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Characteristics of uranium carbonitride microparticles synthesized using different reaction conditions ☆

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ABSTRACT

Three sets of experimental conditions were tested to synthesize uranium carbonitride ($UC_{1-x}N_x$) kernels from gel-derived urania-carbon microspheres. Primarily, three sequences of gases were used, N_2 to N_2–4%H_2 to Ar, Ar to N_2 to Ar, and Ar–4%H_2 to N_2–4%H_2 to Ar–4%H_2. Physical and chemical characteristics such as geometrical density, phase purity, and chemical compositions of the synthesized $UC_{1-x}N_x$ were measured. Single-phase kernels were commonly obtained with densities generally ranging from 85% to 93% TD and values of x as high as 0.99. In-depth analysis of the microstrutures of $UC_{1-x}N_x$ has been carried out and is discussed with the objective of large batch fabrication of high density $UC_{1-x}N_x$ kernels.

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1. Introduction

The chemical and physical properties of uranium mononitride (UN) or uranium carbonitride ($UC_{1-x}N_x$) make them desirable fast reactor fuels [1]. Uranium mononitride is also being considered as the kernel of tri-structural isotropic (TRISO) particles [2,3] for enhanced accident tolerant fuel type in light water reactors (LWR's). For the LWR TRISO applications the need exists to maximize the fissile fuel density; uranium nitride is significantly better than traditional fuel uranium dioxide (UO_2) for this application. In addition to the highest uranium densities, uranium mononitride also has a high melting point: 2850 ± 30 °C under N_2 pressures of $\geqslant$2.5 atm [4]. Moreover, it also has a high thermal conductivity (15 – 25 W/mK at temperatures ranging up to 1600 °C) [5] and good chemical solubility with other actinides such as Pu and Np due to their similar crystallography in the mononitride form.

Synthesis of high-density UN or $UC_{1-x}N_x$ with low carbon content, especially at large-scale fabrication is challenging. In the most commonly used method of fabricating UN, the carbothermic reduction, carbon-incorporated uranium oxides (UO_2 + C) are heat treated in nitrogen environments to synthesize UN. Here, the first step involves converting the UO_2 + C reactants into dense intermediates of uranium carbide (UC) plus UO_2 followed by transforming the carbide [6] into the nitride [7]. Such nitride kernels need to be further heat treat to obtain high densities. This sintering step is normally done at temperatures in excess of 1750 °C.

Here, as part of an ongoing experimental program, the initial studies of alternative synthesis routes have achieved single phase and high density UN/$UC_{1-x}N_x$ kernels. Their microstructural properties were evaluated and the knowledge gained was utilized in optimizing the synthesis experimental conditions, which are to be used in ~100-g-scale fabrication of UN or $UC_{1-x}N_x$ kernels for LWR and/or Molten Salt Cooled (FHR) platforms. In this article, the characteristics of UN or $UC_{1-x}N_x$ with respect to their chemical composition and microstructure as a function of process conditions are discussed.

2. Experimental conditions and instrumentation

Uranium mononitride and/or $UC_{1-x}N_x$ was synthesized using the carbothermic reduction of air-dried, sol–gel [8] synthesized microspheres of UO_{3-x} + C. These reactant kernels were heat treated using different cover gases at four different steps. The first step,

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calcining up to 700 °C, involves the reduction of UO_3 into UO_2 via the reaction

$$UO_3 + 0.5\ C = UO_2 + 0.5\ CO_2 \qquad \text{(Reaction1)}$$

and a resulting decrease in the initial C/U of the air-dried material by 0.5 [9]. In the second step, the cover gas was either N_2-containing to facilitate nitridation according to the following general reaction

$$UO_2 + 2C + 0.5N_2 = UN + 2CO. \qquad \text{(Reaction2)}$$

or converted to UO_2:2UC in either vacuum or Ar-containing atmospheres via the general reaction

$$UO_2 + 3C = UC + 2CO \qquad \text{(Reaction3)}$$

(Note that carbon in excess of 2 for Reaction (2) would lead to $UC_{1-x}N_x$ and possibly free carbon [10].)

In the third step the kernels finished the nitriding process at 1750–1800 °C and sintered further.

In the fourth step, the cover gas was changed to cool the product $UC_{1-x}N_x$ kernels. This was usually done in inert atmosphere (Ar or Ar–4%H_2) to prevent any oxidation of the nitride kernels at elevated temperatures and to prevent conversion of UN to U_2N_3 if nitrogen atmospheres were used.

The work presented here involves the use of three sets of cover gases for the steps discussed above. These were used in three distinct experiments. Flowing N_2, N_2–4%H_2, and Ar gases were used in the first set of experiments. In the second sets of experiments, Ar, N_2, and Ar were used, while the third set of experiments employed Ar–4%H_2, N_2–4%H_2, and Ar–4%H_2. Table 1 summarizes the experimental conditions used in the three sets of experiments. All of the cover gasses used in these experiments were of ultra-high purity grade 5.0 (99.9–99.998%).

A Labmaster Very High Temperature Laboratory Furnace (Thermal Technology Inc) configured for temperatures up to 1800 °C in air (Graphite Hot Zone Furnace) was used as the graphite furnace. The metal furnace used was a tungsten element, top loading multipurpose furnace from Centorr Vacuum Industries.

2.1. Experiment 1: use of N_2, N_2–4%H_2, and Ar

The reactant oxide (UO_{3-x} + C) microspheres used in this set of experiments contained C/U molar ratios of 2.6 and 2.7. Each sample contained microspheres of 300 to 500 mg. These microspheres were heat treated to 1400 °C at a 5 °C/min in flowing N_2 (1 atm) and held for 12 h at 1400 °C. The cover gas was changed into N_2–4%H_2 after 12 h at 1400 °C and further held for 12 more hours. These unsintered $UC_{1-x}N_x$ kernels were then sintered at 1800 °C for 8 h in flowing Ar gas (Table 1). Once the sintering step was done, the samples were cooled to room temperature in flowing Ar atmosphere.

2.2. Experiment 2: use of Ar, N_2, and Ar

Heat treatment of 1.4 g of UO_{3-x} + C (C/U molar ratio is 2.65) microspheres was done up to a temperature of 1500 °C. First, the reactant material was heat treated to 700 °C at a 3 °C/min ramping rate in flowing Ar gas. This step using 3 °C/min was introduced in order for the precursor kernels to undergo calcination process and to produce UO_2 + C with an approximate C/U molar ratio of 2.15 and to minimize any particle cracking. It was then followed by heating of 5 °C/min to 1500 °C in the same cover gas. The samples were held in that temperature for 8 h in Ar to convert about 2/3 of the oxide to UC. Nitrogen gas was then introduced to the system and held for another 24 h at the same temperature to complete the nitridation step via Reaction (3).

Sintering of these kernels was performed at 1800 °C for 15 h in flowing N_2 gas: first the furnace was ramped up to 1800 °C in Ar, and the cover gas was changed to N_2 at 1800 °C. The cooling was done under flowing Ar gas at 5 °C/min rate.

2.3. Experiment 3: use of Ar–4%H_2 or vacuum, N_2–4%H_2, and Ar–4%H_2

Three different samples named UCN-01 through UCN-03 were synthesized in a Mo crucible with 1.5 in. deapth covered with a graphite sheet (graphoil lid). The first step of the synthesis was performed using Ar–4%H_2 gas for the UCN-01 and UCN-02 samples, and vacuum was used from 700 to 1675 °C for the UCN-03 sample. Another two samples, UCN-04 and UCN-05, were synthesized in a gas-through Mo crucible as first used by Ledergerber et al. [11] surrounded by a Mo fixture to the graphite furnace. This new setup contained gas-through on the reactants in order to obtain a good reaction gas missibility with the kernels. A gas flow of 416 cc/min was used for sample UCN-04. For UCN-05 the gas flow rates were increased to 1660 and 2000 cc/min for Ar–4%H_2 and N_2–4%H_2, respectively. Up to 25 g of precursor UO_{3-x} + C kernels with a C/U molar ratio of 2.65 were used. Table 1 summarizes the experimental conditions used in each of the steps.

Four more 25 to 75 mg samples were synthesized using similar experimental conditions but with different sintering times (10 h in N_2–4%H_2 and 2 h in Ar) plus cooling in Ar concurrently in a

Table 1
Experimental conditions used in the three main sets of experiments.

	Temperature (°C)	Ramp rate (°C/min)	Hold time (h)	Cover gas
Experiment 1				
Step 1	700	5	N/A	N_2
Step 2	1400	5	12	N_2
	1400	N/A	12	N_2–4%H_2
Step 3	1800	5	8	Ar
Step 4	20	5	N/A	Ar
Experiment 2				
Step 1	700	3	N/A	Ar
	1500	5	N/A	Ar
Step 2	1500	N/A	24	N_2
Step 3	1800	N/A	15	N_2
Step 4	20	5	N/A	Ar
Experiment 3				
Step 1	700	3	N/A	Ar–4%H_2
	1675	5	N/A	Ar–4%H_2 or vacuum
Step 2	1750–1800	5	N/A	N_2–4%H_2
	1750–1800	N/A	20	N_2–4%H_2
Step 4	20	5	N/A	Ar–4%H_2