Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 374 (2008) 75–78

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Oxidative ammonolysis of uranium(IV) fluorides to uranium(VI) nitride

Charles B. Yeamans [a], G.W. Chinthaka Silva [b], Gary S. Cerefice [b], Kenneth R. Czerwinski [b,*], Thomas Hartmann [b,e], Anthony K. Burrell [c], Alfred P. Sattelberger [b,c,d]

[a] University of California, Berkeley, Department of Nuclear Engineering, 4155 Etcheverry Hall, M.C. 1730, Berkeley, CA 94720-1730, USA
[b] University of Nevada, Las Vegas, Harry Reid Center for Environmental Studies, Box 454009, 4505 Maryland Parkway, Las Vegas, NV 89154, USA
[c] Los Alamos National Laboratory, Chemistry Division, P.O. Box 1663, Los Alamos, NM 87545, USA
[d] Argonne National Laboratory, 9700 Cass Avenue, Bldg 221, Argonne, IL 60517, USA
[e] Idaho State University, INSE, 1770 Science Center Drive, Idaho Falls, ID 83402, USA

Received 12 March 2007; accepted 14 June 2007

Abstract

Actinide nitrides, in particular UN, are being considered as fuel types for advanced reactor systems. Here, we demonstrate a low-temperature synthesis route on uranium that could be developed into a commercial fabrication process for UN and mixed actinide nitride fuels. UN was successfully synthesized from UO_2 by first reacting with NH_4HF_2 in a ball mill at 20 °C to form tetravalent ammonium uranium fluorides. Then, reaction with an ammonia atmosphere at 800 °C oxidized tetravalent uranium fluorides to hexavalent UN_2. The final product, UN, was obtained by decomposing UN_2 at 1100 °C under argon to produce UN through an intermediate phase of U_2N_3.

1. Introduction

Uranium mononitride (UN) is gaining attention as a potential fuel for Generation IV nuclear reactors. The conventional carbothermic synthesis, which relies on the conversion of the uranium dioxide (UO_2), graphite, and nitrogen gas to carbon monoxide and UN at 1800 °C, is difficult to control and produces fuel with substandard thermal and mechanical properties [1,2], because of the carbon impurities invariably introduced [3,4]. High temperatures volatilize low boiling point actinides, particularly americium [5] leading to potentially difficult contamination control problems.

Uranium mononitride has a number of favorable nuclear fuel properties, such as high fissile atom density, high melting point, and high thermal conductivity [6]. Unfortunately, the current routes to uranium nitrides, (UN, UN_2 and U_2N_3) [7] require high temperatures and pressures for their preparation. This is due to the high thermodynamic stability of UO_2 [8], which is the commonly used starting material. For most uranium chemistry significant energy input is required to overcome the thermodynamic stability of the oxide phase. One interesting exception is the reaction of ammonium bifluoride (NH_4HF_2) with UO_2 that ultimately yields $(NH_4)_4UF_8$ [9–11]. The ammonium–uranium-fluoride chemical system ranging in composition from UF_4 to $(NH_4)_4UF_8$ has been studied in some detail [12,13], so it is somewhat surprising that the mildly exothermic conversion of uranium dioxide to uranium fluorides at ambient temperature has not been more widely exploited. Based on published thermodynamic data [14–16], the enthalpy change for Eq. (1.1). (see below) resulting in the formation of $(NH_4)_4UF_8$ is estimated to be −65 kJ/mol.

A previous study investigated the reaction of UF_4 with ammonia gas at 800 °C [17], but the reaction product was incorrectly identified as U_3N_4, thereby failing to properly characterize the unique oxidative ammonolysis reaction described in the current study. The decomposition of UN_2 to UN has been studied in some detail [18]. A 1970

---

* Corresponding author.
E-mail address: czerwin2@unlv.nevada.edu (K.R. Czerwinski).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.06.022

patent proposed that ammonium uranium fluoride (NH_4UF_5), as well as other uranium fluorides, could be reacted with ammonia to form $UN_{1.9}$, and subsequently denitrided to high-purity UN [19]. However, no analytical data was provided to support such claims.

This work reports a three-step process for synthesizing UN at temperatures below 1200 °C. UO_2 is first converted to tetravalent ammonium uranium fluorides at 20 °C by ball-milling with solid ammonium bifluoride. Then, these ammonium uranium fluoride species are reacted with an ammonia atmosphere at 800 °C. This step simultaneously removes the excess ammonium bifluoride reagent by volatilization and oxidizes the uranium compounds to UN_2. In the final step, UN_2 is decomposed at 1100 °C under argon to produce UN, through an intermediate phase, U_2N_3.

2. Experimental methods

2.1. Ammonium uranium fluoride synthesis

A charge of 10.4 g uranium dioxide (International Bio-Analytical Industries, Inc.) and 9.2 g ammonium bifluoride (Fischer Scientific, 99.99%) was ground in a mechanical ball mill (Retsch PM 100) for 20 min at 20 °C. This starting mixture constitutes a 10% stoichiometric excess of ammonium bifluoride. Immediately after milling, a mixture of ammonium uranium fluorides and unreacted NH_4HF_2 was formed. This was sealed in a teflon bottle and left undisturbed for 55 days, at which point the product was confirmed by XRD as a mixture of $(NH_4)_4UF_8$ and NH_4HF_2 consistent with the known structures [20,21].

2.2. Uranium dinitride synthesis

A charge of 200 mg $(NH_4)_4UF_8$ was loaded in a quartz boat coated in a platinum foil and placed inside a 25 mm diameter quartz tube, capped on either end with a 25 mm quartz Solv-Seal (Andrews Glass Co., Inc.). Pyrex Solv-Seal caps fitted with 15 mm high vacuum teflon stopcocks sealed the tube and allowed a controlled atmosphere to blanket the sample. After flushing with argon (99.999% purity, Praxair) for 30 min, the cover gas was switched to ammonia (research grade, Praxair). The tube furnace reached 800 °C in 20 min, and then was held at temperature for 60 min. A fine white powder, identified by XRD as a mixture of ammonium fluoride and ammonium silicon fluoride, was observed adhering to the tube walls downstream of the quartz boat. After cooling for 2 h to 35 °C, the cover gas was switched back to argon and the tube flushed. The sample was removed from the tube and transferred to an argon inert atmosphere glove box.

2.3. Uranium sesquinitride synthesis

A U_2N_3 sample was synthesized by heating UN_2 at 700 °C for 1 h under ultra-high purity argon in the same apparatus described for UN_2 synthesis.

2.4. Uranium mononitride synthesis

Uranium mononitride was made by heating UN_2 at 1100 °C for 23 min. Since the final UN product oxidizes easily, ultra-high purity argon (99.999% purity, Praxair) was used to maintain the inert atmosphere for the denitriding reaction. Further minimization of oxygen contamination was accomplished by covering the sample with a 0.1 mm thick 99.99 % Pt-foil, as well as employing a zirconium metal oxygen getter upstream of the sample.

2.5. Analytical methods

Samples were analyzed using powder X-ray diffraction on a Phillips PANAnalytical X'Pert Pro, utilizing copper Kα radiation. Lanthanum hexaboride (LaB_6 SRM 660a) was added as an internal standard to XRD samples to allow lattice parameter refinement. Qualitative phase analysis was performed using PANalytical's High Score plus software. Rietveld analysis [22] was applied using the TOPAS-2 software suite (Bruker AXS, Inc.) to confirm and quantify phase constitutions. EXAFS spectroscopy was performed at BESSERC-CAT beamline of the Advanced Photon Source user facility, Argonne National Laboratory.

3. Results

The green $(NH_4)_4UF_8$ starting material was converted quantitatively to dark grey UN_2 (Fig. 1). Rietveld analysis of the powder X-ray diffraction pattern of the product showed it to be consistent with the pattern of uranium dinitride [23], with a lattice parameter of 0.53050 nm. The X-ray density of the UN_2 sample was 11.8357(2) g/cm^3, compared with the published value of 11.73(1) g/cm^3. Uranium dioxide was present as an impurity in the product 0.8(2) wt%. EXAFS spectroscopy confirmed the known face-centered cubic (CaF_2-type) structure and lattice parameter of UN_2 synthesized by this route. XANES analysis indicated that UN_2 created a shift of +2.1 eV in the uranium-L_{III} absorption edge relative to that of UF_4; similar to shifts seen in other U(VI) compounds [24].

The lattice parameter of the U_2N_3 body-centered unit cell calculated from XRD measurements is 1.06538(2) nm, which is a good match to the value of 1.0678(1) nm determined by Rundle [23]. The X-ray density of the U_2N_3 sample is 11.3828(4) g/cm^3, compared with the published value of 11.25(1) g/cm^3. Synthesis of UN under high phase-purity argon was studied at different temperatures, and 1100 °C was found to be optimum. It was possible to synthesize more than 97 wt% phase-pure UN at this temperature. The calculated X-ray density and face-centered UN unit cell lattice parameter are 14.3189(4) g/cm^3 and 0.48897(1) nm, respectively. Again, these values match with the known values [25] of 14.315(1) g/cm^3 and 0.4889(1) nm. Thermogravimetry and differential scanning calorimetry (TG/DSC) profiles indicate that UN_2 decomposes to U_2N_3 at

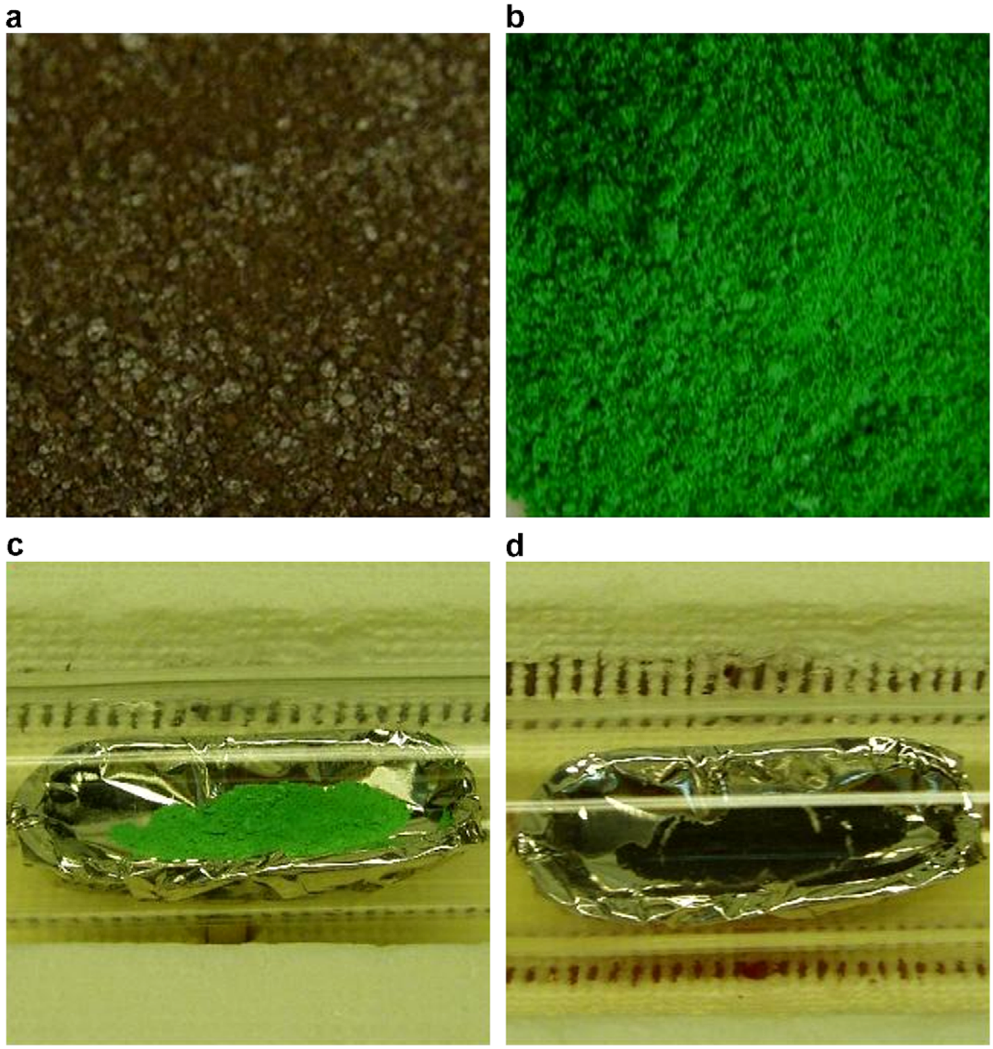

Fig. 1. UN_2 synthesis. (a) UO_2 and NH_4HF_2 immediately after mixing. (b) Ammonium uranium fluoride product mixture after grinding in a mechanical ball mill. (c) Ammonium uranium fluoride mixture before reaction with ammonia. (d) UN_2, after reaction with ammonia at 800 °C for one hour.

650–700 °C, followed by a second decomposition from U_2N_3 to UN at 950–1200 °C.

The exact ammonium uranium fluoride mixture used as a starting material was of no consequence to the product of the ammonia reaction step. Similar uranium nitride products were obtained from analogous experiments performed with pure $(NH_4)_4UF_8$ made by reaction of UF_4 with a saturated ammonium fluoride solution. Furthermore, additional experiments confirmed similar UN_2 product was obtained using the oxide-free mixture of β-NH_4UF_5, δ-$(NH_4)_2UF_6$, γ-$(NH_4)_2UF_6$, and $(NH_4)_4UF_8$ formed within the first hour after milling UO_2 and NH_4HF_2 as the starting material.

4. Discussion

The reaction steps are:

$$UO_2 + 4NH_4HF_2 \xrightarrow{20^\circ C} (NH_4)_4UF_8 + 2H_2O \tag{1.1}$$

$$(NH_4)_4UF_8 + 6NH_3 \xrightarrow{800^\circ C} UN_2 + 8NH_4F + H_2 \tag{1.2}$$

$$UN_2 \xrightarrow{700^\circ C} 1/2U_2N_3 + 1/4N_2 \tag{1.3}$$

$$1/2U_2N_3 \xrightarrow{1100^\circ C} UN + 1/4N_2 \tag{1.4}$$

The overall reaction is

$$UO_2 + 4NH_4HF_2 + 6NH_3 \rightarrow UN_2 + 8NH_4F + H_2 + 1/2N_2 + 2H_2O \tag{1.5}$$

It should be noted that Eq. (1.2). formally is an oxidation of uranium(IV) to uranium(VI). We believe this uranium oxidation is unprecedented in reactions involving gaseous ammonia and may explain why the authors of reference [17] misidentified the uranium nitride product formed from reaction of UF_4 and ammonia. The route exploits the facile reaction of UO_2 with ammonium bifluoride to form uranium fluorides under ambient conditions and suggests application of this reaction step to synthesis of transuranic nitrides. Formation of U_2N_3 at a temperature as low as 650–700 °C is a remarkable reaction considering UN_2 is stable at 800 °C for prolonged periods under ambient atmospheric pressure (100 kPa) of ammonia.

With rapid growth expected in the nuclear power industry, it is important to develop highly-effective processes for fuel fabrication. Nitride fuels are already deployed in high-performance applications such as space reactors, and additional demand for nuclear power creates the need for higher-performance fuels in commercial applications. These fuels must combine the reactor design needs for high performance with the commercial financial demands for low fuel fabrication cost. A less-complicated, lower temperature synthetic route works to accomplish this. In addition, using NH_4HF_2 as the fluorinating agent for converting uranium oxides to uranium fluorides has significant heath and safety advantages over the more commonly-employed fluorinating agents for uranium oxides, aqueous hydrofluoric acid and gaseous fluorine. It is a solid at the reaction temperature, with a much lower vapor pressure and fluoride ion mobility.

5. Conclusion

Oxidation of fluoride species under ammonia to higher valence nitrides represents a novel synthetic approach that merits further study, a logical extension being to synthesis of other actinide nitride potentially useful in nuclear power applications, such as the nitrides of plutonium and thorium. In addition, it will be necessary to produce fuel-quality pellets of uranium mononitride for study of physical and thermal properties of potential fuel material produced from this low-temperature fluoride synthesis. Further process engineering work is necessary to develop this synthetic protocol into a viable plant-scale process, but this route holds great promise for the future of nitride fuel fabrication.

Acknowledgements

The authors are deeply indebted to Dr Frederic Poineau, Dr Martine Duff, and Dr Douglas Hunter for XAFS analysis of the uranium nitride species. This research was supported by the DOE Advanced Fuel Cycle Initiative, US Department of Energy: agreement No. DE-FG07-01AL67358. Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

References

[1] G. Pautasso, K. Richter, C. Sari, J. Nucl. Mater 158 (1988) 12.
[2] P. Bardelle, D. Warin, J. Nucl. Mater 188 (1992) 36.
[3] T. Muromura, H. Tagawa, J. Nucl. Mater 71 (1977) 65.
[4] T. Muromura, H. Tagawa, J. Nucl. Mater 80 (1979) 330.
[5] W. Ward, P.D. Kleinschmidt, R.G. Haire, J. Chem. Phys 71 (1979) 3920.
[6] M. Streit, F. Ingold, J. Euro. Ceram. Soc. 25 (2005) 2687.
[7] J. Bugl, A.A. Bauer, J. Am. Ceram. Soc. 47 (9) (1964) 425.
[8] R.J. Ackermann, P.W. Gilles, R.J. Thorn, J. Chem. Phys 25 (1956) 1089.
[9] D. Copenhafer, US At. Energy Comm. NYO-5027 (1943).
[10] B.N. Wani, S.J. Patwe, U.R.K. Rao, K.S. Venkateswarlu, J. Fluo. Chem. 44 (1989) 177.
[11] C.B. Yeamans, Dry Process Fluorination of Uranium Oxides using Ammonium Bifluoride [thesis], Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, S.M. 2003.
[12] R. Benz, R.M. Douglass, F.H. Kruse, R.A. Penneman, Inorg. Chem. 2 (1963) 799.
[13] R.A. Penneman, F.H. Kruse, R.S. George, J.S. Coleman, Inorg. Chem. 3 (1964) 309.
[14] H. Wanner, I. Forest (Eds.), Chemical Thermodynamics of Uranium, North Holland Elsevier Science Publishers, Amsterdam, 1992, p. 30.
[15] J. Thourey, S. Bendaoud, G. Perachon, J. Fluo. Chem. 36 (4) (1987) 395.
[16] B.N. Sudarikov, E.G. Rakov, L.K. Marinina, V.P. Seleznev, Tezisy Dokl. - Vses. Konf. Khim. Urana. 97 (1974).
[17] H. Funk, H. Böhland, Z Anorg. Allg. Chem. 334 (1964) 155.
[18] P.E. Evans, T.J. Davies, J. Nucl. Mater. 10 (1963) 42.
[19] Nukem Nuilear-Chimie Undmetallurgie Gesellschaft mit Beschprankster Haftung. A process for the production of nuclear fuel nitrides from fluorides. *European Patent Office Great Britain GB1186630* (1970).
[20] A. Rosenzweig, D.T. Cromer, Acta Crystallogr. B 26 (1970) 38.
[21] L. Pauling, Z. Krist. 85 (1933) 380.
[22] H.M. Reitveld, J. Appl. Crystallogr. 2 (1969) 65.
[23] R.E. Rundle, N.C. Baenziger, A.S. Wilson, R.A. McDonald, J. Am. Chem. Soc. 70 (1948) 99.
[24] Y. Suzuki, S.D. Kelly, K.M. Kemner, J.F. Banfield, Appl. Environ. Mircobiol. 71 (4) (2005) 1790.
[25] E.H.P. Cordfunke, J. Nucl. Mater. 56 (1975) 319.