QUANTIFICATION OF PROCESS VARIABLES FOR CARBOTHERMIC SYNTHESIS OF $UC_{1-x}N_x$ FUEL MICROSPHERES

TB Lindemer¹, CM Silva², JJ Henry², JW McMurray^{2,*}, SL Voit², JL Collins², and RD Hunt²

1. MPi Business Solutions, Inc., Knoxville TN 37915

*2. Materials Science and Technology Division, Oak Ridge National Laboratory,
Oak Ridge, TN 37831-6063*

A B S T R A C T

This report details the continued investigation of process variables involved in converting sol-gel-derived, urania-carbon microspheres to ~820- μ m-dia. $UC_{1-x}N_x$ fuel kernels in flow-through, vertical Mo and W crucibles at temperatures up to 2123 K. Experiments included calcining of air-dried UO_3-H_2O-C microspheres in Ar and H_2 -containing gases, conversion of the resulting UO_2-C kernels to dense $UO_2:2UC$ in the same gases and vacuum, and its conversion in N_2 to $UC_{1-x}N_x$ ($x = \sim 0.85$). The thermodynamics of the relevant reactions were applied extensively to interpret and control the process variables. Producing the precursor $UO_2:2UC$ kernel of ~96% theoretical density was required, but its subsequent conversion to $UC_{1-x}N_x$ at 2123 K was not accompanied by sintering and resulted in ~83-86% of theoretical density. Increasing the $UC_{1-x}N_x$ kernel nitride component to ~0.98 in flowing N_2-H_2 mixtures to evolve HCN was shown to be quantitatively consistent with present and past experiments and the only useful application of H_2 in the entire process.

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*corresponding author, email: mcmurrayjw1@ornl.gov

1. Introduction

This paper reports a study of the many experimental parameters involved in conversion of gel-derived urania-carbon microspheres to $UC_{1-x}N_x$ fuel kernels. The technical basis for the needed fabrication of accident-tolerant fuel has been summarized earlier [1, 2] and publications since 1975 report synthesis of $UC_{1-x}N_x$ kernels [3-13]. A common theme is the experimental difficulty in approaching theoretical density for the very refractory UN, which melts at 3035 K at 0.1 MPa N_2 [13], as was also noted for UN pellets [14] and (U,Pu)N pellets [15] fabricated from powder. Most studies used isothermal conversion to $UC_{1-x}N_x$, sometimes followed by attempts to increase the kernel density with higher temperatures and N_2 -free atmospheres. Another common theme was conversion first to a $UO_2:2UC$ kernel either in flowing inert gas or vacuum (also used for making UO_2 -UC- UC_2 fuel kernels at 1823 K [16] and 2163 K [17, 18]), followed by conversion to $UC_{1-x}N_x$ in flowing N_2 . Sometimes H_2 was also a gas component. Ledergerber et al [5] reported the sole use of gas flowing through the microspheres at a known rate in a vertical Mo crucible, while the others exposed the reactant bed at less efficient modes of gas exchange. Generally, maximum batch sizes contained <60 g U content.

Here, the primary experiments are an extension of those in ref. [5] and were conducted in vertical Mo and W crucibles in which gas flows up through the bed of microspheres at temperatures up to 2023 K. The programmatic objective was quantitative description of the parameters for production of dense $UC_{1-x}N_x$ kernels for irradiation experiments.¹ The experiments permitted a detailed investigation of non-isothermal carbothermic conversion to $UO_2:2UC$ during a 1-5 K/min temperature ramp at different flow rates, which are given at standard temperature and pressure (STP), followed by conversion to $UC_{1-x}N_x$ at 1948-2123 K and sintering up to ~2373 K. Several other allied experimental results are also reported.

2. Experimental

2.1. Sample preparation

The internal gelation process was used to produce hydrated uranium trioxide microspheres containing Cabot Mogul L carbon black adequately dispersed throughout the gel spheres as described in ref. [9]. Cabot Mogul L is the fluffy form of Cabot's Black Pearl L. It has a density of 0.2403 g/cm³, a surface area of 138 m²/g, and an average particle size of 24 nm. In solution it tends to form large aggregates which are best dispersed in basic solution with a dispersing agent. In these experiments, the carbon and dispersing agent (Tamol SN) were added to the chilled basic hexamethylenetetramine (HMTA)/urea solution and sonicated for 5 min with a Hielscher UP200S ultrasonic probe. It was subsequently chilled in an ice bath prior to mixing it with the chilled acid-deficient uranyl nitrate solution to make the broth. Care was given to minimize the chance of the carbon reagglomeration, flocculation, and settling in the broth before gel spheres were formed. The air-dried gel microspheres retain both H_2O and NH_3 with an approximate ratio of 15/1 [19], have a molar C/U ratio of 2.65, and a density of ~1.6 g/cm³, equivalent to ~40% of theoretical density. A few experiments were performed with similar air-dried microspheres having C/U ratios of 2.15 and 2.3.

2.2. Equipment, supplies, and methodology

All gases were ultrapure grade. The graphite furnace was capable of 2473 K (Astro furnace, Thermal Technologies). It was fitted initially with a vertical Mo crucible similar to that used in ref. [5] with a ~100 cm³ working volume (3.76 cm inside dia. × 8.64 cm high) that held a maximum of ~120 g of air-dried microspheres on a Mo screen. A 2273 K nitriding run indicated melting of the Mo screen and a review of published phase diagrams revealed a Mo-N eutectic and a W-N peritectic involving liquids,

¹ This document is a condensation of Oak Ridge National Laboratory report ORNL/TM-2015/301.

both at ~ 2200 K [20]. Thus, a hollow W cylinder of similar dimensions positioned on a W screen above a carbon base was used subsequently, nitriding experiments were limited to < 2300 K to avoid the known W-N peritectic, and Ar was used for $UC_{1-x}N_x$ kernel sintering experiments up to 2375 K, with no further indication of liquids. Ultra high purity gases were introduced into the crucible bottom through either a ~ 4.5 -cm-dia. Mo or, later, W screen. Optical and thermocouple methods confirmed the bed temperature, and flow rates as high as 2.5 l/min, beyond those used here, cooled the bed by less than 5 K from any set point above 1775 K. Geometrical densities of input microspheres and product kernels were determined from their weights and radii obtained from stereoscopic images, ref. [11]. The product from each 25 to 110 g run was separated by a roller micrometer into ~ 5 bin fractions that differed by ~ 30 μm in diameter. Geometrical density of each fraction was determined from average kernel weight and stereoscopic measurement of kernel diameters; 794 (± 10) μm Fe spheres were used to calibrate this procedure and gave 96.7% theoretical density for the Fe standards. Subsequent porosimetric measurements of density confirmed those measured optically. Crystalline chemical phases were identified using X-ray diffraction (XRD) and subsequent analysis [11]. The value of x in $UC_{1-x}N_x$ was determined from the lattice parameter, p (nm), via the relation $x = -759.314 + 3223.5 p - 3412.4 p^2$. The latter equation was obtained by fitting 40 (x , p) data pairs, 31 from UC to UN from ref. [21], and 9 in the composition range $\sim 0.3 \leq x \leq \sim 0.87$ reported in ref. [22]. This relation gives $UN_{1.001}$ at 0.4890 nm. (A similar equation from ref. [5] was inaccurate for $x < \sim 0.5$, while the one from ref. [22] only fitted those ~ 30 data pairs.)

A typical experiment when using the Mo crucible in the Astro furnace is described next. Calcining from ambient to ~ 975 K was performed at 3 K/min, then the calcined material was ramped at 5 K/min to 1673 K where the CO partial pressure was high enough to permit conversion to $UO_2:2UC$ via removal of CO gas. This step took place in known flows of either Ar or Ar-4% H_2 . From 1673 to 2023 K ramp rates were constant at either 1, 3, or 5 K/min, with either N_2 or 96% N_2 -4% H_2 , hereafter called N_2 -4% H_2 , introduced at 1948 K and the ramp continued to as high as 2123 K where the final conversion to $UC_{1-x}N_x$ was accomplished in ~ 20 h (i.e., overnight). The $UC_{1-x}N_x$ kernels were cooled at 5 K/min in either Ar or Ar-4% H_2 to prevent formation of the sesquinitride. Specific gas flows used will be described in the experimental section. Also, some experiments terminated when $UO_2:2UC$ was formed by 2123 K so that the characteristics of this $UC_{1-x}N_x$ precursor could be determined. In several experiments the calcined microspheres were taken in vacuum from 900 K to 2123 K to form $UO_2:2UC$.

In all phases of this study, the thermodynamics of the relevant conversion reactions were used to interpret and guide the temperature, gas flow rate, and mass-balance parameters necessary to remove gaseous products (CO_2 , CO and HCN) at different stages of the process.

2.3 Experimental procedure

The experimental program gave information on calcining, the conversion of calcined material to the $UO_2:2UC$ intermediate, its subsequent conversion to $UC_{1-x}N_x$, the conversion of calcined material directly to $UC_{1-x}N_x$, increasing the value of x in flowing N_2 -4% H_2 via removal of HCN, and the size distribution of the resulting kernels. Each subject area is reported and discussed in its own sub-section.

2.3.1 Calcining

Our previous studies of calcining [8, 9] were augmented by again detecting the mass signals from released gases with a mass spectrometer (MS) attached to a Netzsch simultaneous thermal analyzer (STA) (Model STA 449 F1 Jupiter) while ramping at 3.3 K/min. A 400 to 1700 K blank run confirmed that the weight change was accurate within $< \sim 0.25$ mg. Initial sample weights of air-dried microspheres were 115 to 190 mg with initial C/U = 2.65, were held in an alumina cup, and gas flow rates were ~ 120 ml/min/g U. The exit gas flow was sampled every 5 K by the MS via a SiC capillary tube maintained at 573 K. Typical data for a run in Ar-4% H_2 are illustrated in Fig. 1 and similar plots were made for runs in Ar and 100% H_2 . It was assumed that the non-zero signals for masses 17, 18, and 28 below 900 K were background and were subtracted. Comparison of the data from the three runs led to the conclusion that

the MS signal for H₂O was primarily mass 18, those for NH₃ were mass 16 and 17, and those for CO plus CO₂ were mass 6 and 12 (both minor), 28 and 44. The results of the present analysis are shown in Figs. 2-4; all mass curves have been scaled for illustrative purposes and cannot be compared quantitatively. In Fig. 2, the CO₂ peaks in Ar over the 450-650 K range confirm the deduction in ref. [9] that the molar O/U ratio is gradually reduced from 3 by carbon and concludes at 2 by 873 K; integration of the CO₂ trace over temperature permits calculation of the O/U-vs.-T behavior shown in Fig. 2. Figure 3 illustrates that when calcining in 96% Ar-4%H₂, hereafter called Ar-4%H₂, the hydrogen primarily finishes reducing the O/U to 2 starting at ~773 K and finishes ~50 K earlier than in Ar alone, while H₂ reduction begins at ~650 K and terminates ~175 K lower than in Ar, at ~750 K. Similarly, the CO₂ traces (which are not quantitative) for the three different calcining gases illustrate that O/U reduction by carbon begins at 475 K, but its participation terminates at lower temperature with increasing H₂ content. The H₂O evolution illustrated in Fig. 4a shows a corresponding behavior with increasing H₂ content. However, the additional 2.4% weight loss in 100% H₂ shown in Fig. 3 is equivalent to an additional C/U loss of ~0.7, and may result from either evolution of kernel dust from the rapid O/U reduction, see below, or another mechanism for loss of carbon. The O/U reduction to produce only CO instead of CO₂ is not indicated by the MS signals and would only account for an extra ~1.7% weight loss. Even so, some of this may occur via the upper water gas shift reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, which does occur in the present 583-723 K temperature range; for this reaction, the use of 100% H₂ significantly decreases the CO₂/CO ratio relative to that in either Ar or Ar-4%H₂ and the ratio of the MS mass signals 44/28 does decrease as predicted. Another loss of carbon via CH₄ may occur via the Sabatier reaction $\text{CO}_2 + 4 \text{H}_2 = \text{CH}_4 + 2 \text{H}_2\text{O}$, which is favored in the 575-675 K range. Both of these reactions normally require a catalyst. There is also the reaction $2 \text{H}_2 + \text{C} = \text{CH}_4$. All three of these reactions are especially thermodynamically favorable in the presence of 100% H₂ and produce either CO/CO₂ ratios or CH₄ pressures that could account for carbon loss beyond that from CO₂. On the other hand, use of 100% H₂ during calcining of kg-sized batches, to ultimately produce oxycarbide kernels, generally were calculated here to give good carbon balance for the process and suggests that the above reactions, if operable, were minimal [17, 18].

[Figure 1]

The weight losses observed in the experiment in Ar were used to deduce a possibly more detailed composition of the air-dried microspheres. Reduction of O/U from 3 to 2 produces 0.5 moles of CO₂ per mole U and a weight loss of 6.13%. The rest of the weight loss was equivalent to removal of ~2.3 moles of H₂O + NH₃ per mole U. As noted above, the probable H₂O/NH₃ ratio was 15 and the C/U was 2.65. Thus the overall composition of the air-dried microspheres is consistent with UO₃:2.16H₂O:0.14NH₃:2.65C and an initial weight of ~360 g/mole U.

Given the above air-dried microsphere composition, the MS data taken every 5 K were converted to the approximate ml of H₂O and CO₂ released at temperature per ml of kernel during calcining at 3.3 K/min in different atmospheres. For example, the background-adjusted H₂O MS signal for a given run was summed over temperature and the multiplier calculated to make this sum equivalent to the 2 mols H₂O released. The resulting factor was then used to convert each 5 K MS signal to give the incremental mols of H₂O released for a given temperature increment. The results are shown in Fig. 4b and the temperature effect of the ideal gas law is included. Not included is the experimentally observed ~50% reduction in kernel volume during calcining since its contraction characteristics vs. temperature are unknown. In 100% Ar, the data in Figs. 2, 3, and 4a were interpreted to demonstrate that the 2.3 moles of bound H₂O (including the 0.15 moles NH₃) were released by ~650 K, while carbon reduced the O/U from 3 to 2 in two stages, half by ~600 K and the remainder by ~873 K, to produce 0.5 moles CO₂ for a total of 2.8 moles H₂O plus CO₂. Furthermore, the weight loss data in Fig. 3 illustrates that carbon accomplished the initial half of the O/U reduction in all three atmospheres. When using either Ar-4%H₂ or H₂, the final half of the O/U reduction was done mainly by H₂ for a total of 3.05 moles gas. Note that, when using 100% H₂, the rapid reduction of the O/U starting at ~720 K gives a rate three times higher than the other two

atmospheres. Apparently, as a consequence, in oxide-carbide kernel production experiments [17], when 100% H₂ was originally used for calcining at a ramp rate of 4 K/min, ~10-20% of fines resulted and indicated breakup of kernels during processing, probably during calcining. When Ar-12%H₂ was used, the percentage of fines dropped to 2%; both original and coated kernels from one of these production runs have been characterized extensively [23].

Note that experiments with the initial C/U=2.65 lead to a calcined kernel that is UO₂:2.15C, which is converted to UO₂:2.15UC. For convenience, in this document the former is called UO₂:2C and the latter UO₂:2UC. Nitriding then produces UC_{0.15}N_{0.85}.

[Figure 2]

[Figure 3]

[Figure 4]

A few insights were obtained for the calcining process during its subsequent conversion to UN. When a ramp of 5 K/min instead of 3 K/min was used, the calcined kernels contained defects, such as pin holes, and the resulting UC_{1-x}N_x kernels were cracked. This implies that sufficient time is needed for the ~160 ml of H₂O and CO₂ that is formed at standard temperature and pressure per absolute ml of air-dried microspheres to diffuse from the microsphere to prevent physical damage via a rapid increase in internal pressure. XRD of the calcined microspheres showed that UO₂ was the sole uranium-bearing phase. Continued heating of the UO₂-C microspheres to 1570 K in the Netzsch STA resulted in <1% additional weight loss and no CO and CO₂ evolution. Subsequent conversion to UO₂:2UC commenced at 1570 K with accompanying CO evolution since p_{CO}(0.1 MPa) > 0.0004 was sufficient for the sweep gas to remove the CO conversion product. Upon heating to 1273 K, the density of the UO₂:2C kernel was 30% of theoretical [8], and when continued to 1673 K was 45-50% of theoretical, which indicates sintering of the UO₂:2C kernel. XRD of the final UC_{1-x}N_x kernel gave composition results consistent with 0.5 moles CO₂ evolved per mole U during calcining in Ar. Two runs (L16 and L20) with 25 g of air-dried material were calcined in Ar and then converted in N₂ at 2023 K. Calcining of one mole UO₃ with 0.5 moles C should give UO₂ and 0.5 mole CO₂ and decrease the initial C/U = 2.65 to 2.15. Subsequent nitriding removed 2 moles CO and the excess of 0.15 would be expected to appear as 1-x amount of solid-solution [UC], in which [UC] and [UN] represent these components in the ideal solid solution of UC_{1-x}N_x. The lattice parameters of the UC_{1-x}N_x product were equivalent to 1-x values of 0.14 and 0.16, which average to the expected 0.15. Another run (L22) started with C/U = 2.3 material, was calcined in Ar, and converted at 2023 K in N₂. XRD analysis indicated UC_{0.05}N_{0.95} and 12.0 wt% UO₂, in good agreement with mass-balance calculations giving 13.3 wt% UO₂ upon assuming that 0.5 CO₂ was evolved during calcining. In a run using C/U = 2.15 material (UN-21) and calcining in sufficient Ar-4%H₂ to reduce the O/U with the H₂ content, followed by conversion in N₂, resulted in x = 0.95, which is equivalent to C/U = 2.05 after calcining, while O/U reduction entirely by C would have given C/U = 1.65 and XRD evidence of UO₂. The H₂ thus provided 80% of the O/U reduction. Conversely, in another experiment (UN-25) with C/U = 2.65 initially and calcining in Ar-4%H₂ and nitriding in N₂ gave x = 0.83, which indicates C/U = 2.17 after calcining, i.e., only 0.02/0.5 or 4% of the O/U reduction was accomplished by H₂. It appears from these experiments that reduction of O/U in Ar-4%H₂ during calcining is not controllable. If reduction by 100% H₂ were controllable, the O/U reduction from 3 to 2 by H₂ flowing through a vertical bed of air-dried microspheres requires a minimum of one mole H₂ per mole U. Figure 4 illustrates that most of the reduction occurs over 600 to 800 K, which is traversed in 67 minutes at the recommended 3 K/min. It follows that, for H₂ to accomplish all the reduction, a minimum flow of 1.4 ml H₂/min/g U is needed.

2.3.2 Conversion to $\text{UO}_2\text{:}2\text{UC}$ precursor

The literature [4, 5] suggests that carbothermic conversion of calcined material to a $\text{UO}_2\text{:}2\text{UC}$ kernel was nearly completed before N_2 was introduced near the final nitriding temperature. The present work substantiated this view, found that insight into this part of the overall process was useful, and thus the thermodynamics of the $T\text{-}p_{\text{CO}}$ relationship was applied to the present experiments. The rate of conversion is primarily dependent on removal of CO by flowing inert gas as long as the kernel does not sinter sufficiently to result in rate control by slower processes within the kernel. This condition applies for low-density calcined microspheres [6, 8] below ~ 1900 K. This rate, in turn, is fundamentally dependent on the moles of CO produced per mole of U, which is calculated here for both isothermal and non-isothermal experimental temperatures. The relevant reaction is

in which the CO pressure at temperature is represented [8] by

$$\log(p_{\text{CO}} / 0.1 \text{MPa}) = \frac{-19,346}{T / \text{K}} + 8.83 \quad 2$$

Since p_{CO} is subatmospheric at temperatures commonly used for carbothermic conversion, the absolute minimum moles of inert gas needed to remove one mole of CO at a given temperature is numerically approximated by the inverse of p_{CO} . When converting the $\text{UO}_2\text{:}2\text{C}$ microsphere, 2/3 of Eq. 1 produces 4/3 mole CO. In inert gas flowing at a given rate (ml/min), the inverse of p_{CO} can be multiplied by the factor $(4/3)22,460(\text{ml gas/mole})/238(\text{g U/mole U})$ to give an experimentally useful value for ml/min/g U. These values for isothermal conversion are shown as line A in Fig. 5.

For a sample converted over a temperature range at a constant ramp rate (K/min), values of p_{CO} from Eq. 2 were summed over equally-spaced temperatures to give the moles of CO released during the temperature ramp. To do this, the mean-value theorem (MVT) was applied to calculate average $p_{\text{CO}}^{\text{MVT}}$ values over a given temperature range. (The integration of $p_{\text{CO}} = \exp(A/T+B)$ over temperature cannot be accomplished in closed form and numerical integration using the trapezoidal method over 10 K increments is typical.) For the present experimental temperatures, the $p_{\text{CO}}^{\text{MVT}}$ values for Eq. 2 at any given T above 1673 K are represented by

$$\log(p_{\text{CO}}^{\text{MVT}} / 0.1 \text{MPa}) = 0.00395 \times T / \text{K} - 9.346 \quad 3$$

Application of Eq. 3 is illustrated for conversion of $\text{UO}_2\text{:}2\text{C}$ from 1673 to 2023 K, for which

$p_{\text{CO}}^{\text{MVT}} = 0.0444$ at 2023 K. The inverse is 22.52, and multiplying by 4/3 gives 30.03 moles of inert gas/mole U, or 2.82 standard liters per g U. The log of the latter value at 2023 K and other temperatures is shown in curve (B) in Fig. 5. Furthermore, at a ramp rate of 1 K/min over the 350 K range, the minimum flow rate needed for conversion by 2023 K is 2.82 (l/g U)/350 (min) or 8.08 ml/min/g U. A ramp rate of 5 K/min would require five times this flow or 40.4 ml/min/g U. (Consequently, here all experimental flow rates are divided by the temperature ramp rate to normalize the flow rate given in the subsequent figures to the equivalent of 1 K/min.) Equation 3 also predicts a doubling of calculated flow for each 70 K lowering of the conversion temperature below 2023 K. Experimental values have to be higher than these minimum flows so that the equilibrium p_{CO} at any temperature is not attained, which would stop Eq. 1. Finally, as a further example, curve (C) illustrates the minimum flow needed when ramping from 1773 K to any other temperature.

[Figure 5]

Fig. 6 illustrates a different application of Eq. 1 for conversion of one gram of U in calcined $\text{UO}_2\text{:}2\text{C}$ microspheres to give the $\text{UO}_2\text{:}2\text{UC}$ product. Equation 2 was used to calculate the p_{CO} in 5 K increments from 1673 K to higher temperatures and this value was used to calculate the moles CO removed at a given flow rate, and these moles of CO were summed over temperature until complete conversion to $\text{UO}_2\text{:}2\text{UC}$ was attained. All calculations were made at a ramp rate of 1 K/min. If higher ramp rates were used, flow rates would have to be increased proportionately to give results identical to those shown in Fig. 6 since a given total amount of flowing gas is needed to remove a given amount of CO. These curves and similar calculations were especially useful in establishing the experimental parameters and interpreting the results.

[Figure 6]

It was apparent early in this investigation that the highest $\text{UC}_{1-x}\text{N}_x$ kernel density resulted when the $\text{UO}_2\text{:}2\text{UC}$ precursor was fully formed and of $\sim 97\%$ TD, in apparent agreement with experimental parameters used by others [4, 5]. In four initial experiments, either Ar or Ar-4% H_2 at flow rates of 16-22 ml/min/g U were used throughout the runs and are twice the minimum of 8 ml/min/g U calculated above. The resulting $\sim 400\text{-}\mu\text{m}$ -radius kernels of $\text{UO}_2\text{:}2\text{UC}$ were separated into ~ 5 size fractions in the roller micrometer and the TD of each fraction determined as described above. The resulting percent TDs for the four runs were 96, 91.5, 97, and 89.4; these results are plotted in Fig. 7. Densities in these four, as well as in accompanying $\text{UC}_{1-x}\text{N}_x$ synthesis, were not a function of either 1, 3, or 5 K/min above 1673 K and the experimental gas flow was directly proportional to ramp rate; thus all the data are plotted normalized to flows at 1 K/min.

[Figure 7]

Subsequently, a series of six experiments investigated the formation of the $\text{UO}_2\text{:}2\text{UC}$ precursor and the parameters are given in Table 1. In these and other experiments it was noted that a 10 to 15 K/min ramp of calcined material from 973 to 1673 K generally resulted in a lower density of $\text{UO}_2\text{:}2\text{UC}$ and thus ramp rates of 3-5 K/min were used subsequently. The best densities were obtained in UC-L01² with a 3 h hold at 2023 K and in UC-L06 where Ar was used with a 1 K/min ramp rate and no hold at 2023 K, the latter being 5% TD higher than when Ar-4% H_2 was used, UC-L05. Generally, a hold of at least an hour at the final temperature is recommended before N_2 is introduced.

[Table 1]

The $\text{UO}_2\text{:}2\text{UC}$ kernels were characterized further by XRD and ceramography in a scanning electron microscope (SEM) using backscatter electron imaging (BSE). The XRD of UC-L01, Fig. 8, revealed UO_2 and UC. XRD of a few of the other kernels revealed small amounts of UC_2 .

[Figure 8]

Samples observed in the SEM micrographs in Fig.9 were synthesized by heat treating up to 2023 K in flowing Ar-4% H_2 with a 3 h holding time (UC-L01) and without any holding time (UC-L03) indicated the presence of a low contrast UO_2 (the effective atomic number of UO_2 is lower compared to that of UC)

² Experiment numbers such as UC-L01, UCN-L10, and FCM-UN06 are included throughout this document to ensure accurate referral to the original data files for each experiment.

layer at the kernels surfaces. Another sample, which was synthesized by heating in Ar up to 2023 K, without any holding time, and then followed by cooling in vacuum (UC-L05), also showed the similar characteristics. Kernels of all these samples consist of interchangeable grains of UO_2 and UC in their bulk part.

[Figure 9]

The SEM micrographs and elemental maps shown in Fig. 10 are from a typical kernel of the sample synthesized at 2023 K in Ar-4% H_2 without any holding time. This sample was cooled to room temperature also in flowing Ar-4% H_2 . The presence UO_2 and UC grains in the bulk area of the kernel (the upper left BSE SEM image) can be confirmed using the corresponding EDS elemental maps. High-contrast areas in the BSE SEM image correspond to low oxygen concentrations confirming that these grains are of UC. The low-contrast UO_2 grains show high oxygen concentrations as expected. As in the other samples discussed earlier (Fig. 9), this sample also contained a $\sim 30\text{-}\mu\text{m}$ layer of UO_2 at the kernel surface; such a UO_2 layer was a common observation on oxide-carbide fuel kernels such as those used for the AGR-1 irradiation [16-18, 23-25]. The BSE SEM image (at the lower left) and the corresponding EDS maps obtained from an area close to the kernel surface also confirm this observation.

[Figure 10]

The sample UC-L05 was synthesized at 2023 K in flowing Ar, without any holding time at that temperature, and cooled under the same gas flow showed the presence of UO_2 , UC, and UC_2 according to XRD. Also, the thin layer on kernel surfaces of this sample was of high-contrast in the BSE SEM image (top BSE SEM micrographs in Fig. 11). The EDS elemental maps obtained on an area close to a typical kernel surface also showed that high-contrast layer consists of low oxygen levels. Thus, it is shown that the majority of thin layer on the kernels in this sample consists of the UC_x chemical phase.

[Figure 11]

Quantitative ceramography was used to analyze the phase content of UC-L06 kernels. The overall kernel carbide content should be ~ 60 volume %, and the UO_2 $\sim 40\%$. In the kernels of Fig. 11, ceramography revealed an outer skin of UC_x that was $\sim 25\text{ }\mu\text{m}$ thick and an interior that was a UO_2 -UC mixture. The average radius of the kernels was $\sim 427\text{ }\mu\text{m}$ and thus the surface layer was $\sim 17\%$ of the kernel volume. The interior thus contains 43 volume % UC and 40 volume % UO_2 , i.e., $\sim 52\%$ of the interior should be UC, while manual quantitative ceramography of the interior (point count) gave 58%.

2.4. Conversion of $\text{UO}_2:2\text{UC}$ to $\text{UC}_{1-x}\text{N}_x$

The conversion of the near-TD intermediate $\text{UO}_2:2\text{UC}$ kernels of the previous section to $\text{UC}_{1-x}\text{N}_x$ is examined next (experiment identification appears in parentheses).

Ten grams of the 97% TD $\text{UO}_2:2\text{UC}$ produced in Ar (UC-L06) was treated (UCN-L17) in N_2 at a flow of 11 ml/min/g U in the Mo crucible at 2023 K for 20 h. This treatment resulted in 82% TD nitride with $x = 0.95$ and no UO_2 . Multiplying the 97% TD $\text{UO}_2:2\text{UC}$ by the ratio of the molar volumes of UN (17.4 ml/mole U) to $\text{UO}_2:2\text{UC}$ (20.44 ml/mole U) gives 82.6% TD UN and is consistent with the experimental 82% TD.

Similarly, $\sim 84\%$ TD $\text{UO}_2:2\text{UC}$ kernels produced in vacuum (UC-L05) were nitrided (UCN-L19). The kernels were heated in Ar to 1948 K followed by heating them to 2023 K at 1 K/min in N_2 -4% H_2 at 22 ml/min/g U. They were then held at that temperature for 20 h and subsequently cooled to ambient temperature in Ar-4% H_2 at 5 K/min. The TD of this material was 74.7% (± 2), vs. a predicted 71.5%

without sintering. A further indication of negligible sintering was that the average radius of the kernels before and after conversion was unchanged within 0.5%. XRD indicated an x value of 0.95 with no UO_2 .

The above results reveal that conversion of near-TD $\text{UO}_2\text{:}2\text{UC}$ to a $\text{UC}_{1-x}\text{N}_x$ kernel is clearly not accompanied by sintering at 2023 K in 20 h.

3. Integrated processing of $\text{UC}_{1-x}\text{N}_x$ kernels

The remaining 12 experiments started with either 25, 50, or 75 g of air-dried microspheres and ended with $\text{UC}_{1-x}\text{N}_x$. Calcining was performed at the standard ramp rate of 3 K/min to 973 K, the ramp rate increased to 5 K/min to 1673 K in either Ar or Ar-4% H_2 , where conversion to $\text{UO}_2\text{:}2\text{UC}$ commenced. Then the ramp rates were set at either 1, 3, or 5 K/min from 1673 to 2023 K. From 1673 to 1948 K the same gases were used. As explained above, the experimental flow rates shown in Fig. 7 were normalized to a ramp rate of 1 K/min, e.g., 10 cc/min at 1 K/min was equivalent to 50 cc/min at 5 K/min, since there was no apparent effect on kernel density (as long as the normalized 8 ml/min/g U was exceeded during the ramp to 2023 K). At 1948 K either N_2 or N_2 -4% H_2 were substituted, the ramp continued, and the kernels held for 18-20 h at 2073 K. The usual flow rate for N_2 -containing gas was ~25 ml/min/g U, which is twice that needed for 100% conversion of oxycarbide to $\text{UC}_{1-x}\text{N}_x$ in 120 minutes at 2023 K at p_{CO} (0.1 MPa) of 0.1. In a few experiments 125 ml/min/g U were used. The range of flows during conversion to nitride had no apparent effect on final kernel density.

There are some obvious outliers in Fig. 7 that need comment. There is an almost 50% range in TD below the normalized flow rate of 8 ml/min/g U and line A suggests that ~30-40% of the UO_2 -carbon microsphere remained unconverted to $\text{UO}_2\text{:}2\text{UC}$ by 2023 K and was the cause of the lower density. The ~50% TD at 24 resulted from introducing N_2 at 1673 K; line B suggests that all $\text{UC}_{1-x}\text{N}_x$ was formed before ~1950 K. Lastly, the two >90% TD results shown in the upper right may have been enhanced by the 5-30% UO_2 content revealed by XRD.

Effects of process variables on density were revealed in a series of experiments with a second batch of air-dried material with $\text{C/U} = 2.65$ and are summarized in the next several paragraphs.

This second batch of material gave different densities in experiments FCM-UN01 to 08. Initial sample weights were 25 g except for 100 g in FCM-UN06 and all were calcined in Ar at the standard 3 K/min to 973 K. Conversion to $\text{UO}_2\text{:}2\text{UC}$ in Ar from 1673 to 2023 K at an optimum ramp rate of 1 K/min, with no hold, gave only 87% TD $\text{UO}_2\text{:}2\text{UC}$ (FCM-UN02), about 10% lower than with previous air-dried material. (If this material were converted to UN, the TD would be 74%.) However, nitriding at 2123 K gave better densities. Subsequent experiments with the original $\text{C/U} = 2.65$ microspheres gave TD values equivalent to those obtained before, indicating that the TD difference between microsphere batches is real and not because of changes in furnace variables.

Increasing ramp rates to as high as 10 K/min during carbothermic conversion in vacuum of the second material appeared to result in decreased kernel density. In addition, none of the vacuum runs with this second material led to kernel TD as high as the runs in Ar, in contrast with previous good equivalent results [8]. Conversion in vacuum at 3 K/min to 2023 K followed by a 16 h nitriding gave 80% TD nitride kernel (FCM-UN07), with a calculated 92% TD $\text{UO}_2\text{:}2\text{UC}$ precursor. Conversion to $\text{UO}_2\text{:}2\text{UC}$ in vacuum at 5 K/min to 2123 K and a 10 h hold, then nitriding for 10 h at 2023 K gave 70% TD $\text{UC}_{1-x}\text{N}_x$ (FCM-UN08). Conversion of 100 g in vacuum at 10 K/min to 2023 K followed by a 16 h nitriding gave 66% TD $\text{UC}_{1-x}\text{N}_x$ (FCM-UN06). Figure 6 showing calculated vacuum conversion at different ramp rates suggests that the observed better density with lower ramp rates is either a function of the ramp rate, which gives more time for sintering during the ramp, or of more fraction conversion at lower temperatures, the latter seemingly counterintuitive.

Increasing the nitriding temperature to 2123 K gave one of the best $UC_{1-x}N_x$ densities (FCM-UN04). Conversion to $UO_2:2UC$ by 2123 K was done in Ar at 5 K/min, held 10 h, then nitrided for 1 h to give 85% TD UN.

Nitriding of a calcined kernel entirely at 2123 K gave poor density (FCM-UN05). The calcined $UO_2:2C$ kernel was preserved by stopping the Ar flow to prevent removal of CO, 10 K/min used from 973 K to 2123 K, then nitriding commenced for ~12 h, and resulted in 75% TD UN.

A run in the Mo crucible at a final temperature of 2273 K resulted in melts (FCM-UN03), while a subsequent W system gave little evidence of reaction. The precursor $UO_2:2UC$ was formed using the Mo crucible by ramping to 2273 K in Ar at 3 K/min and nitrided overnight. Crucible-kernel melts and very poor quality $UC_{1-x}N_x$ kernels resulted, while selected best kernels exhibited 88% TD. As noted above, Mo-N and W-N liquids can occur at ~2200 K and nitriding was not performed subsequently above 2123 K.

Additional sintering at ~2273 K of kernels made at lower temperatures had a slight effect on density. Treatment of ~20 $UC_{1-x}N_x$ kernels made at 2023 K (FCM-UN08) were heated in Ar in a W crucible for 2 h at ~2273 K and resulted in no melts, but TD increased only from 70 to 72.6%. $UC_{1-x}N_x$ kernels made at 2023 K (UCN-L21) and heated at ~2273 K in $N_2-4\%H_2$ for 4 h exhibited a 3% increase to ~86% TD.

Kernel diameter did not affect the resulting density. 850- to 1000- μm -dia., air-dried microspheres with an initial C/U=2.65 were converted under optimum conditions to produce 420- μm -dia. kernels with ~78% TD and $N/(N+C)=0.76$, thus demonstrating that halving the diameter did not lead to better density.

In the remainder of this section thermodynamic calculations are extended to explore the efficacy of HCN in removing carbon in order to increase the value of x. The authors [8, 26] published thermodynamic arguments demonstrating that HCN was the dominant hydrocarbon present during carbothermic conversion of UO_2-C mixtures in N_2-H_2 gases to produce $UC_{1-x}N_x$. Values of p_{HCN} at given x values are shown in Fig. 12 and show the rapid drop in p_{HCN} as x increases to pure UN. As noted earlier, [UC] and [UN] represent these components in the ideal solid solution of $UC_{1-x}N_x$, with activities of 1-x and x, respectively. The relevant equilibrium for increasing the [UN] content by flowing N_2-H_2 mixtures past the microspheres to remove carbon in [UC] via HCN gas is

for which the equilibrium constant is, with standard thermodynamic data [20, 27, 28] in the 1700-2300 K range,

$$K_{eq} = p_{HCN} \frac{x}{(1-x)p_{N_2}\sqrt{p_{H_2}}} = e^{\frac{7833}{T/K}-6.93} \quad 5$$

and thus

$$p_{HCN} / 0.1MPa = \frac{(1-x)p_{N_2}\sqrt{p_{H_2}}}{x} \times e^{\frac{7833}{T/K}-6.93} \quad 6$$

[Figure 12]

The maximum removal of HCN occurs when the input N₂-H₂ gas exits the sample saturated with the equilibrium partial pressure of HCN. This minimum required moles HCN per mole U at a given x is the inverse of Eq. 6. For N₂-4%H₂ the reciprocal pressure term is 5.2 and the above equation simplifies to $[5.2x/(1-x)] \times \exp(-7833/T + 6.93)$. To obtain the total moles N₂-4%H₂, *n*, per mole U between any two values of x, integration of the term $x/(1-x)$ gives $1-x-\ln(1-x)$ and its combination with the thermodynamic terms gives

$$n / \text{moles } N_2 - 4\%H_2 / \text{mole } U = 5.2(1-x-\ln[1-x])e^{\frac{-7833}{T/K}} \quad 7$$

Integration from x = 0.01 to 0.999 at 2023 K and unit conversion to liters per gram of U leads to Fig. 13 and Table 2.

[Figure 13]

Values at 1773 K are about half those shown since p_{HCN} is higher, see Fig. 12. It can be seen that the approach to higher and higher purity requires considerably increased N₂-4%H₂ amounts. The liters of N₂-4%H₂ per g U needed to purify, for example, from x = 0.9 to x = 0.99 is the difference between the respective y-axis values (37.7 and 14.6 in this case) and if 10 hours were required to convert UC_{0.1}N_{0.9} to UC_{0.01}N_{0.99} in N₂-4%H₂ while simultaneously removing residual [UC], the minimum N₂-4%H₂ flow would be 39 ml/min/g U.

[Table 2]

It was demonstrated during the present calculations that given usual carbothermic conversion parameters p_{CO} was always at least an order of magnitude higher than p_{HCN} at all x values. Consequently, increasing the values of x by removing HCN from the processing bed is likely much less effective than removing the CO during conversion of the oxycarbide kernel to carbonitride.

In the present experiments with 25 g of air-dried material (~18 g U) and, a N₂-4%H₂ flow of 80 ml/min/g for ~20 h, the 96 liters/g U for the run produced x = 0.98. From the above table, this was sufficient gas to increase the typical initial x value of ~0.85 to 0.98. In experiments with 25 g of C/U = 2.65 near the end of this study (FCM-UN03) N₂-4%H₂ was used during overnight nitriding at 2273 K and resulted in the typically sharp XRD carbonitride pattern shown in Fig. 14.

[Figure 14]

Another set of experiments performed at Los Alamos National Laboratory led to similar conclusions. 2073 K conversion of ~200 mg of monolayers of microspheres with C/U of 2.675 was performed in open W trays in 10 h at 0.5 l/min of N₂-7%H₂ in a W furnace. Given the initial C/U values, without HCN effects these should have been converted to give x values of approximately 0.8, but all ended with x = ~0.99. If HCN were removing carbon to give x = 0.99, a minimum of ~(0.2g)(37.7 l/g) or ~8 liters of gas flowing past the specimens would be needed. Since 300 liters flowed through the furnace, it is plausible that kernel formation and then removing HCN gas led to the high-purity UN.

The present calculations were also used to analyze the results of Ledergerber et al [5], who converted 50 g of microspheres (~35 g U) at 0.5 l/min of N₂-5%H₂ for 3 to 11 h. The best [UN] content was x = 0.97 or less. It is estimated that a minimum of ~800 liters of N₂-5%H₂ would have to pass thru the kernels to get that x value, whereas only a total of 90 to 330 liters was used. Furthermore, in some of the other

experiments x values were as low as 0.85. It appears that high x values were obtained by control of initial C/U ratios in the sol-gel microspheres, not from stripping of carbon through HCN removal.

The results of Mukerjee et al [6] were also consistent. After converting microspheres having C/U as high as 2.2, inferring an x value of 0.8, the x values of kernels were increased at 1673 K in 60 ml N_2 -8% H_2 /min/g $UC_{1-x}N_x$ for 3 h and resulted in x values of ~ 0.89 to 0.98. Mass balance calculations for 50 g of carbonitride show that increasing the value of x from 0.9 to 0.98 would require removing ~ 0.016 moles of HCN and Table 2 shows the needed flow at 2023 K is ~ 15 l N_2 -4% H_2 /g U for a total of 750 l. As noted above, at 1673 K this would be at least halved, and with 8% H_2 , the p_{HCN} is increased by $\sqrt{2}$ and the needed flow is thus reduced by another factor of 0.7 to give about 260 l needed, while ~ 540 l was used. Thus, by removing HCN, an enrichment of the [UN] content seems plausible. The CH_4 suggested in ref. [6] for increasing x has a partial pressure about an order of magnitude less than does HCN at a given x and 1673 K and is thus likely to be less effective.

4. Discussion

This work noted several general factors that led to decreased $UC_{1-x}N_x$ kernel density. These included 1) increasing the temperature ramp rate of the calcined kernel to the carbothermic conversion temperature, 2) incomplete carbothermic conversion to $UO_2:2UC$ before reaching the final nitriding temperature, 3) carbothermic conversion of calcined material to $UO_2:2UC$ entirely at the final temperature, and 4) some dependence on the batch of initial air-dried microspheres.

In view of the above, the process recommended from the present work was used routinely for $UC_{0.15}N_{0.85}$ kernels of ~ 83 to 86% TD and is as follows:

- Calcine in flowing Ar flowing at ~ 2 ml/g U from ambient at 3 K/min to 973 K
- Ramp at 5 K/min from 973 to 1673 K in above Ar flow
- Ramp at 1 K/min from 1673 to 2023-2123 K in Ar flowing at 10-15 ml/min/g U. For ramp rates up to 5 K/min, increase Ar flow proportionally. Hold at final temperature for one hour.
- The alternative of post-calcining ramping in vacuum to 2023-2123 K for efficient conversion to the $UO_2:2UC$ precursor is also recommended for further investigation since subsequent nitriding resulted in equivalent density [8].
- At 2023-2123 K, substitute N_2 flowing at 5-10 ml/min/g U and nitride for 10 h. To increase $N/(N+C)$ to ~ 0.98 , use N_2 - H_2 mixtures at flow rates and total times given in Section 3.
- To prevent U_2N_3 formation upon cooldown, at 2023-2123 K substitute Ar flowing at 5 ml/min/g U for 30 min.
- Cool to ambient temperature in above Ar flow at maximum furnace ramp rate.

Use of the above process in the resulted in uniform kernels typified by Fig. 15.

[Figure 15]

Having developed a standard method of kernel fabrication, several runs were made and characterized to provide ~ 350 g of nitride kernels for later coating studies. In a given run, the crucible was completely filled with 110 to 130 g of air-dried microspheres with C/U = 2.65 to produce ~ 75 g of kernels. The density characteristics of each run were determined and the run-to-run reproducibility is shown in Fig. 17.

[Figure 16]

The last 5 runs shown above were processed to provide 350 g of kernels for subsequent coating studies; only ~5% of the kernels were rejected. These were then riffled into 4 equal portions for coating. The percentage of kernels with an average diameter, $\pm 10 \mu\text{m}$, is shown in Fig. 18.

[Figure 17]

Several observations concerning calcining result from the present work. When using Ar, all evidence indicates 0.5 moles CO_2 /mole U result in the O/U reduction from 3 to 2; the resulting minimum C/ UO_2 ratio needs to be 2 to permit later $\text{UC}_{1-x}\text{N}_x$ synthesis. With initial C/U = 2.15 and 2.3 material, calcining in Ar-4% H_2 , as well as Ar, generally led to UO_2 in the final nitride kernel even though the hydrogen also reduced the O/U, and the proportion of H_2 reduction relative to that for carbon was not reproducible. Using up to twice the minimum recommended Ar-4% H_2 flow of 35 ml Ar-4% H_2 /min/g U still led to UO_2 content. Consequently, it appears an initial C/U > 2.5 is to be recommended and 2.65 was used here. When C/U = 2.65 microspheres were calcined and stored to be used later in smaller batches, subsequent room-temperature re-oxidation above O/U = 2 occurred and led to insufficient C/U for conversion to nitride; this approach was abandoned.

Subsequent conversion of the calcined kernels to $\text{UO}_2\text{:}2\text{UC}$ was accomplished in either Ar or Ar-4% H_2 while ramping the temperature at either 1, 3, or 5 K/min in the 1673-2023 K range. The resulting 89-97% TD values are shown in Fig. 7 and were obtained at a normalized flow rate of ~15 to 19 ml/min/g U. There was no apparent dependence on the temperature ramp rate or the presence of 4% hydrogen, but the highest density was obtained in pure Ar alone. Lines A and B in Fig. 7 and indicate ~80% conversion to $\text{UO}_2\text{:}2\text{UC}$ by 1948 K and complete conversion at 2023 K. The UC_2 phase, with a molar volume of 23.2 ml/mole U, should be eliminated by complete conversion to UO_2 and UC (24.64 ml/mole and 18.34 ml/mole respectively) so that $\text{UC}_{1-x}\text{N}_x$ kernel (17.60 ml/mole) density is maximized.

The results of the present conversion of the calcined kernels to $\text{UO}_2\text{:}2\text{UC}$ were compared to those for preparing oxycarbide kernels of ~375 μm diameter for the Advanced Gas Reactor irradiations. The fuel had the approximate composition O/U=1.52, C/U=0.36, equivalent to $3\text{UO}_2\text{:}2\text{UC}$ if the carbide phase were all UC and $4\text{UO}_2\text{:}3\text{UC}_{1.9}$ if the carbide phase were all dicarbide [17, 18, 23]. Ramping at 40 K/min to the final conversion temperature was much greater than the 1 to 5 K/min used here and the final density of 11 g/ml or ~97% TD was not attained until ~2165 K, while that % TD was attained by 1823 K by Stinton et al [16], and here by ~2025 K with a kernel volume 10 times larger and a 66% carbide content. Generally, the present work suggests that slower ramp rates result in better densities, even during ramping of calcined $\text{UO}_2\text{:}2.15\text{C}$ from 873 to 1673 K.

The origin of the 30- to 40- μm -thick oxide layer observed in UC-L01, 03, 04, and 05 was considered. This layer on a 828- μm -dia. kernel represents about 20 to 25% of the volume of the kernel. If this volume were to result from carbon oxidation or hydrocarbon stripping of the surface layer during conversion of the C/U = 2.65 kernel, the resulting kernel C/U would be about 1.61 to 1.72 assuming 75 to 80% conversion. Subsequent formation of UN would give ~20% residual UO_2 which is easily detectable by XRD and the carbon balance of the overall process would be poor; neither is the case. Therefore, the oxide layer is suggested to result from the gel-forming process, where most of the carbon content of the layer is apparently rejected from the surface to the interior of the kernel.

The carbide phase in the $\text{UO}_2\text{:}2\text{UC}$ precursor may substitute solid-solution oxygen directly to give $\text{UC}_{1-y}\text{O}_y$ [29] and the effects and utility of increasing y were considered. Increasing the y value lowers the amount of UO_2 with its higher molar volume binding oxygen to the oxycarbide with its lower molar volume and may have the effect of increasing the resulting $\text{UC}_{1-x}\text{N}_x$ density by a few percent. To this end,

the practicality of increasing y during processing was considered. Thermodynamic calculations using the latest methodology [30] and U-Pu-C-O data base [31] provided the p_{CO} - y - T behavior at 1800, 2000, and 2200 K. Least-squares methods fitted the 39 (p_{CO} , y , T) values to give the numerical values in Eq. 8,

$$\log(p_{CO} / 0.1 \text{ MPa}) = 19.157 + \frac{-33468}{T / K} - 24.62y \quad 8$$

and this equation was used to plot Fig. 19. Figure 19 also plots calculated p_{CO} values from Stoops and Hamme [29] from their equation

$$\log(p_{CO} / 0.1 \text{ MPa}) = 13.63 + \frac{-36690}{T / K} \quad 9$$

at $y=0.25$, which they reported was the boundary of the three-phase $U + UO_2 + UC_{0.75}O_{0.25}$ region. Since free carbon is completely consumed in making the oxycarbide precursor, it would appear from Fig. 19 that y in the present process is at least ~ 0.15 and the precursor that was considered to be $UO_2:2.15C$ may have been $UO_2:4.08UC_{0.85}O_{0.15}$. Whether the value of y could be increased further by removing CO in flowing Ar via the reaction

in which [UC] and [UO] represent the solid-solution components of the oxycarbide, was considered using the methodology of Section 3. Generally, the moles of Ar needed to remove one mole of CO is the reciprocal of p_{CO} , and is multiplied by 22.4 (l/mol)/238 grams U or 0.103 to obtain the total amount of Ar in liters per gram of U. Integration of the reciprocal between two y values to obtain the amount is

$$\text{Liters Ar} / \text{g U} = \frac{0.103}{56.67} e^{-44.1 + \frac{77043}{T / K} + 56.67y} \quad 11$$

in which the terms in the exponent are those in Eq. 8 times $\ln(10)$. These calculations led to the conclusion that increasing the value of y from 0.15 to 0.20 in a full crucible to produce ~ 85 g of precursor at a usual Ar flow of 16 ml/min/g U would take about 2 h at ~ 2200 K, and each increase of 0.01 in y would take 70% longer (or require 70% larger flow) than the previous increase, all of which is impractical. Even in the unlikely event that the p_{CO} values were ten times higher than calculated, the initial y value would be about 0.2, and increasing it beyond 0.24 would also be impractical. Therefore, future experiments to increase y are proposed to be performed in vacuum at temperature after the precursor was formed.

[Figure 18]

Nitriding the $UO_2:2UC$ intermediate at 2023 K in the ~ 0.3 cm-high bed is summarized next. A narrow range of $UC_{1-x}N_x$ kernel density was accomplished only when all of the calcined $UO_2:2C$ was converted to the $UO_2:2UC$ precursor, which occurred above the normalized flow rate of ~ 8 ml/min/g U at a ramp rate of 1 K/min, as shown in Fig. 7. At 2023 K nitriding was accomplished in ~ 20 h, i.e., overnight for convenience, and gave about 83% TD kernels for many different experimental conditions. The usual flow rate for N_2 -containing gas was ~ 25 ml/min/g U, which is twice that needed [5] for 100% conversion of oxycarbide to $UC_{1-x}N_x$ in 120 minutes at 2023 K at $p_{CO}(0.1 \text{ MPa})$ of 0.1. Carbon balance was excellent when using Ar and Ar-4% H_2 from the initial $C/U = 2.65$ of the air-dried microspheres to the final

$C/(C+N) = 0.15$ of the carbonitride. Additionally, if N_2 -4% H_2 mixtures were used to attain $x = \sim 0.99$ via HCN removal of the excess carbide component, then Fig. 13 illustrates the higher total flow needed, and also illustrates the extreme flows needed if $x = 0.999$ were desired.

This minimum recommended flow rate and other factors were compared to those used by Ledergerber et al [5]. They obtained $\sim 96\%$ TD $UC_{0.15}N_{0.85}$ containing 2.7% UO_2 with a 30-60 g sample when using 1000 ml Ar-7% H_2 /hr/g U and a ramp rate of 5 K/min. These conditions are equivalent to 3.3 ml/min/g U when normalized to 1 K/min ramp rate and are well below the 8 ml/min/g U needed here. Line A of Fig. 7 also indicates that $<50\%$ conversion to $UO_2:2UC$ when the experiment attained 2023 K, while our [8] integration of the CO(%) -vs.-time data of ref. [5] gave $\sim 66\%$ overall conversion to $UC_{1-x}N_x$ by 2023 K, (equivalent to 100% conversion to $UO_2:2UC$). Also, the maximum p_{CO} (0.1 MPa) of 0.11 obtained in ref. [5] compares to 0.19 predicted from Eq. 2, which suggests that the effluent gas was not saturated to the thermodynamic maximum and the conversion was incomplete. The discrepancy between the present flow rate requirement and that used in ref. [5] is unresolved.

In general, use of hydrogen appears to have limited application. There seemed to be no useful or controllable effect while calcining. The use of 100% H_2 in the Netzsch STA resulted in an additional C loss. Further, and as noted earlier, kernel fragmentation was an issue when using H_2 -containing gas during the calcining step [17]. No effect of H_2 was noted for conversion to $UO_2:2UC$. As noted above, during nitriding in N_2 -4% H_2 gases, the $N/(C+N)$ ratio can be increased to 0.98-0.99 via removal of HCN at rates that agree with those predicted thermodynamically.

Both vacuum conversion of calcined material to $UO_2:2UC$ and conversion in flowing Ar appear to give equivalent densities [8] when subsequently nitrided to the final $UC_{1-x}N_x$ kernel as long as ramp rates of 3 K/min or less are used to the final temperature. Vacuum conversion could be used to prepare large quantities of $UO_2:2UC$ for subsequent conversion to $UC_{1-x}N_x$ in the upflow crucible. Crucible bed density would be ~ 12 g U/ml, including 50% sphere packing fraction, vs. ~ 0.6 g U/ml when starting with air-dried microspheres. Conversely, conversion in Ar requires flows that are directly proportional to both U content and temperature ramp rate. Even if $UO_2:2UC$ were prepared in flowing Ar, subsequent treatment in vacuum may decrease the UO_2 content and increase the [O] content of the oxycarbide, as noted above, which has the potential of $\sim 92\%$ TD $UC_{1-x}N_x$ even without nitride sintering.

The $UC_{1-x}N_x$ kernel density obtained here, $\sim 83\%$ TD for a ~ 820 - μ m-dia. kernel, is compared with those from previous studies. Figure 20 compares the present results with those from the literature in which an extensive range of high temperatures was used. The present results are shown as line A. Ledergerber et al [5] line D, obtained 97% TD at 2023 K for a 770- μ m-dia. kernel and $\sim 45\%$ TD at 1823 K. Odeychuk [12], curve E, converted 600-650- μ m-dia. UO_2 kernels to 536-580- μ m-dia. carbonitride kernels in a bed of carbon and a N_2 - H_2 atmosphere followed with exposure to 75% H_2 -25% N_2 in a carbon-free atmosphere to decrease the $C/(C+N)$ to ~ 0.02 and to obtain the densities shown in Fig. 16. Shoup [4] obtained 87% TD at 1773 K with a kernel diameter of 150 μ m. Mukerjee [6] started with a 2200- μ m-dia. gel that was washed and dried and obtained 97% TD at 1973 K and 2 kPa N_2 , but the final diameter was not given. Tennery et al [14] sintered UN pellets, which were made from powder made by the hydride-nitride process, at N_2 pressures near the U(l)-UN boundary to obtain the densities shown as line G1; sintering at 0.15 MPa N_2 gave densities shown as line G2. Arai et al [15], line E, made (U,Pu)N pellets from powders derived by a carbothermic process and studied the processing parameters that resulted in the densities shown. Metroka [31] made pellets from UN powder supplied by Tennery [14] and sintered in 33% Ar, 67% N_2 above 1773 K at 0.1 MPa to give the results shown as line H1. He also used hot isostatic pressing of encapsulated UN at 104 MPa, lower line H2, and 207 MPa, upper line H2. All these studies illustrate that there are several processing factors that affect final density.

[Figure 19]

Liquid-assisted sintering of $UC_{1-x}N_x$ kernels may be recommended for future study. The experimentally observed melting temperature of UN (K) is represented by $3035(pN_2 [0.1 \text{ MPa}])^{0.0283}$ from 10^{-13} to 7.5 0.1 MPa values [13] and may give some basis for liquid-assisted sintering at practical T and pN_2 values. As illustrated above, Tennery [14] used N_2 pressures for which the above relationship suggests liquid existence in the 1940 to 2500 K range for sintering UN pellets up to 2373 K and was able to increase density by ~5% more than when sintering at atmospheric pressure.

5. Conclusions

Calcining of ~100 mg of air-dried microspheres in the Netzsch STA thermal analyzer coupled with a mass spectrometer revealed that C along with Ar-4% H_2 simultaneously reduce the O/U from 3 to 2 by 873 K, in agreement with earlier TGA work [9]. However, the proportion of each during calcining was not controllable with the 25 to 100 g samples used to make $UC_{1-x}N_x$ kernels. Thus, a C/U molar ratio slightly above 2.5 is recommended, of which 0.5 C/U is used for O/U reduction and 2 C/U for carbothermic conversion to UN. Calcining in 100% H_2 in the Netzsch STA resulted in gas release during UO_3 reduction that was three times higher than with Ar and Ar-4% H_2 , as high as 75 ml H_2O per ml kernel, and during ~2-kg production of $4UO_2:UC_2$ this apparently resulted in >10% of broken material [17]. It was also noted that calcining with a temperature ramp rate above ~3 K/min resulted in $UC_{1-x}N_x$ kernel defects.

Formation of the intermediate $UO_2:2UC$ of near-theoretical density in either flowing argon or in vacuum was required before N_2 was introduced for conversion to UN to attain the highest density final product. Extensive thermodynamic calculations guided, and were consistent with, subsequent experiments at different Ar flow rates and temperature ramp rates. Conversion of calcined material to $UO_2:2UC$ in vacuum gave results comparable with those in flowing Ar at ramp rates of 3 K/min or less [8] and would appear to be more easily scalable to large-scale production, but here density depended on the initial air-dried precursor batch. Further, vacuum conversion could decrease in the $UO_2/UO_{1-y}C_y$ ratio and might result in higher $UC_{1-x}N_x$ kernel density. It was deduced that the outer oxide layer commonly observed possibly has its origin in the 1.5 M NH_4OH washing process used to remove the HMTA, urea, and NH_4NO_3 from the gel spheres after they are formed, aged, and washed with trichloroethylene to remove the silicone oil. In future preparation, four washes will be used rather than six.

Subsequent conversion of $UO_2:2UC$ in N_2 to $UC_{1-x}N_x$ in ~820 μm diameter kernels was not accompanied by sintering up to 2123 K. The resulting density was consistent with that expected from the difference in molar volumes, with no change in diameter before and after conversion. Heating the kernel to ~2325 K in Ar for 0.5 h may have increased the density by a few percent.

In general, production of $UC_{1-x}N_x$ kernels requires long times. Calcining to $UO_2:2C$ requires ~3.5 h, ramping to 1673 K requires ~2.5 h, conversion of $UO_2:2C$ to $UO_2:2UC$ at 1 K/min and coincident sintering to ~96% TD another ~10 h, conversion of $UO_2:2UC$ to ~86% TD carbonitride ~10 h, and cooling to room temperature ~2 h, for a total of ~28 h. Present attempts to speed up the process generally resulted in lower product density.

The present experiments with initial C/U = 2.65 had ~0.15 C/U in excess of that needed for the conversion process and this excess resulted in a final N/(C+N) of ~0.85. This ratio was increased to at least ~0.98 by subsequent treatment in N_2 -4% H_2 , which removed the excess carbon content via HCN formation. However, higher purity $UC_{1-x}N_x$ would likely require impractical times and gas flows as

shown in Fig. 13. Thermodynamic calculations provided the flow and temperature parameters for the process.

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List of Tables

Table 1 Process Variables Affecting Density of $\text{UO}_2\text{:2UC}$ Precursor

Run #	Gas	ramp rate (K/min) from 1673 to 2023 K	TD (%)	comments
UC-L01	A4H	5	96	30 μm UO_2 outer layer
UC-L02	A4H	ended at 1673 K	46	no conversion of $\text{UO}_2 + 2.15 \text{ C}$
UC-L03	A4H	3	89	40-50 μm UO_2 outer layer
UC-L04	A4H	1	92	30 μm UO_2 outer layer
UC-L05	Ar	5 in vacuum	84	30-40 μm UO_2 outer layer
UC-L06	Ar	1	97	25 μm UC outer layer
Initial C/U = 2.65; flow rate 16 ml/min/g U; ramp rate 3 K/min to 973 K; from 973 to 1673 K, 5 K/min for UC-L01, 15 K/min otherwise; A4H represents Ar-4% H_2 ; UC-L01 held 3 h at 2023 K, no hold for remainder, cooled in same gas at 10-20 K/min				

Table 2 Amounts of $\text{N}_2\text{-4\%H}_2$ per mole U at 2023 K vs. x in $\text{UC}_{1-x}\text{N}_x$.

x	moles $\text{N}_2\text{-4\%H}_2$ per mole U	liters per g of U
0.01	0.006	0.001
0.10	0.594	0.056
0.20	2.567	0.242
0.30	6.285	0.592
0.40	12.3	1.2
0.50	21.4	2.0
0.60	35.1	3.3
0.65	44.3	4.2
0.70	55.9	5.3
0.75	70.6	6.6
0.80	89.8	8.4
0.85	116.1	10.9
0.90	155.5	14.6
0.95	226.9	21.4
0.97	281.3	26.5
0.99	400.9	37.7
0.999	655.3	61.7

Figures

Fig. 1. Original mass spectrometer (MS) signals vs. time during calcining of ~190 mg of ~1800- μm -dia. air-dried microspheres with $\text{C/U}=2.65$ in a 10 ml/min flow of $\text{Ar-4\%H}_2$ at 3.3 K/min ramp rate in the Netzsch STA. Each curve is identified with its mass number; the signals for mass numbers 6 and 29 were near zero. The apparent backgrounds for 17, 18, and 28 were subtracted before processing in subsequent figures.

Fig. 2. The lower three curves are the MS CO₂ signals for calcining in either Ar, Ar-4%H₂ or H₂ in the Netzsch STA with attached mass spectrometer. The upper curve shows O/U reduction during calcining in Ar of air-dried microspheres in flowing gas with initial C/U = 2.65, as derived from integration of the CO₂ MS signal in Ar (solid line).

Fig. 3. Weight loss (%) during calcining of air-dried microspheres in flowing gas with initial C/U = 2.65 in either Ar, Ar-4% H_2 or H_2 in the Netzsch STA with attached mass spectrometer.

Fig. 4. (a) The mass 18 MS signals for H₂O evolution during calcining of air-dried microspheres at 3.3 K/min in flowing gas with initial C/U = 2.65 in either Ar, Ar-4%H₂, or H₂ in the Netzsch STA with attached mass spectrometer. Also shown is the signal for NH₃, mass 16 and 17, in Ar, lowest dotted curve. **(b)** Conversion of data in Fig. 4a to release rate in ml of H₂O plus CO₂ per ml of kernel, including ideal gas law effects, during calcining. Not included is the 50% volume shrinkage of the kernel during calcining.

Fig. 5. Total minimum liters of inert gas per gram of U needed for conversion of $\text{UO}_2:2\text{C}$ microspheres to $\text{UO}_2:2\text{UC}$. (A) Isothermal conversion at temperature. (B) Conversion at 1 K/min from 1673 K to any higher temperature. (C) Conversion at 1 K/min from 1773 K to any higher temperature.

Fig. 6. Calculated fraction conversion of calcined $\text{UO}_2\text{:2C}$ microspheres to $\text{UO}_2\text{:2UC}$. Solid lines are for inert gas flowing at the four illustrated ml/min/g U rates (STP) through the sample bed and exiting saturated at the equilibrium CO pressure, all at a temperature ramp rate of 5 K/min from 873 K to 1673 K and 1 K/min above 1673 K. The dotted lines are for calculated conversion of microspheres in vacuum and are independent of $\text{UO}_2\text{:2C}$ amount. Lines A, B, and C are for ramp rates above 1200 K of 2, 5, and 20 K/min, respectively. Line D assumes no conversion during a ramp rate of 15 K/min in inert gas from 873 K to 1673 K, followed by vacuum conversion at a 5 K/min ramp rate.

Fig. 7. Experimental percent densities and calculated percent conversion vs. gas flow rates used during $\text{UO}_2\text{:2UC}$ and $\text{UC}_{1-x}\text{N}_x$ synthesis, and normalized to 1 K/min temperature ramp rate used from 1673 to 2023 K. Dotted lines are $\text{UO}_2\text{:2UC}$, dashed lines are data for $\text{UC}_{1-x}\text{N}_x$ made from $\text{C/U} = 2.65$ microspheres, and solid lines are carbonitride made from $\text{C/U} = 2.15$ microspheres. All $\text{UC}_{1-x}\text{N}_x$ data resulted from N_2 substitution for Ar at 1948 K, per ref. [5]. The diamond point in each density range is the average for the majority of the specimen and the range includes densities from the small tails of the size distribution. Line A plots the fraction conversion to $\text{UO}_2\text{:2UC}$ by 2023 K vs. flow rate. Line B is analogous for 1948 K, where N_2 was introduced, and the density data suggest that higher density results with $>90\%$ conversion to $\text{UO}_2\text{:2UC}$.

Fig. 8. The XRD pattern of the sample synthesized using 3 h holding at 2023 K and consecutive cooling in Ar-4%H₂ (UC-L01). Red, green, and pink patterns present the experimental, fit, and the residue, respectively. Red, black, and blue tick marks represent peak locations for UO₂, UC, and LaB6 660b internal standard, respectively.

Fig. 9. BSE SEM micrographs of UC/UO₂ samples synthesized using different experimental conditions: (a-b) 3 h holding at 2023 K and consecutive cooling in Ar-4%H₂ (UC-L01); (c-d) heating at 2023 K with no holding time and consecutive cooling in Ar-4%H₂ (UC-L03), (e-f) heating at 2023 K with no holding time in Ar and cooling under vacuum (UC-L05).

Fig. 10. BSE SEM images and the corresponding EDS elemental maps of a typical kernel from the sample synthesized at 2023 K in flowing Ar-4%H₂ without any holding time followed by cooling in the same environment (UC-L04).

Fig. 11. BSE SEM images and EDS elemental maps of a kernel from the sample synthesized by heat treating up to 2023 K in Ar without any holding time followed by cooling in Ar (UC-L06).

Fig. 12. Plot of $\log(p_{\text{HCN}} [0.1 \text{ MPa}])$ for the UC-UN-carbon system at 0.1 MPa of N_2 -4% H_2 . (A) $2\text{C} + \text{N}_2 + \text{H}_2 \rightarrow 2\text{HCN}$. (B) $[\text{UC}] + \text{N}_2 + 0.5\text{H}_2 \rightarrow [\text{UN}] + \text{HCN}$ at given x .

Fig. 13. Log (Liters of N_2 -4% H_2 per g U) needed at 2023 K to convert pure UC ($x = 0$) to $\text{UC}_{1-x}\text{N}_x$ over the range $0.8 \leq x \leq 0.999$ via HCN stripping. The amount of gas needed is the difference between the amounts at higher and lower x values.

Fig. 14. The full profile fit of the XRD pattern of $\text{UC}_{0.09}\text{N}_{0.91}$ (lattice parameter = 0.48979(1) nm). Red, green, and pink patterns represent the experimental, fit, and the residue, respectively.

Fig. 15. Typical 840- μm -dia. $\text{UC}_{0.04}\text{N}_{0.96}$ kernels using the process parameters developed in this study. (UCN-L13, Bin 7, 86% TD, nitriding in N_2 -4% H_2 at 2023 K)

Fig. 16. Average density (orange dot) and density range vs. run number that each produced ~75 g of kernels. The nitriding temperature for run 9 was 2023 K and the % TD of ~83% was typical of that temperature. The remaining runs were at 2223 K and the % TD typically averaged ~3% higher.

Fig. 17. Distribution of kernel diameters in 350 g of material combined from the last five runs shown in Fig. 16.

Fig. 18. The calculated behavior of p_{CO} vs. temperature and oxygen content in the two-phase region UO_2 and $\text{UC}_{1-y}\text{O}_y$. The lower composition boundary occurs where the three-phase region that includes C appears, and the upper boundary where U appears, as illustrated on the figure. The Stoops and Hamme [29] p_{CO} values at three temperatures are calculated from Eq. 9, see text.

Fig. 19. Percent theoretical density of nitride kernels and pellets vs. final processing temperature. For $UC_{1-x}N_x$ microspheres: (A) present study; (B) Shoup [4]; (C) Mukerjee et al [6]; (D) Ledergerber et al [5]; (E) Odeychuk [12], For nitride pellets: (F) Arai et al, $U_{0.8}Pu_{0.2}N$ [15]; (G1 and G2) Tennery et al, UN [14]; (H1 and H2), Metroka, UN [32] .