Fabrication and Characterization of Uranium-based Nuclear Fuels

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Background and Introduction

Nuclear energy continues to play a large role in the energy landscape of the world. Of particular interest is creating more efficient and accident tolerant nuclear fuels such as uranium mononitride (UN) or large-grained uranium dioxide (UO_2). A carbothermic reduction of UO_2 and nitridation thermal process was used to convert UO_2 powder into phase-pure UN, which was confirmed through X-ray diffraction.

The UN powder was cold pressed into green pellets prior to sintering at 1900 °C. UO_2 pellets were pressed and sintered at 1500 °C using a three step process (reducing-oxidizing-reducing atmospheres) to make high density, stoichiometric UO_2 pellets. The fabrication and characterization of high quality nuclear fuels provides opportunities for further testing and optimization of high performance, accident tolerant fuels.

Material Systems UN and UO_2

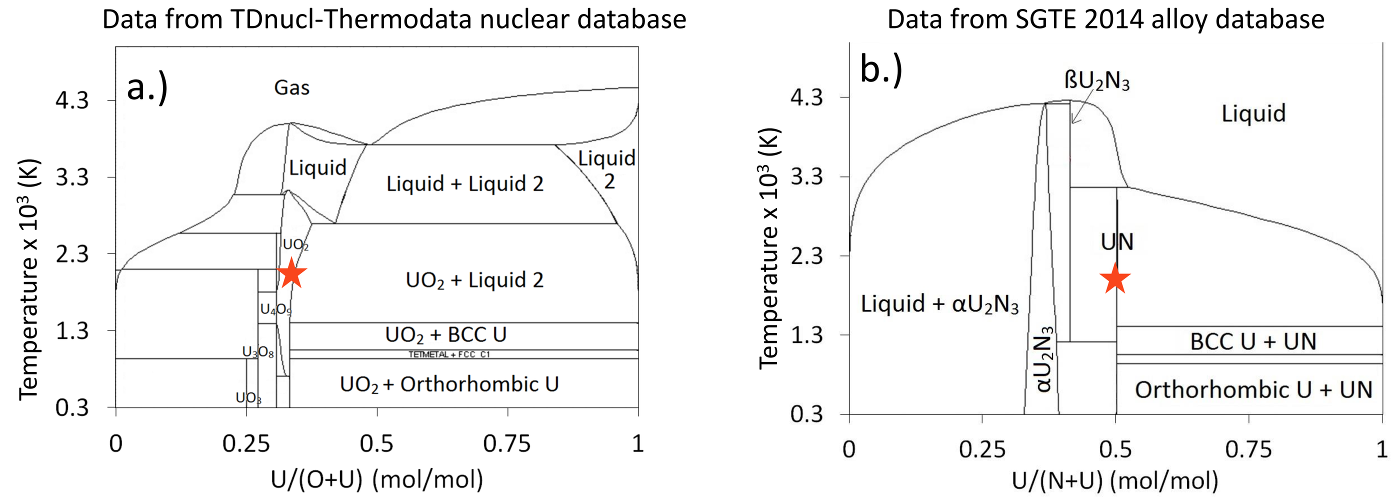

Figure 1: Phase diagrams for the oxygen-uranium (a) and nitrogen-uranium (b) systems in the relevant temperature range [1]. The orange stars signify UO_2 and UN respectively. Both of these material systems are very complex with the product formed being very dependent on the partial pressures of the constituent gasses [2].

UO_2 was used as the feedstock in this study because of its availability and current widespread use as a nuclear fuel. Improving the thermal conductivity of nuclear fuel can greatly decrease the impact of a thermal transient, such as a loss of coolant accident (LOCA), during operation.

Physical Properties	UN	UO_2
Density (g/cm³)	14.33	10.97
Uranium Density (g/cm³)	13.53	9.67
Melting Point (°C)	2650	2700
Heat Capacity (J/kgK) at 500°C	230	300
Thermal Conductivity (W/mK) at 500 °C	20.5	2-4

Table 1: Bulk physical properties of UN and UO_2. The high uranium density, thermal conductivity, and low heat capacity of UN are favorable over UO_2 as a nuclear fuel [3].

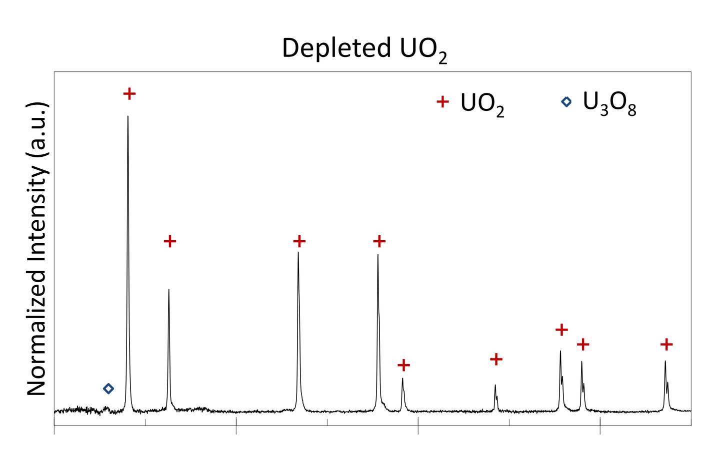

Figure 2: X-ray diffraction (XRD) pattern of the feedstock UO_2 used in this study. This feedstock contains a small amount of U_3O_8, a higher oxidized state of uranium.

Starting Materials

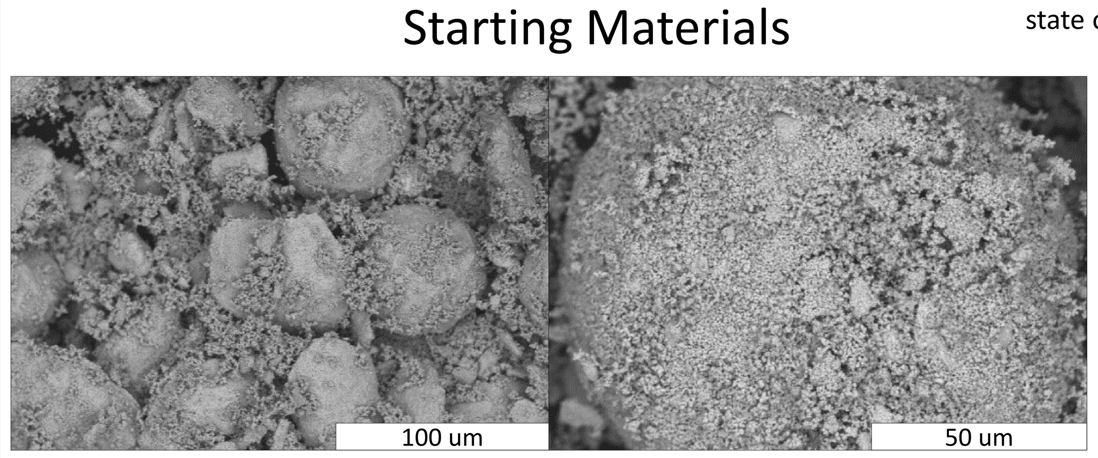

Figure 3: Scanning electron micrographs of the feedstock UO_2 powder. The UO_2 powder has very small primary particles that are clumped in much larger clusters.

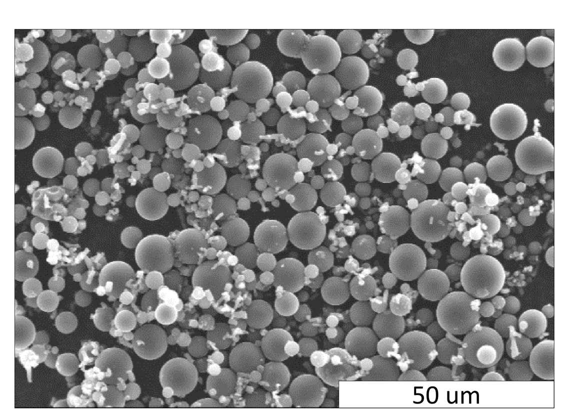

Figure 4: Scanning electron micrograph of the feedstock carbon source.

Carbothermic Reduction of UO_2 to UN

Steps [4,5]

1. Under vacuum: Removal of oxygen
$$UO_2 + 3C \leftrightarrow UC + 2CO \qquad eq.\ 1$$

2. In N_2 + 6%H_2: Removal of carbon, form UN
$$2UC + 2N_2 + H_2 \leftrightarrow 2HCN + 2UN \quad eq.\ 2$$

3. In UHP argon: Maintain phase purity
$$U_2N_3 \leftrightarrow 2UN + \tfrac{1}{2}N_2 \qquad eq.\ 3$$

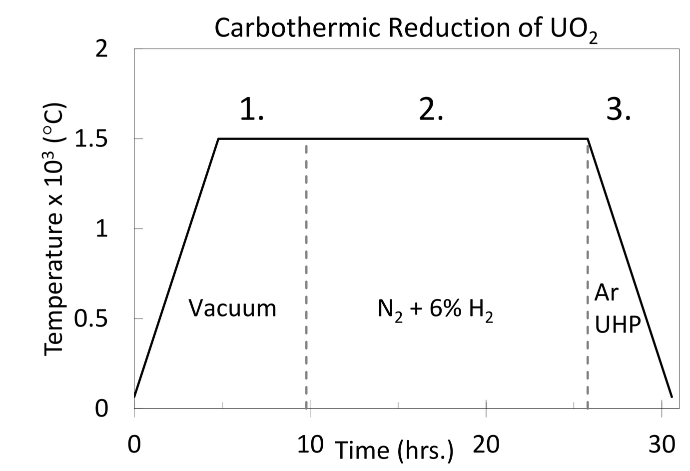

Figure 5: Furnace temperature and gas profile for the carbothermic reduction of UO_2 to UN [4]. Three batches of UN were synthesized with batch sizes of 5, 12, and 12 grams respectively.

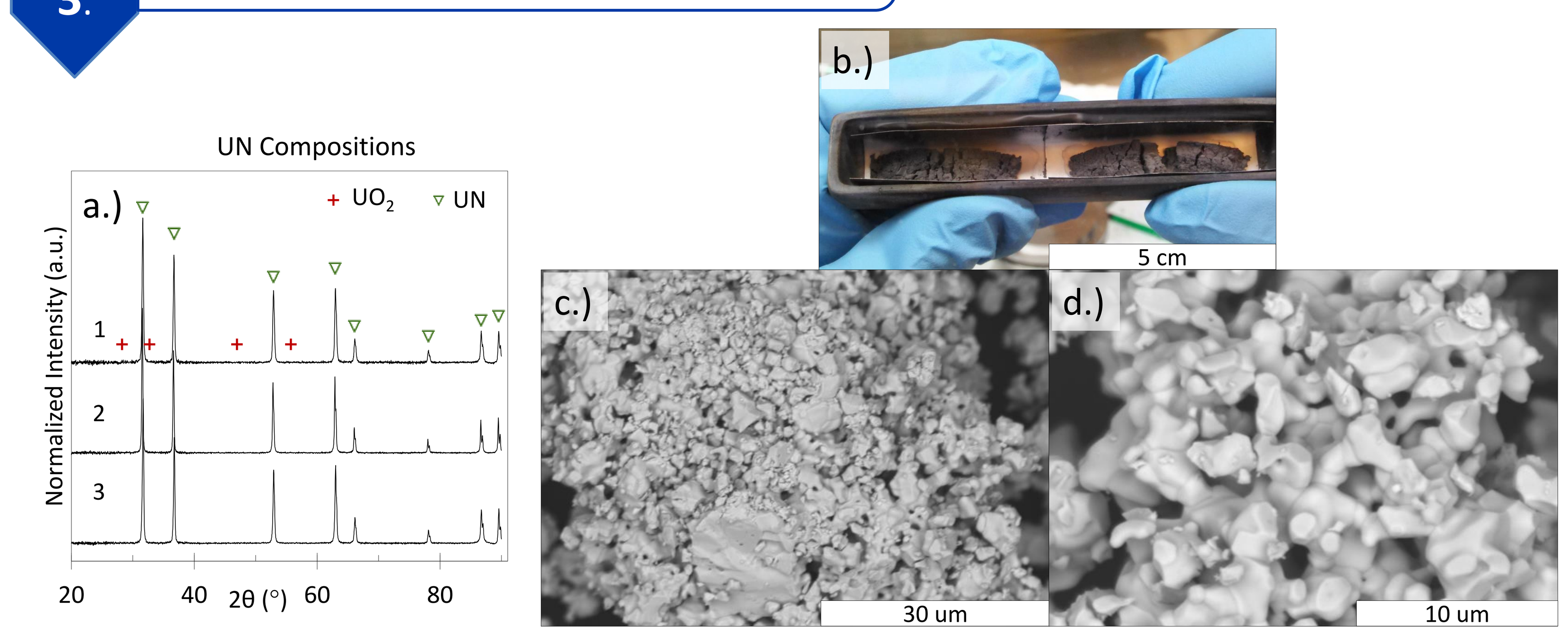

Figure 6: Results of the carbothermic reduction of UO_2 to UN. a.) X-ray diffraction scans of the three batches (1, 2, and 3) of UN synthesized suggesting phase pure UN. b.) Photograph of the crucible and UN powder after synthesis. c.) and d.) SEM micrographs of the UN powder showing particle size and some sintering.

Shape forming and Sintering

- Grind with mortar and pestle (UN)
- Press at 400-670 MPa with zinc stearate as lubricant on die walls and punch
- Sinter in appropriate atmosphere

Pressed Pellet Density	UN	UO_2
Theoretical Density (g/cm³) [3]	14.33	10.97
Green Density (% of theoretical)	60 ± 2	55 ± 5

Table 2: Density of the pellets after being pressed into shape. High green densities generally contribute to high final densities.

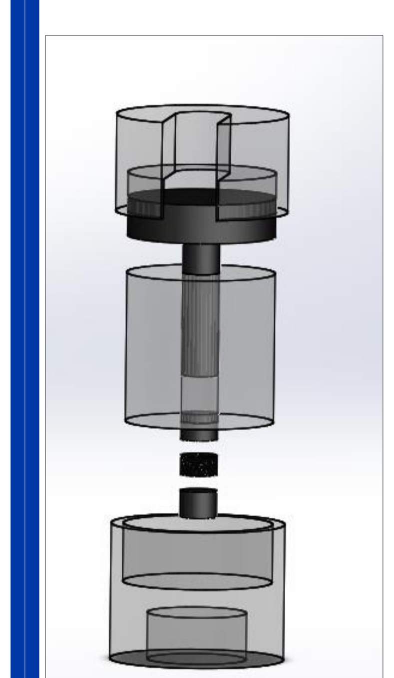

Figure 7: Solidworks® model of the die used to press the pellets.

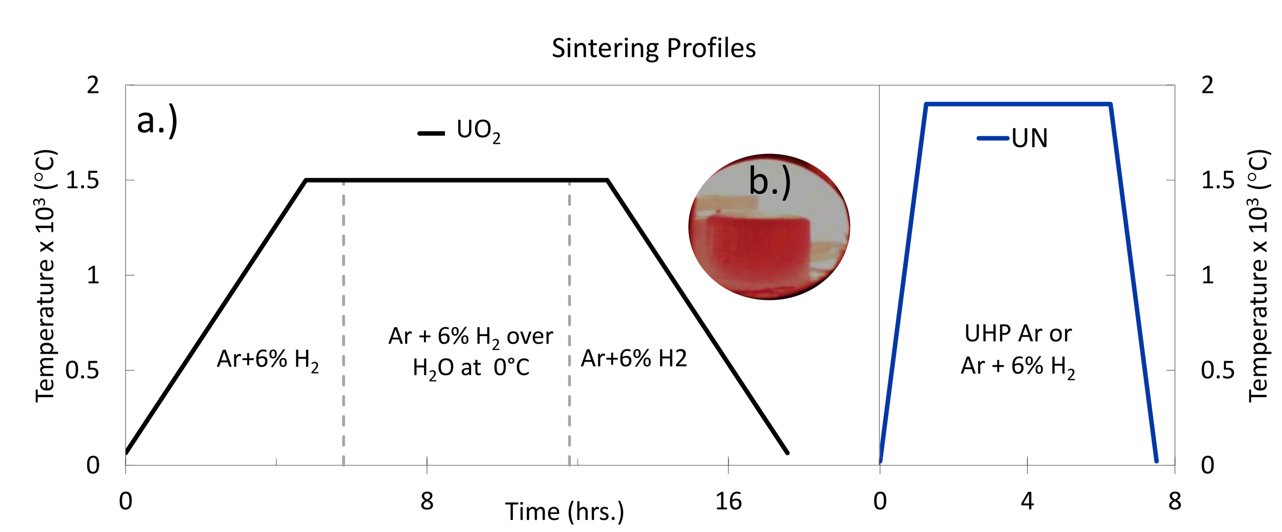

Figure 8: a.) Temperature and gas profile used to sinter the UO_2 and UN pellets. For UO_2, a three step process is used to achieve higher densities at lower temperatures. b.) Photograph of a 9 mm diameter UN pellet, in the furnace at 750 °C.

Results and Discussion

UN: High purity, 9 mm diameter pellets were fabricated with greater than 90% theoretical density.

Ultra-high-purity argon atmosphere formed pellets with the less porosity than those sintered in Ar + 100 ppm N_2. Further analysis such as elemental analysis and further sintering studies need to be carried out for a complete understanding.

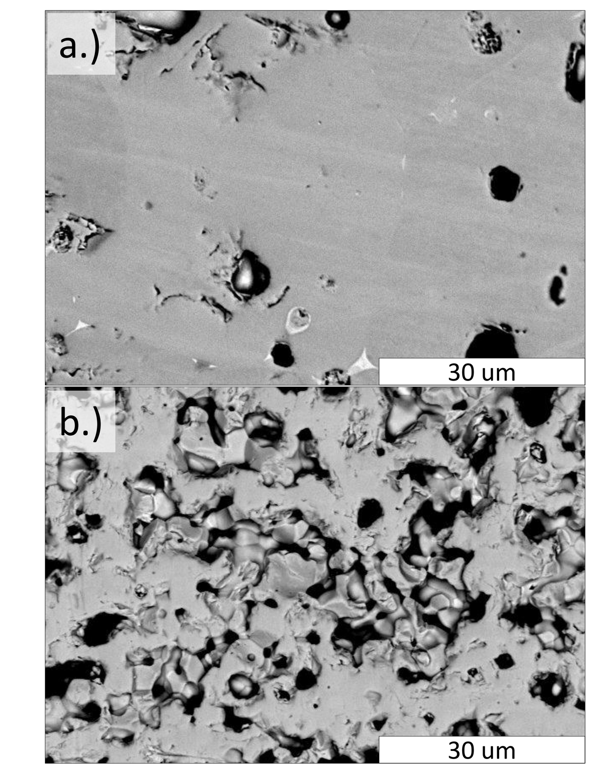

Figure 9: Scanning electron micrographs of UN pellets sintered in a.) ultra-high-purity argon, and b.) ultra-high-purity argon + 100 ppm N_2. Undesirable porosity resulted when N_2 was in the sintering atmosphere.

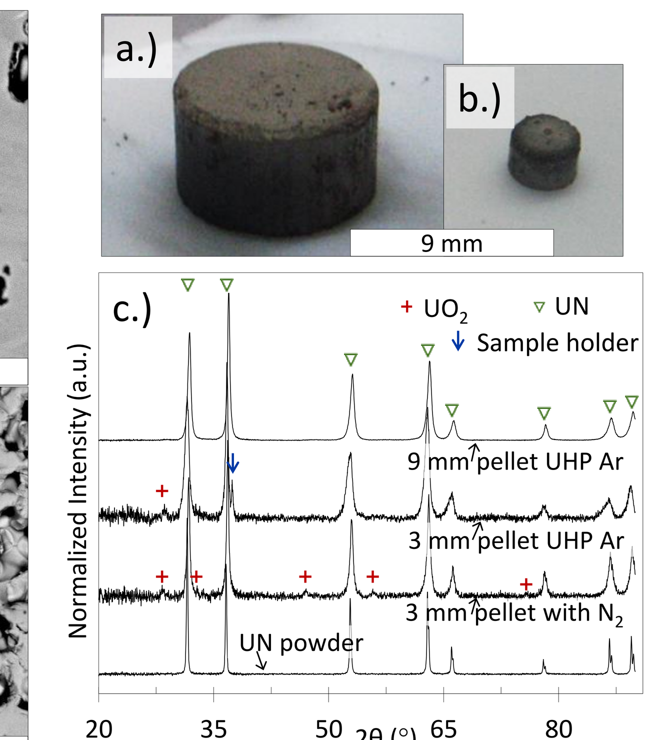

Figure 10: Macro images (a and b) and x-ray diffraction patterns (c) of sintered UN pellets. There is significant UO_2 impurity present in the 3 mm pellets, but surface grinding of the 9 mm pellet produced an XRD pattern with no detectable second phase.

UO_2: The sintering process effectively removed the U_3O_8 impurity in the starting powder. This occurs during the first and third stages of sintering (see Figure 8a) where the reducing environment causes the following reaction to take place [6]:

$$U_3O_8 + 2H_2 \rightarrow 2H_2O + 3UO_2 \qquad eq.\ 4$$

The resulting microstructure of the 3 mm pellet was small pores (<1um) that are spherical in shape. The grain size could not be determined without additional etching. A similar process will be used to fabricate 9 mm pellets as the project continues.

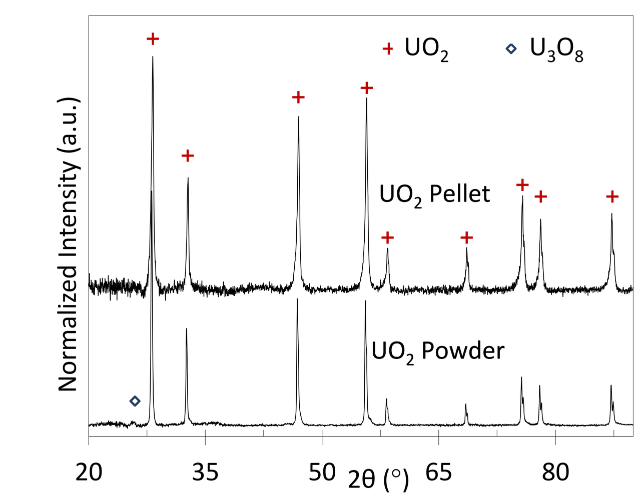

Figure 11: X-ray diffraction pattern of sintered 3 mm UO_2 pellet. Although U_3O_8 was detected in the starting powder, the sintering process effectively removed this impurity.

% Theoretical Density of Pellets	UN	UO_2
Archimedes Density	92 ± 3	93 ± 5

Table 3: Final densities of the UN and UO_2 pellets. Error for Archimedes density was determined through error analysis, after three sequences of weighing.

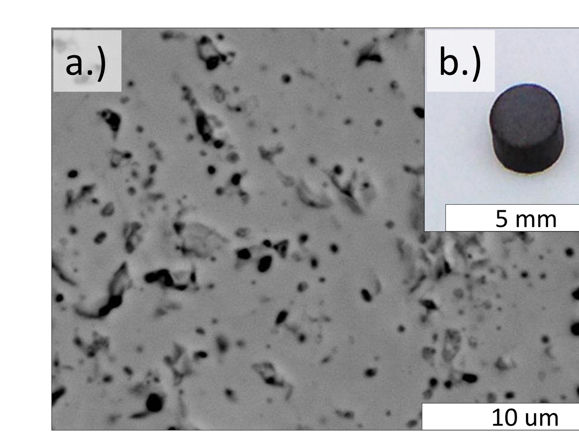

Figure 12: a.) Scanning electron micrograph revealing fine pore structure. b.) Photograph of the UO_2 pellet.

Conclusions

Carbothermic reduction is a suitable route for preparing UN from UO_2. High purity, dense pellets of UN and UO_2 nuclear fuels were successfully made. For UN sintering, nitrogen free atmosphere results in less porosity. This project demonstrates the feasibility to fabricate phase pure UN and UO_2 nuclear fuel pellets for further studies.

References

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