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Journal of Nuclear Materials

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November 2015

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



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Title

Uranium Silicide Pellet Fabrication by Powder Metallurgy for Accident Tolerant Fuel Evaluation and Irradiation

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Abstract

In collaboration with industry, Idaho National Laboratory is investigating uranium silicide for use in future light water reactor fuels as a more accident resistant alternative to uranium oxide base fuels. Specifically this project was focused on producing uranium silicide (U_3Si_2) pellets by conventional powder metallurgy with a density greater than 94% of the theoretical density. This work has produced a process to consistently produce pellets with the desired density through careful optimization of the process. Milling of the U_3Si_2 has been optimized and high phase purity U_3Si_2 has been successfully produced. Results are presented from sintering studies and microstructural examinations that illustrate the need for a finely ground reproducible particle size distribution in the source powder. The optimized process was used to produce pellets for the Accident Tolerant Fuel-1 irradiation experiment. The average density of these pellets was $11.54 \pm 0.06 \text{ g/cm}^3$. Additional characterization of the pellets by scanning electron microscopy and X-ray diffraction has also been performed. Pellets produced in this work have been encapsulated for irradiation, and irradiation in the Advanced Test Reactor is expected soon.

Highlights

A process to consistently produce high density U_3Si_2 pellets was developed.
Proper milling of the U_3Si_2 to produce the correct particle sized distribution was essential for final product consistency.
This process was used to produce pellets for irradiation in the Advanced Test Reactor.

Abbreviations

ASTM American Society for Testing and Materials
ATF Accident Tolerant Fuel
ATR Advanced Test Reactor
EDS electron dispersion spectrometer/spectroscopy
FCRD Fuel Cycle Research and Development
INL Idaho National Laboratory
L/D length to diameter
LWR Light Water Reactor(s)
MC-ICP-MS Multi Collector Inductively Coupled Plasma Mass Spectrometer
OES Optical Emission Spectrometer
PEG polyethylene glycol
SEM scanning electron microscope/microscopy
XRD X-ray diffraction

1. Introduction

Further improvement and development of the safety and performance of fuel for Light Water Reactors (LWR) continues to be an important area of research especially as it relates to creating Accident Tolerant Fuels (ATF). The Fuel Cycle Research & Development (FCRD) program has made investigation of ATF concepts a high priority [1].

Several accident tolerant fuel concepts are currently being evaluated by industry lead teams in collaboration with national laboratories and universities. This work is part of one such collaboration whose partners includes Westinghouse Electric Company and Idaho National Laboratory among others. The primary uranium compound used in nuclear fuel worldwide is uranium dioxide (UO₂). Alternative uranium compounds, such as uranium silicides, exist whose properties make them a potential alternative to UO₂ in nuclear fuel. In this work, samples of high density (>94% theoretical density) uranium silicide (U₃Si₂) have been fabricated by powder metallurgy techniques. The developed fabrication techniques were used to create samples for irradiation testing in the Idaho National Laboratory (INL) Advanced Test Reactor (ATR) as part of the ATF-1 irradiation [2]. Post irradiation examination of these samples will provide important information on the performance of U₃Si₂ under typical LWR conditions.

Uranium and silicon form several different stoichiometric compounds including USi₂, USi (or U₃₄S_{34.5}), U₃Si₂, U₃Si [3, 4]. The uranium density and thermophysical properties of high uranium content uranium silicides (U₃Si₂ and U₃Si) make them an attractive material from both an economic and safety perspective as a replacement for UO₂. Experience from research reactor fuel work indicates U₃Si swells too much under irradiation for use as a nuclear fuel [5, 6, 7]; additionally it disassociates into U₃Si₂ and solid solution U above 900°C, which is below some expected temperatures in uranium silicide fueled pins. Fortunately, U₃Si₂ has a very promising record under irradiation in research reactor fuels and maintains several advantageous properties over UO₂ [6, 7, 8, 9]. Some of these properties are shown in Table 1. There are approximately 17% more uranium atoms in a set volume of U₃Si₂ than there are in the same volume of UO₂, given a constant percentage of theoretical density for both samples. This superior uranium loading has the potential to enable power uprates, extend cycle length in LWRs, or reduce enrichment, all of which are economically beneficial. The higher uranium loading may also allow for the practical application of advanced cladding materials such as SiC or ATF cladding materials that carry a neutronic penalty compared to zircaloy such as FeCrAl steels. The lower melting temperature of U₃Si₂ compared to UO₂ is off-set by its much higher thermal conductivity that drastically drops the anticipated centerline temperature in a fuel pin compared to UO₂ fueled pins. These properties can have positive impacts on fuel pin performance in a variety of reactor accident conditions. The high thermal conductivity of U₃Si₂ in comparison to UO₂ and thus lower operating temperatures make it attractive as an ATF concept especially when paired with SiC or FeCrAl cladding. The performance of U₃Si₂ clad in SiC and FeCrAl in postulated PWR accident conditions has been shown to be superior to that of the UO₂ Zircaloy system [12, 13].

The goal of this work was to develop a process that could be used to produce U₃Si₂ pellets that was industrially scalable after the U₃Si₂ compound was produced. Once this process was demonstrated, it was then used to fabricate pellets for an irradiation experiment. The fuel fabrication process used in this work is schematically illustrated in Fig. 1. The process used to formulate U₃Si₂ is likely restricted to lab scale because it involves the production of powdered U metal which is highly pyrophoric and must be handled in an inert atmosphere glovebox. The lab scale formulation steps are segregated by the green box in Fig. 1.

Uranium silicide was formed from mixing powders of elemental uranium and silicon in near stoichiometric quantities. Uranium powder was created by a hydride/dehydride process, and the necessary silicon was procured as a powder. The mixture was then pressed into a compact. The compacts were agglomerated in a furnace at 1450°C, and then sent to an arc melter to completely react the uranium and silicon. In the arc melter, a tungsten electrode

Table 1. Key Properties of UO₂ and U₃Si₂

<i>Property</i>	<i>UO₂</i>	<i>U₃Si₂</i>
Theoretical Density (g/cm³)	10.96	12.2
Theoretical Uranium Number Density (atom/cm³)	2.44×10 ²²	2.86×10 ²²
Thermal Conductivity (W/m·K 400-1200°C)	6 to 2.5	13.0 to 22.3 [10] 16.1 to 28.2 [11]
Melting Point	2847	1665

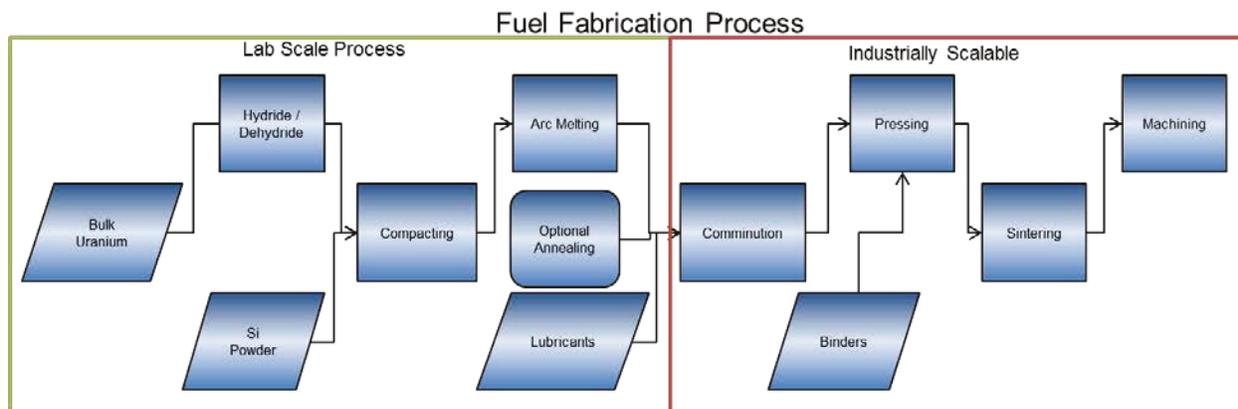


Fig. 1. Fabrication Flow Chart for Uranium Silicide Pellet Production in This Work

passed current through the uranium and silicon sample into a water cooled copper or graphite hearth. The arc melting process was repeated two additional times to ensure complete reaction. This process produces uranium silicide that is more U_3Si_2 phase pure (97% U_3Si_2) than what was typically produced by arc melting bulk uranium and silicon pieces which usually had about 10% U_3Si [3, 14].

The formulated U_3Si_2 was then sent through a standard powder metallurgical process that could be scaled up to an industrial scale. These steps are depicted inside the red box in Fig. 1. The ingots from arc melting are comminuted or turned into a powder by planetary ball milling. The resulting powder is pressed into green (formed but not sintered) pellets and then sintered. Various different sintering parameters were explored to achieve the desired theoretical density. A programmatic goal density of greater than 95.5% theoretical density (11.65 g/cm^3) was established based on the current criteria used for UO_2 in commercial fuel fabrication. The sintered pellets were machined using centerless grinding which had not been previously demonstrated on U_3Si_2 .

2. Uranium Silicide Formulation

As was discussed briefly in the Introduction, U_3Si_2 was produced using a lab scale process. Separate work is underway that seeks to find a pathway to produce industrial quantities of U_3Si_2 from standard nuclear industry uranium sources (i.e., UF_6). U_3Si_2 formulation is carried out by a unique technique for arc melting uranium metal powder with elemental silicon powder. The formulation process took place inside inert atmosphere (Ar) gloveboxes with tightly controlled O_2 partial pressures. Typically, the O_2 content of the glovebox is kept below 2 ppm. The reactive nature of U metal and, especially, U metal powders necessitates this precaution. Making U_3Si_2 by this process is practical for lab to bench scale quantities from tens of grams up to a few kilograms of material. These quantities are adequate to characterize U_3Si_2 properties and produce fuel for initial scoping irradiations.

2.1 Uranium Powder Fabrication

To start the U_3Si_2 fabrication process, feedstock uranium rods were washed in a weak nitric acid (10 weight percent (wt.%) solution to remove any outer oxide layer. The rods were then sized into 10 to 25 gram portions for processing through a hydride/dehydride apparatus. Bulk uranium metal was turned into a powder by a hydride/dehydride process. The hydride/dehydride process is a reversible chemical reaction that creates uranium hydride (UH_3) by applying heat and a hydrogen atmosphere to bulk uranium. By completing the hydriding reaction and then reversing the reaction by applying heat and vacuum, the hydrogen is removed from the uranium, and the bulk uranium is transformed into a fine powder. As hydrogen is adsorbed by the U, changes in the lattice parameter between the larger UH_3 crystal and U crystal induce stresses in the bulk U metal that breaks it apart into a fine powder. This process is known as decrepitation. This process is commonly used for other metals such as titanium to produce a fine powder. The peak reaction rate for this process occurs at a relatively low temperature of around 225°C which is easily obtainable in most furnaces, and inhibits sintering of the U powder after dehydriding [15, 16]. Care must be taken with the uranium product and any uranium hydride, as both chemicals are pyrophoric in air. The INL hydride/dehydride apparatus resides in an inert atmosphere glovebox and consists of a process tube that is connected to a gas manifold system that can supply H_2 , Ar, or vacuum to the interior of the process tube. A tube furnace provides heating for the process tube. Uranium hydride is less dense than U metal and yields a “fluffy” structure around the bulk U as the hydride process proceeds. After the dehydride process is complete, a brittle sponge-like structure is left behind along with some powder. In this work, the brittle sponge like structure was



Fig. 2. Uranium from the Hydride/Dehydride Process

crushed in a mortar and pestle and sieved through a 300 micrometer sieve. Any material that could not pass through the sieve was returned to the process for further hydride/dehydriding.

During the process, the hydriding step and dehydriding step were repeated over the course of a run to yield the final powder. The typical hydriding step consisted of applying hydrogen to the process tube until the hydrogen flow into the tube stagnated. Hydrogen atmosphere was maintained for about one hour. Vacuum was then applied to the process tube starting the dehydride step. The dehydride step lasted about an hour until the pressure in the tube had dropped below 10 mtorr. By iterating the steps a finer powder was created and bulk pieces of U metal were better broken apart. An example of some uranium after hydride/dehydride processing through several steps is shown in Fig. 2.

2.2 Arc Melting Process

The resulting fine uranium powder was then mixed with powdered silicon. In initial development the silicon powder was produced by hammer milling highly pure Si chunks and sieving the resulting powder to a diameter of less than 300 micrometers. Later development and irradiation tests used highly pure Si powder (99.999 wt. %) with a particle size between 149 and 44 micrometers. The uranium and silicon powders were blended in near stoichiometric quantities (92.7 wt.% U, 7.3 wt.% Si). A small amount of excess Si was added to account for Si loss during arc melting per the recommendations from previous experience fabricating U_3Si_2 fuel for research reactors [14]. In practice, it is difficult to produce phase pure uranium silicides. The additional Si also helps minimize the formation of U_3Si or U solid solution phases. The mixture used in this work was 92.5 wt. % U and 7.5 wt. % Si.

After the powder was mixed, it was compressed into a small rectangular compact using a hand press with a pressing pressure of approximately 225 MPa (32,600 psi). This mixed powder technique is a departure from the historic model for fabricating U_3Si_2 for research reactors. In that process, U metal was laid over Si pieces and arc melted so that the U would slump over the Si, encapsulating it before further melting and mixing. The new compacting technique puts the U and Si in more intimate contact for arc melting facilitating more complete silicide formation. A general representation of the U Si rectangular compact is shown in Fig. 3.



Fig. 3. Uranium and Silicon Compact before Arc Melting



Fig. 4. Uranium Silicide Ingot after Arc Melting

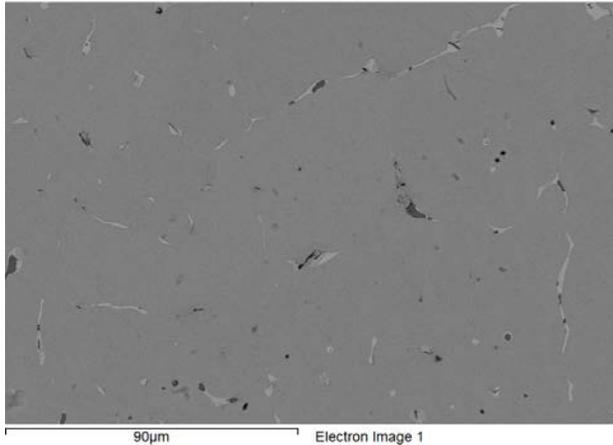


Fig. 5. Electron Backscatter Image of Arc Melted Uranium Silicide

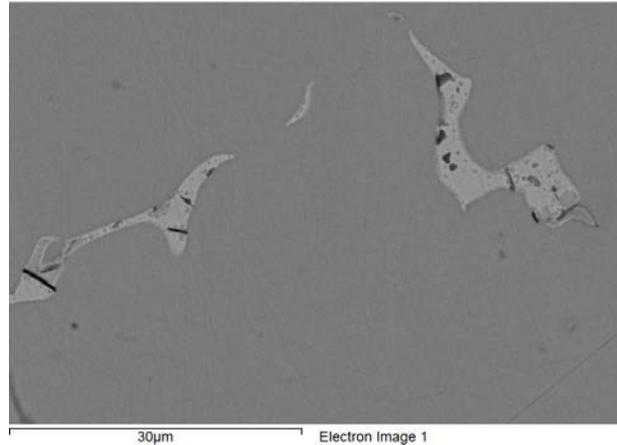


Fig. 6. Electron Backscatter Image of U_3Si Inclusions in Arc Melted Uranium Silicide

Arc Melting was chosen as the process by which the elemental Si and elemental U would be transformed into the U_3Si_2 compound because of both historical experience and the ease with which many different lab scale quantities of compounds or alloys can be created by this technique. In arc melting, elements to alloyed or compounded are placed in a conductive water cooled hearth and an arc is struck between the hearth and a tungsten electrode. The arc is passed over the target material melting them at a high temperature. After the arc is removed the material quickly cools into an ingot of the desired compound. In the development stages of this work, the U and Si compacts were placed in a deep, water-cooled copper hearth. Initially the compacts were melted at a relatively low current for arc melting to reduce Si loss and powder spray in the arc melting chamber. The compacts did not have adequate strength to fully withstand the arc passing over initially. The deep hearth helped to contain the compact during the initial pass of the arc. The arc melted ingots were flipped and remelted two additional times at progressively higher currents to ensure a homogenous compound. A representative arc melted ingot is shown in Fig. 4. After arc melting, some ingots were annealed for 72 hours at $800^\circ C$. This step follows the recommendations from early in research reactor U_3Si_2 fuel development. This step is intended to insure any solid solution U in the ingots has completely reacted with Si in the ingots [3]. Later in U_3Si_2 research reactor fuel development, the annealing step was found to be unnecessary [14] when additional Si was added to the charge as was done in this work. In later development, in this work, the powder compacts were agglomerated after pressing and before arc melting. The powder compacts were agglomerated by quickly heating the compacts up to $1450^\circ C$. The temperature of the furnace was held for 30 minutes and then allowed to naturally cool. This step greatly reduced the amount of powder dispersed in the arc melter during processing the U and Si compacts. It also allowed the use of an easier to use shallow flat copper hearth instead of the deeper hearth.

Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) examinations have been performed on the post arc melting microstructure. Uranium rich compositions will contain U in solid solution that will react with U_3Si_2 to produce U_3Si . Silicon rich compositions will contain USi or Si in solid solution. Historically, uranium silicide fuel with a volume fraction of less than 10% U_3Si phase was considered adequate for fuel qualification testing [3]. SEM examinations of the uranium silicide phases revealed about 1.5% volume fraction U_3Si . Phases were identified using electron dispersion spectroscopy (EDS). Once the phases were identified, they were clearly distinguishable using the SEM electron backscatter detector, and image analysis was used to estimate the volume fraction of the U_3Si phase. Chemical compositions can be gathered from EDS analysis, but definitive morphological information on exact crystal structures cannot be gathered. However, XRD also revealed the presence of U_3Si_2 and U_3Si phases confirming the EDS analysis. Rietveld refinement of the collected XRD spectra revealed between 0.5 to 3.3 wt.% U_3Si in the fabricated uranium silicide. No UO_2 phase was identified in XRD examinations of the development material from arc melting. This phase purity of U_3Si_2 is considered better than the typical uranium silicide produced for research reactors. It is postulated that the agglomeration and powder compacting followed by arc melting process may be a contributing factor to the good phase purity. Two SEM micrographs of the uranium silicide are shown in Fig. 5 and Fig. 6. The dark grey areas in the micrographs are the U_3Si_2 phase. The lighter grey areas are the U_3Si phases, and the black areas are porosity. Interestingly, the U_3Si phase appears to be forming as a precipitate along grain boundaries of larger U_3Si_2 grains. The inclusions detailed in Fig. 6 are typical of U_3Si inclusions seen in as cast and annealed uranium silicide fabricated in this work.

3. Uranium Silicide Pellet Fabrication

Uranium silicide ingots from the arc melter are comminuted into a fine powder before being pressed into a green pellet and subsequently sintered. The comminution process to create a fine sinterable powder underwent extensive refinement. Obtaining the correct particle size distribution of the final U_3Si_2 powder was essential to produce highly dense pellets as is typical for ceramics. Uranium silicide presents several challenges to the creation of a fine powder. Most notably, it is reactive in oxygen requiring the use of inert atmosphere gloveboxes for the majority of the powder work. The high density of uranium silicide compared to most other common materials complicates the grinding process. Ideally, grinding media should be close in density, if not more dense than the material being ground. Additionally, all the precautions associated with handling a radioactive substance must be followed.

3.1 Comminution

Planetary milling was chosen as the means to reduce the arc melted ingots into a fine powder. Before milling the arc melted ingots are manually broken up using a hammer mill. Appropriately sized U_3Si_2 particles are then loaded into a milling jar along with the milling media. In planetary milling, about 10-20% of the milling jar volume is taken up by the grinding media, and 10-40% of the milling jar volume is taken up by the material being ground. Zirconia grinding media and zirconia lined milling jars were utilized in this work. The density disparity between zirconia and U_3Si_2 is undesirable. However, partially stabilized ZrO_2 is very wear resistant and introduces very little contamination during milling.

In order to achieve the desired final particle size (Fig. 7 red curve) in this work, it was necessary to progressively reduce the size of the milling media. A single milling step with 10 mm media was initially attempted (Fig. 7 green curve), but, even after switching to a smaller 5 mm grinding media (Fig. 7 orange curve), the final particle size was still too coarse for high density sintering. A multi-step approach was then adopted where material from the hammer mill was processed through a mortar and pestel to reduce the size of any material below 5 mm. This material was then initially milled with 5mm media followed by sieving. The fines ($<39 \mu m$ particle size) were then milled a second time with 1mm milling media. Milling aids were also added to increase the process efficiency. Initially, in this work no milling aids were utilized; however, the powder tended to stick to the side of the milling jar,

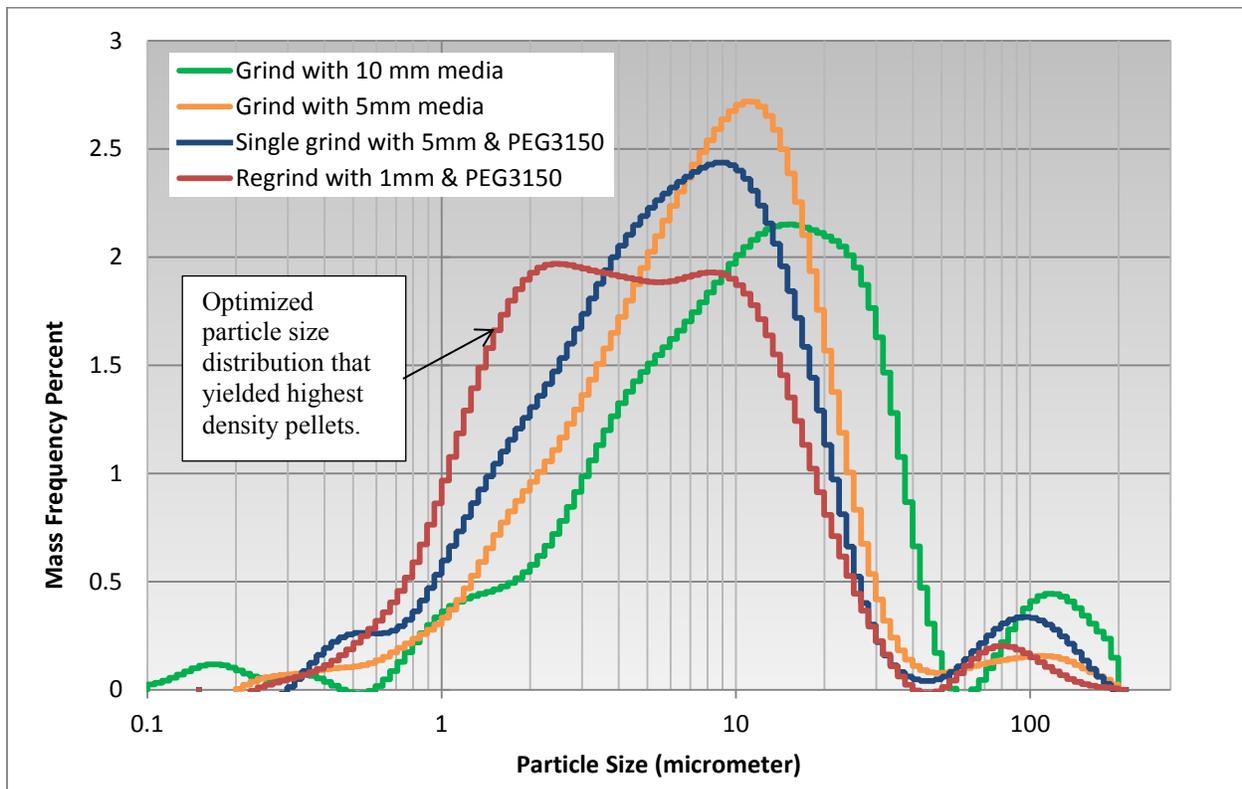


Fig. 7. Particle Size Distribution of U_3Si_2 from Different Milling Recipes

preventing further milling. Several lubricants or milling aids were tried, including Oleic acid and several molecular weights of polyethylene glycol (PEG). The general guidance for adding milling aids to a powder is 0.2 wt.% of the material being comminuted [17]. Because U_3Si_2 is much denser than normal ceramics, the same lubrication effect can be achieved with a smaller wt.% of lubricant. On a volume percent basis, 0.2 wt.% PEG in a typical ceramic like Al_2O_3 or ZrO_2 is equivalent to approximately 0.1 wt.% PEG, and, therefore, was used in this work.

The particle size distributions of the resulting powders from milling were evaluated using a Micromeretics Sedigraph III that utilizes sedimentation theory to calculate particle size distribution and are displayed in Fig. 7. The high density of U_3Si_2 required the use of a high viscosity (9.1668 mPa·s) solution (Sedisperse A-13) from the particle size analyzer vendor. The curves in Fig. 7 show different particle size distributions attained from different milling parameters. The blips in the curves in the range near 100 μm and below 0.5 μm are statistical anomalies inherent in this particle size distribution technique. In initial studies, 10 mm grinding media were used to comminute the U_3Si_2 . Powder from this distribution (shown in green in Fig. 7) did not sinter to high enough densities for this work. To produce a finer particle size distribution, smaller grinding media were employed and regrinding was investigated. Without any milling aids, 5 mm milling media were able to drop the median particle size, but high densities could not be consistently achieved with this powder (orange curve in Fig. 7). After further process refinement, the multi-step process described above was established. The particle size distribution of the powder after the initial 5mm planetary milling step is shown by the blue curve in Fig. 7. The sieved powder was then reground with 1mm media to produce a particle size distribution shown by the red curve in Fig. 7. Pellets pressed from this particle size distribution have consistently sintered to high densities, and the production of this particle size distribution has proved to be reproducible by following the same milling parameters on multiple batches of arc melted uranium silicide. This process was used to produce highest density pellets for both characterization activities and pellets for the irradiation experiment.

3.2 Pellet Pressing

Forming the fine powder from milling into a green pellet for sintering required several iterations of development. To produce green pellets, charges of powder are loaded into a lubricated die with two floating punches. The floating punches and die are pressed in a manual press, ejected, and then examined before sintering.

Pellets were pressed from a 9.525 mm (0.375 inch) diameter die. Before pressing, the die wall was lubricated with zinc stearate. In powder metallurgy, pellets with an aspect ratio (length to diameter ratio) of less than 1.0 help facilitate pellet production because stresses induced in pressing continue to concentrate the larger a pellet becomes. As this work was developmental and final sintered density was the key metric for success, a charge of 4 grams of U_3Si_2 was selected that created pellets with an aspect ratio of about 0.75 to help facilitate pellet production. Two floating punches provided dual action compaction to the charge when pressure was applied. Pellets were pressed with a pressure ranging from approximately 124 to 248 MPa. The pressures were held for 30 to 60 seconds and then released. The length of time the pressure was held was not observed to impact the quality of the green pellet. Most successful pellets were pressed between 124 to 156 MPa. Pellets pressed at higher pressures tended to delaminate or

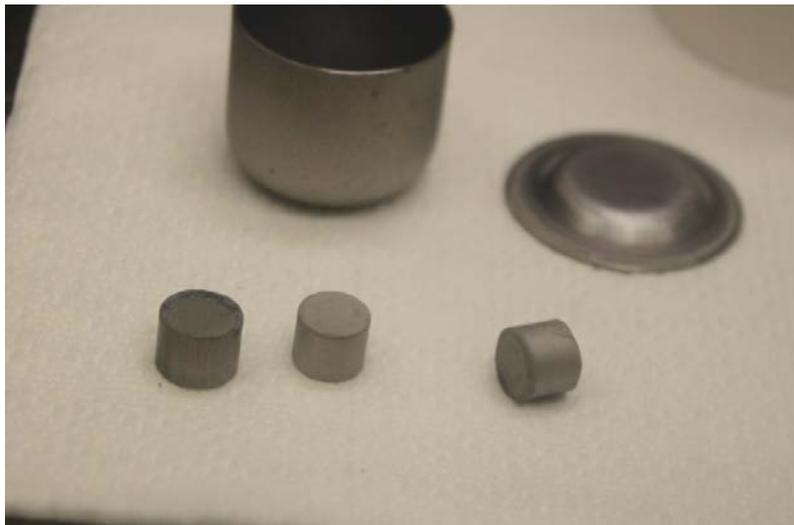


Fig. 8. Typical unsintered U_3Si_2 pellet on left compared to two sintered pellets in center and to the right with Ta crucible in the background.

have end cap defects after ejection from the die as is commonly observed in powder metallurgy when too great a load is applied. Increasing the pressure did not necessarily lead to higher green densities or green strengths. The best sintering results tended to occur with pellets with a green density between 60 and 65% theoretical density. This was achievable with most powder distributions only using 124 MPa. This behavior with increasing pressure and optimum green density is consistent with some earlier work reported in literature for uranium silicide [18]. A typical unsintered pellet is shown on the left side of Fig. 8.

The final powder from the comminution process, shown by the red curve in Fig. 7, was highly susceptible to delamination and had very low green strength after pressing. This powder still contained the PEG lubricant from milling. Difficulty with pressing had been observed previously with other milling lubricants as well. Therefore, it was necessary to burn off the PEG from the powder. This was accomplished by heating the powder under vacuum to 350°C for about 1 hour (the autoignition temperature of the utilized PEG is 305°C). Even after the removal of the PEG, the powder needed some additional cohesion to create green pellets. A water-soluble poly (ethylene oxide) polymer was added to the powder to act as a binder during pressing. Approximately 0.1 weight percent of the polymer was added to the powder after the PEG removal step. This produced pellets with adequate green strength that were appropriate for sintering.

3.3 Pellet Sintering

Sintering studies on the different powders from milling have been carried out in parallel with the milling and pressing development. In each development cycle, ~30 gram batches of powder were ground in the planetary mill, pressed into pellets, and sintered. Sintering of the U_3Si_2 was conducted in a box furnace inside a glovebox with an Ar atmosphere with 40 ppm O_2 and in a separate graphite furnace that is operated under vacuum (Ar back filled and evacuated to $\sim 10^{-5}$ mbar). After sintering, the density of the pellets is measured, and the microstructure of select pellets is examined. The final density of the sintered pellets appears to depend on several parameters including the particle size distribution, pellet green density, the maximum sintering temperature, and the time at maximum sintering temperature. Sintering temperatures ranging from 1200°C to 1550°C have been investigated. Sintering times ranging from 2 to 8 hours at maximum temperature have also been investigated. Two-step sintering was briefly investigated, but the final density was always similar to simply sintering the pellet for the same time at the maximum sintering temperature. The best sintering results occurred when the pellets were inside a tantalum crucible on a bed of small tantalum pellets. The Ta works as an effective oxygen getter during sintering. Without the Ta pellets, the U_3Si_2 pellets tended to stick to the Ta crucibles or Ta foil that were used prior to the introduction of the Ta pellets. The Ta pellets act as a setter sand for the U_3Si_2 pellets, decreasing interactions and encouraging U_3Si_2 densification. The central pellet and the pellet to the right side of Fig. 8 are representative of U_3Si_2 sintered by this process. A Ta crucible used to hold the sintering pellets is shown in the background of Fig. 8.

3.4 Pellet Machining

After sintering, the pellets still require some machining to reach final dimensions. A centerless grinder was

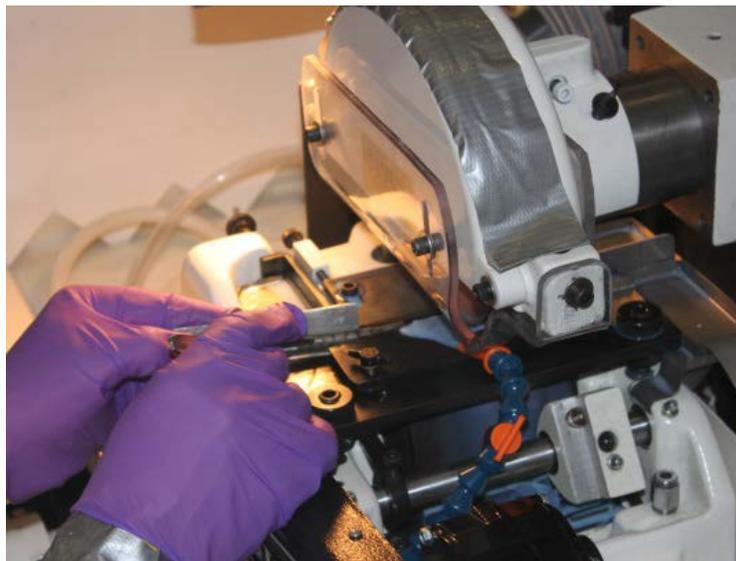


Fig. 9. Centerless grinding of U_3Si_2 pellets

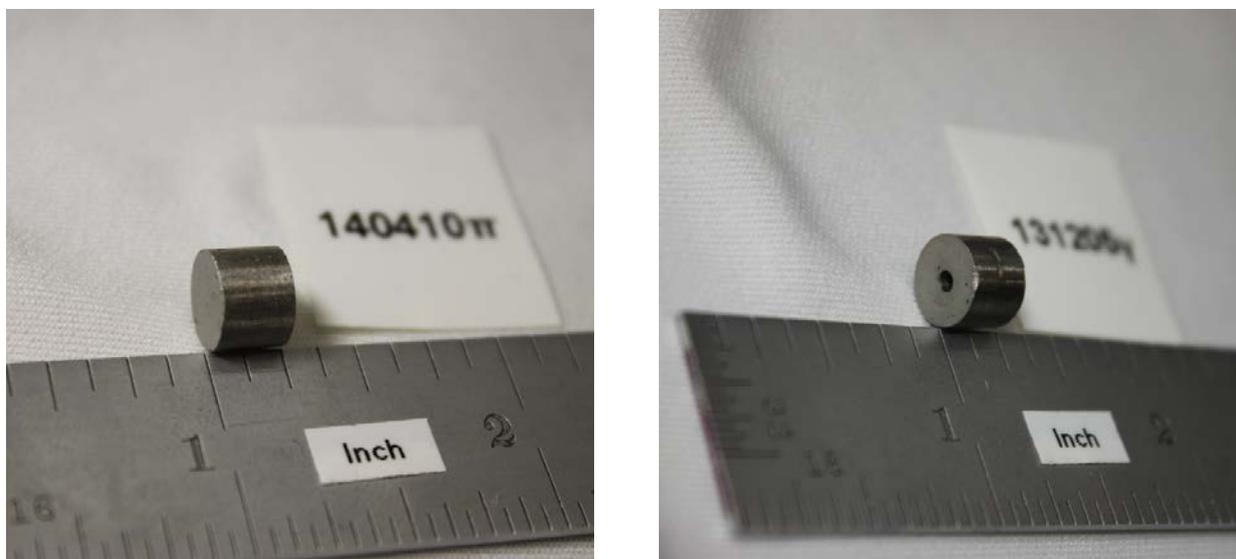


Fig. 10. Sintered and Machined Pellets without a melt wire hole (left) with a melt wire hole (right).

procured to size the sintered U_3Si_2 pellets to the correct diameter. With some modifications, the same centerless grinder was used to grind the faces of the pellets as well. Centerless grinding is the standard machining technique that is used to size fuel pellets in the nuclear industry. Demonstrating that centerless grinding of U_3Si_2 is possible was an important outcome of this work to collaboration partners (Westinghouse Electric Company) of the authors. Centerless grinding of U_3Si_2 pellets is being demonstrated in Fig. 9. The centerless grinder was a Unison Model 188 DedTru Grinding system. Significant modifications were performed to make the equipment appropriate for radiological work. To the authors' knowledge, this work is the first time U_3Si_2 has been centerless ground. The final pellets for the irradiation were inspected and had an average diameter of 0.819 ± 0.00037 cm (0.3225 ± 0.00014 in.). The centerless grinder setup was modified to also grind the pellets faces to a desired height. The average pellet height for the irradiation was 0.612 ± 0.022 cm (0.241 ± 0.009 in.). Examples of machined pellets from the centerless grinder are shown in Fig. 10.

In addition to machining the pellets to their cylindrical dimensions, select pellets were drilled out to include a central hole for melt wires. An example of a pellet with a central hole is shown in the right picture of Fig. 10. The melt wire packages were inserted into the top two depleted insulator pellets in each irradiation rodlet. Refer to Section 5 for more information on the irradiation design.

4. Pellet Characterization

The primary metric for evaluating U_3Si_2 pellets in this work has been density. A programmatic goal density of greater than 95.5% theoretical density (11.65 g/cm^3) was established based on the current criteria used for UO_2 in commercial fuel fabrication. This theoretical density criteria is based on the resintering densification properties of UO_2 . While this criteria was used to evaluate this developmental work on utilizing standard powder metallurgy techniques to produce U_3Si_2 pellets, a new density criteria specific to U_3Si_2 will need to be established to meet applicable US Nuclear Regulatory Commission requirements such as Regulatory Guide 1.126. Additionally, the microstructure of the final product has been evaluated via scanning electron microscope (SEM) examinations and XRD to confirm the crystal phase. Vickers microhardness testing was also performed.

4.1 Density Evaluations

The density of the sintered pellets was measured using immersion density following ASTM B962 and helium pycnometry. Whenever immersion density is performed on sample prepared by powder metallurgy, it is important to follow ASTM B962 [19] that requires the collection of a samples dry mass, mass after oil impregnation, and mass when immersed in water. If the oil impregnation step is not performed, the densities from immersion density will be artificially high because air trapped in open porosity will distort the immersion mass. Unfortunately, the oil impregnation leaves the sample unusable for irradiation. Helium pycnometry will provide the same data as ASTM B9622 immersion density without contaminating the sample. The helium pycnometer used in this work was a Quantachrome Micro-Ultrapyc 1200e.

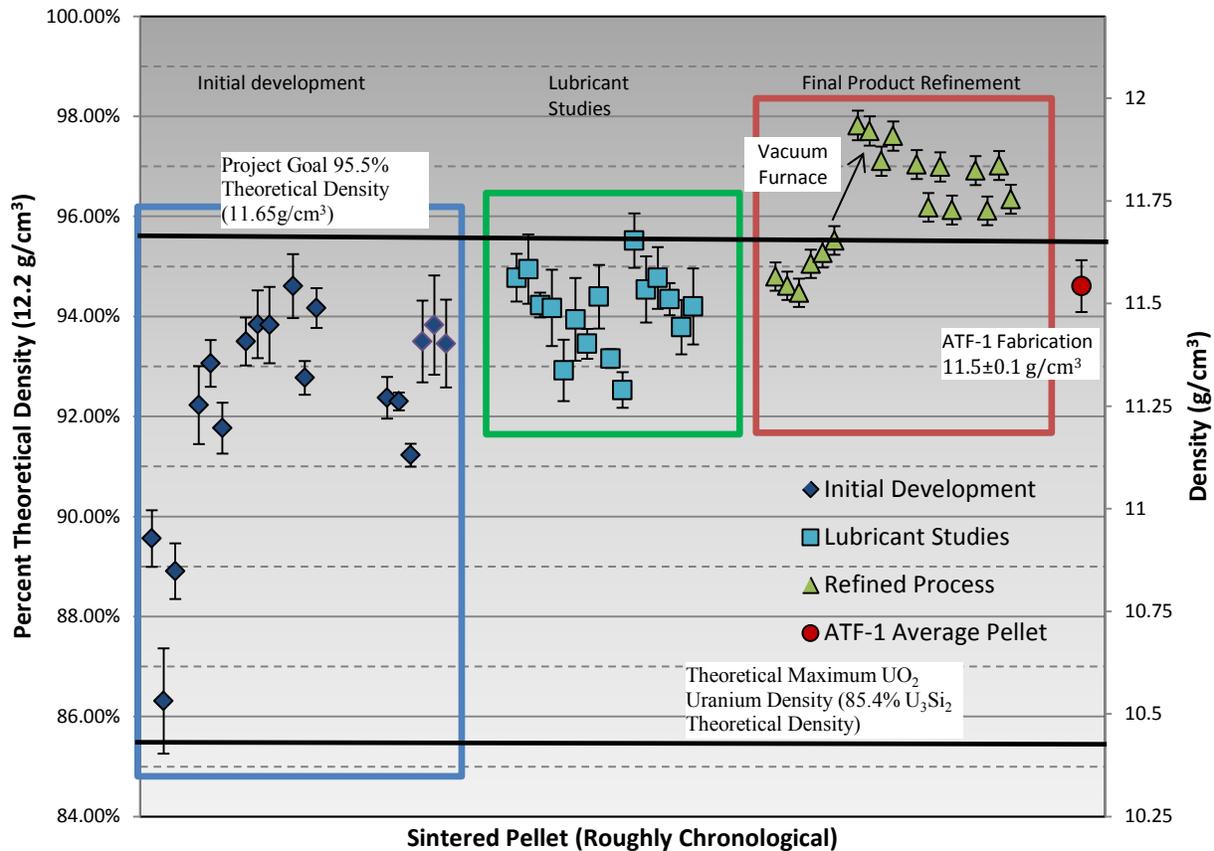


Fig. 11. Development of Sintered Pellet Density

The process of developing a technique to create a high density, reproducible U_3Si_2 pellet required considerable iteration to find both the correct sintering parameters and the needed initial powder particle size distribution. Fig. 11 documents the general development of sintered pellet density from the initial tests through final product refinement and the average density of pellets fabricated for the ATF-1 irradiation. Pellets pressed from the initially milled powder (green curve in Fig. 7 and “Initial Development” Series in Fig. 11) were sintered at several different temperatures and times resulting in a range of densities for the different conditions. Pellets sintered for 1 hour at 1400°C had densities ranging from 86.3 to 89.6 % theoretical density. Pellets sintered at 1450°C for 1 hour had an average density of 92.4 % theoretical density, and pellets sintered at 1450°C for 2 hours had an average density of 93.7 % theoretical density (11.44 g/cm³). All this sintering was carried out in the Ar atmosphere furnace. This early work established 1450°C and higher as the desired sintering temperature with a time at temperature of 2 hours or longer.

However, these densities were short of the programmatic goal of demonstrating 95.5% theoretical density U_3Si_2 pellets, and short of the programmatic requirement of at least 94% theoretical density for the irradiation. Evidence from SEM microstructure examination suggested a finer particle size distribution was required. Several pellets were sintered from powder typified by the orange curve in Fig. 7. However, without milling aids, these powders appear to have had highly variable particle size distributions, and consistent densities under similar conditions were difficult to obtain. Some pellets were sintered with densities as high as 94.6 % theoretical density, but the majority of pellets sintered from this powder had theoretical densities ranging from 91 to 93.5% theoretical density. Sintering temperatures of 1450°C and 1500°C were investigated, and sintering times ranging from 2 hours to 4 hours were investigated.

It was clear that milling aids would need to be added to the planetary milling jar to create the needed particle size distribution. Pellets pressed from powders that were milled with various different milling aids (Oleic Acid and PEG of various molecular weights) had densities typified by the “Lubricant Studies” series in Fig. 11. The particle size distribution of the powder used to press these pellets was similar to the blue curve in Fig. 7.

The key to the final powder product (powders with a particle size distribution represented by the red curve in Fig. 7) was the addition of PEG and regrinding with smaller media. After PEG had been established as an effective milling aid that did not adversely impact the powder pressing properties, regrinding with smaller media clearly became effective (blue curve to red curve in Fig. 7). After a more consistent powder product was established, it was possible to consistently produce pellets with a density above 94% theoretical density. This was done both in an Ar atmosphere furnace and in a furnace with a vacuum atmosphere using the same sintering parameters. Using pellets pressed from the powder that had the PEG removed and the poly (ethylene oxide) resin added, pellets sintered for 4 hours at 1500°C under Ar had an average theoretical density of 94.7% (11.57 g/cm³). Similar pellets with the water-soluble poly (ethylene oxide) resin, but still containing PEG from milling, sintered nicely as well. However, these pellets had lower densities ranging from 92.9 to 94.4 % theoretical density.

To achieve higher densities above 95.5% theoretical density, the vacuum furnace was utilized. Pellets pressed from powder with Fig. 7 red curve particle size distribution, with the PEG burned off, and with the poly (ethylene oxide) resin added were sintered in the vacuum furnace at pressures in the 10⁻³ to 10⁻⁴ mbar range. The furnace was ramped up to 600°C at a rate of 2.5°C per minute and held there for 2 hours, then ramped at 30°C per minute up to 1500°C and held for 4 hours, and then allowed to naturally cool. This produced pellets with a theoretical density range of 96.1 to 97.8 % and an average theoretical density of 96.9% (11.8 g/cm³). This satisfied a project goal of producing pellets with densities above 95.5% theoretical density. However, upon dimensional examination of these pellets, they were too small to be utilized in the irradiation test. Due to programmatic time constraints, pellets for the irradiation were fabricated at a lower density in the Ar atmosphere furnace. The following sintering schedule was followed for the pellets sintered for the irradiation. The furnace was ramped at 25°C per minute to 600°C and held there for 2 hours; the furnace was then ramped at 25°C per minute to 1500°C, and held for 5 hours. About 100 pellets were sintered for the ATF-1 irradiation about half of these pellets were evaluated using helium pycnometry. The average density of these pellets was 11.54 ±0.06 g/cm³ and is shown in Fig. 11. This shows the developed powder metallurgical technique can repeatedly produce high density pellets, and the techniques used in this process should scale up to industrial scales.

4.2 SEM Examination

During process development, examination of the porosity and microstructure of the sintered U₃Si₂ by Scanning Electron Microscope (SEM) also informed the milling development and confirmed the sintering was proceeding as planned. Additionally, SEM examination of the early development sintered pellets revealed no U₃Si, pure U, or pure Si, phases in the sintered pellets. SEM examination of early development pellets did reveal some minor Cu containing contamination phases from the arc melting process. These phases were eliminated in the final development product after the agglomeration step was added. The amount of porosity in the sintered microstructure followed the density of the pellets as can be seen in Fig. 12 and Fig. 13. SEM examination early in development provided evidence for the need to produce a smaller particle size distribution. In Fig. 14 the grain structure is faintly

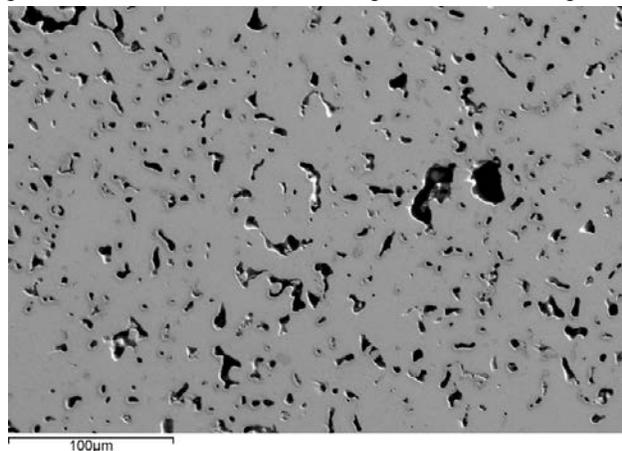


Fig. 12. SEM secondary electron image showing the sintered microstructure of 88.6% theoretical density U₃Si₂

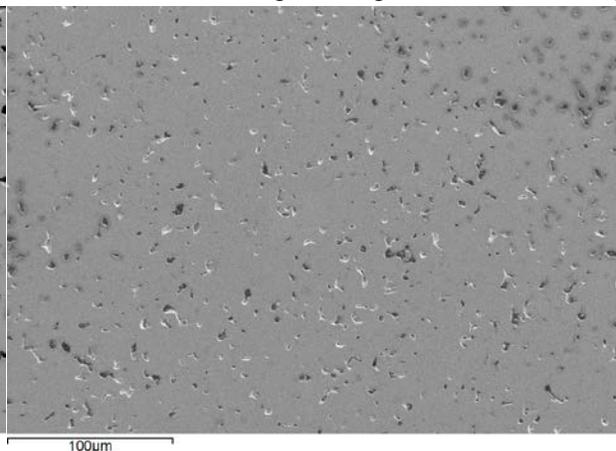


Fig. 13. SEM secondary electron image showing the sintered microstructure of 92.1% theoretical density U₃Si₂

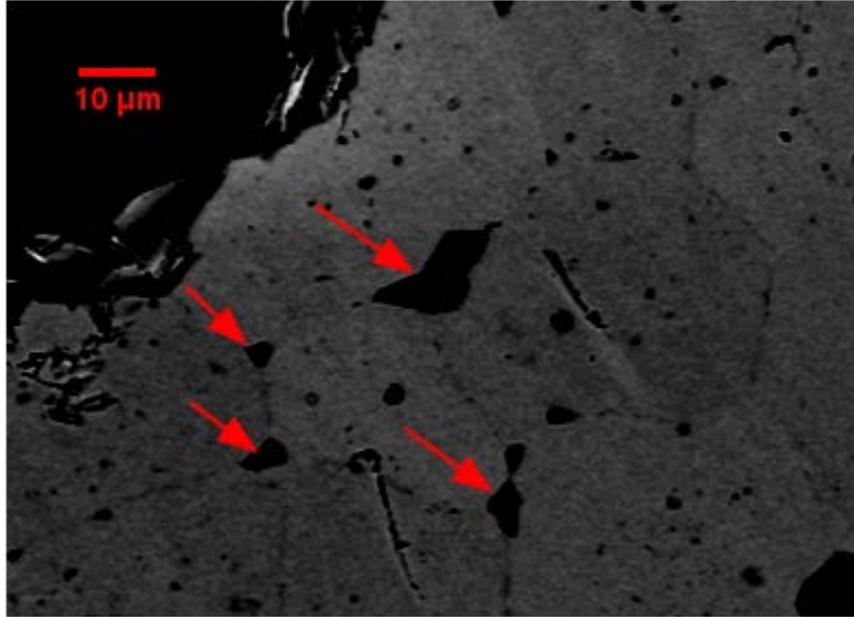


Fig. 14. SEM backscatter electron image showing the location of porosity in U_3Si_2 .

visible in the backscatter electron image, and it is clear that the majority of porosity falls along the grain boundaries and at triple points. Arrows point towards intergranular porosity in the figure. This porosity is difficult to close via thermal diffusion that occurs during conventional sintering. This illustrated the need to produce a finer particle size distribution in milling to help eliminate intergranular porosity.

SEM analysis of the as fabricated pellets for the irradiation was also performed. The microstructure of the as fabricated pellets is similar to what was seen in the development pellets and is shown in Fig. 15 and Fig. 16. There is a small amount of uranium oxide that has entered the process, and there appears to be a Si rich phase in the as fabricated pellets as well. Where these phases entered the system is still under investigation, but it may be due to the atmosphere of the furnace used during sintering. X-ray Diffraction analysis was performed to positively identify the minor phase and their abundance and is discussed in the next section. The uranium oxide phase and porosity appears as dark areas in Fig. 15 and Fig. 16. The light gray areas in the figures are U_3Si_2 , and the medium gray areas are uranium silicide that is Si rich compared to U_3Si_2 . Unlike the development pellets there does not appear to be any Cu bearing phases from the arc melting. Some of the oxide observed in the SEM may be due to surface oxidation during polishing. Analysis by XRD clarified that the Si rich phase was USi.

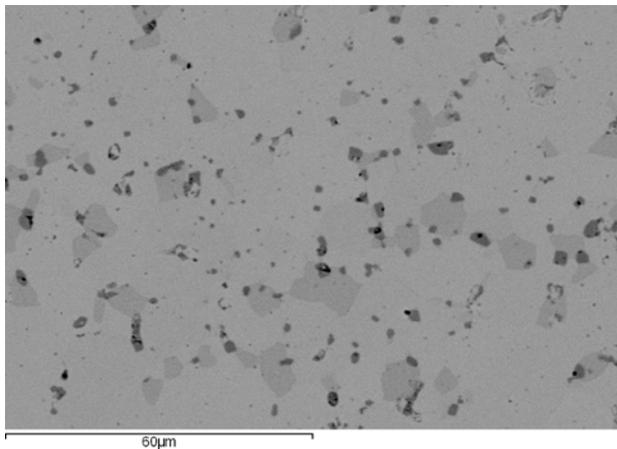


Fig. 15. SEM backscatter electron image showing an as fabricated pellet from the irradiation batch.

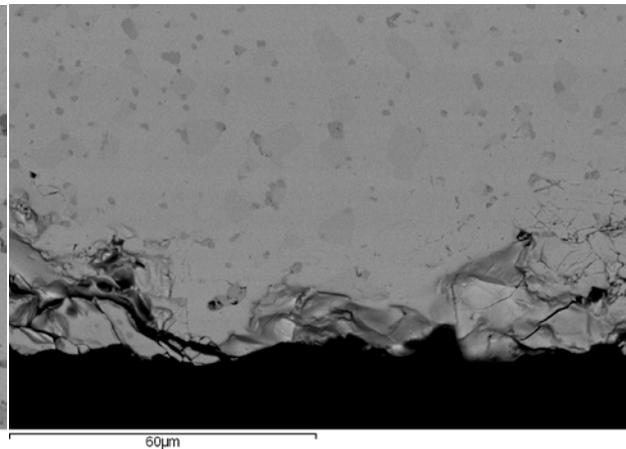


Fig. 16. SEM backscatter electron image showing an as fabricated pellet from the irradiation batch near the pellet edge.

4.3 Chemical, XRD, and Microhardness Analysis

Chemical analysis was performed on source powders for enriched pellets and depleted pellets going into the ATF irradiation. Isotopic, major element, and trace element analysis was performed using different mass spectrometry techniques. For uranium isotopics and trace impurity analysis, powder samples were dissolved in hydrofluoric, nitric, and boric acid. For Si major element analysis, the powder samples were dissolved in hydrofluoric and hydrochloric acid. Uranium isotopics were examined using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS), and trace impurity was established using an ICP-MS. The Si was examined using an ICP-OES (Optical Emission Spectrometer). The enriched pellets had an enrichment of 5.44 wt.% U-235. The powders were analyzed for several trace elements including Al, Cr, Cu, Er, Mn, Mo, Ni, Ta, W, and Zr. Elevated levels of W (721 ppm) and Zr (254 ppm) were found in the enriched material, and elevated levels of W (335 ppm) were found in the depleted material. The elevated W is likely due to the arc melting process where either the tip spalls off or accidental dipping of the tip in the melt. Difference in the W trace amounts is likely due to differences in technicians. The elevated Zr may be due to the enriched uranium metal feedstock or may be from the planetary milling media (ZrO_2). The major element analysis of Si showed $6.6 \pm 0.6\%$ Si. This is less than the expected 7.5%, but this analysis is likely biased low. The dissolution for Si analysis may have not fully dissolved all the Si as this dissolution is still under development.

During development x-ray diffraction (XRD) was performed on samples of arc melted U_3Si_2 . This examination confirmed that the primary phase present in the sintered pellets was U_3Si_2 . No uranium oxide phases were observed in the XRD spectra. A 0.5% U_3Si phase was observed in the arc melted samples. Some preliminary XRD work on as fabricated pellets from the irradiation has also been performed. The phases seen in the SEM work are confirmed with the XRD work. An XRD pattern from powder from arc melting after comminution before sintering is shown in Fig. 17. This pattern was predominantly U_3Si_2 . XRD did not detect any UO_2 or USi in pre-sintered powders from before and after PEG burnout. XRD and SEM examination of arc melted ingots from agglomerated powders also have not revealed USi or UO_2 phases. In XRD of the as sintered ATF-1W fuel pellets, the major phase is U_3Si_2 (84-88%) with a minor USi phase (8-13 %) and a minor UO_2 phase (2-4%). An example XRD spectrum from a pellet is shown in Fig. 18.

Exactly where the UO_2 and USi phases formed in the as fabricated microstructure of ATF-1 pellets is not entirely known. The oxide may have formed during the agglomeration step, the PEG burnout step, or may have formed during sintering. However the XRD results to date suggest it is likely the minor phases formed during sintering. The uranium silicide is purposefully formulated with extra Si to ensure all the U is tied up in a silicide compound and to help with Si loss during arc melting. With the agglomeration step, less Si is lost in arc melting and may be contributing to the formation of the Si rich phase. The atmosphere of the glovebox that contained the sintering furnace is another likely contributor to the minor phases. The atmosphere is primarily Ar, but it does have approximately 35 ppm O_2 and efforts to getter O_2 locally by surrounding the pellets with Ta crucibles and high surface area Ta pellets were likely not adequate to prevent oxidation. Excess Si from formulation and the loss of U to UO_2 are likely contributors to the USi phase.

Microhardness measurements were also performed on sintered pellets. A Vickers hardness tester was used to produce indents. A 500 g force was used with a 13 second dwell time. The average Vickers hardness for the sintered material was 550 HV for 37 indents with a standard deviation of 46. No indents were observed where the one diagonal was significantly different than the other. No variation in hardness was observed across the radius of

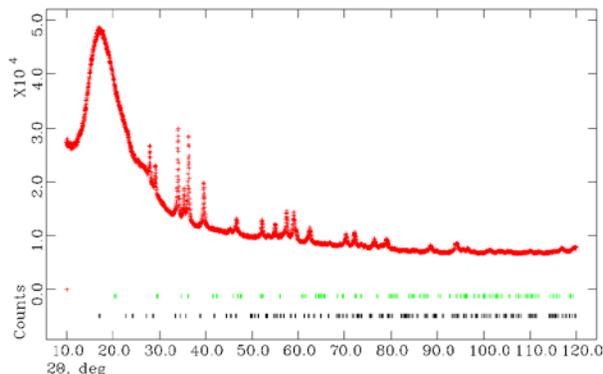


Fig. 17. XRD pattern from as arc cast U_3Si_2 powder after comminution with reflection points for U_3Si_2 (black) and U_3Si (green)

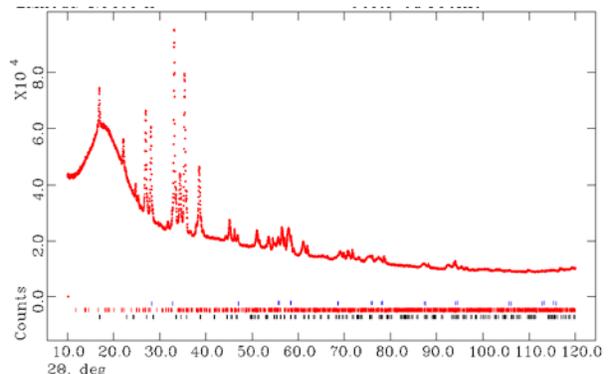


Fig. 18. XRD pattern from an as fabricated ATF-1W fuel pellet with reflection points for U_3Si_2 (black), USi (red), and UO_2 (blue)

the pellets.

5. ATF-1 Irradiation

The ATF-1 irradiation is a series of drop-in style ATR irradiation experiments designed to provide preliminary irradiation performance data on potential accident tolerant fuel concepts under typical LWR conditions [2, 20, 21]. The ATF-1 design consists of a fueled rodlet (fuel plus cladding) that is encapsulated in a stainless steel capsule. Drop-in tests use the heat generated from fission and gamma heating in the experiment and a temperature control gap between the rodlet and the capsule to maintain temperature. No active control mechanisms exist in drop-in designs. The typical design of an ATF-1 experiment is shown in Fig. 19.

Machined pellets from this work were incorporated into rodlets and capsules as part of the ATF-1 irradiation experiment. Pellets were pressed from depleted and enriched U_3Si_2 powder prepared to have a particle size distribution that is represented by the red curve from Fig. 7. They were sintered in an Ar atmosphere with ~ 35 ppm O_2 for 5 hours at $1500^\circ C$ to create pellets with a final density of 11.54 ± 0.06 g/cm³. The rodlet component acts similar to cladding under normal LWR irradiation conditions. The zirconium alloy Zirlo was used for the tube walls of the rodlet, and Zircaloy-4 was used for the rodlet endcaps. There are 6 rodlets in the Westinghouse U_3Si_2 ATF-1 experiment. Each rodlet contained a stack of pellets consisting of a depleted U_3Si_2 pellet (0.41% U-235) followed by 12 enriched pellets (5.44% U-235), and then 2 depleted pellets with central holes filled with a melt wire package.

The 6 rodlets were designed to operate at a variety of initial power and temperature conditions and remain under irradiation for a variety of burnups. The test matrix for the ATF-1W irradiation is shown in Table 2. Three of the rodlets are designed to operate at ~ 275 W/cm ($\sim 600^\circ C$ centerline). Two are designed to operate at ~ 430 W/cm ($800^\circ C$ centerline), and one is designed to operate at 461 W/cm ($\sim 1000^\circ C$ centerline). The high temperature rodlet utilizes an Ar/He mix to achieve higher temperatures, and the other rodlets use only He. The desired burnup of the 3 low temperature rodlets is 20, 40, and 70 GWd/tU. For the 2 medium temperature rodlets, burnup is 20 and 70 GWd/tU, and for the high temperature rodlet the desired burnup is 20 GWd/tU. Examination of the melt wire packages after irradiation should help put some bounds on the maximum temperatures experienced by the fuel. After the rodlets were assembled, they were loaded into He filled, stainless steel capsules, and transferred to ATR for irradiation. After irradiation, the capsules will be sent back to the INL Hot Fuels Examination Facility for postirradiation examination. The experiments will undergo a variety of examinations including neutron radiography, gamma scanning, fission gas release analysis, optical microscopy, burnup analysis, hardness testing, and density evaluation. Samples from the rodlets will also likely be examined for thermal properties and by electron microscopy [22].

The primary purpose of this irradiation is to generate data on the swelling of U_3Si_2 under typical LWR

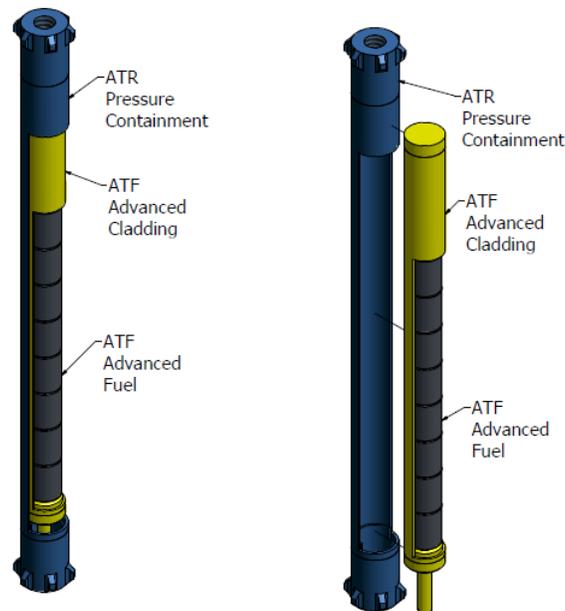


Fig. 19. Design of Typical ATF-1 Experiment

Table 2. ATF-1W Test Matrix

Rodlet ID Bot End Cap	Initial LHGR (W/cm)	Target Burnup (GWd/tU)	Rodlet Weld/Fill Gas	Predicted Peak Fuel Temperature (°C)
ATF-W01	250	20	100% He	660
ATF-W02	250	40	100% He	660
ATF-W03	250	70	100% He	670
ATF-W04	470	20	100% He	930
ATF-W05	460	70	100% He	960
ATF-W06	500	20	25% He 75% Ar	1260

conditions (temperature, linear heat generation rate, and neutronic conditions). The swelling behavior of U_3Si_2 at elevated temperatures and lower fission density is unknown. The majority of U_3Si_2 irradiation data was collected at the lower temperatures and higher neutron flux conditions experienced in research reactors. The results of this experiment will test the findings of Reference 7 that U_3Si_2 will resist amorphization at irradiation temperatures above 250°C. Additionally these irradiations will explore fission density ranging from 0.6×10^{21} to 2.1×10^{21} fissions per cm^3 which the low end of fission density explored previously (2×10^{21} to 7×10^{21} fission per cm^3 [6]).

6. Conclusions

Uranium silicide pellets have been produced by powder metallurgy techniques as part of an accident tolerant fuel concept. The process to produce these pellets has undergone extensive optimization to yield reproducible pellets with a sintered density of greater than 94% theoretical density (11.47 g/cm^3). In order to produce pellets of this density, the particle size distribution of the source powder was optimized. Pressing and sintering parameters were also optimized until high density, phase pure pellets were reproducible. With optimized powder and optimized sintering parameters, it was possible to fabricate pellets with a density of 11.8 g/cm^3 (96.9% theoretical density). Around 100 pellets were fabricated for the ATF-1 irradiation with a density of $11.54 \pm 0.06 \text{ g/cm}^3$. A centerless grinder was used to machine sintered U_3Si_2 to final dimensions. SEM and XRD examination of the as fabricated pellets shows the majority of the pellets are U_3Si_2 with minor phases of USi and UO_2 . Enriched and depleted pellets were produced to fuel 6 rodlets for the ATF-1 irradiation. The results of these irradiations will help determine if U_3Si_2 has acceptable performance at prototypic LWR conditions and help validate the future use of the fabrication techniques discussed in this work.

Further work is underway to better identify the source of the USi phase (~10%) in the as fabricated pellets. Additional characterization work is also on-going. Thermophysical characterization of sintered pellets has been initiated. Corrosion studies of U_3Si_2 in water and steam will also be performed. In collaboration with university partners, samples will be produced to study the elastic and creep properties of U_3Si_2 . Neutron diffraction may also be considered.

7. ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy. This work is also part of a collaboration led by Westinghouse Electric Company comprising several national laboratories, vendors, and universities awarded in response to the DE-FOA-0000712 funding opportunity. The authors would like to acknowledge the assistance of the support staff associated with the Fuels Applied Science Building at INL. Several technicians helped to contribute to this work including Blair Park, Jakeob Maupin, Kevin Hays, and Micheal Chapple. The authors would also like to acknowledge Michael Benson, Leah Squires, and Thomas Hartmann for their assistance with XRD analysis.

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