Development of an accident-tolerant fuel composite from uranium mononitride (UN) and uranium sesquisilicide (U_3Si_2) with increased uranium loading.

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Abstract

The processing steps necessary to prepare a potential accident-tolerant fuel composite consisting of uranium mononitride (UN) combined with uranium sesquisilicide (U_3Si_2) are described. Liquid phase sintering was performed with U_3Si_2 as the liquid phase combined with UN powder or UN μ -spheres. Various UN to U_3Si_2 ratios were tested which resulted in up to 94% dense pellets. Composite UN- U_3Si_2 samples had greater than 30% more uranium content than UO_2 .

Keywords: accident-tolerant fuels, nuclear fuel, uranium sesquisilicide, U_3Si_2 , uranium mononitride, UN, high density nuclear fuel, composite

1. Introduction

Uranium dioxide (UO_2) has been the uranium bearing compound of choice for commercial nuclear power generation due to several beneficial properties. These properties include a high melting point, thermal stability, chemical stability, and low swelling under irradiation. These come at the expense of a relatively low thermal conductivity of 7-8 W/m·K at 573 K, which decreases with increased temperature and burn-up [1]. A fuel with a higher thermal

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8 conductivity will improve heat removal efficiency, thus lowering centerline
9 temperatures. This will bring down temperatures overall during operation
10 and therefore lessen the severity of thermal gradients within the fuel. This
11 will reduce detrimental temperature dependent effects, such as grain growth,
12 pellet cracking, and fission product transport, which in turn can decrease
13 fission gas release [2]. In an accident scenario, these qualities become more
14 important. A high thermal conductivity fuel will reject heat more rapidly
15 and operate at a lower temperature; when combined with lower heat capacity,
16 such fuels will have less stored energy. A lower operating temperature can
17 also improve safety margins, but only if the lower operating temperature is
18 reduced enough to compensate for possible lower fuel melting points [3].

19 The use of uranium mononitride (UN) as a nuclear fuel is desirable due
20 to its high uranium loading and high thermal conductivity which increases
21 with temperature [4]. The reactivity of UN with water has been a concern in
22 water cooled nuclear reactor applications. Workers at Oak Ridge National
23 Laboratory found when U_3Si_2 was exposed to steam for 384 hours the material
24 exhibited a slight discoloration and 0.014% weight gain [5]. For this reason
25 U_3Si_2 has been combined with UN to provide a protective barrier. A continu-
26 ous U_3Si_2 phase was desired to improve water tolerance within the composite.
27 Several uranium sesquisilicide fractions were tested to reach these goals. A
28 U_3Si_2 content between 25 and 35 mass % achieved the highest densities in
29 these tests. Uranium sesquisilicide also has a high thermal conductivity and
30 high uranium density relative to UO_2 . A fuel based on U_3Si_2 alone is an
31 option, but the current work is focused on a UN- U_3Si_2 composite.

32 A fuel composed of UN and U_3Si_2 will significantly improve the fuel's
33 thermal conductivity over UO_2 (Table 1). Another fuel improvement over UO_2
34 is a higher uranium density and therefore higher fuel loading. For example,
35 an inter-metallic composite consisting of UN combined with 25 mass% U_3Si_2
36 at 95% of the theoretical density will have 33% more uranium than UO_2 per
37 unit volume. This will translate to a 33% increase in the fuel content without
38 increasing the U^{235} enrichment. A fuel with increased fissionable content
39 can also aid the neutron economy when the fuel is combined with claddings
40 with higher neutron cross-sections, or which require greater thicknesses which
41 reduce fuel volume. Two paths to the fuel composite were tested; both
42 employed U_3Si_2 from Idaho National Laboratory (INL), but two types of UN
43 were tested. One series of experiments was done with UN powder from Los
44 Alamos National Laboratory (LANL) and another with UN μ -spheres from
45 General Atomics (GA).

Table 1: Properties of uranium compounds

	Density (g/cm ³)	U content (gU/cm ³)	M.P. (°C)	Thermal conductivity @ 573 K (W/m·K)
UN	14.3	13.55	2850	18 [4]
U ₃ Si ₂	12.2	11.31	1662	15 [6]
UO ₂	10.97	9.66	2865	7 [7]

2. Materials & Methods

Uranium mononitride was provided by LANL and GA. The UN obtained from LANL was prepared by single pass carbothermic reduction and nitridization, resulting in a carbon content of 836 ppm, Standard Deviation (SD) 19, and an oxygen level of 2228 ppm, SD 232. A portion of the powder was subsequently sintered at high temperature to reduce the carbon and oxygen impurities. This resulted in a carbon content of 218 ppm with a SD 6.8 ppm, and oxygen at 1794, and a SD 30 ppm. The impurity levels for the GA-provided UN μ -spheres and uranium sesquisilicide were not available at the time of writing.

The LANL UN was ground and sieved to produce a 100-200 μ m powder. General Atomics provided UN μ -spheres prepared by a sol-gel process for testing. The uranium sesquisilicide was furnished by Idaho National Laboratory. The U₃Si₂ had been ground and sieved to less than 37 μ m in size (Figure 1). The powders were mixed with Zn-stearate as a binder (<1 mass%). The bimodal mixture was then pressed to form green pellets for sintering. These pellets were prepared in 6 mm and 13 mm diameter dies. Liquid phase sintering temperatures used were as high as 2073 K with dwell times at the peak temperature of up to 6 hours. The pellet densities were measured using the Archimedes method with ethanol.

2.1. Powder Preparation

The powder morphology was analyzed by embedding the powders in epoxy and polishing, as well as by directly applying the powders to carbon adhesive on aluminum stubs. Both methods were followed by sputter coating with carbon for Scanning Electron Microscopy (SEM).

The as-received LANL UN powder consisted of relatively large particles, approximately 100-200 μ m in size with a porous structure (Figure 2). To

Figure 1: U_3Si_2 powder as received from INL.

improve particle mobility during sintering, the LANL UN was further ground and sieved to obtain a powder $<70\text{ }\mu\text{m}$ in size. The porous nature of the raw powder resulted in rapid size reduction with less than an hour of tumbling with yttria-stabilized zirconia grinding media. The ground powder had a significant fraction of fines (Figure 3).

The GA μ -spheres were analyzed for size and circularity with optical microscopy and ImageJ software [8]. A Hirox KH 1300 digital microscope was used to obtain sixteen optical images encompassing 616 μ -spheres. The average diameter was $275\mu\text{m}$ with a SD of $29\mu\text{m}$ and an average circularity of 0.84 with a SD of 0.07. The spheres displayed a significant amount of porosity under SEM analysis (Figure 4).

Powders were stored inside an argon-filled glove box which was kept below 10 ppmV O_2 . Powder weighing and pellet pressing were also carried out inside the glove box. Prior to pelletization the powders were mixed outside of the glove box with a rotary jar mill (CV-80461, U.S. Stoneware) inside of small autoclavable glass bottles (120 ml) with hermetically sealed caps. The bottles were placed inside of a 1 L HDPE bottle to set on top of the rollers for tumbling. The plastic bottle also provided secondary containment. Mixing of the powders was done in two steps to promote an even distribution of binder. Half of the Zn-stearate binder was added to the mononitride alone and mixed for approximately one hour. The uranium sesquisilicide and remaining binder were then added to the mononitride powder mixture (inside the glove box) and mixed for another hour on the rotary mill. The bottle with the mixed powder was then returned to the glove box for pellet pressing. The binder concentration was kept to $< 1\text{ mass}\%$, typically $0.5\text{ mass}\%$. The binder was

(a) LANL UN Particles

(b) LANL UN particle detail

Figure 2: SEM images of LANL UN powder particles as received.

98 increased to 0.75 mass% to improve powder adhesion when preparing samples
 99 with UN μ -spheres. Even with the increased binder, the UN μ -spheres formed
 100 fragile pellets which required extra care during handling to avoid crumbling.

101 2.2. Pellet Preparation

102 The dies used for green pellet compaction were trapezoidal split sleeve dies
 103 from Across International LLC. These simplified the removal of the pellets
 104 after pressing. A saturated solution of Zn-stearate in benzene was applied as
 105 a die wall lubricant. The die sleeve was assembled, then the bottom platen
 106 was dipped in the lubricant solution. The excess lubricant was removed by
 107 touching a corner on a flat surface allowing the excess liquid to run off, leaving
 108 only a thin film on the platen. The lubricated platen was then fitted into
 109 sleeve assembly and pushed to the bottom with the punch. The solution
 110 was allowed to dry. Next, the desired amount of mixed precursor powder
 111 was added to the die assembly. Minimal handling of the mixed powder was
 112 necessary to avoid segregation of larger particles from the fines. The top
 113 platen was coated with the lubricating solution in the same manner as before,
 114 then inserted into the die assembly and allowed to slide on top of the powder.
 115 The punch was inserted into the die assembly and pushed down, then the
 116 die assembly was transferred to a Carver Model C hydraulic press. Pressures

Figure 3: LANL UN after grinding (SEM).

117 applied ranged from 260 to 700 MPa. The pressure was held for approximately
 118 one minute.

119 2.3. Sintering

120 After the pellets were pressed, they were placed on an yttria crucible,
 121 which was set in a refractory metal crucible, which was then placed in a large
 122 alumina crucible with a heavy lid. The refractory metal provided a barrier
 123 between the yttria and the alumina which have a low temperature eutectic,
 124 and the alumina provided a protective enclosure to reduce oxidation of the
 125 pellet surface. The alumina crucible had small grooves ground onto the edge
 126 of the rim to allow gases to escape. The pellets were sintered in a tungsten
 127 element, tungsten shielded, M-5X12 Materials Research Furnace (MRF) with
 128 a flowing ultra-high purity argon cover gas. The samples were exposed to room
 129 temperature air briefly when they were transferred from the glove box to the
 130 furnace. Once the samples were inside the furnace, the door was immediately
 131 closed and placed under vacuum. The furnace was then back-filled with
 132 ultra-high purity argon flowing through an oxygen/moisture trap. The argon
 133 was evacuated and backfilled twice to remove residual moisture and oxygen
 134 with the system turbo pump. The sintering temperature profile included a
 135 thirty minute hold at 350°C (623 K) to remove the Zn-stearate binder. After
 136 evaporating the binder, the temperature was ramped at $\approx 17.5^\circ\text{C}$ per minute

(a) SEM of UN μ -spheres at 100X. (b) Detail of a broken UN μ -sphere at 500X.

Figure 4: SEM images of as received UN μ -spheres.

137 to 1400°C (1673 K), then slowed to between 6 and 6.67°C per minute to the
 138 final peak dwell temperature. Dwell times tested ranged from 1 to 6 hours.
 139 The cool down rates closely mimicked the heating profiles, cooling at 6 to
 140 6.67°C per minute to 1400°C and then cooling to room temperature at 17.5°C
 141 per minute.

142 2.4. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

143 The pellets were cut with a diamond wafering saw and mounted in epoxy to
 144 prepare samples for SEM with Energy-Dispersive X-ray spectroscopy (EDS).
 145 After setting, the samples were polished with successive grits ending with
 146 a 3 μ m diamond spray. Samples were then sputter coated with carbon to
 147 improve conductivity. Scanning electron microscopy was carried out with a
 148 JEOL 6400. The system settings were 10kV and 120nA for imaging. During
 149 EDS the settings were 10kV and 60nA. Imaging of Figures 2a, 2b, and 3 was
 150 performed with a Cameca SX50 at 15kV and 1nA.

151 3. Results

152 The mixed powders were pressed into 65 - 70 % TD green pellets with
 153 $\approx$ 300 MPa pressure. Their geometry was determined with calipers. Higher
 154 pressures were tested but led to fragile pellets which delaminated easily. Pellets
 155 prepared from the GA UN μ -spheres were extremely fragile, so additional
 156 binder was used to alleviate chipping and crumbling of the green pellets.

157 In general, handling of the unsintered pellets was minimized to avoid these
158 problems. Unsintered pellet densities were only checked when experimental
159 parameters were changed.

160 Several heating profiles were tested. Initial tests done below the melting
161 point of U_3Si_2 , up to 1662°C (1935 K), did not result in significant densification.
162 Sintering temperatures were increased to 1700°C (1973 K), thus shifting the
163 sintering into the liquid phase. Experiments carried out at temperatures
164 $>1700^\circ\text{C}$ exhibited increased interactions with the crucible material and some
165 slumping occurred. For these reasons, and the increased possibility of phase
166 changes, experiments at temperatures greater than 1700°C were consequently
167 avoided. Sintering at 1700°C for 2 hours was sufficient to consistently approach
90% TD (Figure 5).

Figure 5: Ground LANL UN 30 mass% U_3Si_2 composite, sintering dwell time of 2 hours
 $\rho=11.9 \text{ g/cm}^3$ (89% TD).

168
169 Longer sintering times were tested to increase the product density. This
170 method was marginally effective. The extended sintering resulted in the
171 accumulation of the residual porosity at the top of the sample. Post-sintering
172 grinding with sandpaper was necessary to obtain right cylinders. Voids were
173 often exposed after removing the surface defects from the these samples
174 (Figure 6). Pellet densities improved after removing surface bubbles, but this
175 method was not reliable, as some sanded sample surfaces did not remove
176 deeper voids.

177 Typical sample property results are listed in Table 2. Samples prepared

Figure 6: UN 35 mass% U_3Si_2 composite before and after sanding off bubbles revealing voids, 12.62 g/cm^3 93% TD.

178 with $<70 \text{ }\mu\text{m}$ powder mixed with U_3Si_2 approached 95% TD after 3 hours of
 179 sintering at 1700°C . Samples prepared from the UN μ -spheres were slightly
 180 less dense, but did not exhibit the surface bubbling which occurred with the
 181 $<70\mu\text{m}$ UN powder-derived pellets.

182 Sintering LANL UN with 30 mass% sesquisilicide for 3 hours at 1700°C
 183 resulted in a theoretical density of 92%, where the U_3Si_2 formed a some-
 184 what continuous phase, with the UN existing as separate regions within the
 185 sesquisilicide phase (Figure 7). Sintering composites with the GA μ -spheres
 186 for 6 hours at 1750°C resulted in slumping, but had a similar morphology
 187 to that of the LANL UN particle based samples (Figure 8). The higher
 188 temperature did create regions with a higher silicon content indicating a
 189 separate silicide phase was present (Figure 8d). The UN and U_3Si_2 did not
 190 appear to have intermixed during sintering since the SEM images display a
 191 clear two phase morphology (Figures 7, 8). The UN became consolidated
 192 under both testing schemes (Sub-figures 7c, 8c), losing the porous character
 193 of the precursor powders.

194 4. Summary

195 In this feasibility study several UN- U_3Si_2 sample composites were pre-
 196 pared via liquid phase sintering. The steps required to prepare $>90\%$ dense

Table 2: Composite pellet densities and uranium content

UN particle	U ₃ Si ₂ conc. (mass %)	Dwell (hours)	Density (g/cm ³)	T.D. (%)	U increase over UO ₂ (%)
powder	30	2 [†]	11.9	89%	21%
powder	35	3 [†]	12.6	93%	28%
powder	30	3 [†]	12.9	94%	31%
powder	25	6 [‡]	12.6	91%	28%
μ-spheres	25	3 [†]	12.0	87%	22%
μ-spheres	25	1 [†]	12.5	91%	27%
μ-spheres*	30	6 [‡]	13.2	96%	34%

[†]1700°C, [‡]1750°C, *Slumped

197 experimental fuel forms are described. Extended sintering time and post
 198 processing to remove surface voids, or an alternate processing method is
 199 required to obtain consistent 95% dense pellets. Composite fuel derived from
 200 UN mixed with approximately 30 mass% U₃Si₂ will provide a fuel with >30%
 201 more uranium per unit volume.

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Figure 7: Composite sample sintered for 3 hours at 1700°C (92% TD), sample consisted ground UN and 30 mass% U_3Si_2 . Images display qualitative elemental concentrations, brighter representing a higher concentration of the element specified (a) Backscatter electron image at 750× (b) Uranium concentration (c) Nitrogen concentration (d) Silicon concentration.

Figure 8: Composite sample (96% TD) consisting of GA μ -sphere UN and 30 mass% U_3Si_2 ; sample exhibited regions of high silicone content, pellet also slumped upon sintering. Images display qualitative elemental concentrations, brighter representing a higher concentration of the element specified (a) Backscatter electron image at 1000 $\times$ (b) Uranium concentration (c) Nitrogen concentration (d) Silicon concentration.