ELSEVIER

Journal of Nuclear Materials 247 (1997) 127–130

journal of nuclear materials

Formation of uranium and cerium nitrides by the reaction of carbides with NH_3 and N_2/H_2 stream

Takashi Nakagawa [a,*], Hirotaka Matsuoka [a], Masaji Sawa [a], Masayuki Hirota [b], Masanobu Miyake [c], Masahiro Katsura [a]

[a] *Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan*
[b] *Industrial Technology R and D Department, New Energy and Industrial Technology Development Organization, National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan*
[c] *Department of Applied Physics and Chemistry, Fukui University of Technology, 3-6-1, Gakuen, Fukui, Fukui 910, Japan*

Abstract

UC or CeC_2 were converted into U_2N_3 or CeN by the use of NH_3 or an N_2/H_2 gas mixture. A stream of NH_3 works not only as a nitriding agent but also as a carbon clearing agent due to its high nitriding and hydriding activities. When the carbide is converted into nitride, carbon is liberated. Some experiments were performed in order to examine the role of the carbon activity of carbon materials (amorphous carbon or graphite) in the formation of CH_4. © 1997 Elsevier Science B.V.

1. Introduction

Uranium mononitride, UN, is considered to be one of the promising nuclear fuel materials for liquid metal fast breeder reactors. Desirable fuel characteristics of liquid metal fast breeder reactors are a high melting point, high thermal conductivity, high heavy-metal atom density, compatibility with cladding and coolant, low swelling, low fission gas release, short time for doubling fuel and fabricability. A review of available data suggests that UN has many favorable properties and potentially the best performance characteristics of the conventional ceramic fuels [1]. A great deal of attention has been given to ways of preparing UN economically and in large quantities [2–5]. The carbothermic synthesis of UN from $UO_2 + C + N_2$ (or NH_3) may be most suitable for this purpose. The UN synthesis process may be divided into three steps. The first step is to heat a mixture of UO_2 and carbon to form UC according to the reaction $UO_2 + 3C = UC + 2CO$, followed by the formation of UN by the reaction of UC $+ \frac{1}{2}N_2 = UN + C$ (the second step) and the final step is the removal of the free carbon formed in the second step by the reaction $C + 2H_2 = CH_4$. Also, uranium nitride fabrication methods are summarized in Ref. [6]. Little attention, however, has been paid to the high hydrogen activity of flowing NH_3 or the different role between NH_3 and the mixture of N_2 and H_2. UN can be obtained by decomposition of U_2N_3 above 1350°C [7] and pure U_2N_3 results in pure UN formation. One of the most important problems is the removal of free carbon from reaction products ($U_2N_3 + C$) for pure U_2N_3 fabrication by the carbothermic reduction. Cerium is often used as a dummy of plutonium. Moreover, the rare earth elements including cerium are present in the nuclear fuels as fission products. In the case where nitrides are used as fuel materials, nitrogen potential may be an important factor for the formation of nitrides of fission products. Cerium mononitride, CeN, is generally prepared by the reaction of cerium metal with NH_3 or N_2 [8,9]. No information is available for the fabrication of CeN by the carbothermic reduction. Katsura estimates nitriding and hydriding abilities of an unstable state ammonia in terms of activities [10]. Ammonia possesses very high nitrogen and hydrogen activities when its decomposition is suppressed. Use of an ammonia stream may be expected to lead to both nitride formation and carbon removal in a shorter time. In this study, uranium monocarbide was reacted with flowing ammonia to form uranium nitride and simultaneously to remove the

---

[*] Corresponding author. Tel.: +81-6 877 5111; fax: +81-6 875 5696; e-mail: nakagawa@nucl.eng.osaka-u.ac.jp.

0022-3115/97/$17.00 © 1997 Elsevier Science B.V. All rights reserved.
PII S0022-3115(97)00036-6

liberated carbon. CeN was prepared by the reaction of NH_3 and CeC_2 which was obtained by the carbothermic reaction of CeO_2 and two kinds of carbon, namely, graphite or amorphous carbon. For comparison, this CeC_2 was reacted with $75\%H_2 + 25\%N_2$ mixed gas to prepare CeN.

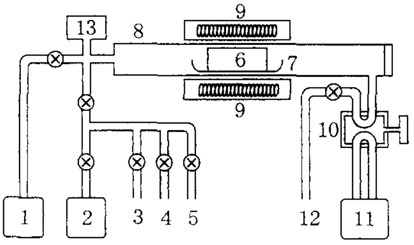
2. Experimental

2.1. Materials

The chemical analysis for the as-received uranium monocarbide powder used in this work shows; 95.00 wt% U, 4.80 wt% combined carbon and 0.03 wt% free carbon. That the chemical analysis accounts for 99.83% material only is thought to be due to analysis error or dissolution of O and N in carbide. Cerium dicarbide was prepared by the carbothermic reduction of cerium dioxide at 1400°C for 12 h in vacuum. The purity of cerium dioxide was 99,999%. Two kinds of carbon, graphite and amorphous carbon, were used in cerium dicarbide (CeC_2) preparation. UC and CeC_2 were treated in Ar atmosphere to prevent their oxidation, Commercial ammonia, nitrogen and hydrogen, (respective purities: 99.998%, 99.9998% and 99.9999%) were used as reactant gases.

2.2. Apparatus

The experimental apparatus used in this work, shown schematically in Fig. 1, consisted of a gas-supply system, a cylindrical resistance furnace, a vacuum system and a gas sampling system. The apparatus could be evacuated to 10^{-6} Pa. A quartz reaction tube was fitted in the resistance furnace. This furnace could be divided into the upper and lower halves connected by a hinge, in such a way that it could be opened for quenching and visual observation. The temperature of the furnace was controlled by an on–off type thermoregulator controlled by a chromel–alumel thermocouple whose ends were mounted on the center of the outer surface of the reaction tube. The temperature of the specimen was measured by this thermocouple. A capacitance manometer is used to measure the total pressure within the range from 10^{-2} kPa to 10^2 kPa. The gas analysis system consisted of a gas sampler with two sampling cocks and a gas chromatograph. An X-ray diffraction powder pattern for the reaction product was obtained with a diffractometer using crystal monochromatized Cu Kα radiation at room temperature.



1. Diffusion Pump
2. Rotary Pump
3. Nitrogen Gas Inlet
4. Hydrogen Gas Inlet
5. Ammonia Gas Inlet
6. Sample
7. Quartz Boat
8. Reaction Tube
9. Electric Furnace
10. Gas Sampler
11. Gas Chromatograph
12. Gas Outlet
13. Capacitance Manometer

Fig. 1. The sketch of the experimental apparatus.

2.3. Procedure

A quartz boat containing UC powder (1 g) was placed in the center of the reaction tube. After the specimen was outgassed at 900°C for 14 h while maintaining the system below $10 - 4$ Pa, the desired temperatures were kept between 600 and 900°C. Then ammonia gas was fed into the reaction tube as a stream at a flow rate of 100 ml/min for 12 h. During each reaction the total pressure (P_{total}) was measured with the capacitance manometer and partial pressures of NH_3, N_2 and CH_4 (P_{NH_3}, P_{N_2} and P_{CH_4}) were determined by the gas chromatograph. That of H_2 (P_{H_2}) was calculated by the relation $P_{total} = P_{NH_3} + P_{N_2} + P_{CH_4} + P_{H_2}$. Part of the reaction product was leached in 10 N HNO_3 solution, held at 100°C for about 10 h to dissolve U_2N_{3+x} and the solutions were filtered off through a glass-filter to check whether indissoluble residue (free carbon) was present or not. The other reaction product 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. Similar experiments for CeC_2 containing an excess free carbon (1–2 wt%) were performed at 900°C under NH_3 flow or N_2–H_2 mixture flow.

Table 1
Detection of CH_4 as a function of time, hydrogen activity and nitrogen activity at each temperature

Reaction temp. (°C)	Reaction time (h)			Reaction products	Hydrogen activity	Nitrogen activity
	3	9	12			
900	detected		not detected	α-U_2N_3	14.7	1766.7
800	detected			α-U_2N_3 + C	13.1	1375.5
700	detected			α-U_2N_3 + C	10.6	711.7
600	not formed			α-U_2N_3 + C	9.7	742.5

3. Results and discussion

The results of the reactions of UC with NH_3 are summarized in Table 1. UC powder could be converted into U_2N_{3+x} under the ammonia flowing atmosphere at all temperatures examined. Free carbon was present in solid products except for at 900°C. At 700 and 800°C, CH_4 was detected throughout the runs, suggesting that the liberated carbons were not completely removed within the allowed period (12 h). In the reaction at 900°C, CH_4 was detected continuously for 9 h and ultimately fell below the detection limit. However, when NH_3 is passed over the UC sample at 600°C, CH_4 was not detected during the run for 12 h presumably because the rate of reaction between liberated carbon and NH_3 was so slow that PCH_4 could not develop above the detectable level. These results suggest that the liberated carbon coexisting with U_2N_{3+x} can be removed through the formation of CH_4 by the reaction with a stream of NH_3. Katsura [10] derived nitrogen and hydrogen activities, a_N and a_H, for the gaseous phase of NH_3, N_2 and H_2 mixture, that is, $a_N = (1/K_{p,NH_3})(P_{NH_3}/P_{H_2}^{3/2})$ and $a_H = \{(1/K_{p,NH_3})(P_{NH_3}/P_{N_2}^{1/2})\}^{1/3}$ where K_{p,NH_3} is an equilibrium constant of the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$. Although the values of both nitrogen activity of 1 bar nitrogen and hydrogen activity of 1 bar hydrogen are unity, the nitrogen activity at the end of each run becomes more than 700 and the hydrogen activity more than 9 as shown in Table 1. Such large activity values may make the formation of nitride and methane feasible.

CeC_2 was fabricated by carbothermic reduction, $CeO_2 + 4C = CeC_2 + 2CO$, and this carbide was reacted with NH_3 or a mixture of nitrogen and hydrogen. Table 2 summarizes the conditions and results of CeC_2 preparation and CeN formation. The CeC_2 sample contained an excess free carbon because carbon had been added to cerium oxide in the mole ratio (CeO_2:C = 1:4.8). If the C/CeO_2-ratio is below the stoichiometric value, the reduction of CeO_2 is incomplete, that is, a certain amount of CeO_2 remains unreacted or sesquicarbide is formed. In runs 1 and 2, graphite was used as a starting material while amorphous carbon was used in runs 3, 4 and 5. CeC_2 could be prepared from either amorphous carbon or graphite. X-ray diffraction pattern of the solid product of run 2 shown in Fig. 2 indicates the formation of CeN and presence of graphite. It is considered that this graphite was not what was crystallized during the reaction but what had been present in solid phase from the beginning of nitridation because X-ray diffraction patterns of the solid products in runs 4 and 5 indicate only the presence of the CeN phase. It is found that graphite is difficult to be removed even by flowing ammonia at 900°C. Fig. 3 shows the variations of respective partial pressures of N_2, H_2, NH_3 and CH_4 and total pressure with time in run 2. In region I, the main reaction may be the conversion of CeC_2 into CeN judging from the fact that the detected nitrogen pressure is lower than the nitrogen pressure which should be obtained by ammonia decomposition. CH_4 formation in region II may suggest that the carbon clearing reaction

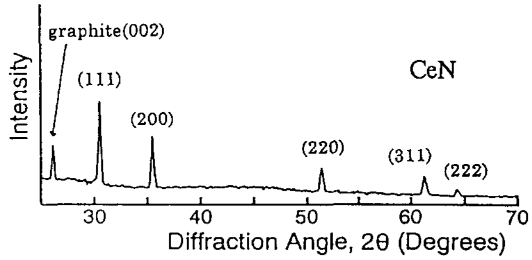


Fig. 2. The X-ray diffraction pattern of the product of run 2.

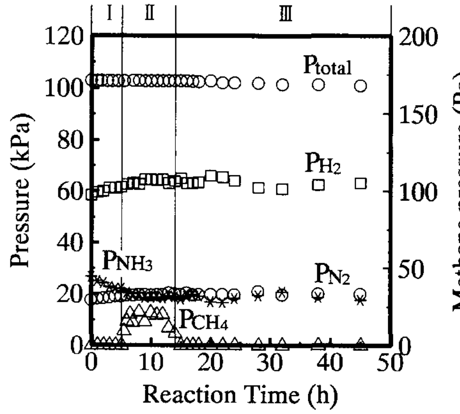


Fig. 3. The variation of each pressure with time during run 2.

Table 2
The conditions and products of the cerium carbide preparation and nitride formation

Run No.	Solid reactants	Gas reactants (flow rate: ml/min)	Reaction time (h)	Reaction temp. (°C)	Solid products
1	CeO_2, graphite	in vacuum	12	1400	CeC_2, graphite
2	CeC_2 (graphite [a])	NH_3(200)	45	900	CeN, graphite
3	CeO_2, amorphous carbon	in vacuum	12	1400	CeC_2, amorphous carbon
4	CeC_2 (amorphous carbon [a])	NH_3(200)	45	900	CeN
5	CeC_2 (amorphous carbon [a])	N_2(50), H_2(150)	45	900	CeN amorphous carbon

[a] An excess of carbon (1–2 wt%).

comes to the fore. The equilibrium is almost reached in the last region where $P_{N_2}:P_{H_2}$ is 1:3. Free carbon in run 4 was removed and there was a little amount of free carbon in the product of run 2 as much as that in the carbide before nitridation. Therefore, free carbon in run 2 may be considered to be graphite. Free carbon in run 5 was hardly removed. This fact indicates that H_2 reacts with carbon much more slowly than NH3 and the above results may suggest a high ability of NH3 as carbon clearing agent.

When carbon comes in contact with NH_3 to form CH_4, the following reaction occurs:

$$C(s) + \tfrac{4}{3}NH_3(g) = CH_4(g) + \tfrac{2}{3}N_2(g). \qquad (1)$$

The use of flowing NH_3 shifts this equation to the right with a sufficient rate until an apparent equilibrium is established. At equilibrium the following relation holds:

$$\mu(C) + \tfrac{4}{3}\mu(NH_3) = \mu(CH_4) + \tfrac{2}{3}\mu(N_2), \qquad (2)$$

where μ denotes the chemical potential. Eq. (2) is rearranged as

$$\tfrac{4}{3}\Delta G_f{}^{\circ}(NH_3) - \Delta G_f{}^{\circ}(CH_4) = RT \ln \frac{P_{CH_4}}{a_C}\left\{\frac{P_{N_2}^{1/2}}{P_{NH_3}}\right\}^{4/3}, \qquad (3)$$

where P is the partial pressure, a_C is carbon activity, $\Delta G_f{}^{\circ}$ is the standard free energy of formation, R is the gas constant and T is temperature. Substituting respective equilibrium constants, K_{p,NH_3} and K_{p,CH_4}, of the reactions, $\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$ and $C + 2H_2 = CH_4$, into the standard free energies of formation yields

$$P_{CH_4} = \frac{a_C}{K_{p,CH_4}}\left\{\frac{K_{p,NH_3}P_{N_2}^{1/2}}{P_{NH_3}}\right\}^{4/3}. \qquad (4)$$

As the carbon activity becomes larger, the methane pressure increases. Eq. (4) explains well the experimental results in this work because amorphous carbon has larger carbon activities than graphite.

For the removal of the free carbon as CH_4 in the conversion process of the carbide into nitride, the combination of an NH_3 stream and amorphous carbon is effective due to high hydrogen activity of the former species and carbon activity of latter.

4. Conclusions

The conclusions drawn from this work are as follows.

(1) UC can be converted into U_2N_{3+x} using an NH_3 stream at temperatures above 600°C.

(2) CeN can be obtained by the reaction of CeC_2 with an NH_3 stream or a gaseous mixture of N_2 and H_2 at 900°C.

(3) It is found that liberated carbon during the nitriding reaction is amorphous carbon and it can be removed by NH_3 at temperatures above 700°C although graphite is difficult to remove, even at 900°C.

(4) An NH_3 stream provides favorable properties for carbide conversion into nitride due to its high nitrogen and hydrogen activities.

References

[1] A.W. Cronenberg, W.A. Ranken, in: Proc. 1st Symp. on Space Nuclear Power Systems, Albuquerque, NM, 1984, eds. M.S. El-Genk and M.D. Hoover (Orbit, Malabar, FL, 1985) p. 307.

[2] T. Muromura, H. Tagawa, J. Nucl. Mater. 71 (1977) 65.

[3] T. Muromura, H. Tagawa, J. Am. Ceram. Soc. 61 (1978) 30.

[4] T. Muromura, H. Tagawa, J. Nucl. Mater. 80 (1979) 330.

[5] T. Muromura, H. Tagawa, J. Nucl. Sci. Technol. 17 (1) (1980) 57.

[6] Hj. Matzke, Science of Advanced LMFBR Fuels (North-Holland, Amsterdam, 1986) ch. 3, p. 125.

[7] A.A. Bauer, Reactor Technol. 15 (1972) 87.

[8] M. Katsura, M. Hirota, T. Nakagawa, M. Miyake, J. Alloys Compounds 207&208 (1994) 413.

[9] R. Kieffer, P. Ettmayer, Sw. Pajakoff, Monatsschr. Chem. 103 (1972) 1285.

[10] M. Katsura, J. Alloys Compounds 182 (1992) 91.