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Production of Low-Enriched Uranium Nitride Kernels for TRISO Particle Irradiation Testing

Fuel Cycle Research & Development Advanced Fuels Campaign

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ABSTRACT

A large batch of UN microspheres to be used as kernels for TRISO particle fuel was produced using carbothermic reduction and nitriding of a sol-gel feedstock bearing tailored amounts of low-enriched uranium (LEU) oxide and carbon. The process parameters, established in a previous study, produced phase-pure NaCl structure UN with dissolved C on the N sublattice. The composition, calculated by refinement of the lattice parameter from X-ray diffraction, was determined to be $UC_{0.27}N_{0.73}$. The final accepted product weighed 197.4 g. The microspheres had an average diameter of 797±1.35 μm and a composite mean theoretical density of 89.9±0.5% for a solid solution of UC and UN with the same atomic ratio; both values are reported with their corresponding calculated standard error.

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Production of Low Enriched Uranium Nitride Kernels for TRISO Particle Irradiation Testing

1. INTRODUCTION

The fully ceramic microencapsulated (FCM) fuel form uses tri-structural isotropic (TRISO)-coated particles embedded in a dense SiC matrix. The FCM concept leverages existing Light Water Reactor (LWR) infrastructure with an Accident Tolerant (AT) drop-in replacement for conventional UO_2. With an FCM compact, much of the U volume associated with traditional UO_2 pellets has been replaced by TRISO coatings and the SiC matrix thus necessitating a higher fissile-density fuel, such as UN, to be used as the kernel of the TRISO particles. Thorough technical details can be found in previous publications [1, 2].

This work reports on the successful production of a large batch of UN TRISO particle fuel kernels using carbothermic reduction and nitriding of a sol-gel feedstock bearing tailored amounts of low enriched uranium (LEU) oxide and carbon. The process parameters were established by Lindemer et al. in a previous report [3]. The final product was phase-pure NaCl structure $UC_{0.27}N_{0.73}$, weighed 197.4 g, had an average diameter of 797±1.35 μm and a composite theoretical density (TD) of 89.9±0.5 % for a solid solution of UC and UN with the same atomic ratio (see Section 4). Each value is reported with a corresponding standard error. The microspheres will be coated with the appropriate TRISO layers using chemical vapor deposition and prepared for planned irradiation testing.

2. OVERALL FCM TRISO PROCESS DESCRIPTION

The production of FCM TRISO particles can be subdivided into two distinct steps as shown in Figure 1. Feedstock UO_3+C spheres produced using a sol-gel method are converted to UC_xN_{1-x} by carbothermic reduction, occurring in two calcining steps governed by the reactions given in Equations 1 and 2, and subsequent nitriding that proceeds via Equation. 3.

$$UO_3 + C \rightarrow UO_2 + 1/2\,C + 1/2\,CO_2 \quad (1)$$

$$UO_2 + (3-2y)C \rightarrow UO_yC_{1-y} + (2-y)CO \quad (2)$$

$$\left(\frac{1-2y-x}{3-2y}\right)UO_2 + \left(\frac{2+x}{3-2y}\right)UO_yC_{1-y} + \left(\frac{1-x}{2}\right)N_2 \rightarrow UC_xN_{1-x} + \left(\frac{xy-2y-2x+2}{3-2y}\right)CO \quad (3)$$

The resulting UC_xN_{1-x} kernels are coated with carbon buffer, inner pyrolytic carbon (IPyC), SiC, and an outer pyrolytic carbon (OPyC) layers using chemical vapor deposition (CVD) as has previously been done in extensive TRISO development work [4-6]. The CVD process is sensitive to the properties of the material to be coated (e.g. morphology, size, weight, density, etc.). As such, the coating parameters for FCM TRISO were established using depleted uranium (DU) bearing UC_xN_{1-x} microspheres produced during the TRISO kernel research and development (R&D) phase reported in [3]. Figure 2 shows a cross-sectioned final product FCM TRISO particle with a high density UC_xN_{1-x} kernel.

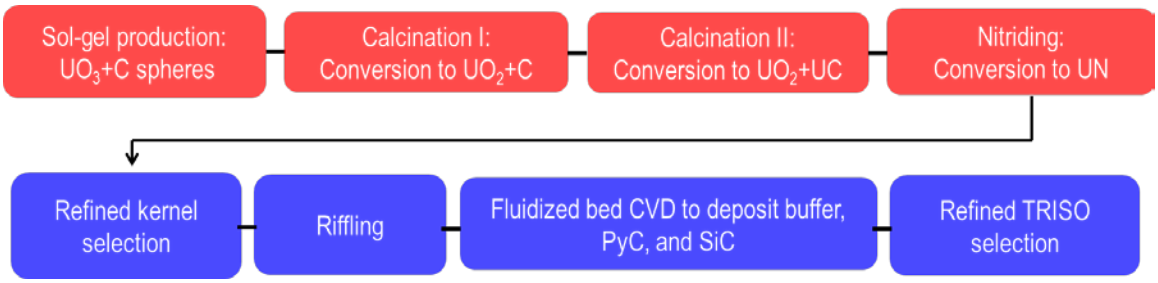

Figure 1. Flow chart of the integral FCM TRISO particle process.

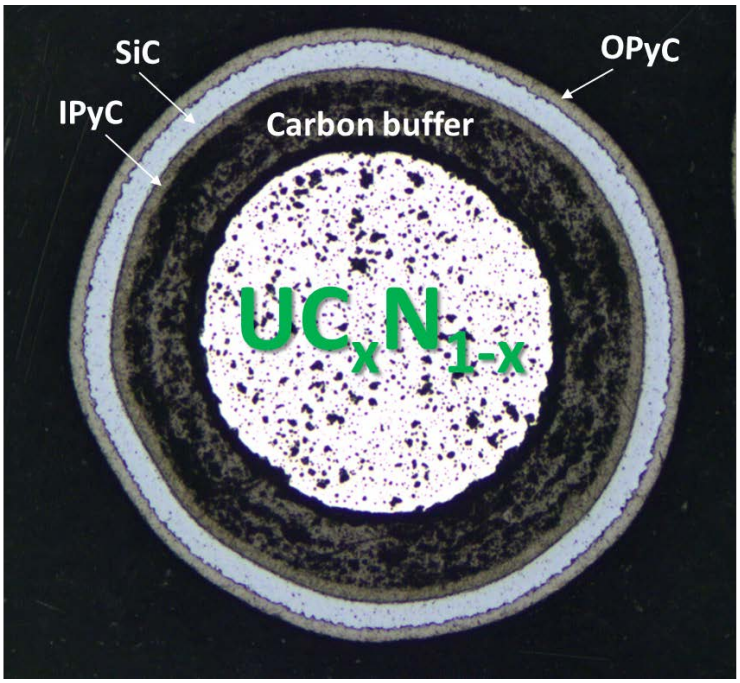

Figure 2. Cross-sectioned FCM TRISO particle resulting from process variables from early kernel development [3].

3. LOW-ENRICHED URANIUM NITRIDE FABRICATION PROCESS

The internal gelation process was used to produce 1400–2000-µm-diameter spheres of hydrated UO_3 with homogenously-embedded carbon powder. The starting material consisted of uranium oxides, with a ^{235}U enrichment of 7.35 at. % U, and Cabot Mogul L carbon black; these components were dispersed throughout the gel spheres as described in ref. [7]. As pointed out in [3], this form of C tends to aggregate. This was mitigated by using the dispersing agent, Tamol SN, which was added to the chilled basic hexamethylenetetramine (HMTA)/urea solution and sonicated for 5 min with a Hielscher UP200S ultrasonic probe. Since sonification heats the solution, it was subsequently rechilled. To this, a chilled acid deficient uranyl nitrate solution was added to form the broth which was then added as droplets in a controlled fashion into a flowing stream of hot (~62 °C) immiscible silicone oil to facilitate the gelation reaction. The gelled spheres were then washed and dried resulting in a product with a C/U ratio of 2.65 with ~2 moles of adsorbed H_2O /mole U and traces of NH_3. A flow diagram of the process is shown in Figure 3.

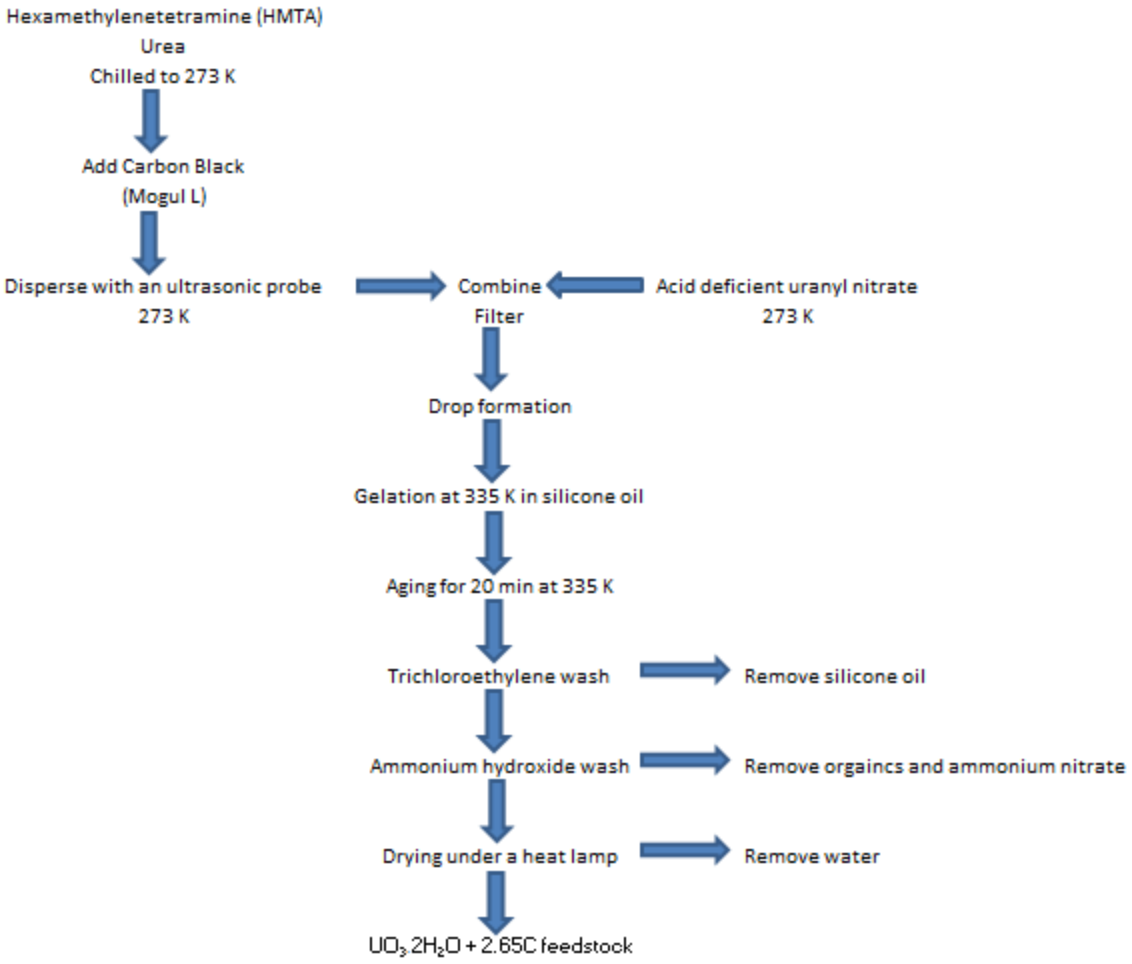

Figure 3. Flow diagram for the internal gelation sol-gel feedstock.

This material weighed 468 g and was used as a feedstock to produce five independent batches totaling 197.4 g of phase-pure UN microspheres with a diameter of 750–870 µm and an average geometric TD of 89.9±0.5%. Figure 4 depicts the overall conversion process using the parameters determined in [3].

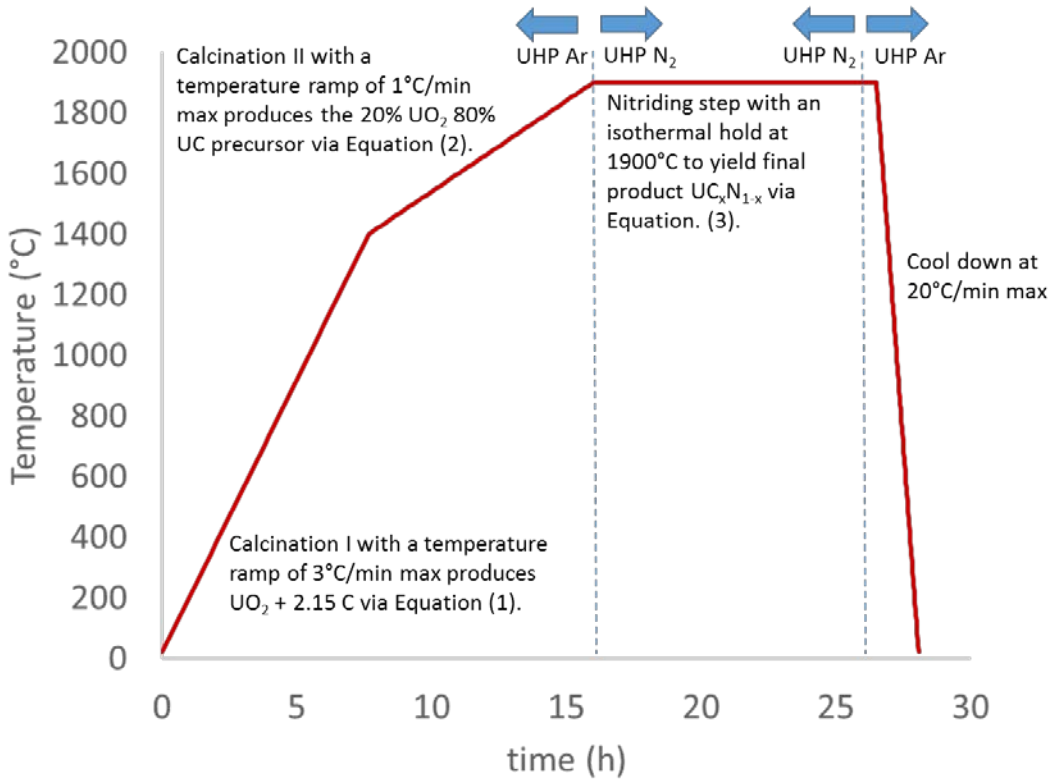

Figure 4. Process used to convert the sol-gel feedstock to ~800µm and 89.9% TD phase-pure UC_xN_{1-x} microspheres with 13.5 at. % dissolved C. Note that reference [3] gives ~1950°C for isothermal hold but 1900°C was used for this work for consistency with the majority of previous DU exploratory batches.

All gases were Air Liquide Ultra High Purity (UHP) grade with nominal impurity limits shown in Table 1. The conversion took place in an Astro furnace (Thermal Technology, LLC) with a graphite heating element capable of reaching 2200 °C. The reaction chamber consisted of a hollow W cylinder (Figure 5) whereby process gas was introduced by continuous flow through the W tube shown in Figure 5(a), entering at the orifice in Figure 5(b), and exited at the opening in the gravity sealed lid, Figure 5(c). The feedstock material was positioned above a 60-inch by 60-inch-mesh W screen with a wire diameter of 0.004 inches and an opening of 0.0127 inches. This was done in order to separate the spheres from the inlet of the chamber for containment while still allowing for intimate contact with the process gas.

Table 1. Impurity limits for the process gases used for the sol-gel feedstock to UN conversions.

Impurity	**UHP Ar**	**UHP N_2**
Moisture	< 3 ppm	< 3 ppm
O_2	< 2 ppm	< 2 ppm
Hydrocarbons	< 0.5 ppm	< 0.5 ppm
CO_2	< 1 ppm	< 1 ppm
CO	< 0.5 ppm	< 1 ppm
N_2	< 5 ppm	

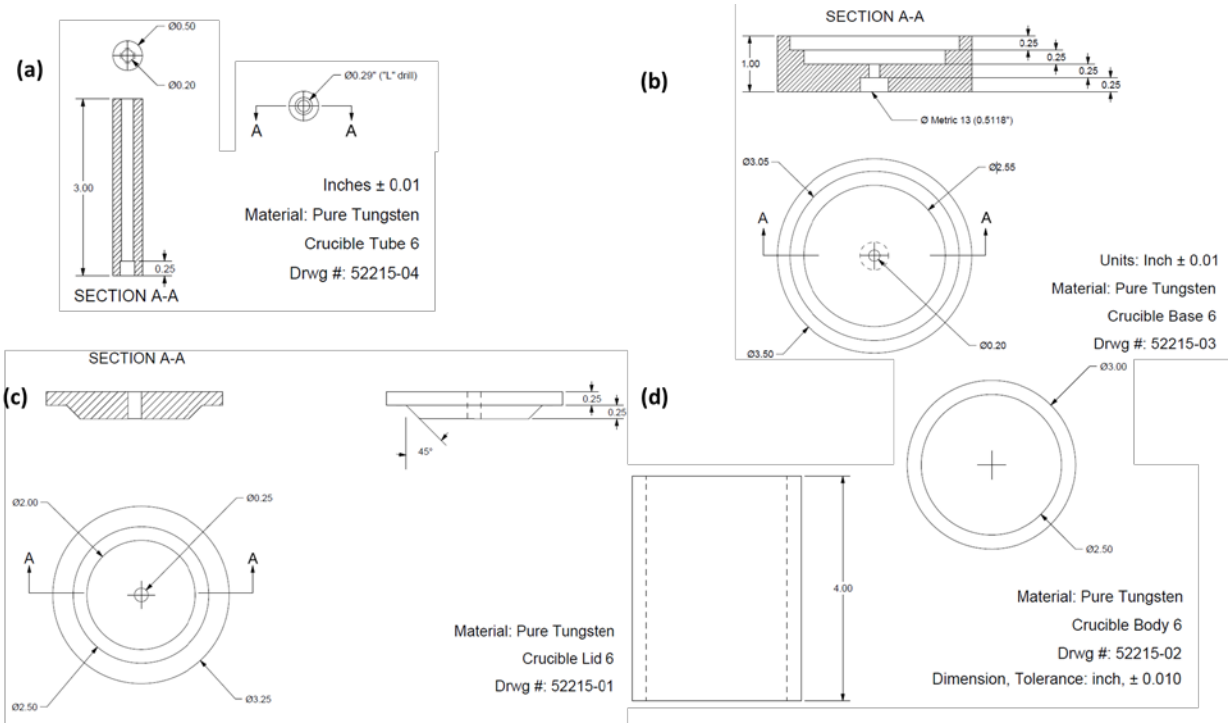

Figure 5. Engineering drawings of the W crucible used for the conversion step of UN microsphere production.

4. CHARACTERIZATION OF FINAL PRODUCT UN MICROSPHERES

The product, or batches, from each carbothermic and nitriding conversion run were upgraded by hand-tabling to remove non-spherical kernels, followed by roller micrometer division into eleven bins based on diameter. Each bin was configured to retain kernels within a ~25 µm diameter range, and material with diameters between 750-850 µm was set aside to be composited into the final product. A subset from each bin was characterized by determination of average particle weight and diameter using established procedures from the Advanced Gas Reactor program detailed in references [3, 8]. Given the assumption of spherical particles, this data was used to estimate average density for each bin, as shown in Figure 6. The TD was calculated relative to a 27% UC-73% UN solid solution.

A final upgrading step was applied to each batch of material before compositing. Kernels were spread into a monolayer and visually surveyed to remove those that were oblong but yet round enough to pass the earlier hand-tabling. Next, material from all five batches was combined and riffled into sub-lots for characterization and coating charges. The composite average kernel diameter and density, reported here with their standard error, were found to be 797±1.35 µm and 12.67±0.07 g/cm^3 respectively. The calculated 100% TD for $UC_{0.27}N_{0.73}$ is 14.1 g/cm^3; therefore, the final accepted product was determined to be 89.9±0.5% TD. The median size and mean TD distribution by weight are shown in Figure 6. The phase purity and chemical composition of the final product were determined with powder X-ray diffractometry (XRD) as was done in [3].

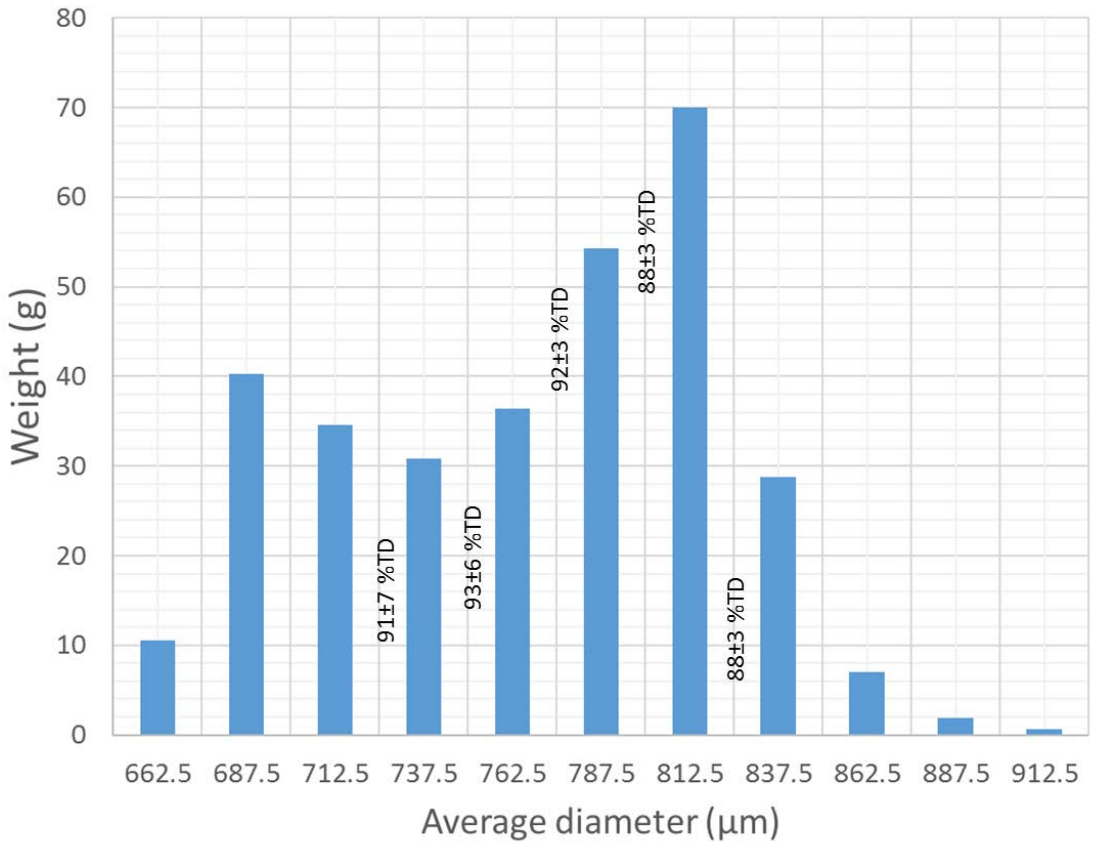

Figure 6. Kernel mass distribution as a function of average diameter. The %TD with associated standard errors are given for the microspheres that fell within a specified size range.

The XRD pattern in Figure 7 indicates the final product is phase-pure NaCl structure UC_xN_{1-x}. The refined lattice parameter (4.9125±0.0001Å) suggests a composition corresponding to $UC_{0.27}N_{0.73}$. If desired, in [3] it was demonstrated that the N content can be increased by additional processing in flowing N_2-4%H_2 via removal of the solid-solution C as HCN and substituting N for it on the anion sublattice. As mentioned in Section 2, the integral FCM TRISO fabrication involves coating the kernels using CVD, which required considerable R&D to determine parameters that produced acceptable results. Therefore, the N enrichment step with N_2-4%H_2 was not used in order to preserve the CVD process developed for depleted U-bearing UC_xN_{1-x} of comparable compositions.

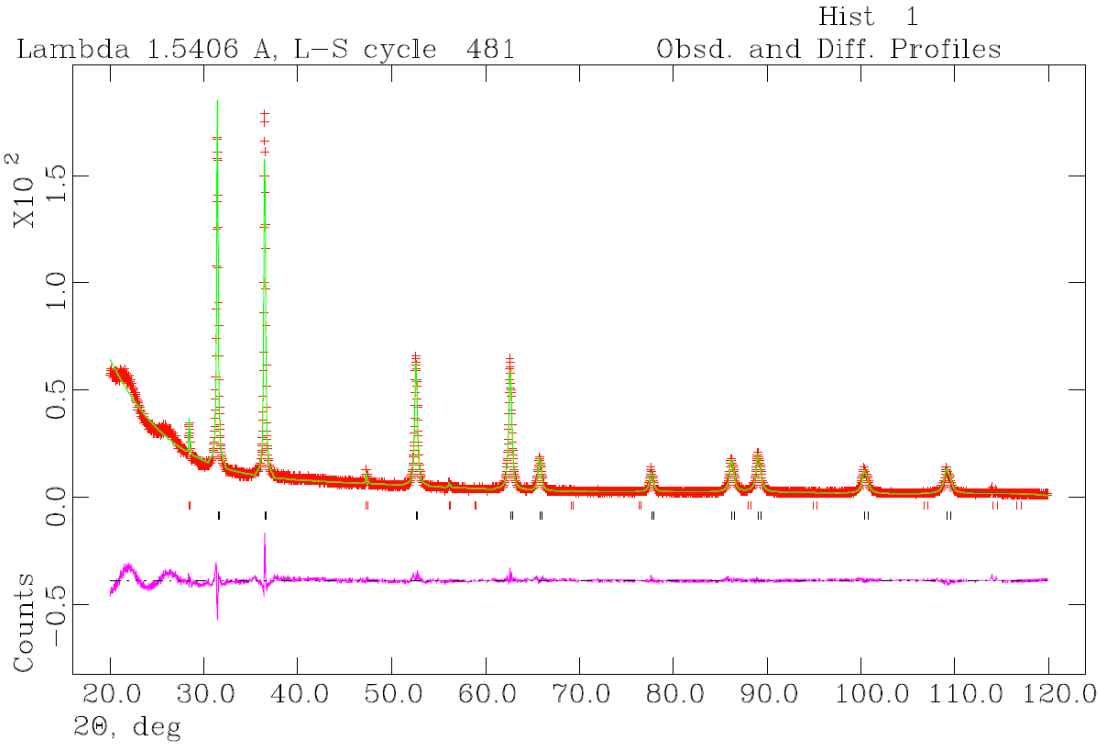

Figure 7. XRD pattern for a representative specimen taken from the final product.

Uranium monocarbide is isostructural with UN exhibiting complete miscibility over an extensive temperature range with comparable physical properties summarized in Table 2 from [9]. In the presence of excess C, i.e., the buffer layer in a TRISO particle, UC_xN_{1-x} and graphite coexist up to x values of ~0.89 and 0.83 for 800 and 1400°C, respectively, as illustrated in Figure 8. The significance of this is that a deleterious second phase precipitate, i.e. UC_2 or U_2C_3, is not expected under anticipated operation temperatures, departures thereof associated with accident scenarios, or during the CVD TRISO coating that uses temperatures within the range covered in Figure 8. Due to the similar properties of UC and UN, UN with 27% C on the anion sublattice is considered to be acceptable.

Table 2. Selected properties of UN and UC.

Property	UN	UC
Molecular mass, amu	252	250
Density, g/cm^3	14.3	13.63
Melting point, °C	2850	2365
Heat capacity, J/(mol·K)	48	50
Thermal conductivity, W/(m·K)	13	25.3
Linear expansion coefficient, 1/K	7.52×10^{-6}	10.1×10^{-6}
Electrical resistivity, Ω·m	1.46×10^{-6}	727.7×10^{-8}

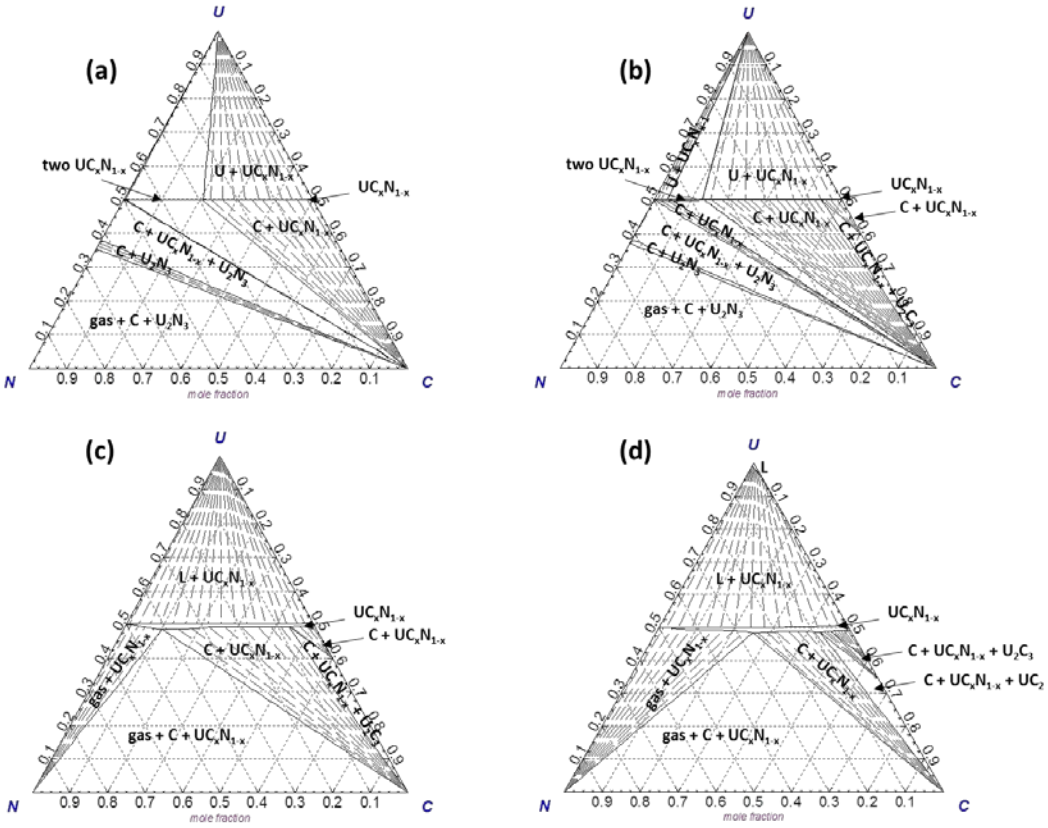

Figure 8. Computed phase relations in the U-C-N system at (a) 300°C, (b) 800°C, (c) 1400°C, and (d) 1600°C.

The SEM images in Figure 9(a,b) show the pore distribution with the highest concentration and larger ones near the center of the kernels. In Figure 9(c), the mosaic gives insight into a few features. First, there seems to be mostly high-density kernels, Figure 9(d) for example, with a smaller fraction exhibiting a central void that is ~10% of the total volume of the kernel. An analysis of the sol-gel feedstock and the UO_2-UO_yC_{1-y} precursor is underway to determine whether or not they exhibit similar features. It is probable that these voids were created from so-called "lift out" that can occur with the back-potting technique of the mounting and polishing step used to prepare the samples for optical and SEM imaging.

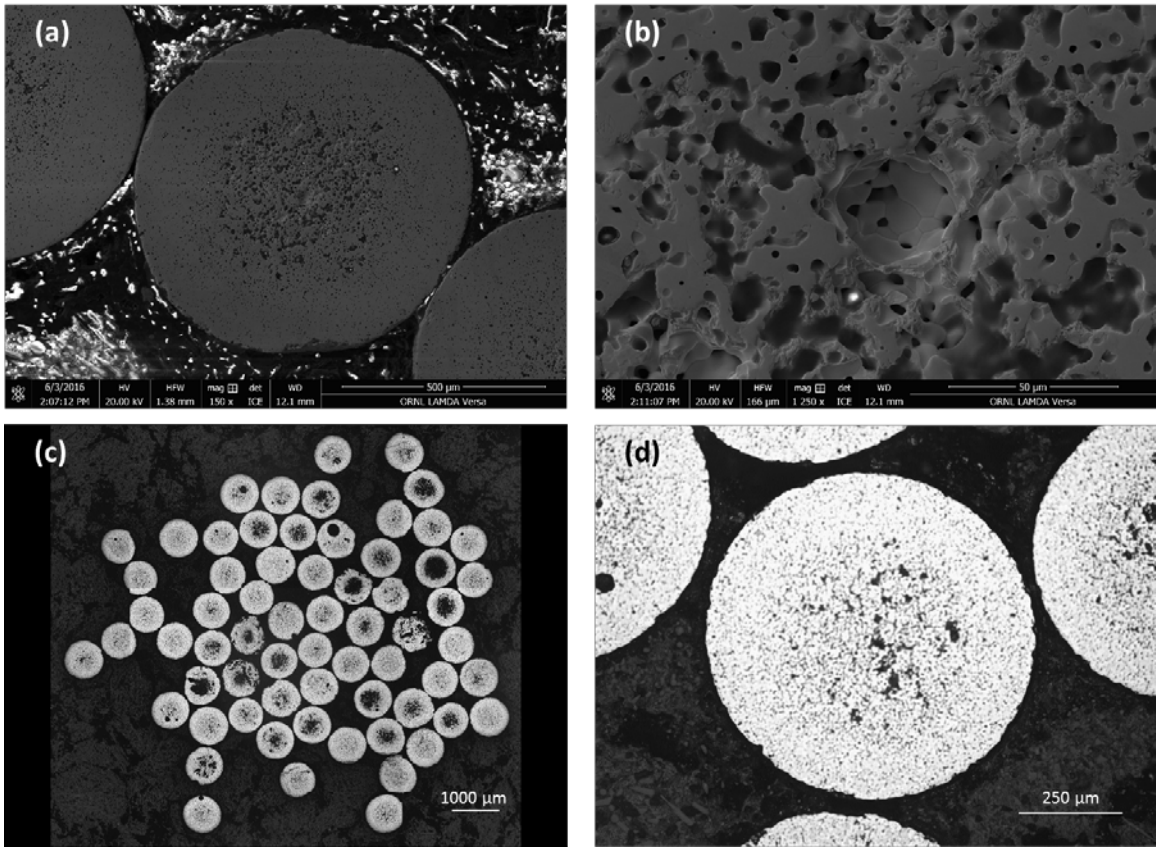

Figure 9. SEM images **(a,b)** showing the pore structure in a kernel from the final product $UC_{0.27}N_{0.73}$. The optical microscope images in **(c)** and **(d)** show what appears to be mostly high density microspheres.

5. CONCLUSIONS

A 197.4-g batch of LEU-bearing, ~800-µm-diameter UC_xN_{1-x} microspheres was produced using the optimized process determined in [3]. The XRD analysis showed the material to be phase-pure $UC_{0.27}N_{0.73}$. The average density was determined to be 12.67±0.07 g/cm^3 or 89.9±0.5 % TD for $UC_{0.27}N_{0.73}$. This large batch of microspheres will be coated with TRISO layers using a CVD process developed at ORNL for irradiation testing that should aid qualification of UN as the kernel in TRISO particle fuel for the FCM design.

6. ACKNOWLEDGMENTS

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