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Carbothermic synthesis of 820 μm uranium nitride kernels: Literature review, thermodynamics, analysis, and related experiments ☆

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ABSTRACT

The US Department of Energy is developing a new nuclear fuel that would be less susceptible to ruptures during a loss-of-coolant accident. The fuel would consist of tristructural isotropic coated particles with uranium nitride (UN) kernels with diameters near 825 μm. This effort explores factors involved in the conversion of uranium oxide–carbon microspheres into UN kernels. An analysis of previous studies with sufficient experimental details is provided. Thermodynamic calculations were made to predict pressures of carbon monoxide and other relevant gases for several reactions that can be involved in the conversion of uranium oxides and carbides into UN. Uranium oxide–carbon microspheres were heated in a microbalance with an attached mass spectrometer to determine details of calcining and carbothermic conversion in argon, nitrogen, and vacuum. A model was derived from experiments on the vacuum conversion to uranium oxide–carbide kernels. UN-containing kernels were fabricated using this vacuum conversion as part of the overall process. Carbonitride kernels of ~89% of theoretical density were produced along with several observations concerning the different stages of the process.

1. Introduction

One of the lessons from the natural disaster induced accident at Fukushima is the value of a nuclear fuel cladding that is more resistant to high temperature oxidation. As a result, efforts are underway to develop accident tolerant fuel that would greatly extend the temperature regime and time period before fuel failure and fission product release during a loss of coolant accident. One of the concepts being explored is tristructural isotropic (TRISO) fuel particles embedded in a silicon carbide (SiC) matrix to directly replace uranium dioxide (UO_2) pellets in light water reactor (LWR) fuel [1,2]. The SiC matrix has a high thermal conductivity and is resistant to oxidation so the fuel can operate at substantially lower temperatures than UO_2 and is less likely to fail. The TRISO particles will, as well, retard fission product release at high temperatures and under oxidizing conditions even if the cladding and SiC matrix fail. The nature of the fuel configuration, however, will result in a limited volume fraction for uranium, and thus efforts are needed to maximize actinide concentration to maintain adequate fissile loading. This can be accomplished by minimizing particle coating thickness and by substituting uranium nitride (UN) for the typical TRISO kernel of UO_2, since the fissile density of UN is 30% greater than that of UO_2.

In this paper, the literature on the preparation of UN kernels is reviewed and analyzed to obtain detailed information on the high-temperature process. This analysis involved relevant thermodynamic and kinetic calculations. With prior work as a basis, an ongoing calculational and experimental program was established to investigate the several reactions involved in the carbothermic conversion of sol–gel-derived urania-carbon microspheres to UN kernels. This paper reports the several related investigations. Because of the diverse nature of these studies, and for better clarity, detailed discussion of each is included within the relevant section, and it is followed by general conclusions in Section 7.

2. Literature review

Initially, UN was synthesized from uranium metal using the hydride–dehydride–nitride process [3]. The UN powder that was sintered at a nitrogen pressure just above the pressure for the decomposition into nitrogen and uranium produced the UN pellets with the highest densities. At 1873 and 2373 K, the theoretical densities (TDs) of the UN pellets were 85% and 93%, respectively. Subsequently, a dense UO_2 pellet with a thickness of 740 μm was reacted with carbon in nitrogen at 1973 K, and it was determined

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that the solid-state diffusion was rate controlling [4]. Water contamination of approximately 20 ppm in the nitrogen produced hydrogen cyanide (HCN), which was efficient in carbon transport to the pellet and formed a continuous $UC_{1-x}N_x$ layer. Extrapolation of the data [4] indicated that it would have taken 370 h to complete the reaction. The very slow kinetics is a primary reason for the use of micron-sized uranium oxide–carbon microspheres from the internal gelation process.

Several studies on the preparation of dense $UC_{1-x}N_x$ kernels with a high nitride content from UO_2–carbon gel-derived microspheres have been published over the past 45 years. These references are summarized in chronological order. Unless noted, the conversion was performed using flowing gas over the microspheres at 0.1 MPa. In 1975, UO_2–carbon sol-derived microspheres were heated to 1673–1973 K for up to 40 h in combinations of argon and nitrogen; the $UC_{1-x}N_x$ kernels from this study had TDs up to 90% [5]. In 1977, $UC_{1-x}N_x$ kernels with a diameter of 150 μm and TDs of 65–90% were prepared by heating UO_2–carbon microspheres to 1673–1798 K for up to 40 h [6]. This study [6] noted that the conversion to UO_2–UC in argon at 1773 K and the subsequent conversion to UN in nitrogen produced kernels with TDs up to 85%. In contrast, when only nitrogen was used in the conversion process from UO_2–carbon microspheres to UN, the maximum TD density for these kernels was only 70%.

In 1991, a study, which will be discussed in more detail below, prepared $UC_{1-x}N_x$ microspheres using flowing nitrogen at 1573–1823 K [7]. In 1992, researchers [8] passed argon, nitrogen, and their combinations with hydrogen through UO_2–carbon microspheres in a vertical molybdenum crucible. This study [8] and an earlier effort [4] realized the efficacy of HCN instead of methane (CH_4) or acetylene (C_2H_2) for carbon transport at these temperatures. The primary objective of this study [8] was the production of low-density kernels for subsequent fuel pellet fabrication. However, they also produced $UC_{1-x}N_x$ kernels with 97% TD at 2023 K, as discussed later. Another effort [9] evaluated the conversion of UO_2–carbon to UC kernels in vacuum at 1473–1773 K. With a ramp rate of 1 K/min, the reaction to UC was completed by 1723 K in a vacuum and by 1823 K in flowing argon. The most recent study [10] reacted carbon powder and UO_2 microspheres with 70–95% TDs in nitrogen at 1973 K for approximately 6 h. It was determined that the resulting increase in carbon monoxide (CO) pressure lowered the reaction rate. Subsequent treatment in 25% nitrogen/75% hydrogen produced nearly pure UN. When the UN microspheres were sintered at 2123 and 2373 K, the TDs were 80% and 97%, respectively.

3. Thermodynamic calculations

Values of CO and HCN pressures (pCO and pHCN) were calculated for equilibria relevant to carbothermic conversion. During an actual conversion, the reaction kinetics should slow significantly if these pCO and pHCN equilibrium values are approached. For the present calculations, the on-line FactSage database [11] was used to determine the Gibbs free energy of formation of all reaction components from the elements in their standard states.

3.1. Calculation of log (pCO) values from thermodynamic data

Fig. 1 illustrates the results of several calculations relevant to the conversion of oxide–carbon microspheres to carbide-nitride kernels. Line A in Fig. 1 is for reaction (1), and it is represented by the Eq. (1).

$$UO_2(s) + 3C(s) \rightarrow UC(s) + 2CO(g) \qquad \text{(Reaction1)}$$

$$\log pCO = -19,346/T + 8.83 - 0.5\log(aUC) \qquad (1)$$

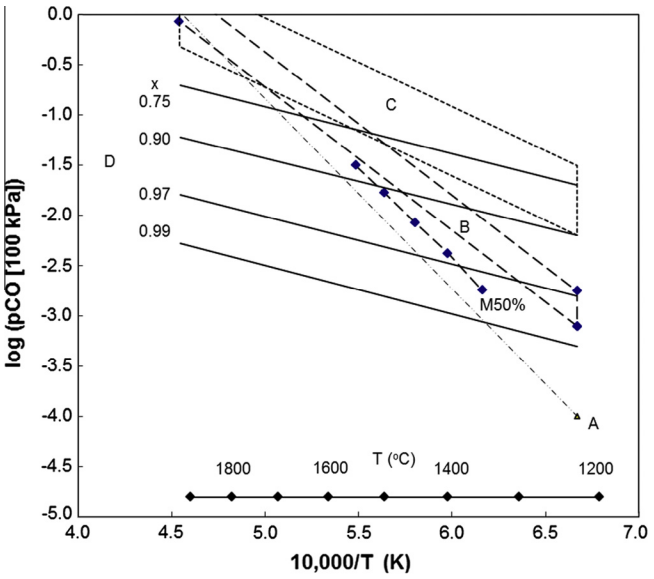

Fig. 1. Plot of log (pCO [bar]) vs 10,000/T for several equilibria. When $UC_{1-x}N_x$ and nitrogen are present, pN_2 is 100 kPa, where equilibria with U_2N_3 may appear below 1622 K (1349 °C). A: $UO_2 + 3\ C \rightarrow UC + 2\ CO$. B: Range for $4\ C + 2\ UO_2 + N_2 \rightarrow 2\ [UN] + 4\ CO$ from $x = 0.99$ (lower boundary) to 0.20 (upper boundary). C: Range for $UC_2 + UO_2 + N_2 \rightarrow 2\ [UN] + 2\ CO$ from $x = 0.99$ (lower boundary) to 0.20 (upper boundary). D: $4\ [UC] + 2\ UO_2 + 3\ N_2 \rightarrow 6\ [UN] + 4\ CO$ at given x values. M50%: Experimental pCO at 50% conversion in N_2 from Ref. [7].

in which aUC represents the activity of UC. Line A illustrates the difficulty of conversion at low temperatures in argon flowing at 100 kPa. For example, at log (pCO) = 0.1 kPa, 1000 volumes of argon must flow through the material to remove one volume of CO. Conversely, vacuum conversion efficiently removes the CO.

The other results in Fig. 1 are focused on the carbothermic conversion of oxide–carbon microspheres in nitrogen to produce high-purity UN kernels from the $UC_{1-x}N_x$ solid solution. For example, one study [8] preferred conversion to a UO_2–UC mixture before introducing nitrogen. Consequently, the range of x varies from 0 to nearly 1 for pure UN, and several intermediate reactions are possible. A study of the reaction of UC with nitrogen from 1748 to 1973 K noted that UC_2 and free carbon were present at different stages of the reaction as x increased [12]. Extensive calculations were thus performed to determine log (pCO) for likely intermediate reactions. For these calculations, [UC] and [UN] represent the components of the ideal solid solution $UC_{1-x}N_x$, where the activity of [UC] is $1-x$ and the activity of [UN] is x. One result is region B in Fig. 1 for the reaction (2) where $x = 0.99$ is the lower boundary of the region and $x = 0.20$ is the upper boundary.

$$4C(s) + 2UO_2(s) + N_2(g) \rightarrow 2[UN] + 4CO(g) \qquad \text{(Reaction2)}$$

Similarly, region C is for the reaction (3) over the same range of x.

$$UC_2(s) + UO_2(s) + N_2(g) \rightarrow 2[UN] + 2CO(g) \qquad \text{(Reaction3)}$$

It can be seen that regions B and C have higher log (pCO) values than line A, which indicates possible processing advantage in nitrogen. The set of lines marked D are for the reaction (4).

$$4[UC] + 2UO_2(s) + 3N_2(g) \rightarrow 6[UN] + 4CO(g) \qquad \text{(Reaction4)}$$

This equilibrium illustrates the need to remove CO at its low pressures in order to have high-purity UN. Fortunately, pCO is not too sensitive to temperature while the solid-state kinetics of the conversion reaction is greatly enhanced with temperature.

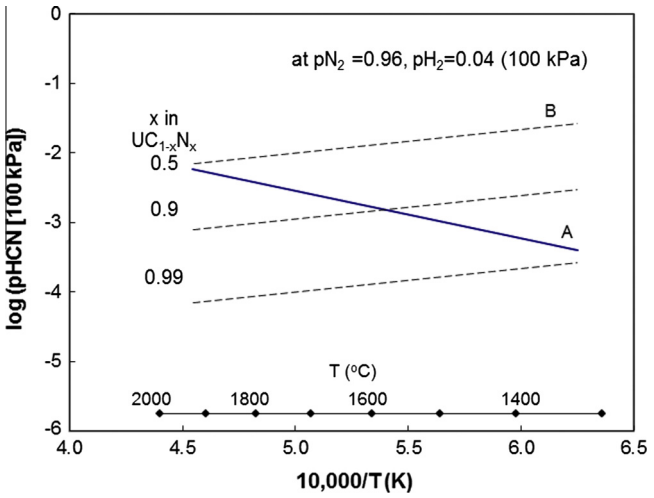

Fig. 2. Plot of log (pHCN [100 kPa]) for the UC-UN-carbon system at 100 kPa of 4% hydrogen in nitrogen. A: 2 C + N_2 + H_2 → 2 HCN. B: 2 [UC] + 2 N_2 + H_2 → 2 HCN + 2 [UN] at given x.

3.2. Calculation of log (pHCN) values

Earlier studies [8,10] utilized nitrogen and hydrogen mixtures in the conversion process, and thus typical log (pHCN) values were calculated. These pressures are shown in Fig. 2 for 4% hydrogen in nitrogen at a total pressure of 100 kPa. Pressures of CH_4 and C_2H_2 in equilibrium with carbon were also calculated, but they were always <10 Pa in this temperature range. Line A confirms that HCN pressures in the presence of free carbon are significant enough to transport carbon during carbothermic conversion, as shown earlier [4], but HCN could also be a source of carbon loss from the system during conversion. However, a comparison with pCO in Fig. 1 illustrates that it is always larger than pHCN and conversion in flowing gas removes significantly more CO than HCN. Line B in Fig. 2 illustrates that the HCN pressure over $UC_{1-x}N_x$ at different compositions is sufficient to remove carbon in the flowing gas mixture and to thus beneficially increase the value of x in $UC_{1-x}N_x$.

4. Kinetic models

Two kinetic models are considered here to analyze literature and current data and to obtain reaction rate constants. One model commonly used is the first-order rate Eq. (2)

$$k_f(s^{-1})t = -\ln(1-\alpha) \quad (2)$$

In which α is the fraction reaction, k_f is the first-order rate constant, and t is time in sec. In a reacting sphere, $\alpha = 1-(r/r_0)^3$, in which r is the radius of the unreacted core and r_0 the original radius, and Eq. (2) becomes Eq. (3)

$$k_f(s^{-1})t = -\ln((r/r_0)^3) = -3\ln(r/r_0) \quad (3)$$

The Eq. (3) becomes indeterminate as r approaches zero and prevents extrapolation to determine the times near 100% conversion.

The second model is for a reacting sphere being converted to another material with the rate controlled by solid-state diffusion through the product layer. An earlier work [13] applied this model to experimental data for oxidation of nickel spheres. In spite of the difference in molar volumes of the nickel reactant and the nickel oxide product, this study concluded that the expression derived by another effort [14] was adequate to represent experimental data via Eq. (4) in which k_d is the rate constant for diffusion control.

$$k_d(cm^2/s)t/(r_0)^2 = 1 - 2\alpha/3 - (1-\alpha)^{2/3} \quad (4)$$

Unlike Eqs. (2) and (3), Eq. (4) is applicable at all values of α. Eq. (4) was used in the form of Eq. (5). A plot of isothermal experimental data for each of the above models

$$k_d(s^{-1})t = 1 - 2\alpha/3 - (1-\alpha)^{2/3} \quad (5)$$

versus time should be linear if either model was rate controlling.

The interface-control model used by an earlier study [9] was not used here. Time for conversion was proportional to $1-(1-\alpha)^{1/3}$; in a solid sphere this becomes $1-r/r_0$. Present results with the interface-controlled model were found to be visually sigmoidal with time rather than reasonably linear with the diffusion-control model. Furthermore, when the data were fitted with both models, the least-squares parameters for the interface model always displayed larger errors, which suggested that rate control at the interface was less likely.

5. Analysis of literature data

Two of the previous publications [7,8] were unique in that they provided sufficient experimental details to permit the following analysis of the thermodynamic and kinetic parameters, which affect the carbothermic conversion.

5.1. Ledergerber et al. [8]

Ledergerber et al. [8] provided detailed information that permitted additional insight into the conversion process. The initial carbon to uranium molar ratio of the microspheres was not given, but in Section 6.5 it is deduced that this value was approximately 2.15. Conversion was attained by flowing gases through a vertical bed of microspheres held in a molybdenum crucible at a typical flow rate of 0.2 mol gas/min/mol uranium. $UC_{0.15}N_{0.85}$ kernels with a TD of 97% were produced at 2023 K. In general agreement with another effort [6], the highest densities were achieved by the complete conversion of the UO_2:2C microspheres into UO_2:2UC kernels

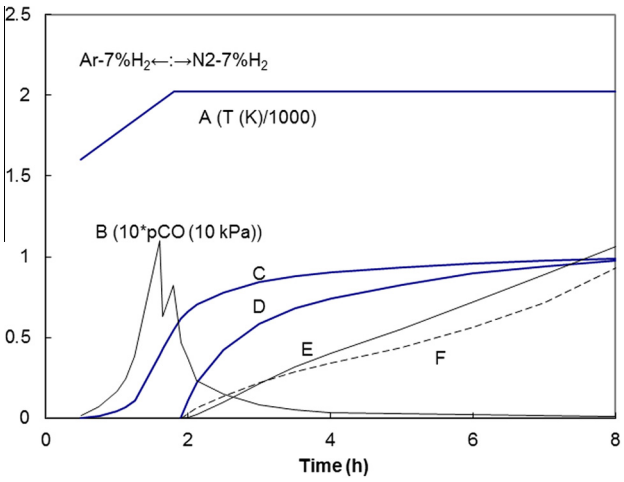

Fig. 3. Experimental T and pCO from Ledergerber et al. (Ref. [8], Fig. 2) and present additional kinetic analyses. The several units of the ordinate are defined below. A Temperature, K/1000 B. Measured pCO, 10 kPa, times 10. C Fraction total conversion obtained by integrating pCO over time. D Fraction reaction of UO_2:2UC to $UC_{0.15}N_{0.85}$. *E* Value of Eq. (5) for diffusion control, times 4 for clarity, for UO_2:2UC conversion to $UC_{0.15}N_{0.85}$. F value of Eq. (2) for a first-order reaction, times 0.25 for clarity, for UO_2:2UC conversion to $UC_{0.15}N_{0.85}$.

using 7% hydrogen in argon for 1.8 h and then conversion to UN in 7% hydrogen in nitrogen for 6.2 h, as shown in Fig. 3. This overall process produces two mols CO per mol UO_2 and is divided into two parts. In the first part, all of the carbon was reacted in flowing 7% hydrogen in argon via the reaction (5) to remove 66% of the total CO and to produce UO_2:2UC microspheres. In the second part, the microspheres were heated in 7% hydrogen in nitrogen to form UN as shown in reaction (6).

$$2UO_2(s) + 6C(s) \rightarrow 2UC(s) + 4CO(g) \quad \text{(Reaction5)}$$

$$2UO_2(s) + 4UC(s) + 3N_2(g) \rightarrow 6UN(s) + 4CO(g) \quad \text{(Reaction6)}$$

To demonstrate that the initial conversion to UO_2:2UC had occurred, the pCO data from the original figure [8] was integrated vs time to obtain the fraction conversion vs time as shown in Fig. 3. This figure shows that about 66% of the total CO was produced via reaction (5) by the time 2023 K was attained. The pCO at any given temperature during the ramp to 2023 K is essentially the equilibrium value for the reaction (5) and peaked at 1.6 h at 11 kPa as displayed in Fig. 3, which is a reproduction of Fig. 1 from Ref. [8]. Then the pCO fell rapidly, which indicated the reaction was essentially finished. Therefore, CO removal by flowing 7% hydrogen in argon was controlling the conversion rate during the temperature ramp. The spike in pCO after nitrogen was introduced may indicate rapid formation of the UO_2–$UN_{1.5}$ solid solution, which has been observed in similar experiments [4]. The nitriding results for the earlier effort [8] were also analyzed using Eq. (2) and (3). It was assumed that the CO generated after 1.9 h was from the conversion of UO_2:2UC to the final $UC_{0.15}N_{0.85}$. As can be seen in the Fig. 3, the diffusion-control model was remarkably linear with time and the model for first-order rate reaction less so. The value of $\log(k_d\ [s^{-1}])$ was determined to be −4.91 for Eq. (5).

5.2. Murkerjee et al. [7]

Additional insight into the conversion process was obtained from the detailed work of Mukerjee et al. [7]. This study flowed nitrogen over 50 g of gel-derived microspheres of UO_2 and carbon in a tantalum crucible at six temperatures from 1573 to 1823 K. The carbon to uranium molar ratios ranged from 2.0 to 2.2. They determined the conversion fraction vs time by converting the CO to carbon dioxide (CO_2) and measuring the latter. The flow rate was either 40, 60, or 80 cm^3/min/g sample, with the latter flow rate being equivalent to 1.07 mol N_2/min/mol uranium. Their Fig. 3 shows the effect of flow rate on fraction conversion vs time at 1723 K at a given fraction conversion. The experimental time is inversely proportional to nitrogen flow while a higher flow increases the fraction conversion at a given experimental time. Mukerjee et al. [7] concluded "that diffusion of CO(g) through the product layer was the rate-controlling step and that decrease in N_2(g) flow rate, i.e., increase in CO partial pressure results in decrease of reaction rate," and they fitted their data with the first-order expression, Eq. (2). Similar experiments [15] at 1748 K with UO_2–carbon powders at N_2 flow rates of 55 to 190 cm^3/min/g sample gave rate constants (with time in sec) in agreement with those of Mukerjee et al. [7] and which also increased similarly with flow rate. To further demonstrate the correlation of pCO in the above experiments with the thermodynamic values shown in the relevant region B in Fig. 1, the results of Mukerjee et al. [7] at 60 cm^3/min/g were used to determine pCO vs T at 50% conversion. At this conversion, 1 mol CO/mol U was generated, and the resultant average pCO was calculated from its dilution with the mols of flowing nitrogen. These pCO values ranged from 0.18 kPa at 1573 K to 3.16 kPa at 1823 K, and the five values are plotted in Fig. 1. The parallelism of these values just below those for region B of Fig. 1 supports the general conclusion that the rate of CO removal affected the reaction rate in the early stages of conversion. For similar calculations at 90% conversion, the calculated pCO values were about half an order of magnitude lower and suggested that rate control at the higher reaction percentages was not as affected by the ambient pCO. It follows that the average pCO calculated here results from higher pCO values in the initial stage of the reaction and lower values at any - given latter stage of reaction. Also, these pCO values were less than the equilibrium values in region B of Fig. 1; otherwise, the conversion reaction would stop. The final step in the work of Mukerjee et al. [7] was the reduction of the solid-solution UC content at 1673 K in flowing 8% hydrogen in nitrogen. It was proposed that CH_4 was the species that reduced the UC content in $UC_{1-x}N_x$, but instead it was probably HCN, which has partial pressures approximately two orders of magnitude higher than does CH_4 in this temperature range. After the kernels were sintered at 1973 K for 3 h in 2 kPa of nitrogen, their TD was 97%.

Several general conclusions follow from this analysis. As pCO approaches the equilibrium value, the reaction rate decreases when conversion is done in flowing gas and conversion is practical only >1775 K. On the other hand, vacuum conversion of UO_2–carbon microspheres to UO_2–UC kernels is rapid in the 1475–1775 K range. Such conversion to this intermediate mixture would efficiently remove ~66% of the total CO produced in the overall reaction to make UN. This intermediate product when reacted in nitrogen generally produced UN kernels of higher density than when nitrogen was used throughout, which would have given $0.5 < N/(C + N) < 1$ as intermediate compositions. In order to approach 100% TD, the UN kernels must be sintered at temperatures of least 1800 K. Additional sintering in low nitrogen pressures or vacuum may help approach theoretical density.

6. Experiments, analyses, and discussion

Several different experimental investigations were performed and analyzed and reported in this section. The investigations were calcination of gel-derived UO_3:$2H_2O$:2.65 C microspheres to UO_2:2.15 C microspheres up to 873 K, vacuum conversion of the latter to UO_2:2UC at 1456–1668 K, the evolution of microsphere characteristics during processing, and nitriding of vacuum-synthesized UO_2:2UC microspheres following the process of Ledergerber et al. [8].

6.1. Equipment and materials

Thermogravimetry was the principal method used to measure mass changes of carbon-bearing uranium microspheres as a function of time, temperature, and defined atmosphere. Calcination below 800 K was studied with a Harrop Model ST-736 differential thermal analyzer/thermogravimetric analyzer (DTA/TGA) with an alumina specimen holder; reagent-grade gases were used. A Netzsch Simultaneous Thermal Analyzer (STA) model 449 F1 TGA was used at all temperatures. The specimens consisted of 75 mg (~15 microspheres) to 1000 mg (~200 microspheres) loaded into an alumina crucible positioned on top of an alumina sample carrier. The sample carrier rests upon a high-resolution balance and contains a thermocouple allowing the simultaneous acquisition of both temperature and mass data. Residual oxygen was removed from ultra-high-purity argon and nitrogen by flowing the gas over a bed of copper at 923 K. The amount of oxygen in the supply and exhaust gas streams was measured using a zirconia solid electrolyte cell method. A mass spectrometer was incorporated downstream for analysis of product gases. For vacuum conversion studies, TG measurements were performed under vacuum down to 0.0001 Pa. A few high-temperature conversion and sintering

experiments were performed in a graphite furnace capable of 2100 K. X-ray diffraction (XRD) was used to determine phase content.

The internal gelation process was used to produce hydrated uranium trioxide (UO_3 $2H_2O$) microspheres with Cabot Mogul L carbon black adequately dispersed throughout the gel spheres. The preparation process was recently discussed in detail elsewhere [16]. The majority of the air dried microspheres had a carbon to uranium molar ratio between 2.6 and 2.7. If hydrogen is used during the UO_3 reduction to UO_2, then both carbon and hydrogen can and do serve as a reductant, and the carbon to uranium ratio after the calcination step should be analytically determined. For our microspheres and test conditions, hydrogen did most of the reduction. Without hydrogen, the microspheres will only be reduced by carbon, and the amount of carbon in the calcined microspheres does not require additional chemical analysis.

6.2. Calcination of UO_3 $2H_2O$ microspheres with carbon

The Harrop DTA/TGA and purified argon were used to convert the gel-derived UO_3:$2H_2O$:2.65 C microspheres to UO_2:2.15 C microspheres as shown in reaction (7). The microspheres were heated to 873 K at a rate of 200 K/h and then held at 873 K for 2 h.

$$UO_3 \cdot 2H_2O(s) + 2.65C(s) \rightarrow UO_2(s) + 2.15C(s) + 2H_2O(g) + CO_2(g) \quad \text{(Reaction7)}$$

The dwell time was increased from 50 min [16] to 2 h because the sample size was increased from 0.3 g to 7 g. The reduction to UO_2 using adequately dispersed carbon begins at 723 K [17].

Several general observations were noted about the calcination step. If a ramp rate faster than 200 K/h to 873 K was used, then a small fraction of the microspheres had surface imperfections, and a significantly higher ramp rate resulted in cracked kernels upon carbothermic conversion. However, after calcination, a ramp rate as high as 20 K/min to conversion temperatures could be used above 873 K. In order to circumvent the slow calcination step, a master batch of properly calcined material was stored in argon. However, an unavoidable, partial oxidation of the UO_2 apparently occurred during storage. When the calcined microspheres were reheated above 723 K, an additional carbon loss of 0.1 to 0.2 carbon/uranium would occur, and this carbon loss would typically lead to a small percentage of UO_2 phase in the nitride. For this reason, critical experiments were started with the recommended 200 K/h calcination of air-dried uranium microspheres with carbon. Simultaneous thermogravimetry, temperature profile, and mass spectrometry for this process were obtained with the Netzsch instrument and are shown in Fig. 4. The H_2O trace displays two peaks representing removal of adsorbed and chemically bound water. The oxygen trace (not shown for clarity) was analyzed for behavior that may indicate partial decomposition of UO_3 to an oxide such as triuranium octoxide (U_3O_8). Four distinct peaks are associated with oxygen species and all correspond to indicated H_2O and CO_2 peaks. Decomposition of UO_3 to lower oxides, carbonate decomposition, and residual organic decomposition, if present, overlap with other TG and MS traces. Two distinct CO_2 peaks are revealed with onset temperatures of 442 K and 792 K respectively.

6.3. Vacuum conversion

Isothermal experiments were performed in vacuum from 1456 to 1668 K. One-gram samples of previously calcined UO_2:carbon microspheres were heated to the desired temperature in 50 min in the STA. A vacuum of 0.1 Pa or lower was maintained. A sample was converted to UO_2:2UC, which was confirmed by XRD. The STA results were analyzed using the rate equations for first-order and diffusion-controlled approaches. As shown in Fig. 5, results illustrate that the two equations represent the data similarly up to about 95% conversion, but the first-order equation deviates significantly from linearity thereafter. In the case of the diffusion-controlled model, the linearity is possibly the result of the effective radius being that of the individual UO_2 + UC crystallites and not of the microsphere itself.

Only the diffusion-controlled model was used to determine the rate constants at each temperature. The constants shown in Table 1 exhibited linearity with 10,000/T and are represented by Eq. (6). The activation energy (E_a)/gas constant (R) value of 12,900 is equivalent to an E_a of 247 kJ/mol, which is 90 kJ/mol lower than the previously reported E_a for uranium oxide

$$\log(k[\mathrm{sec}^{-1}]) = 3.31 - 12,900/T(\mathrm{K}) \quad (6)$$

microspheres with carbon in vacuum [9] and is 50 to 125 kJ/mol lower than the reported values for other conversion experiments [9]. In addition, the E_a/R value of 12,900 is considerably different

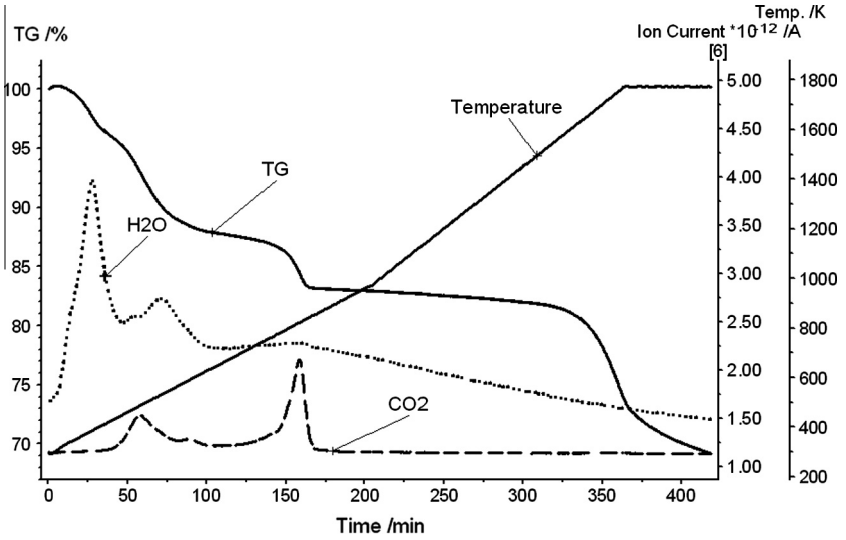

Fig. 4. Characteristics of calcination of air-dried UO_3:2.65 carbon in Ar at 200 K/h from theromogravimetry and mass sepectrometry with the Netzsch instrument. The traces for H_2O and CO_2 are qualitative and have the experimental relative intensities.

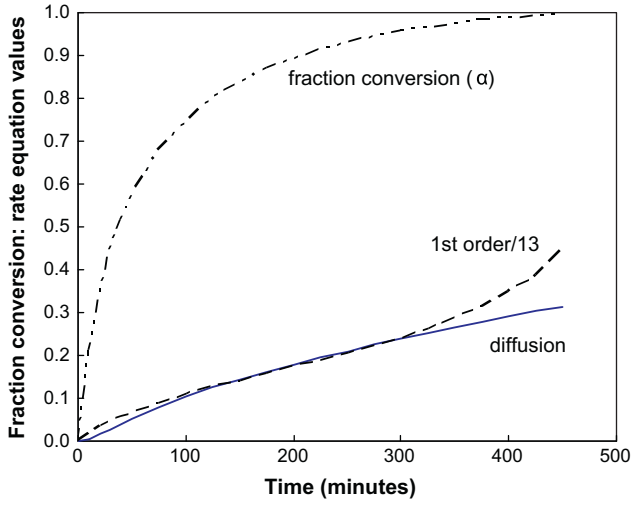

Fig. 5. Plot of experimental data at 1558 K showing the time dependence of fraction conversion and its values in the diffusion-controlled and first-order rate equations. (The first-order values were divided by 13 to scale them to the diffusion-controlled values.).

Table 1
Rate constant in vacuum.

10,000/T (K)	log(k [s^{-1}])
5.995	−4.39
6.188	−4.74
6.418	−4.94
6.627	−5.19
6.868	−5.58

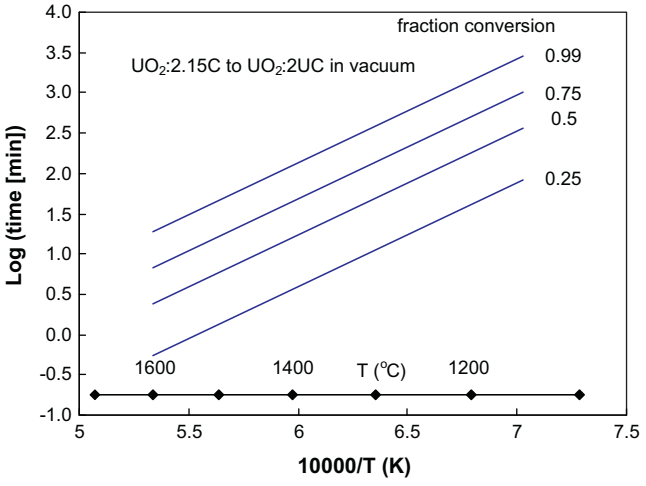

Fig. 6. The interdependence of temperature and fraction conversion (α) on the time for reaction of calcined microspheres of UO_2:carbon to form UO_2:2UC in vacuum.

from the E_a/R value of 19,346 for Eq. (4), which indicates the rate control was not related to pCO of the conversion reaction. This current observation differs from earlier results [7]. The new, lower activation energy was most likely due to the dispersion of smaller carbon black nanoparticles among the UO_2 crystallites in the microspheres.

The time to attain any fraction conversion at temperature is represented by Eqs. (7a) and (7b). Eq. (7b) was used in Fig. 6 to demonstration the vacuum conversion behavior.

$$\log(t[\mathrm{sec}]) = \log(1 - 2\alpha/3 - [1-\alpha]^{2/3}) - 3.31 + 12,900/T(K) \quad (7a)$$

$$\log(t[\mathrm{min}]) = \log(1 - 2\alpha/3 - [1-\alpha]^{2/3}) - 5.09 + 12,900/\mathrm{T(K)} \quad (7b)$$

An additional experiment was performed at 1773 K, and approximately 66% of the sample was converted when a temperature of 1773 K was attained. An iterative application of Eq. (7b) both during the ramp to temperature and also the isothermal portion showed good agreement with the data. Therefore, Eqs. (7a) and (7b) should be valid up to a temperature of 1773 K.

A non-isothermal conversion in vacuum was conducted for comparison with earlier experimental results [9] and application of Eq. (7b). The initial calcined material was taken to 1423 K at 25 K/min and then 1723 K at 1 K/min. X-ray diffraction results indicated that the kernel was 68.7 wt% UC and 31.3 wt% UO_2. The

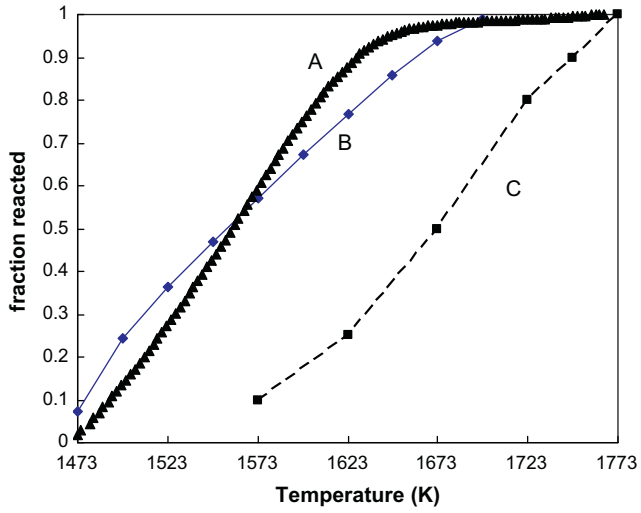

Fig. 7. Characteristics of conversion of UO_2:carbon to form UO_2:2UC in vacuum at 1 K/min. A Current experimental results. B Predicted from iterative application of Eq. (7b). C Experimental results from ref [9] at initial carbon/UO_2 ratios of 3 to 4.

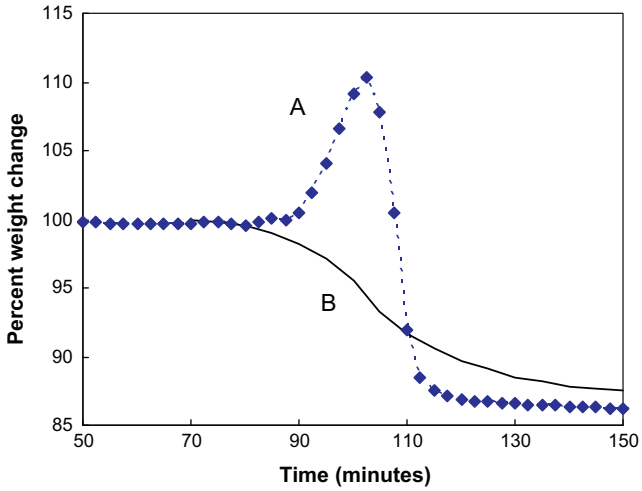

Fig. 8. Characteristics of conversion of UO_2:carbon to UO_2:2UC in vacuum while ramping to 1773 K at ~15 K/min. A Experimental data. B Predicted from iterative application of Eq. (7b).

kernels had an average diameter of 935 μm, and the density was 8770 kg/m^3 or 69% of TD. Curve A in Fig. 7 shows the experimental conversion results, and curve B is the behavior predicted from Eq. (7b) using an iterative manual spreadsheet calculation. Curve B, and thus the application of Eq. (7b), adequately represents the experimental data of curve A. It can also be seen that conversion in the present work was comparable to the earlier study [9]. However, the current uranium microspheres with carbon began to react 100 K lower than the previous uranium kernels with carbon [9].

Fig. 8 illustrates the utility of Eq. (7b) in the analysis of complicated experimental results. In this experiment, UO_2:carbon microspheres were taken in vacuum to 1773 K at a ramp rate of ~15 K/min and held at that temperature until conversion to UO_2:2UC was completed. The model predicts that conversion would begin at approximately 1323 K or 80 min into the experiment and that the conversion would be about 60% complete when 1773 K was attained after 107 min. As seen in Fig. 8, the predicted behavior for the initial half of the conversion falls where the observed weight gain in the data reflects the most rapid CO evolution rate. (These gains also appear when CO_2 is evolved rapidly during caclining in vacuum at 723–873 K. The rapid evolution of gas in vacuum exhibits a downward pressure, i.e., a false weight gain, on the STA.) The conversion rate then slows and the STA weight percentage drops precipitously until 110 min, which is at about 66% conversion, where the weight change and the predictions of Eq. (7b) again begin to coincide. This experimental behavior would have been difficult to interpret without the model of Eq. (7b).

Vacuum conversion is shown here to be much faster than any possible conversion by flowing argon through a particle bed used for production quantities of UO_2:3C mixtures to UC. The minimum mols of gas needed to remove 1 mol of CO at low pressure is the reciprocal of pCO. The calculated flow of argon needed to just saturate the argon with the equilibrium CO pressure for 100% conversion in the time calculated by Eq. (7b) can be determined using Eq. (8). The combination of Eqs. (1) and (8) become Eq. (9).

$$\log(\text{flow}[\text{molsAr}/\text{min}]) = -\log(\text{pCO}[100\ \text{kPa}]) - \log(\text{t}[\text{min}]), \quad (8)$$

$$\log(\text{flow}[\text{molsAr}/\text{min}]) = 3.26 - 6,446/\text{T} \quad (9)$$

At 1873 K, Eq. (9) predicts 1.5 mols argon/min (140 mL/g uranium/min) and at 1473 K 13 mols argon/min (1200 mL/g uranium/min) just to saturate the argon with the equilibrium pCO, at which pCO the reaction would actually stop. These values need to be multiplied by 2 for complete conversion of 1 mol UO_2 (which produces 2 mols of CO) and by another estimated factor of ~5 so that pCO is well below the equilibrium value (line A, Fig. 1), as deduced from a comparison of the experimental M50% and region B of Fig. 1. This gives a total factor of 10 to ensure that pCO is considerably less than equilibrium so that the conversion can proceed. Such flows are practically impossible and demonstrate the advantage of vacuum conversion to the carbide. Conversely, in the present experiments with only ~100 mg samples (~20 microspheres) on a flat specimen holder in flowing gas so that CO removal is unhindered, conversion rates were only slightly lower than those with vacuum.

6.4. Evolution of diameter and density

The commonly observed shrinkage of the original air-dried microspheres at different stages of conversion was measured. Air-dried microspheres had an average diameter of 1760 μm. Their approximate molar composition was UO_3 $2H_2O$ + 2.65 carbon with trace amounts of ammonia nitrate, urea, and hexamethylenetetramine. The density of the air-dried microspheres was typically 1600 kg/m^3. However, the density of the air-dried uranium microspheres is greatly impacted by the gelation temperature. After the microspheres were heated at 1373 K in argon, their composition became UO_2 + carbon, and their average diameter only reduced to 1550 μm. The density of calcined microspheres was 2400 kg/m^3, which corresponded to a 30% TD. Conversion to UO_2:2UC at 1573 K produced kernels with an average diameter of 1200 μm and a density of 4600 kg/m^3 or 36% of TD. The same conversion at 1673 K yielded kernels with an average diameter of 1070 μm and a density of 6200 kg/m^3 or 49% of TD. With a conversion temperature of 1773 K, the average diameter decreased to 990 μm while the density increased to 7400 kg/m^3 or 58% of TD. In one combined experiment, the conversion to UO_2:2UC at 2023 K produced microspheres with an average diameter of 900 μm and a density of 9700 kg/m^3 or 76% of TD. Then, these microspheres were converted to UN at 1873 K with no change in diameter and a lower density of 8300 kg/m^3 or 58% of TD.

6.5. Investigations using the Ledergerber parameters [8]

Uranium carbonitride kernels were made from air-dried UO_3:2-H_2O:2.65 carbon microspheres by using the general experimental parameters of Ledergerber et al. [8]. In one run, about 7 g of air-dried microspheres were placed in a molybdenum boat in a graphite furnace and calcined at 3 K/min to 973 K in 4% H_2 in Ar. The sample was then heated at 5 K/min to 1948 K, the gas switched to 4% H_2 in N_2, and the temperature ramp continued to 2073 K, where it was held for 20 h. The gas was switched back to 4% H_2 in Ar to prevent the formation of U_2N_3 during cooling at 20 K/min to room temperature. The resulting kernels were $UC_{0.57}$ $N_{0.43}$ with a 90% TD and a lattice parameter (LP) of 0.49329 nm. A second run was taken to 2023 K with otherwise identical parameters and gave $UC_{0.54}N_{0.46}$ with an 89% TD and a LP of 0.49325 nm. A third run again used the same parameters, with the single exception that the microspheres were converted to UO_2 and UC in vacuum between 973 and 1948 K; an iterative application of Eq. (7b) predicted conversion to a UO_2–UC mixture by 1873 K. Conversion at 2023 K gave $UC_{0.6}N_{0.4}$ with an 88% TD and a LP of 0.49366 nm.

The above experiments lead to a few observations. Although the approximately 97% TD of Ref. [8] was not achieved, the present density results are equivalent to those from earlier work [5,6]. It does appear that vacuum conversion may be useful to remove 2/3 of the CO in the carbothermic conversion to UN and may be particularly useful for large batches. The especially significant observation is the high carbide content of the kernels resulting from using 4% H_2 in Ar during calcining to 973 K. It appears that the hydrogen primarily reduces the UO_3, so that there is an excess of carbon after calcination, and this excess is most of the ~57% UC in the $UC_{1-x}N_x$. (This observation concerning reduction is contrary to our earlier TGA studies of calcining [17], where both carbon and hydrogen reduced the O/U simultaneously in dehydrated microspheres, resulting possibly from the physical difference between microspheres in a TGA cup of that study and as a monolayer in the present graphite furnace.) The present observation of high carbide content when calcining in 4% H_2 in Ar also leads to the conclusion that Ledergerber et al. [8] obtained their final values of $0.01 < x < 0.15$ in the $UC_{1-x}N_x$ kernels by starting with a carbon to uranium molar ratio of 2.15 in the initial microspheres, which were dried in a rotary drier and calcined in a static bed to 773 K; the latter temperature is just below where O/U reduction to 2 begins [17].

7. Conclusions

Detailed discussions of the present and several related investigations appear in the previous sections. Several conclusions result from these investigations and analyses.

Extensive thermodynamic calculations illustrated that the carbothermic conversion of UO_2–carbon mixes in flowing inert gases

to UC has pCO values lower than when converting in nitrogen to $UC_{1-x}N_x$. However, when carbon is absent and only UO_2 and $UC_{1-x}N_x$ are present, further reaction at usual sintering temperatures to increase the values of x and lower the oxide content by CO removal occurs at very low pCO values, thus requiring relatively large flows of nitrogen. It was also calculated that HCN is second to CO as the dominant carbon-containing gas during carbothermic conversion and sintering.

Analysis of the carbothermic conversions experiments of Refs. [7,15] indicated consistency in their rate constants and a direct influence of gas flow rates, which they concluded affected the ambient pCO values.

Analysis of the experiments of Ledergerber et al. [8] indicated that CO removal by the 7% H_2 in Ar flow was controlling the conversion to $\sim UO_2$:2UC during the temperature ramp to the final temperature, while subsequent conversion to $UC_{1-x}N_x$ kernels in 7% H_2 in N_2 was consistent with control by solid-state diffusion within the kernel.

Several observations of the calcining process were made. Experiments of the calcining process with simultaneous TGA and mass spectrometry at a temperature ramp of 200 K/h revealed many previously unknown details of the release of H_2O, CO, and CO_2. Calcining at rates above 200 K/h led to microsphere surface imperfections, and substantially higher rates resulted in cracked kernels after conversion. Calcining of a master batch to be used later in making $UC_{1-x}N_x$, and storage in argon, led to some reoxidation, loss of C/U via recalcining in subsequent experiments, and UO_2 in the product. Consequently, use of uncalcined, air-dried microspheres is recommended for carbothermic conversion.

Carothermic conversion of microspheres in vacuum to UO_2:2UC was studied isothermally, modeled, and the model applied successfully to non-isothermal experiments.

The parameters of Ref. [8] were the experimental basis for producing ~7 g of $UC_{1-x}N_x$ kernels with ~89% TD. Use of hydrogen-containing gases throughout with an initial carbon to uranium molar ratio of 2.65 led to x values of ~0.57 because hydrogen and not ~0.5 mols of carbon did most of the reducing UO_3 during calcination. Intermediate carbothermic conversion of calcined material in vacuum to a UO_2–UC mixture, followed by conversion and sintering in 4% H_2 in N_2 gave the same density and values of x.

It seems remarkable that the present rate equations based on an unchanging sphere diameter and density can represent experimental kinetic data when one considers that the calcined 1550 μm, UO_2:2.65C, 30% TD microsphere subsequently shrinks to a 990 μm, 50% TD kernel when converted carbothermically at 1773 K. Application of the work of Refs. [13,14]may lead to better rate equations for such conditions.

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