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Examination of HIP for production of high density UN kernels

Fuel Cycle Research & Development Advanced Fuels Campaign

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ABSTRACT

Depleted uranium nitride (UN) kernels with diameters ranging from 420 to 858 microns and theoretical densities between 87 and 91 percent were post-processed using hot isostatic pressing (HIP) in argon gas. This treatment was shown to increase the TD up to 96%. Uranium nitride is highly reactive with oxygen. Therefore, a novel crucible design was implemented to remove impurities in the argon gas via *in situ* gettering to avoid oxidation of the UN kernels. Established characterization techniques for determining average weight, volume, and ellipticity of particle fuel was used for calculating the density before and after HIP processing. Micrographs confirm the nearly full densification of the particles using the gettering approach and processing parameters investigated in this work.

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Examination of HIP for production of high density UN kernels

1. INTRODUCTION

The fully ceramic microencapsulated (FCM) fuel form uses well-developed 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(AT) drop-in replacement for UO_2 [1, 2] However, one challenge is that in an FCM compact much of the U volume has been replaced by TRISO coatings and the SiC matrix compared to a conventional UO_2 pellet since. Due to its high theoretical density (TD), UN is attractive as an FCM fuel kernel and recent neutronics calculations confirm it as a suitable choice for the FCM design [3].

Depleted uranium nitride (UN) microspheres with diameters ranging from 420 to 858 microns and TD between 87 and 91 percent were synthesized in FY15 and FY16 part of a larger effort to explore fabrication routes for Fully Ceramic Microencapsulated (FCM) fuel [4-6]. This work investigates the viability of a post processing step with a hot isostatic press (HIP) shown in Fig.1 to achieve higher TD to improve their suitability for use as FCM fuel kernels.

Figure 1. Hot Isostatic Press from American Isostatic Presses, Inc. used in this work to increase the density of the UN microspheres. The HIP is capable of temperatures and pressures up to 2200°C and 33 ksi respectively.

2. EXPERIMENTAL

Kernels produced in FY15 and FY16 [6] consistently resulted in between 86-88% TD UN microspheres with closed porosity. For this work, three different batches, summarized in Table 1, were chosen to investigate increasing density with a HIP post processing step. Preliminary tests on small sample sizes, ~100 mg, confirmed suspicions that impurities, particularly O_2 and O bearing vapors (i.e. CO, CO_2, H_2O etc.) in the ultra-high purity (UHP) Ar gas HIP media. The Airgas compositional specifications for UHP Ar are given in Table 1. The kernels resulting from the scoping run in are shown in Fig. 2. Phase fractions from X-ray diffraction (XRD) analysis (Fig. 3) determined up to 40% by mass of the sample was oxidized to UO_2.

Figure 2. Visually oxidized UN kernels from the small batch scoping run without the oxygen gettering crucible.

Table 1. Starting size and density analysis with one standard error for the samples used in this study.

sample	diameter (μm)	density (g/cc)	%TD	SE
FCM UN11	828.7	12.38	87%	0.58%
FCM UN17N-K	858.3	12.58	88%	0.67%
FCM-3B-UN14K	420.0	13.01	91%	1.38%

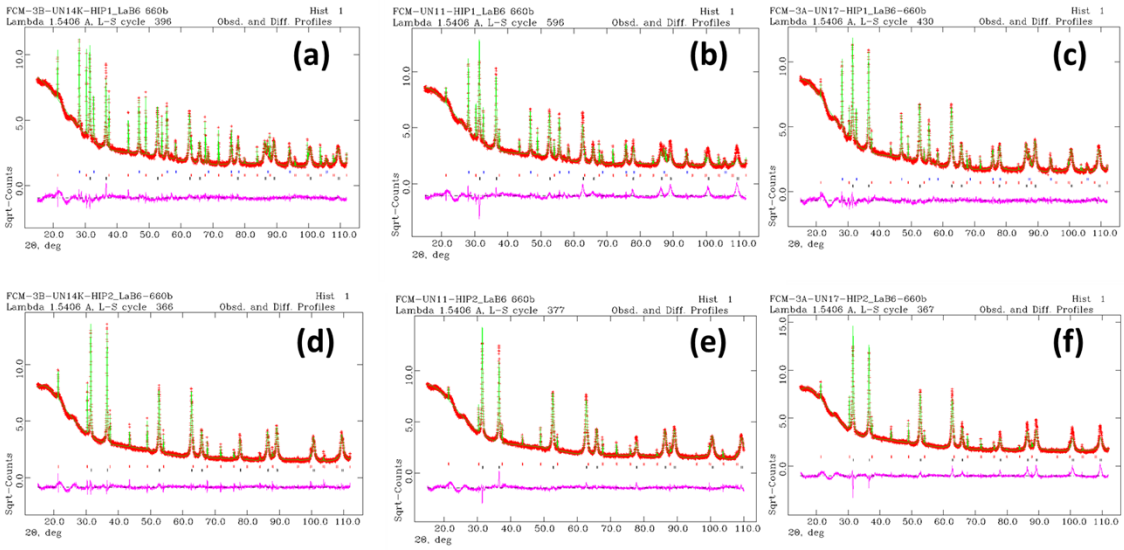

Figure 3. XRD results for scoping run #1 without gettering crucible (a) – (c) and with the gettering crucible (d) – (f). The red, blue, and black tick marks correspond to the LaB6 standard, UO2, and UN diffraction angles in that order.

While the impurity levels in the UHP Ar given in Table 2 are relatively low, the oxygen potential μ_{O_2} of the HIP media is always higher than that for UN-UO_2 equilibrium. Therefore, there is always a driving force for UN oxidation. The progression of the reaction $UN + O_2 = UO_2 + ½ N_2$, however can be made to be kinetically limited via clever equipment design. There are two criteria for this: (1) minimizing volume and (2) reducing the O bearing impurity levels. Both (1) and (2) are based on the ideal gas law. As pressure goes up, so does the number of gas atoms or molecules in the system.[a] A custom crucible, shown schematically in Fig. 3, was designed to operate within the 90 mm diameter by 125 mm high furnace hot zone of the HIP with the objective of reducing the extent of oxidation to an insignificant degree, i.e. less than 2-3 weight % and therefore undetectable with X-ray diffraction.

Table 2. Manufacturers molar compositional specifications for ultra-high purity Ar.

Impurity	Limit
Moisture	< 3 ppm
O_2	< 2 ppm
Hydrocarbons	< 0.5 ppm
CO_2	< 1 ppm
CO	< 0.5 ppm
N_2	< 5 ppm

[a] Amount of gas atoms or molecules go down with temperature. In this case the pressure increase effect driving up the amount of gas is much greater in magnitude than that of temperature reducing it.

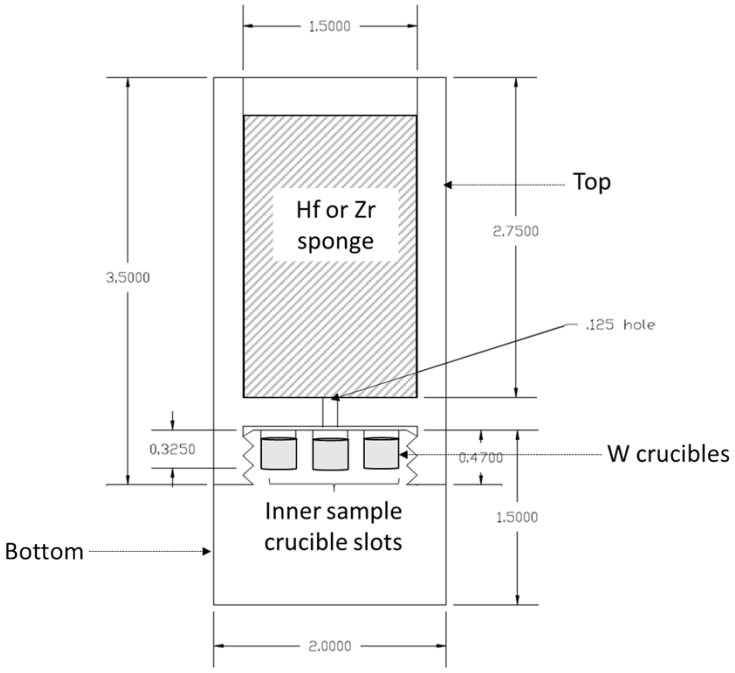

Figure 4. Custom designed HIP crucible made from graphite. The HIP gas must travel a torturous path through hot Hf or Zr sponge that binds O bearing molecules before it enters the sample chamber. There is minimal dead volume above the sample to further reduce the amount of gas and therefore O impurities that is available to react with the specimen(s).

In the first two small batch (~100 mg) scoping runs, the effectiveness of the crucible at eliminating oxidation was demonstrated. The kernels were intact, with some sporadic color change from grey to black, but otherwise no apparent visual signs of oxidation. The XRD analysis in Fig. 2 show no detectable levels of oxides of uranium. The samples were then successively HIPed and characterized in ~5 g quantities in runs 3 – 5 according to Table 3.

Table 3. Time at the isothermal, isobaric holds for each run.

Run #	Temperature (°C)	Pressure (ksi)	HIP time (minutes)
1 (scoping)	1800	30	100
2 (scoping)	1800	30	100
3	1800	5	69
4	1800	15	180
5	1800	30	360

3. RESULTS AND DISCUSSION

Established characterization techniques for determining average weight, volume, and ellipticity of particle fuel was used for calculating the density (based on the theoretical value for pure UN of 14.3 g/cc) before and after HIP processing; details can be found in [6, 7]. The results are plotted in Fig. 5.

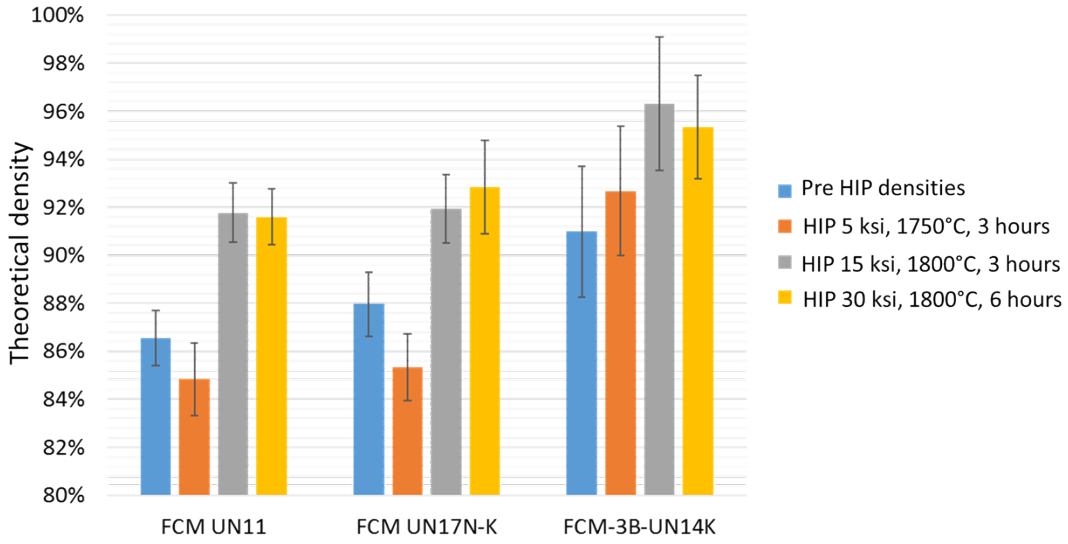

Figure 5. Comparison of the sample %TD's before and after successive HIP processing along with the 95% confidence interval.

The HIP processing recipe, shown graphically in Fig. 6, resulted in TD increases from 5 – 7%. It should be pointed out that the system should not be pressurized until the temperature is sufficient to kinetically activate the getter material thus minimizing ingress of O bearing impurities into the sample chamber. For that reason, the HIP is vented until ~1000°C. Pressurization begins thereafter.

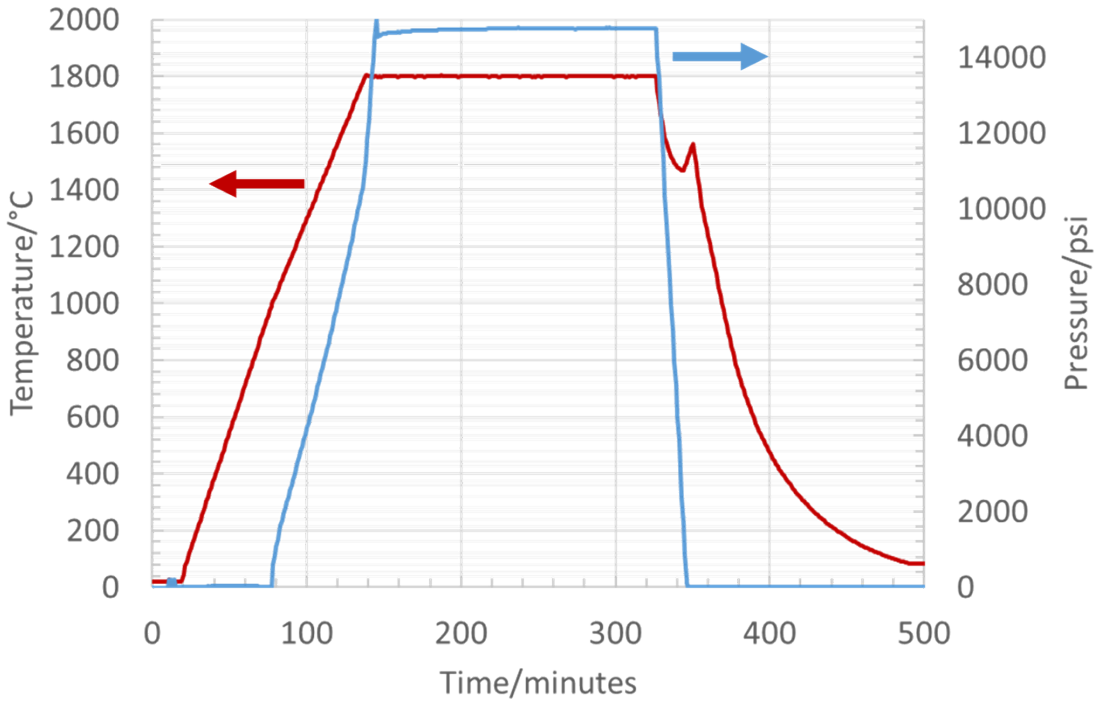

Figure 6. Temperature and pressure versus time for HIP run # 4.

The final density was dependent upon the starting density and/or particle size. Higher HIPed TD resulted from the smaller ~420 µm kernels that were initially chemically converted to 91%TD at atmospheric pressures, however, the increase in TD was only ~5%. For the larger ~850 µm kernels, larger increases in TD of 6 – 7 % were observed but the starting densities were lower at 88 and 87% TD. The micrographs in Fig. 7 confirm the nearly full densification of the 96% TD particles using the gettering approach and processing parameters investigated in this work. At least one previous study [8] showed cold pressed UN powder could be densified to 97% TD with a HIP in a tantalum can at 1500°C and 10 ksi; however, this work demonstrates successful HIP processing of a closed porosity highly reactive material, i.e. UN, using *in situ* oxygen gettering of the HIP media enabled by an innovative crucible design.

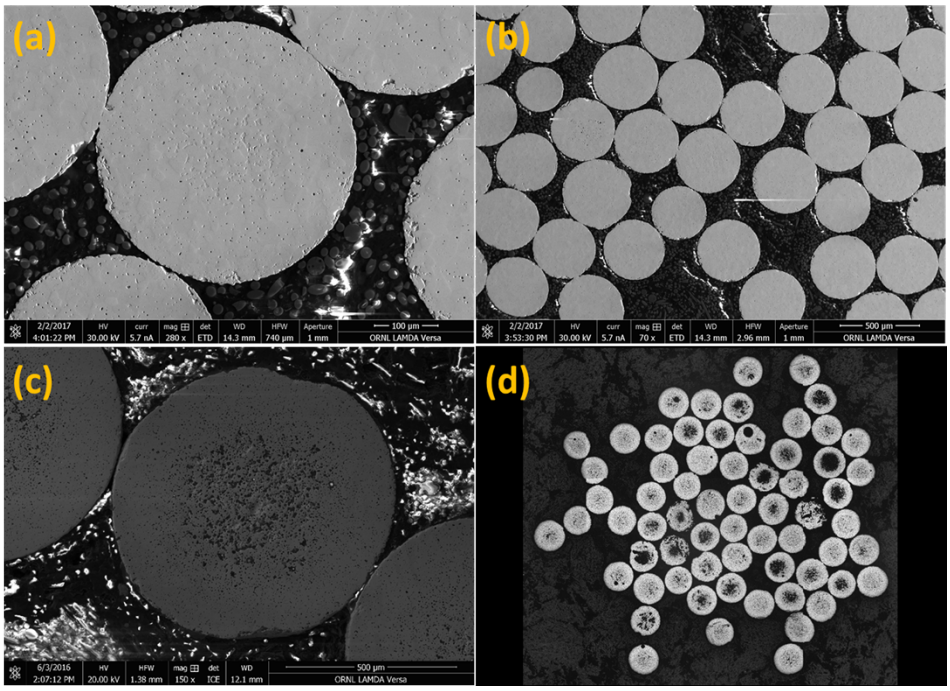

Figure 7. SEM images of HIP processed 96% TD FCM-3B-UN14K (a) compared to 89% TD LEU UN kernels (c) that did not undergo HIP processing. Note (d) was taken with an optical microscope to show the voids that are present in the 89% TD material but that are noticeably absent in the HIPed kernels (b).

4. CONCLUSIONS

Hot isostatic pressing of closed porosity UN microspheres with *in situ* gettered Ar HIP media is effective at increasing the TD up to 97%. Their initial density and size, or both impacted the results. The ~420 µm diameter kernels starting at 91%TD achieved 96%TD while those that started at 87 and 88%TD with ~850 µm diameters only attained 92% TD. In situ gettering of O bearing vapors is crucial for successful HIP processing; otherwise oxidation occurs and destroys the integrity of the kernels. A crucible design was implemented and proven to reduce O impurities and enable increasing the density of closed porosity UN microspheres with a HIP. *The crucible design can be broadly applied for hot isostatic pressing of closed porosity reactive materials in general.* Processing with a HIP at 1800°C and 15ksi for 3 hours was sufficient to achieve measurable increases in TD. Longer HIP times at higher pressures, i.e. 30ksi and 6 hours, did not result in statistically significant density increases. Future work should investigate the effect of increasing temperature up to 2200°C on UN densification with HIP processing.

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6. REFERENCES

1. Terrani, K.A., et al., *Fabrication and characterization of fully ceramic microencapsulated fuels.* Journal of Nuclear Materials, 2012. **426**(1): p. 268-276.
2. Terrani, K.A., L.L. Snead, and J.C. Gehin, *Microencapsulated fuel technology for commercial light water and advanced reactor application.* Journal of Nuclear Materials, 2012. **427**(1): p. 209-224.
3. George, N.M., et al., *Neutronics studies of uranium-bearing fully ceramic microencapsulated fuel for pressurized water reactors.* Nuclear Technology, 2014. **188**(3): p. 238-251.
4. Lindemer, T., et al., *Quantification of process variables for carbothermic synthesis of UC 1-x N x fuel microspheres.* Journal of Nuclear Materials, 2017. **483**: p. 176-191.
5. Lindemer, T., et al., *Carbothermic synthesis of 820μm uranium nitride kernels: Literature review, thermodynamics, analysis, and related experiments.* Journal of Nuclear Materials, 2014. **448**(1): p. 404-411.
6. Lindemer, T.B., et al., *Carbothermic Synthesis of~ 820-μm UN Kernels: Investigation of Process Variables*. 2015, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN (United States).
7. Silva, C.M., et al., *Characteristics of uranium carbonitride microparticles synthesized using different reaction conditions.* Journal of Nuclear Materials, 2014. **454**(1): p. 405-412.
8. Speidel, E.O. and D.L. Keller, *Fabrication and properties of hot-pressed uranium mononitride*. 1963, Battelle Memorial Inst., Columbus, Ohio.