was lowered somewhat as the nitrogen pressure increased, but the shapes of the curves

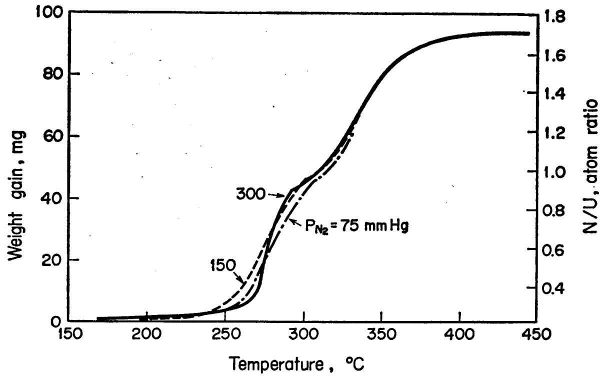

Fig. 3. Thermograms for the nitrogenation of uranium hydride in nitrogen of various pressures in mmHg: The weight of uranium metal, 1.070 g; a heating rate, 2 °C/min.

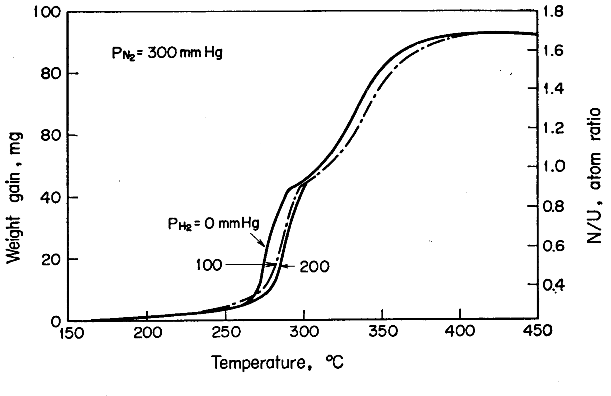

Fig. 4. Thermograms for the reaction of uranium hydride with nitrogen in the presence of hydrogen in mmHg: the weight of uranium metal, 1.070 g; p_{N_2}=300 mmHg; a heating rate, 2 °C/min.

were hardly altered at all by varying the nitrogen pressure. The change in the slope shows two steps of the reaction–the formation of the mononitride, followed by that of the sesquinitride. The nitrogen content increased as the temperature was raised to 420 °C. However, the nitride formed, having more nitrogen than that expressed by the chemical formula of U_2N_3, seemed not to be in an equilibrium state. When the nitride was kept at a temperature below 500 °C, the nitride observed to dissolve more nitrogen with the passage of time.

Figure 4 shows the effect of the pressure of hydrogen on the nitrogenation of the hydride at the nitrogen pressure of 300 mmHg. The hydrogen pressures used were 100 and 200 mmHg. The shape of the curve was not dependent on the variation in the hydrogen pressure. The temperature at which there was a sharp weight gain was 260 °C in the absence of hydrogen, but it shifted higher by about 10 °C when hydrogen was present in the system. The equilibrium hydrogen pressures over UH_3 have been reported to be 4.8, 6.6, and 10.0 mmHg at 250, 260, and 270 °C, respectively.[12,16] When hydrogen was not present, the reaction would occur between nitrogen and the uranium metal produced by the spontaneous thermal decomposition of the hydride. At 100 and 200 mmHg of hydrogen, however, the hydride reacted directly with nitrogen, because the decomposition pressure of the hydride was lower than the system pressure.

The reaction behavior of the hydride with nitrogen at a fixed temperature between 260 and 340 °C was examined by the procedure in which nitrogen of 300 mmHg was added a system which contained the hydride in a hydrogen atmosphere of 150 mmHg. The results are shown in Fig. 5. The velocity of the weight gain at $N/U<1$ is shown to be greater than that at $N/U>1$. The former corresponds to the formation of UN by the reaction of the hydride with nitrogen, and the latter to the formation of the sesquinitride by the reaction between the mononitride and nitrogen.

As mentioned above, the reaction sequence of the nitride formation is expressed as follows:

$$UH_3 + 1/2N_2 = UN + 3/2H_2, \quad \Delta H^\circ_{298} = -40.24\,\text{kcal}$$

$$UN + 1/4N_2 = 1/2U_2N_3, \quad \Delta H^\circ_{298} = -16.7\,\text{kcal}$$

$$U_2N_3 + x/2N_2 = U_2N_{3+x}$$

where the heats of formation, $-\Delta H^\circ_{f298}$, for UH_3,[16] UN,[19] and $1/2U_2N_{3.08}$[15] are 30.59, 70.59, and 86.3 kcal/mol, respectively. Thermochemically, the formation of the mononitride is indicated to take precedence over the sesquinitride in the early stage of the reaction. As seen in Fig. 5, the rate of the weight increase at $N/U<1$ is greater than that at $N/U>1$. Therefore, it may be deduced that the hydride converts to the mononitride, which then reacts with nitrogen to form the sesquinitride after the composition approaches $UN_{1.0}$.

Reaction between Uranium Hydride and Ammonia. The reaction was examined in an ammonia atmosphere of 150 and 300 mmHg. The results are shown in Fig. 6. The reaction began at about 150 °C, and became fast above 250 °C. With ammonia of 300 mmHg, the shape of the curve was obviously different from that of the reaction between the hydride and nitrogen. The reaction is shown to form the sesquinitride directly. In ammonia of 150 mmHg, a plateau on the curve appeared around 400 °C. The plateau seems to indicate that the amount of ammonia becomes too small to continue the reaction with the hydride, but the further reaction of the more reactive uranium powder, produced by the decomposition of the hydride, with the residual ammonia takes place above 400 °C. This is because the partial pressure of hydrogen in the system is about 300 mmHg, and the hydride, of which the equilibrium pressure is 300 mmHg, does not yet proceed to decompose at 390 °C. When the equilibrium pressure is more than the system pressure as the temperature is raised, the thermal decomposition of the residual hydride occurs. As far as the pressure change was followed with time, the decomposition of ammonia was not seen to be catalysed by the nitride or the hydride.

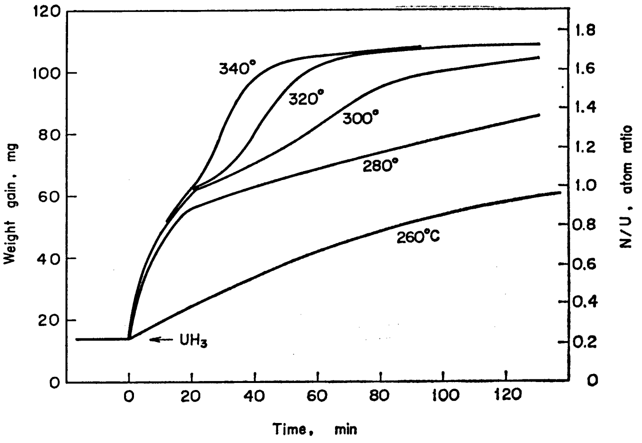

Fig. 5. Nitrogenation of uranium hydride in the mixture of nitrogen of 300 mmHg and hydrogen of 150 mmHg at constant temperatures between 260 and 340 °C: the weight of uranium metal, 1.070 g.

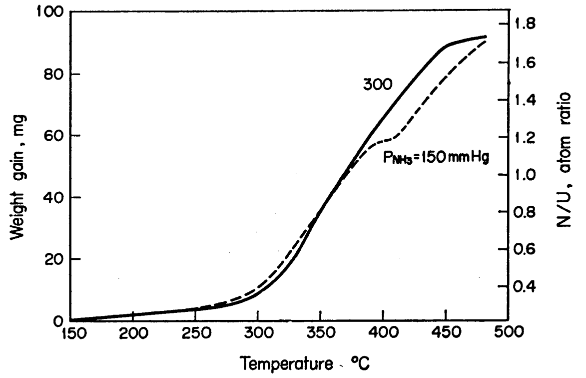

Fig. 6. Thermograms for the nitrogenation uranium hydride in ammonia of various pressures in mmHg: the weight of uranium metal, 1.030 g; a heating rate, 2 °C/min.

---

[19] Average value measured in calorimetry: H. Tagawa, *Nippon-Genshiryoku-Gakkai Shi*, **12**, 658 (1970).