Synthesis and Sintering of UN-UO₂ Fuel Composites

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Abstract

The design and development of an economical, accident tolerant fuel (ATF) for use in the current light water reactor (LWR) fleet is highly desirable for the future of nuclear power. Uranium mononitride has been identified as an alternative fuel with higher uranium density and thermal conductivity when compared to the benchmark, UO₂, which could also provide significant economic benefits. However, UN by itself reacts with water at reactor operating temperatures. In order to reduce its reactivity, the addition of UO₂ to UN has been suggested. In order to avoid carbon impurities, UN was synthesized from elemental uranium using a hydride-dehydride-nitride thermal synthesis route prior to mixing with up to 10 wt% UO₂ in a planetary ball mill.

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1 UN and UN - UO₂ composite pellets were sintered in Ar - (0-1 at%) N₂ to study the effects of
2 nitrogen concentration on the evolved phases and microstructure. UN and UN-UO₂ composite
3 pellets were also sintered in Ar - 100 ppm N₂ to assess the effects of temperature (1700 -
4 2000 °C) on the final grain morphology and phase concentration.

1. Introduction

The United States Department of Energy (USDOE) has always emphasized safe, reliable, and economical nuclear reactor designs for sustainable operations. However, following the Fukushima-Daiichi accident in 2011, the Consolidated Appropriations Act of 2012 (report 112-75) directed the Nuclear Energy branch of the USDOE to give “special technical emphasis and funding priority to activities aimed at the development and near-term qualification of meltdown-resistant, accident tolerant nuclear fuels (ATFs) that would enhance the safety of present and future generations of light water reactors (LWRs)” [1, 2]. In the wake of this Act, ATFs have been internationally defined as fuel-cladding systems that, when compared to traditional UO_2 -zircaloy clad fuels, will provide substantially improved safety response to design basis (DB) and beyond design basis (BDB) scenarios while maintaining comparable, or improved, operational characteristics and economics during normal reactor operating conditions [1-6]. In addition to LWRs, development of ATFs will also have significant impacts on the design and operation of heavy water reactors (HWRs) and supercritical water reactors (SCWRs).

More specifically, ATFs are sought that will improve the high temperature reaction kinetics, enhance fuel and cladding thermal properties, slow hydrogen generation, and increase fission product retention as compared to the traditional uranium dioxide (UO_2)-zircaloy clad fuel [2, 7]. It is realized that researching, testing, and qualifying an ATF by 2022 [2, 8] for insertion of lead test rods into a commercial reactor with improved performance compared to UO_2 is a daunting task: UO_2 has been extensively studied and optimized over the past 60 years. An additional challenge presented by this Act is that the ATF concept should be compatible with existing LWR infrastructure including some 400 active reactors world-wide (many of which are seeking 20+ year operation extensions) [4, 7]. Zinkle *et al.* suggest that further safety enhancements might

best be achieved by a combination of fuel system innovations along with operational and/or reactor design changes [4].

High density fuels that are being considered for ATF solutions include uranium-molybdenum fuels, uranium nitride fuels, uranium carbide fuels, and uranium silicide fuels [3]. Uranium mononitride (UN) fuel forms have been demonstrated in the sodium cooled BR-10 reactor in Russia for nearly 20 years [9] as well as in the FFTF and EBR-II test reactors [3] and are considered in this work due to potential advantages as a reactor fuel. According to Zakova and Wallenius [10], who modeled the neutronics behavior of UN in a BWR core, a primary advantage of using a nitride fuel assembly in a LWR is an increased fuel cycle time. Youinou [3] predict that the fuel cycle could increase from a standard 18 month cycle (as with UO_2) to 25 month cycles based on a burnup of 50 GWd/t, calculated primarily on the increased uranium density of UN (UN contains 40% more uranium than UO_2). The increased cycle period leads to fewer refueling shut downs and is thus an economical driver for nitride fuel implementation. Although the fabrication costs are higher for UN fuels largely due to the added costs of nitrogen enrichment (greater than 90% N-15 is needed to sufficiently increase the neutron economy), the costs are offset by lower uranium enrichment requirements (3.4% U-235 in UN versus 4.2% in UO_2), and the need for a reduced number of assemblies in each reload, resulting in an estimated \$5 million per year savings [3].

In addition to the economical drivers associated with nitride fuels, its desirable thermophysical properties promote its accident tolerance. A UN fuel assembly promotes large power uprates, increased cycle lengths, and allows for higher burn-up when compared to traditional UO_2 LWR fuels. These attributes are due to its high melting temperature (2762 °C), good thermal conductivity (20.5 W/m·K at 500 °C), high uranium density (13.5 g/cm³), and

1 lower heat capacity (230 versus 300 J/kg·K at 500 °C) [11, 12]. Zhao *et al.* [13] modeled the
2 response of UN and UO₂ fuel behavior in SCWR accident scenarios and predicted that the larger
3 thermal conductivity of UN (which is five times greater than UO₂) results in a significantly lower
4 fuel centerline temperature and smaller pellet temperature gradient, resulting in lower reactor
5 operating temperatures. Additionally, fuels with smaller heat capacities will result in a smaller
6 peak power and stored energy release in the event of a reactivity initiated accident, such as a
7 control rod ejection. Since the temperature will rise faster in the UN fuel, the temperature
8 feedback will be faster and the power pulse height will be reduced [3, 13]. The combination of
9 both the larger thermal conductivity and lower heat capacity lead to a significantly larger safety
10 margin in DB and BDB accident scenarios.

11 An additional advantage of nitride fuels are their compatibility with most potential cladding
12 materials, their good irradiation stability, and fission product retention [3]. However, the major
13 drawback to UN fuels are their low oxidation resistance; UN powder readily oxidizes in air and
14 pellets in super-heated steam [14-16]. Three primary methods have been postulated to improve
15 its oxidation resistance: Addition of USi_x to UN powder followed by liquid phase sintering,
16 alloying UN with compounds that will increase its oxidation resistance, and coating UN with a
17 more inert material (such as ZrC) to produce a chemical barrier [3, 9, 17]. The focus of the work
18 presented here is to use a nitride synthesis technique that avoids excessive carbon impurities and
19 to develop an accident tolerant fuel. The effects of adding small amounts of UO₂ (up to 10 wt%)
20 to UN fuel forms is presented. Additionally, the influence of atmosphere and temperature on the
21 final grain morphology and stoichiometry of uranium nitride composite fuels are demonstrated.

2. Material and Methods

This study was completed with depleted uranium sources. UO_2 (99.8%, 50 mesh) was obtained from International Bio-Analytical Industries Incorporated (Boca Raton, FL), which was synthesized by reduction of U_3O_8 prepared via a uranyl acetate dihydrate solution route. The UN in this study was prepared from atomized elemental uranium (99.4%, 50 mesh) received from the Idaho National Laboratory (INL). The morphology of each starting material is shown in the scanning electron microscopy (SEM) image in Figure 1a and b. The powders were mixed with a vacuum grease to avoid excessive oxidation during the ambient X-ray diffraction (XRD) characterization. Each of the XRD patterns were background subtracted and diffraction peaks were identified using the Inorganic Crystal Structure Database (ICSD) [18].

UN was synthesized using a thermal synthesis route in which elemental uranium was hydrided and dehydrided prior to nitridation. The thermal profile used in this work (Figure 2) was adapted from a series of previously published techniques [19-26]. Prior to loading into a tungsten-lined alumina crucible in an argon filled glovebox, the atomized uranium was cleaned in a 50% nitric acid solution and rinsed in methanol to remove any present oxides. A 16 gram batch was loaded into a high temperature alumina tube furnace (CM Furnaces Inc., Bloomfield, NJ, USA), which was immediately vacuum purged. As shown in Figure 2, the reaction was initiated by flowing ultra-high purity (UHP) hydrogen gas (H_2) over the uranium while ramping the temperature to 500 °C to “crack” the oxide barrier and form a hydride. Argon was then introduced to dehydride the powder, according to reaction 1 below. The temperature was then reduced to 225 °C and the atmosphere was switched back to UHP- H_2 where the hydrogen uptake is most rapid [25]. The hydride-dehydride process was completed 2 more times in order to remove any residual oxygen. The dehydrided uranium was then converted to nitride according to

reaction 2 by introducing UHP-N₂ and ramping the temperature to 850 °C. In order to reduce the U₂N₃ to UN as described in reaction 3, argon with a reduced N₂ concentration was introduced and the temperature was briefly raised to 1200 °C before ramping to room temperature. The resulting UN powder was characterized using SEM (Figure 1c) and XRD (Figure 3).

Composite powders were made by mixing 5 grams of the synthesized UN with the as-received UO₂ in nominal concentrations of 5 and 10 weight percent (wt%) UO₂ in an argon backfilled glovebox (maintained with less than 30 ppm O₂). Each of the three nominal compositions were mixed and milled in a planetary ball mill (Retsch PM100, Germany) in a chrome steel milling vessel. Each powder was milled for 1 hour at 400 RPM with 5 mm diameter yttria milling media in a 14:1 media:powder mass ratio. The resulting powders were characterized using SEM (Figure 1d) and XRD (Figure 4).

Prior to sintering, right cylindrical composite pellets were pressed at approximately 550 MPa in a 3.6 mm pellet die without the use of a binder or lubricant to reduce further C and O contamination. Green pellets with a geometric density of 61 ± 2 %TD were placed on a tungsten setter plate and sealed with vacuum grease and a thin polyvinylidene chloride (PVDC) film to prevent excessive oxidation while transferring into the sintering furnace. In all cases, three pellets (one of each composition) were placed on the setter together, sealed, and sintered in a tungsten refractory metal furnace (Thermal Technologies LLC., Santa Rosa, CA, USA). Once

loaded into the furnace, 4 vacuum purge cycles were completed prior to ramping at $25^{\circ}\text{C}/\text{min}$ to the desired sintering temperature, where the temperature was held constant for 5 hours prior to ramping back to room temperature at $25^{\circ}\text{C}/\text{min}$. Once cooled, the pellets were removed and immediately transferred into an argon glovebox.

Densities of the sintered pellets were obtained using Archimedes' principle in water at 21°C . The measured densities of composite pellets are reported in percent theoretical density (%TD) based on the theoretical densities of UN (14.33 g/cm^3 [21]) and UO_2 (10.96 g/cm^3 [27]), respectively. The pellets were prepared for SEM and XRD by grinding approximately 1/3 of the distance through the pellet to create a cross section that was perpendicular to the two parallel faces of the right cylinder. The section face was polished with 1200 grit silicon carbide after grinding. The pellets were fixed to an aluminum sample holder using carbon tape for SEM and EDS characterization (Hitachi S-3400N-II, Japan). Following SEM, the pellets were fixed to a soda lime silica glass holder with putty and centered in the goniometer circle of an XRD (Rigaku, Miniflex 600, The Woodlands, TX, USA) equipped with a $\text{Cu}_{\text{K}\alpha}$ radiation source and a high speed linear detector.

3. Results and Discussion

From the SEM image shown in Figure 1a as well as subsequent imaging not shown, it was determined that the as-received UO_2 powder possesses a bi-modal particle size distribution with a mode near $10\text{ }\mu\text{m}$ and a mode near $100\text{ }\mu\text{m}$. XRD characterization of the UO_2 powder suggests that it is primarily a cubic UO_2 (ICSD powder diffraction file (PDF) 00-041-1422) phase but does have some small percentage of a secondary phase. The secondary phase may be an off-stoichiometric U_3O_8 phase when compared to ICSD PDF 00-047-1493. However, since not all of

1 the primary diffraction peaks for U_3O_8 are present in the diffraction pattern and the peaks that are
2 present are shifted from published values for stoichiometric U_3O_8 , the extra diffraction peaks are
3 labeled as unknown in Figure 3.

4 The SEM image in Figure 1b shows that the atomized uranium is mostly spherical with the
5 exception of a few platelets and appears to have particle size distribution with a single mode near
6 100 μm . By comparison with ICSD [PDF 01-089-3810](#), the XRD pattern suggests that the
7 atomized uranium is primarily a base-centered orthorhombic α -phase uranium (α -U).
8 Additionally, there appears to be a small fraction of a second phase, labeled as unknown in
9 Figure 3, which may correspond to a slight surface oxide on the uranium spheres. However, as
10 demonstrated in the following sections, the secondary phase has no known effects on the nitride
11 synthesis and therefore no further analysis of the phase was conducted.

12 Traditionally, large quantities of high purity UN are synthesized using a carbothermic
13 reduction of a UO_2 and carbon mixture [28, 29]. A disadvantage to the carbothermic reduction
14 route is the unavoidable residual carbon and oxygen concentrations, which were reported as 70-
15 760 ppm and 200-940 ppm, respectively. Accordingly, uranium monocarbide (UC) is
16 thermodynamically predicted to form from the residual carbon, which has proven detrimental to
17 the water corrosion resistance of uranium nitride fuels [29, 30]. It is also challenging to obtain
18 quantitative analysis of the light elements in radioactive materials due to concerns of
19 contamination. Previous work has shown that uranium nitride can be synthesized from elemental
20 uranium in a high energy ball mill [31]. However, due to impurities introduced during the
21 extensive milling process and handling of the powders, the ball milling route was not selected for
22 UN synthesis here. In order to start with the highest purity nitride powder (especially with

minimal light element impurities), the hydride-dehydride-nitride thermal route to UN synthesis was selected as the ATF fuel fabrication route in this study.

Although difficult to scale-up to meet industry production needs, the hydride-dehydride-nitride route is a thermal synthesis route with the potential to form high purity UN with little residual oxygen and carbon, ideal for ATF applications. Many process iterations have led to the thermal profile shown in Figure 2. Throughout the thermal process, the atomized uranium lost its spherical shape and resulted in powder with a more irregular morphology and a significantly reduced particle size, as seen in Figure 1c. Further characterization via XRD suggests that the powder is a phase-pure cubic UN when compared to ICSD PDF 00-032-1397, as shown in Figure 3.

Ball milling the nominal compositions of UN, UN - 5 wt% UO₂, and UN - 10 wt% UO₂ was primarily completed for two reasons: to obtain a homogenous mixture and to increase the sinterability of the green pellets. As seen in the SEM image of Figure 1c and d, the milling process significantly reduced the particle size from 5-10 μm to less than 1 μm, increasing the sintered density by 5% of the theoretical density (TD) at 1900 °C for 5 hours, when compared to as synthesized UN. Additionally, milling significantly reduced the crystallite size of the powder from approximately 95 nm down to 27 nm, as determined using the Scherrer equation and the first two UN diffraction peaks shown in Figure 3 and Figure 4. However, the high energy milling process reduced the crystallinity of the powder, thus reducing the amount of information that can be inferred from XRD analysis. In the diffraction pattern for pure UN in Figure 4, a clear second phase formed from the milling process, noted by broad diffraction peaks at approximately 29, 47.5, and 57 °2θ. Thermodynamics predict that milling a nitride in a pure argon atmosphere would cause a portion of the nitrogen to dissociate from the uranium, resulting in an elemental

uranium phase. However, the peaks do not align with an elemental uranium phase: they are more indicative of a hyper-stoichiometric UN (UN_{1+x}) phase. This very interesting but counterintuitive result will be discussed further below. As seen in the diffraction pattern for UN - 10 wt% UO_2 , broad diffraction peaks from the added UO_2 phase along with the broad diffraction peaks from the UN_{1+x} phase are present. Although it is not clear how much oxygen may have been picked up from handling and milling, the powder is presumed to contain more oxygen after milling than before.

Further characterization of the milled powders was completed using SEM and energy dispersive X-ray spectroscopy (EDS). Although the EDS showed that the powder was homogeneously mixed by the absence of large oxide agglomerates, an artifact from milling was detected. EDS showed that there was a 0.8 ± 0.3 at% zirconium concentration, which is an impurity due to the degradation of the zirconia milling media during milling and is a common artifact of high energy milling. It can be mitigated by careful choice of milling media and milling vessel materials. Additionally, the added handling step, along with increased surface area, will increase the residual oxygen concentration in the UN powders, as seen in the XRD.

Composite powders were pressed into green pellets of 60 ± 2 %TD in an Ar-filled glovebox (<30 ppm O_2) prior to loading into the furnace. From past experience, pellets that were not ball milled were able to be briefly exposed to air (as in the case of transferring into the sintering furnace). However, green pellets pressed from the milled powders were pyrophoric and immediately ignited when exposed to oxygen. Therefore, oxygen exposure was minimized by sealing the sintering crucible with vacuum grease and a PVDC film prior to removal from the glovebox for insertion into the sintering furnace. Both the vacuum grease and the PVDC film

were subsequently burned off in the furnace while ramping to the sintering temperature, contributing to light element impurity concentration in the final sintered product.

Although the effects of nitrogen concentration in the sintering environment have been shown to affect the final microstructure and stoichiometry of UN and (U,Pu)N in the past [29, 32-35], it has not been studied in the fabrication of UN-UO₂ composites, to the best of the authors' knowledge. Secondary phases can be detrimental to the fuel performance; the presence of a liquid uranium phase is undesirable because if heated and irradiated, it would cause the fuel to swell, creep, and react with the fuel cladding. Additionally, the presence of U₂N₃ is undesirable because, upon heating in reduced nitrogen conditions, it will dissociate according to Equation 2. Not only will the nitrogen evolution cause the fuel pin to pressurize and result in undesirable cladding embrittlement, it can also cause fuel to crack during sintering or irradiation [29].

As noted in the U-N binary equilibrium phase diagram [29], UN is a line compound at low temperatures and has a small phase field with increased temperature. However, previous work predicts that the UN phase field is much larger when considering equilibrium nitrogen concentrations. It has been estimated that the nitrogen pressure can span nine orders of magnitude during sintering within the UN phase field at 1550 °C [33, 34]. Additionally, it is stated that the nitrogen concentration during sintering is best kept in a narrow range near the UN dissociation boundary (Equation 4) to reduce the amount of dissolved nitrogen. Tennery *et al.* [33] also found that microstructural features and density were increased when choosing a nitrogen pressure close to the UN dissociation boundary.

To demonstrate the effects of reduced nitrogen environments during sintering, a UN pellet was subjected to 1550 °C for 5 hours in UHP - Ar. As seen in the SEM image of the polished

1 section of Figure 5, a “coring” effect was observed near the pellet surface. It is worth noting that
2 the thickness of the dense ring decreased with increased distance from the top surface due to the
3 increased activity at the corners of the right cylinder. The dense ring observed around the
4 perimeter of the pellet is due to hypo-stoichiometric nitrogen conditions causing the formation of
5 free uranium, described by Equation 4. As shown in the higher magnification images in Figure 5,
6 region 1 shows a microstructure in the center of the pellet where the UN was only partially
7 sintered to a low density, whereas region 2 shows a dense microstructure where the free uranium
8 formed a liquid phase and accelerated the sintering kinetics. However, the density was measured
9 as nearly 80 %TD, which is much greater than the apparent density from region 1 and much less
10 than predicted in region 2. Therefore, the reported density is an average of the dense shell and
11 the porous core structures.

12 Since the core of the pellet subjected to 1550 °C for 5 hours was only partially sintered,
13 atmospheric sintering studies were completed at 1900 °C to provide a denser microstructure. The
14 three gases used were UHP-Ar (<4 ppm N₂), Ar - 100 ppm N₂, and Ar - 1 at% N₂ according to
15 the acceptable range of nitrogen pressure proposed in previous work [33, 34]. The effects of
16 nitrogen pressure during sintering on the microstructure and phase evolution is shown in Figure 6
17 and Figure 7, respectively. Edge effects are pronounced in the pellets sintered in pure Ar;
18 therefore, for comparison purposes, only cross sections of the pellet cores (near the middle of the
19 pellet cross section) are compared using SEM, EDS, and XRD. EDS was used to identify the
20 dark regions in the backscattered electron (BSE) SEM images as a U-O phase, shown in Figure 6
21 and Figure 8. Further quantification of the U-O phase is not reported here because the relative
22 error for C, N, and O concentrations using EDS is relatively large and stoichiometry can only be
23 inferred.

EDS was primarily used to detect the presence of oxygen and nitrogen, not their concentrations. Accordingly, small oxygen concentrations were detected in the UN phase in all of the samples in this study. It is unknown if the oxygen detected was formed on the surface of the polished section or if it is dissolved oxygen but it has been shown that the oxygen solubility in pure UN can reach values in excess of 5 at% and can be determined by a slight lattice expansion in XRD [36-38]. Dissolved oxygen and surface oxides were likely detected on these samples due to the very reactive nature of the powders and green pellets after milling. Comparing Figure 7 with Figure 4 shows that the broad peaks observed in the milled powders evolved into relatively well-defined diffraction peaks after sintering. XRD shows UN as the primary phase in all cases although, as expected, there are prominent UO_2 peaks, which increase with nominal UO_2 additions. Peaks are also present which correspond slightly to hyper-stoichiometric UN (UN_{1+x}) as compared to the ICSD along with unidentified peaks in each diffraction pattern. Furthermore, the unidentified peaks are generally positioned between closely spaced UN and UO_2 peaks. Since the UN powders were milled and sintered in virtually nitrogen free environments (Ar atmosphere of glovebox and UHP-Ar, respectively), it is unlikely that the peaks are due to a hyper-stoichiometric nitride phase. Additionally, the pellets sintered in UHP-Ar show the same peaks corresponding to a UN_{1+x} phase although thermodynamics and past experience suggest that the hyper-stoichiometric nitride phase will be reduced to UN or $\text{UN} + \text{U} + \text{N}_2$ when exposed to temperatures greater than 1100 °C. It seems as though the addition of UO_2 either stabilizes a hyper-stoichiometric nitride phase or a uranium oxynitride phase is being formed. The reported ICSD peak positions for α -U are indicated for the samples sintered in pure Ar since the dissociation reaction (Equation 4) was predicted to occur. Although the coring effect was observed in macro images of these samples similar to Figure 5, peaks for α -U have only a

1 slight correlation with the diffraction pattern (Figure 7). Although not clearly identified using
2 XRD, EDS shows distinct regions of elemental uranium on grain boundaries within the UN
3 microstructures.

4 As shown in Figure 6, the U-O phase is uniformly distributed throughout each of the
5 microstructures and although it is also observed in pure UN samples, its concentration increases
6 with nominal additions of UO_2 . However, a few trends are observed in the microstructures: The
7 microstructure becomes finer with (1) increased UO_2 additions and (2) increased nitrogen
8 concentration during sintering. These findings are in agreement with past literature that reported
9 a decrease in grain size with increased oxygen (up to 1 wt%) and finer microstructures with
10 increased nitrogen concentrations [33, 38]. Tennery *et al.* [33] also noted that the final densities
11 of the pellets were indicative of the resulting grain sizes rather than the sintering temperature or
12 nitrogen pressure.

13 Based on the studies presented above and work presented in previously published work [29, 33,
14 34], the effect of sintering temperature were studied from 1700 - 2000 °C in Ar - 100 ppm N_2 .
15 The resulting pellet microstructures and phase evolution are shown in Figure 8 and Figure 9,
16 respectively. As seen in the BSE SEM images in Figure 8, pore sizes increased with increased
17 sintering temperature. Contrary to previously published work on sintering of pure UN [29, 33],
18 increased sintering temperatures resulted in decreased densities. Sintering for 5 hours at 1700 °C
19 resulted in a density of approximately 93 %TD for each composition whereas sintering at
20 2000 °C resulted in a density of 88 %TD. Although a coarsening effect was observed in the UN
21 grains, the U-O grains, and the pores with increased temperature, the UN grains also appear to
22 coarsen with increased UO_2 additions, as seen in Figure 8. The U-O grains remained
23 homogeneously distributed throughout the microstructures and appeared only on grain

boundaries. However, the frequency of U-O grains decreased with increasing temperature, also due to a coarsening effect. An additional note is that the pores shown in the microstructures tend to be lined with an oxide phase, as determined via EDS. The oxide present at the free surfaces is an attribute that will likely increase the accident tolerance of UN fuels.

Similar to the nitrogen concentration study presented above, XRD confirmed the presence of a UO_2 phase in each of the pellets (Figure 9) and EDS confirmed the presence of a surface oxide or dissolved oxygen in the bulk of the samples. The XRD also shows unidentified diffraction peaks most notably from 39-46 $^{\circ}2\theta$. An interesting observation from Figure 9 is that the number of unknown diffraction peaks decreases with increasing temperature as well as with increased additions of UO_2 . As previously mentioned, the dissolution of oxygen into the UN structure results in a lattice expansion [36-38], which would result in lower 2θ values in the observed diffraction peaks. However, the diffraction peaks for UN in Figure 9 are shifted slightly to the right of the positions provided by the ICSD, suggesting a lattice contraction and providing support for the hypothesis that the unidentified peaks represent a potential hyper-stoichiometric nitride phase or a uranium oxynitride phase.

4. Conclusions

A process to convert elemental uranium to high purity, carbon free uranium mononitride was demonstrated using a hydride-dehydride-nitride synthesis route. The resulting UN was blended with 0, 5, and 10 wt% UO_2 in a high energy ball mill, creating a homogenous mixture with a significantly reduced particle size and a damaged structure. The powder became pyrophoric and readily picked-up oxygen, which contributed to additional oxide phases as well as dissolved oxygen in the sintered pellets. Even the consolidated, green pellets were pyrophoric and prone to

rapid oxidation upon exposure to air. UN and UO₂ composite pellets were sintered at 1900 °C for 5 hours in UHP-Ar, Ar - 100 ppm N₂ and Ar - 1 at% N₂ to gain insight into the effects of nitrogen on the stability of the nitride phases and distribution of oxides. Sintering in UHP-Ar resulted in a coring effect in which UN was dissociated to elemental uranium at grain boundaries, resulting in pronounced liquid-phase sintering and increased densification around the perimeter of the UN pellet. The addition of small amounts of UO₂ as well as nominally increased nitrogen in the sintering atmosphere resulted in finer microstructure, including nitride grains, oxide grains, and pores. Further studies were performed to assess the effects of sintering temperature in Ar - 100 ppm N₂ from 1700 - 2000 °C. In each case, U-O grains were homogeneously distributed throughout the pellet microstructure and existed primarily on UN grain boundaries. The pores were also lined with an oxide phase. Increasing UO₂ additions resulted in microstructural coarsening, as did the sintering temperature. Higher sintering temperatures also resulted in lower sintered densities, presumably due to a preferential formation of oxygen-stabilized nitrides or uranium oxynitrides.

The work presented here demonstrates a viable synthesis process for fabricating carbon free UN-UO₂ accident tolerant fuels for the current fleet of LWRs. Although a new fuel concept has been developed, there is a lengthy process in order to demonstrate its improved accident tolerance. Further work must be completed to determine if controlled UO₂ additions enhance the accident tolerance of UN to high temperature oxygen and steam exposures while maintaining thermophysical properties comparable or better than the benchmark LWR fuel, UO₂.

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