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 microstructures 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 ($\text{UC}_{1-x}\text{N}_x$) make them desirable fast reactor fuelsⁱ. Uranium mononitride is also being considered as the kernel of tri-structural isotropic (TRISO) particles^{ii, iii} 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: $2850 \pm 30^\circ\text{C}$ under N_2 pressures of $\geq 2.5 \text{ atm}$ ^{iv}. Moreover, it also has a high thermal conductivity ($15 - 25 \text{ W/mK}$ at temperatures ranging up to 1600°C)^v 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 $\text{UC}_{1-x}\text{N}_x$ 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 ($\text{UO}_2 + \text{C}$) are heat treated in nitrogen environments to synthesize UN. Here, the first step involves converting the $\text{UO}_2 + \text{C}$ reactants into dense intermediates of uranium carbide (UC) plus UO_2 followed by transforming the carbide^{vi} into the nitride^{vii}. 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/ $\text{UC}_{1-x}\text{N}_x$ kernels. Their microstructural properties were evaluated and the knowledge gained was utilized in optimizing the synthesis experimental conditions, which are to be used in $\sim 100\text{-g}$ -scale fabrication of UN or $\text{UC}_{1-x}\text{N}_x$ kernels for LWR and/or Molten Salt Cooled (FHR) platforms. In this article, the characteristics of UN or $\text{UC}_{1-x}\text{N}_x$ 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^{viii} synthesized microspheres of $UO_{3-x}+C$. These reactant kernels were heat treated using different cover gases at four different steps. The first step, calcining up to 700°C, involves the reduction of UO_3 into UO_2 via the reaction

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

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

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

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%).

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

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 multi-purpose furnace from Centorr Vacuum Industries.

2.1 Experiment 1: Use of N₂, N₂-4%H₂, 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 N₂ (1 atm) and held for 12 h at 1400°C. The cover gas was changed into N₂-4%H₂ 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, N₂, 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 UO₂+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 N₂ gas: first the furnace was ramped up to 1800°C in Ar, and the cover gas was changed to N₂ at 1800°C. The cooling was done under flowing Ar gas at 5°C/min rate.

2.3 Experiment 3: Use of Ar-4%H₂ or vacuum, N₂-4%H₂, and Ar-4%H₂

Three different samples named UCN-01 through UCN-03 were synthesized in a Mo crucible with 1.5 inch depth covered with a graphite sheet (graphoil lid). The first step of the synthesis was performed using Ar-4%H₂ 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^{xi} 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 tungsten furnace. The precursor UO_3+C microspheres used for these four samples contained initial C/U molar ratios of 2.10, 2.15, 2.20, and 2.675.

2.4 Characterization methods

Stereoscopic images of the microspheres were taken at a known magnification. These images were used in determining mean average particle size (radii). A Mettler Toledo XP504 Analytical Balance was used to weigh samples. The balance was validated with reference weights before and after its use to measure samples weights. Geometrical particle densities were determined by dividing average particle weight by average particle volume. Characterization of microstructure of samples (microspheres) was done using a JEOL 6500 FEG-SEM scanning electron microscope (SEM). Crystalline chemical phases were identified using X-ray diffraction (XRD) by a Scintag, USA XRD instrument with a $Cu-K\alpha$ radiation. The XRD instrument was operated at 40 kV and 40 mA power settings. The microsphere particles were powdered and mounted on a zero-background XRD sample mount to acquire XRD powder patterns.

UC and UN have similar crystallography. Their space group is $Fm-3m$ and the lattice parameters are 4.8897Å (ICSD #321397) and 4.9598Å (ICSD #26476) for UN and UC, respectively. Because of these crystallographic similarities, UC is miscible in UN, resulting in solid-solutions of UN and UC: $UC_{1-x}N_x$. According to the literature, lattice parameter of $UC_{1-x}N_x$ solid-solution varies linearly as a function of its composition^{xii, xiii, xiv, xv} obeying Vegard's law with a sufficient accuracy. In the current work, a correlation plot of lattice parameter vs $UC_{1-x}N_x$ chemical composition reported elsewhere^{xvi} was used to determine the chemical compositions of the product $UC_{1-x}N_x$ samples.

3. Results

3.1 Experiment 1: Use of N₂, N₂-4% H₂, and Ar

The first attempt of synthesizing UN involved the nitridation of the reactant UO_{3-x}+C with an initial C/U molar ratio of 2.7 under flowing N₂ gas followed by N₂-4% H₂ at 1400°C (Table 1). As shown in Figure 1a, the resulting product kernels remained intact during the synthesis steps at 1400°C with no significant defects such as powdering or cracking. Powder XRD analysis of the ground kernels indicated that the product is single-phased uranium carbonitride (Figure 1b) with a refined lattice parameter of 4.9026(1)Å. The correlation plots between lattice parameters and UC_{1-x}N_x chemical compositions published elsewhere^{xvi} estimated a chemical composition of UC_{0.2}N_{0.8} for the product phase. The geometrical density estimated for the as-synthesized kernels was 6.9 gcm⁻³.

Figure 1. Optical micrograph and powder XRD analysis of product kernels synthesized using flowing gaseous environments of N₂, N₂-4% H₂, and Ar. The 2nd phase in the XRD pattern is the Si SRM640 internal standard. Red and black ticks on the XRD pattern correspond to Si and UC_{1-x}N_x phases, respectively. The pink pattern at the bottom corresponds to the difference between the calculated and the experimental patterns.

Two reactant compositions containing C/U molar ratios of 2.6 and 2.7 were tested to evaluate sintering of the nitride kernels (Table 1). Even though the product kernels retained spherical shapes without any considerable defects, the product phase consisted of a secondary oxide (UO₂) chemical phase up to 5 wt.% according to XRD analysis. A definite cause for the formation of secondary UO₂ was not identified, but a more likely cause can be the insufficient reaction time. The geometrical densities of sintered product kernels ranging from 8.9 to 11.2 gcm⁻³ indicated ~30% increase in the sintered kernel density (theoretical density (TD) up to 78%) compared to the as-synthesized kernels

(48% TD; before sintering). The chemical compositions of the product carbonitride phase estimated by refined lattice parameters also indicated a lowering of the carbon content in the sintered samples (e.g., $\text{UC}_{0.08}\text{N}_{0.92}$). Only a slight variation in the product chemical compositions and the geometrical densities was identified with respect to the different C/U molar ratios of the reactants used.

3.2 Experiment 2: Use of Ar, N_2 , and Ar

Here, the precursor $\text{UO}_{3-x}+\text{C}$ kernels with an initial C/U molar ratio of 2.65 were used, and ramping rate of $3^\circ\text{C}/\text{min}$ was used up to 700°C to optimize the reduction step. Table 1 summarizes the experimental conditions used in the rest of the steps. The unsintered $\text{UC}_x\text{N}_{1-x}$ kernels had geometrical densities of 7 to 8 gcm^{-3} , while the sintered samples consisted of kernels from 9 to 10 gcm^{-3} densities. SEM micrographs of as-synthesized $\text{UC}_{1-x}\text{N}_x$ kernel cross-sections together with that of the reactant sample are shown in Figure 2 for an example to show the change in the microstructure between the reactant and the product phases: the calcined UO_2+C kernels consist of needle-shape morphology (Figure 2a and 2b), whereas the product $\text{UC}_{1-x}\text{N}_x$ kernels show agglomerated grains of randomly oriented particles with angular-shaped morphology (Figure 2c and 2d).

Figure 2. SEM micrographs of calcined reactant oxide plus carbon (UO_2+C , $\text{C}/\text{U} \sim 2.15$) and the product $\text{UC}_{0.07}\text{N}_{0.93}$. (a) SEI SEM and (b) Back-scatter electron (BSE) SEM images of the $\text{UO}_2+2.15\text{C}$. (c) SEI SEM and (d) BSE SEM images of $\text{UC}_{0.07}\text{N}_{0.93}$.

3.3 Experiment 3: Use of Ar-4% H_2 or vacuum, N_2 -4% H_2 , and Ar-4% H_2

3.3.1 Physical properties and XRD analysis of product carbonitride kernels

Further experimentation on synthesizing dense uranium mononitride or carbonitride was carried out using reducing environments. The experimental conditions tested were as reported by Ledergerber et al^{xi} in synthesizing dense nitride kernels. Three samples were synthesized using the experimental conditions given in detail in section 2.3 and Table 1. A summary of results for the first three samples is given in Table 2. Since the cover gas for the reduction step contained H_2 , O/U reduction to 2 occurs both by carbon, Reaction 1, and by hydrogen^{xvii} (given good cover gas miscibility with the sample), the latter by the general reaction

This results in C/U values higher than that of the desired 2.15.

Table 2. Summary of results obtained for uranium nitrides synthesized using reducing environments. The reactant used was $\text{UO}_{3-x} + \text{C}$ (C/U molar ratio = 2.65)

Sample	XRD results			Avg. particle wt. (g)	Density (g/cm^3)	
	χ^2	L.P. ($\text{\AA}$)	Composition		Experimental	% TD
UCN-01	1.0	4.9325(1)	$\text{UC}_{0.54}\text{N}_{0.46}$	3.80×10^{-3}	12.6	90.2
UCN-02	1.0	4.9233(1)	$\text{UC}_{0.41}\text{N}_{0.59}$	3.78×10^{-3}	13.0	92.6
UCN-03	1.1	4.9366(2)	$\text{UC}_{0.60}\text{N}_{0.40}$	3.72×10^{-3}	12.3	83.4 – 91.0

χ^2 is the goodness of fit between the calculated and the experimental XRD patterns.

All three samples contained only uranium carbonitride phase in the product samples as identified by powder XRD (Figure 3). As indicated in Table 2, each of these samples contained close to 50% carbon, which was estimated using refined lattice parameters, in the uranium carbonitride. The probable cause for high carbon content in the product phase may be due to the reducing conditions (4% H_2), which may have hindered the carbon removal during the calcination step in addition to not having good reaction gas miscibility with the sample. Moreover, the presence of background carbon from the furnace may hinder carbon removal in the sample as HCN since furnace carbon produced HCN reacting with the reaction gas. However, reducing conditions were used to see if the conversion kinetics could be improved. The average particle volume determined for the UCN-01, UCN-02, and UCN-03 samples were 3.0×10^{-4} , 2.9×10^{-4} , and $3.0 \times 10^{-4} \text{ cm}^3$, respectively. The difference in the geometrical densities of the samples corresponds to the slight differences in both the average particle weight and average particle volume (Table 2).

Figure 3. Powder XRD patterns of UCN-01, UCN-02, and UCN-03 samples reported in Table 2. Asterisks indicate the first two major reflections for the Si SRM640b internal standard. Other peaks correspond to $UC_{1-x}N_x$.

3.3.2 Microstructural evaluation of the samples

Microstructures of few typical particles from samples UCN-01 and UCN-02 are depicted in Figure 4. The first particle of the sample UCN-01 shown in Figure 4a contains pores uniformly distributed throughout the whole particle. The 2nd particle (Figure 4b) contains slightly more and larger pores in upper left corner of the particle (highlighted by arrows in Figure 4b). The other two particles shown in Figure 4c and 4d have significant amount of pores close to the particle surface. In both these particles, especially in the one in Figure 4c, most of these large pores are ~10 to 40 μm away from the particle surface. These features in the particle microstructures indicate that the sintering has begun from inside the kernel (close to the center) and directed towards the particle surface. The presence of comparatively large amount of pores close to some of these particle surfaces are suggestive of the sintering process: either some of the

particles' surfaces did not have enough time for grain growth before changing the reaction medium to Ar-4% H_2 from N_2 -4% H_2 or at the sintering temperature; some of the kernels in the reaction medium did not get good miscibility with the reaction gases due to their particular spatial orientation.

In sample UCN-02, the 1st particle (Figure 4e) consists of considerably high uniformity in its pore distribution. Also, the amount and the sizes of the pores of this particle are smaller compared to that of the particles in UCN-01 sample. The pore distribution in the 2nd particle (Figure 4f) is close to the uniformity observed in the first particle. However, a thin layer of distribution of large pores trapped in the kernel from 10 to 20 μm distance away from the kernel surface can be observed at the particle edge, especially at lower right side of it, as highlighted by arrows in Figure 4f. The third (Figure 4g) and fourth (Figure 4h) particles consist of more pores close to the center of the particles than the other two. The large grown grains at the particle surface are obvious in this third particle (Figure 4g) because of the large amount of pores distributed in the center. Also, the pore sizes are larger close to the boundary of the large grain layer of the particle (highlighted by an arrow in Figure 4g). Similar characteristics can be observed in the fourth particle (Figure 4h) in the same sample (UCN-02), but the pore distribution is continuous throughout the particle and the large grain layer thickness is smaller compare to those of the third particle (Figure 4g).

Figure 4. Full particle BSE SEM micrographs of the samples UCN-01 (figures (a) through (d)) and UCN-02 (figures (e) through (h)). The large black blocks in the images are due to dust particles. The arrows highlight the areas of comparatively large amount of pores in the particles.

Figure 5 shows examples of microstructures of kernels from UCN-01 and UCN-02 at high resolution. These high resolution micrographs of the two representative particles further verify the differences in characteristics of pores (size and amount) and grains (size and the level of contrast) of these samples. The amount of pores at the center of the particle with uniform pore distribution (Figure 5a) in UCN-01 sample is less than that of the particle with an uneven pore distribution (Figure 5c) in UCN-02 sample. On the particle surfaces, whether it is with more pores or less pores, a considerable amount of small size pores can be observed in both samples: UCN-01 (Figure 5b) and UCN-02 (Figure 5d). One discernible reason for the presence of such a large amount of small size pores on the kernel surfaces could be the presence of large grown grains on the surface or in the areas close to the surface of the particles. The large amount of pores in the low-contrast area close to the large grain boundary observed in Figure 4g is more prominent in Figure 5d.

Figure 5. High resolution BSE SEM micrographs of samples UCN-01 and UCN-02. (a) Center of particle in Figure 4a, (b) surface of particle in Figure 4c, (c) center and (d) surface of particle in Figure 4g.

In the UCN-03 sample, particles have comparatively large amount of pore spacing at the particle center. Two particles with different amounts of pores at the center are shown in Figure 6a and 6b. Compared to the pore distribution observed at the center of the particles in UCN-02 sample (Figure 4g and 4h), the pores seem to distribute around the center of the particles in UCN-03 sample. Furthermore, the spread of pores from the particle center (Figure 6c) to the surface (Figure 6d) is not continuous; the very small pores are less at the particle surface (Figure 6d) in UCN-03 compared to samples UCN-01 (Figure 5b) and UCN-02 (Figure 5d).

Figure 6. BSE SEM micrographs of the Sample 3. BSE SEM images of 2 particles (a) and (b) from UCN-03. High resolution micrographs of particle 1 at the center (c) and at the surface (d). The large black block in particle 2 is from a dust particle.

3.3.3 High carbon levels in the dense samples and the remedy

Table 3 summarizes the characterization results of the four samples synthesized in the tungsten furnace. All four samples contained $UC_{1-x}N_x$ in the product phase. The refined lattice parameters of $UC_{1-x}N_x$ synthesized using reactant $UO_{3-x}+C$ with C/U molar ratios of 2.10, 2.15, and 2.20 were close to each other with values of 4.8904(1), 4.8905(1), and 4.8905(1) Å, respectively. These lattice parameters correlate to a chemical composition of $UC_{0.01}N_{0.99}$ for all three samples. The last sample synthesized using the reactant C/U molar ratio of 2.675 also had a close lattice parameter value (4.8907(1) Å), which reflects a chemical composition of $UC_{0.01}N_{0.99}$. This composition with high-end nitrogen in the

carbonitride indicates that the use of a carbon-free furnace system lowered the carbon levels in the final nitride product independent of the C/U molar ratio used in the reactant oxides. A previous work by Lindemer et al^{ix} suggested that HCN formation removed excess carbon from these small samples with the 0.5 L/min flow rate to result in high UN content. This did not happen in the graphite furnace possibly because the furnace itself provided HCN content plus the Ar-4% H_2 gas exchange with the microparticles in the Mo crucible covered by graphoil lid was minimal.

The density of the last sample (with C/U 2.675) is the lowest among the four samples synthesized in the tungsten furnace (Table 2). The average particle size is also highest for this sample. With high carbon amount in the reactant and same amount of carbon in the product as in the other three samples (Figure 4), the lowest density in this sample indicates more pores in the product kernels due to comparatively large amount of carbon that has been replaced by nitrogen during carbonitride formation. This also suggests that longer sintering time or better reaction gas exchange would be needed when the reactants of higher C/U molar ratios are used to fabricate dense uranium carbonitrides.

Table 3. Characteristics of the four samples synthesized in a tungsten furnace

Reactant C/U mol. ratio	XRD results			Average radius (μm)	V (cm^3)	Avg. particle wt. (g)	ρ (gcm^{-3})
	L.P. ($\text{\AA}$)	Comp.	χ^2				
2.10	4.8904(1)	UC _{0.01} N _{0.99}	2.24	446.2	3.72×10^{-4}	4.25×10^{-3}	11.4
2.15	4.8905(1)	UC _{0.01} N _{0.99}	2.25	437.2	3.50×10^{-4}	3.88×10^{-3}	11.1
2.20	4.8905(1)	UC _{0.01} N _{0.99}	2.13	441.5	3.6×10^{-4}	4.17×10^{-3}	11.6
2.675	4.8907(1)	UC _{0.01} N _{0.99}	2.08	461.2	4.11×10^{-4}	3.98×10^{-3}	9.7

Considering the observed results, two more nitride samples (UCN-04 and UCN-05) were synthesized in carbon-free environment using a Mo fixture to the furnace and a Mo crucible to hold the reactant $\text{UO}_{3-x} + \text{C}$ with a C/U molar ratio of 2.65. The experimental conditions used for these two samples were same except the cooling was performed in Ar for UCN-04 and Ar-4% H_2 for UCN-05. Also, 25g reactant batches were used in preparing these two samples. Since the batch size (25g) was larger than what has been

used previously, XRD was performed on different samples of particles picked up from center and sides of the sample holder. UCN-04 showed to contain nitride with compositions ranged from $UC_{0.01}N_{0.99}$ to $UC_{0.04}N_{0.96}$. Some particles showed few percentage (up to 3 wt.%) of UO_2 as the secondary chemical phase, probably due to insufficient reaction of the precursor material with the reaction gas in the production of intermediate UC. A geometric density of 92% TD was determined as the highest particle density for this sample. UCN-05 also showed similar characteristics with respect to level of carbon in the nitride and geometrical density.

4. Discussion

Uranium mononitride or uranium carbonitride was synthesized using three different experimental conditions, mainly by varying the reaction gas and temperature. All gas combinations successfully prepared single phase uranium carbonitride with chemical compositions of $UC_{1-x}N_x$ with a range of x values of 0.8 to 1.0. However, nitriding below $1675^{\circ}C$ even when followed by sintering at $1800^{\circ}C$ with up to 15 h holding time produced kernels limited to a density of 11.2 kg/m^3 or 78% TD, as Shoup^v similarly demonstrated at $1500^{\circ}C$. On the other hand, nitriding above $1675^{\circ}C$ produced higher-density $UC_{1-x}N_x$ kernels with densities up to 13.0 gcm^{-3} (~91% TD) when using a shallow Mo crucible to hold the reactant kernels in the graphite furnace. The drawback of using reducing conditions with reactant kernels in the shallow Mo crucible in the graphite furnace was that the product $UC_{1-x}N_x$ kernels contained high carbon levels (up to 50% C). In order to obtain kernels with lower carbon content, similar experiments in a carbon-free tungsten furnace with N_2 -4% H_2 produced $UC_{1-x}N_x$ with very low carbon levels (up to 1%), even if the reactant oxides contained large amount of carbon such as C/U molar ratios of 2.675.

As was noted by Lindemer et al^{ix}, the high carbon content was proposed to result because, during calcination, reaction 4 was more dominant in the presence of H_2 than reaction 1, and thus carbon not used during calcination was incorporated into the product carbonitride. Further experimentation in the same graphite furnace but utilizing a Mo enclosure with better reaction gas exchange with the reactant kernels produced $UC_{1-x}N_x$ with low carbon contents (up to 4%). This indicates that good reaction gas miscibility

with kernels is needed to remove extra carbon as HCN in the product phase when N_2-H_2 gas mixtures are used in the sample synthesis.

Microstructural evaluation of uranium carbonitrides indicated differences in the particle morphology and pore distribution with respect to varying chemical composition of $UC_{1-x}N_x$. With respect to the needle shape grains in the reactant UO_2+C , the product $UC_{1-x}N_x$ kernels synthesized using the first two experimental conditions (sections 2.1 and 2.2) showed agglomerated bulk grain properties. An enlargement of grains was observed during the sintering of the carbonitrides in the dense (93% TD) $UC_{1-x}N_x$ kernels, which were synthesized using a third set of experimental conditions (section 2.3).

Pore size and pore distribution in the $UC_{1-x}N_x$ kernels with high carbon levels had differences with respect to each sample and each kernel, even in the dense samples. In some kernels, more pores were identified at the kernel center than the surface. Pore distribution was sometimes symmetrical and sometimes was not. Some kernels consisted of thin layers of dense areas with large grown grains on the kernel surface. Kernels with more pores close to their surfaces were also identified in these dense samples. These observations indicated that the reaction gas was not easily miscible with the reactant microspheres when using a shallow Mo crucible to hold the reactant kernels, as was determined by the presence of large amount of C in the product phase.

Therefore, a Mo fixture and a Mo crucible with better gas exchange with the reactant kernels were made. Using this new experimental setup, which is similar to that used by Ledergerber et al^{xi}, nitride kernels with a chemical composition of $UC_{0.01}N_{0.99}$ was obtained. The presence of low carbon levels verified the good exchange of reaction gas with reactant kernels. These modifications are to be further evaluated to gain better understanding of the system and optimizing the experimental conditions for synthesizing large batches of high density $UC_{1-x}N_x$.

Conclusions

Carbothermic reduction was successfully used to synthesize single phase $UC_{1-x}N_x$ kernels. Different experimental conditions of gas flow, composition, and sequence, specimen configuration, and reaction temperatures were utilized in this effort. No defects such as cracked or broken kernels were observed in these uranium carbonitride samples.

Small batches (~5 g) of $UC_{1-x}N_x$ kernels with densities generally ranging from 85 to 93% TD could be synthesized. The reason for the high levels of carbon in the product $UC_{1-x}N_x$ kernels, when using a shallow Mo crucible to hold the reactant kernels, was identified as to due to reducing conditions used in a carbon-rich furnace system and not having enough reaction gas miscibility with the sample. This observation was verified using a vertical flow-through Mo crucible in which $UC_{1-x}N_x$ kernels with low carbon levels and high density were obtained.

Further experiments are being carried out to using the modified furnace setup in synthesizing 50-200 g batches of $UC_{1-x}N_x$ kernels having near-theoretical densities.

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