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

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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 UO2 by first reacting with NH4HF2 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 UN2. The final product, UN, was obtained by decomposing UN2 at 1100°C under argon to produce UN through an intermediate phase of U2N3.

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 (UO2), 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, UN2 and U2N3) [7] require high temperatures and pressures for their preparation. This is due to the high thermodynamic stability of UO2 [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 (NH4HF2) with UO2 that ultimately yields (NH4)4UF8 [9–11]. The ammonium-uranium-fluoride chemical system ranging in composition from UF4 to (NH4)4UF8 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 (NH4)4UF8 is estimated to be −65 kJ/mol.

A previous study investigated the reaction of UF4 with ammonia gas at 800°C [17], but the reaction product was incorrectly identified as U3N4, thereby failing to properly characterize the unique oxidative ammonolysis reaction described in the current study. The decomposition of UN2 to UN has been studied in some detail [18]. A 1970
patent proposed that ammonium uranium fluoride (NH₄UF₅), as well as other uranium fluorides, could be reacted with ammonia to form UN₁₉, 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. UO₂ 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 UN₂. In the final step, UN₂ is decomposed at 1100 °C under argon to produce UN, through an intermediate phase, U₂N₃.

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 NH₄HF₂ 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 (NH₄)₄UF₈ and UN₁₉. This was sealed in a teflon bottle and left unchanged for 55 days, at which point the product was confirmed by XRD as a mixture of (NH₄)₄UF₈ and UN₁₉, consistent with the known structures [20,21].

2.2. Uranium dinitride synthesis

A charge of 200 mg (NH₄)₄UF₈ 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 Solyv-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 U₂N₃ sample was synthesized by heating UN₂ at 700 °C for 1 h under ultra-high purity argon in the same apparatus described for UN₂ synthesis.

2.4. Uranium mononitride synthesis

Uranium mononitride was made by heating UN₂ at 1100 °C for 23 min. Since the final UN product oxidizes easily, ultra-high purity argon (99.9999% 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 PANalytical X’Pert Pro, utilizing copper Kα radiation. Lanthanum hexaboride (LaB₆ 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 (NH₄)₄UF₈ starting material was converted quantitatively to dark grey UN₂ (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 UN₂ sample was 11.8357(2) g/cm³, compared with the published value of 11.73(1) g/cm³. Uranium dioxide was present as an impurity in the product by 0.8(2) wt%. EXAFS spectroscopy confirmed the known face-centered cubic (CaF₂-type) structure and lattice parameter of UN₂ synthesized by this route. RXANES analysis indicated that UN₂ created a shift of +2.1 eV in the uranium-LIII absorption edge relative to that of UF₄; similar to shifts seen in other U(VI) compounds [24].

The lattice parameter of the U₂N₃ 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 U₂N₃ sample is 11.3828(4) g/cm³, compared with the published value of 11.25(1) g/cm³. 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/cm³ and 0.48897(1) nm, respectively. Again, these values match with the known values [25] of 14.315(1) g/cm³ and 0.4889(1) nm. Thermogravimetry and differential scanning calorimetry (TG/DSC) profiles indicate that UN₂ decomposes to U₂N₃ at
650–700 °C, followed by a second decomposition from U2N3 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 (NH4)4UF8 made by reaction of UF4 with a saturated ammonium fluoride solution. Furthermore, additional experiments confirmed similar UN2 product was obtained using the oxide-free mixture of β-NH4UF5, δ-(NH4)2UF6, γ-(NH4)3UF6, and (NH4)4UF8 formed within the first hour after milling UO2 and NH4HF2 as the starting material.

4. Discussion

The reaction steps are:

\[
\begin{align*}
\text{UO}_2 + 4\text{NH}_4\text{HF}_2 & \xrightarrow{20^\circ\text{C}} (\text{NH}_4)_4\text{UF}_8 + 2\text{H}_2\text{O} \quad (1.1) \\
(\text{NH}_4)_4\text{UF}_8 + 6\text{NH}_3 & \xrightarrow{800^\circ\text{C}} \text{UN}_2 + 8\text{NH}_4\text{F} + \text{H}_2 \quad (1.2)
\end{align*}
\]

\[
\begin{align*}
\text{UN}_2 & \xrightarrow{700^\circ\text{C}} 1/2\text{U}_2\text{N}_3 + 1/4\text{N}_2 \\
1/2\text{U}_2\text{N}_3 & \xrightarrow{1100^\circ\text{C}} \text{UN} + 1/4\text{N}_2 \quad (1.3) \\
\text{UN}_2 & \xrightarrow{800^\circ\text{C}} \text{UN} + 1/4\text{N}_2 \quad (1.4)
\end{align*}
\]

The overall reaction is

\[
\text{UO}_2 + 4\text{NH}_4\text{HF}_2 + 6\text{NH}_3 \rightarrow \text{UN}_2 + 8\text{NH}_4\text{F} + \text{H}_2 + 1/2\text{N}_2 + 2\text{H}_2\text{O} \quad (1.5)
\]

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 UF4 and ammonia. The route exploits the facile reaction of UO2 with ammonium bifluoride to form uranium fluorides under ambient conditions and suggests application of this reaction step to synthesis of transuranic nitrides. Formation of U2N3 at a temperature as low as 650–700 °C is a remarkable reaction considering UN2 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$_4$HF$_2$ as the fluorinating agent for converting uranium oxides to uranium fluorides has significant health 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.

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