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Fabrication of Stoichiometric U_3Si_2 Fuel Pellets

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Method Article

Fabrication of stoichiometric U_3Si_2 fuel pelletsAdrian R. Wagner*, Jason M. Harp, Kip E. Archibald,
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A B S T R A C T

Uranium silicide, U_3Si_2 , is an accident tolerant fuel type which is gaining momentum as a replacement fuel for uranium dioxide (UO_2). Idaho National Laboratories has been fabricating phase pure U_3Si_2 fuel pellets for use in various irradiation and material characterization experiments. Stoichiometric U_3Si_2 fuel pellets were fabricated using a powder metallurgy and arc melting technique. The use of the stoichiometric ratio to alloy uranium and silicon, and sintering in a vacuum environment allowed for the fabrication of high density (>94% theoretical density), phase pure pellets, greater than 94% U_3Si_2 . Silicon volatilization was not observed in the as-sintered microstructure, which has been verified through XRD and SEM, thus eliminating the need to alloy a substoichiometric U/Si ratio.

- Stoichiometric ratio of U to Si used to form U_3Si_2 phase.
- Decrease in secondary phases present confirm absence of silicon volatilization.
- Analysis via XRD and SEM confirm the phase purity of the U_3Si_2 fuel pellets.

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A R T I C L E I N F O

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Method details

Uranium silicide, U_3Si_2 , is a candidate accident tolerant fuel type to replace uranium dioxide (UO_2), in light water reactors (LWR) [1]. U_3Si_2 is desired for its increased thermal conductivity and higher uranium loading as compared to UO_2 [2], leading to an economic benefit in terms of lower enrichments, extended cycle lengths, or power uprates. The economic advantages of U_3Si_2 may also enable the cost-effective adoption of accident tolerant cladding concepts [1]. Industry partners are interested in deploying U_3Si_2 in the current LWR fleet relatively soon, and desire a more pure U_3Si_2 fuel pellet than what was previously fabricated [2]. However, due to the corrosion characteristics of U_3Si_2 [3], pure U_3Si_2 fuel pellets will likely not be used unless as a part of a high uranium density composite. This work focuses on the fabrication of stoichiometric U_3Si_2 . This knowledge can be applied to future U_3Si_2 applications. Previously fabricated U_3Si_2 fuel pellets were produced using a substoichiometric ratio of U/Si and produced pellets which were 84–88% U_3Si_2 , 8–13% USi, and 2–4% UO_2 [2]. To improve on this and achieve greater than 94% U_3Si_2 , a stoichiometric ratio of U/Si was used to fabricate fuel pellets via the powder metallurgy process discussed by Harp et al. [2]. Along with the composition change, the sintering environment changed from Ar containing 40 ppm O_2 to sintering in a high vacuum ($<1e-4$ Torr), which also contributed to the phase purity of the pellets.

U_3Si_2 formulation

As previously reported by Harp et al. [2] a powder metallurgy process combined with arc-melting was used to fabricate U_3Si_2 . However, unlike Harp et al., a stoichiometric ratio was used to form U_3Si_2 fuel pellets. The previous fabrication effort followed the research reactor experience and used a 92.5 wt% U and 7.5 wt % Si (59.27 at% U, 40.73 at% Si) mixture, while the current process fabricated pellets composed of 92.7 wt% U and 7.3 wt% Si (60 at% U, 40 at% Si). The factors leading to this change—in the previous ATF-1 fabrication effort [2], Si did not volatilize in the arc melting process as anticipated [4]; and a reduction of the USi phase present in the pellet was desired. The uranium and silicon was alloyed and down-blended from a 19.75% enriched substoichiometric U_3Si_2 , 92.06 wt% U, 7.94 wt% Si (57.77 at% U, 42.23 at% Si) and depleted uranium (0.22 wt% U-235) to the desired composition and enrichment.

The remainder of the fabrication effort was similar to that presented by Harp et al. with exception of an additional 0.020 g of PEG (polyethylene glycol) 3350 powder. This additional PEG was added to the final milling/comminution step (1 mm ZrO_2 milling media, milled for 2 h) to aid in the removal of the material from the milling jar. This positively affected the fabrication process by limiting material loss in the milling process; material loss decreased from about 10% to less than 2% for the entirety of the milling/comminution process. Powder characteristics will be discussed later.

Pellet pressing

For the ATF-2 fabrication effort, pellets were pressed to an aspect ratio of 1.15 L/D and had an average green density of 58.79%TD (U_3Si_2 theoretical density: 12.2 g/cc). Prior to pressing, 0.1 wt% binder (PolyOx WSR-301) was added to the U_3Si_2 powder. After each pressing, the tooling was cleaned and lubricated with an aerosol zinc stearate. Each pellet was pressed using an Across International 10 mm diameter punch and die set. Pellets were pressed to approximately 113 MPa (16.4 ksi), and allowed to relax for 30 s. Fig. 1 shows the loading relaxation over 30 s, indicating a drop from 113 MPa to approximately 96 MPa.

Pellet sintering and grinding

After green pellets were pressed, pellets were loaded and sealed into a graphite crucible (Fig. 2) and placed into a RD Webb Vacuum Furnace. The sealant used was an Apiezon L vacuum grease, which was burned off during the 600 °C hold. Sealing the crucible is necessary due to the reactivity of the fine powder when exposed to oxygen, as the furnace is not located in the glovebox. This allows for the pellets to be

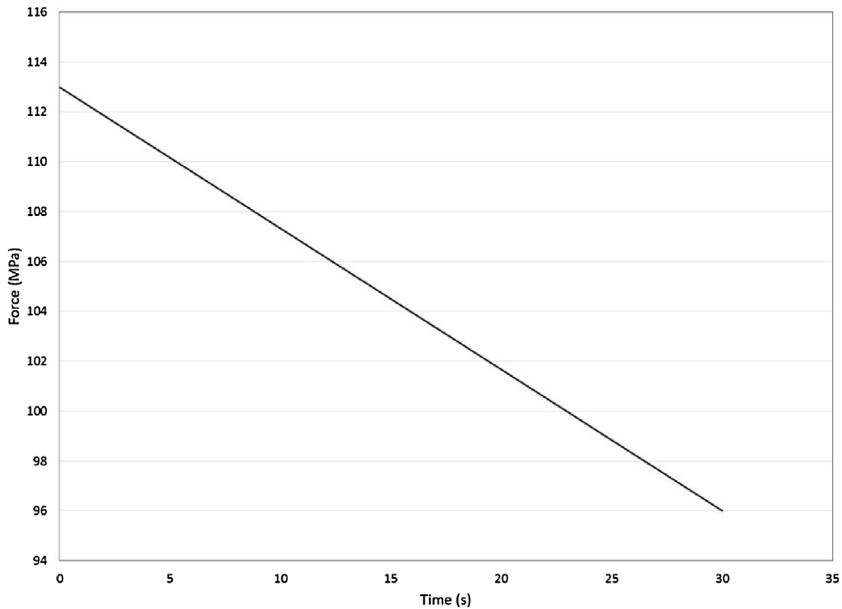


Fig. 1. Relaxation of force during the pellet pressing process; initial pressing force was about 113 MPa and after a 30 s dwell time the force was approximately 96 MPa.



Fig. 2. Green U_3Si_2 pellets loaded into the graphite sintering crucible, before sealing in an inert atmosphere glovebox.

transferred from an inert environment (Ar glovebox) in laboratory air. The wall of the graphite crucible was lined with 0.254 mm thick Ta foil, and the U_3Si_2 pellets were placed onto a bed of Ta pellets, to allow for point contact only between the U_3Si_2 and Ta pellets. Ta is used as an oxygen getter and prevents the fuel pellets from coming into contact with the graphite, ultimately minimizing carbide formation in the fuel pellets. The sintering schedule used (Fig. 3)—4 h hold at 200 °C to ensure the furnace pressure was below 1 e-4 Torr; ramp at 20 °C per minute to 600 °C, hold for 2 h to remove the binder and vacuum grease; ramp

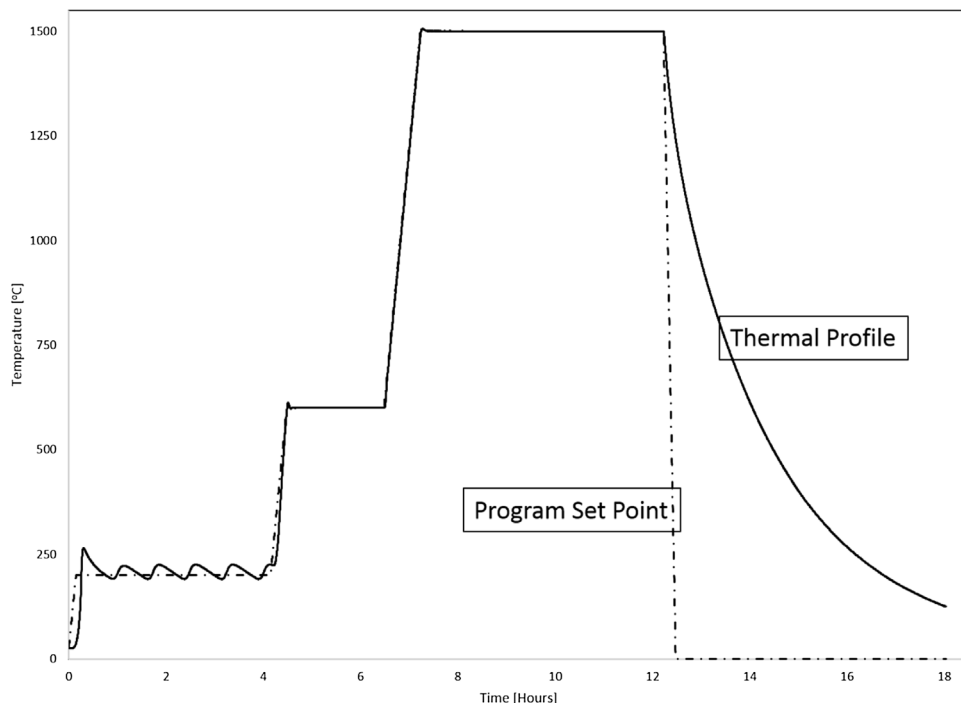


Fig. 3. Sintering profile for U_3Si_2 fuel pellets. Plot shows the program set point and thermal profile as measured by a Type S thermocouple.

at 20 °C per minute to 1500 °C, and hold for 5 h, then cooled naturally to room temperature. This sintering schedule densified the U_3Si_2 pellets to greater than 94.0%TD. Density was determined by geometric calculation and helium pycnometry (Quantachrome Micro-Ultrapyc 1200e). The pellets were ground to the desired diameter via a centerless grinding process. Fig. 4 shows the evolution of an U_3Si_2 fuel pellet from the green state to the centerless ground state.

Material characteristics—Powder and sintered pellets

Powder characteristics

The U_3Si_2 powder fabrication process, mentioned in the U_3Si_2 formulation section produced powder with approximately an 8–10 μm particle size (Fig. 5). This is roughly in line with particle size (10 μm) reported by Harp et al., and indicates that the addition of 0.020 g PEG did not adversely affect the particle size. The particle size distribution was calculated using sedimentation theory and utilizing a Micromeritics Sedigraph III.

Microstructure

Using the thermal cycle previously mentioned, the microstructure of the pellets varied from fine grain to coarse. Grain size was quantified in accordance with ASTM E112-13 [5]. Fig. 6 shows pellets which have been sintered under vacuum (Fig. 6a) using the previously mentioned RD Webb furnace, and under argon using a Thermal Technology Model 1100 refractory metal furnace (Fig. 6b). The aim was to fabricate pellets with a uniform fine grain size, less than 40 μm (Fig. 6). However, many of the pellets had a heterogeneous microstructure—fine <40 μm grains on the edge of the pellet, surrounding larger 100+ μm grains (Fig. 7). The pellets observed in Figs. 6a and 7 were fabricated from

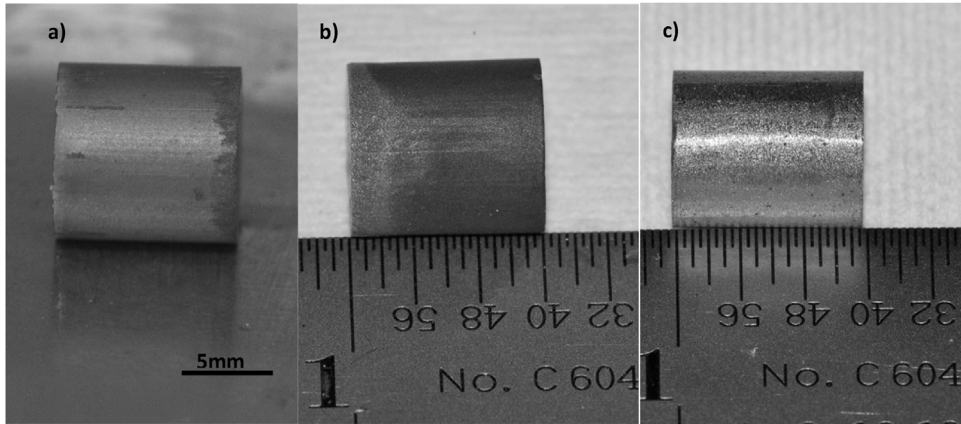


Fig. 4. Evolution of U_3Si_2 fuel pellets a) green pellet; b) as-sintered pellet; c) centerless ground pellet.

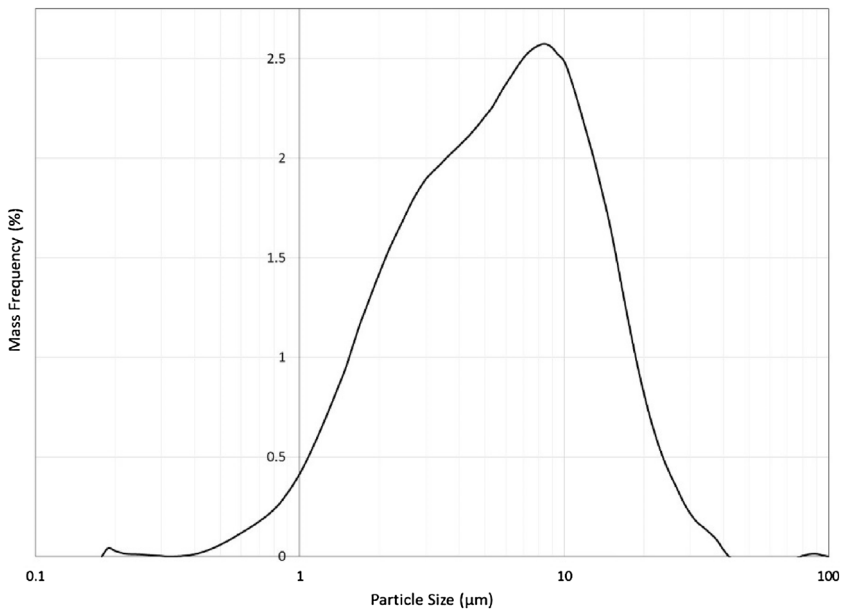


Fig. 5. Mass frequency vs. particle size as determined via sedimentation theory.

the same batch of U_3Si_2 powder and using similar sintering conditions, the primary difference was the amount of U_3Si_2 material present in the furnace during sintering [6]. It is unknown how these coarse grained U_3Si_2 pellets would perform in an irradiation experiment. However, the quality of the machined surface is known—machining induced surface fissures (Fig. 8) were observed after the centerless grinding process. This phenomena appears to be dependent on the microstructure and independent of composition [6]. Hoggan et al. [7] measured grain size to be about $20\ \mu\text{m}$ in substoichiometric pellets, while recent fabrication efforts of have fabricated pellets of a stoichiometric composition having an average grain size of about $29\ \mu\text{m}$ (Fig. 6b). The observed microstructure was caused by a combination of conditions—radiative cooling through the use of a vacuum atmosphere, exacerbated by a larger pellet loading in a confined space ultimately promoting the grain growth [6].

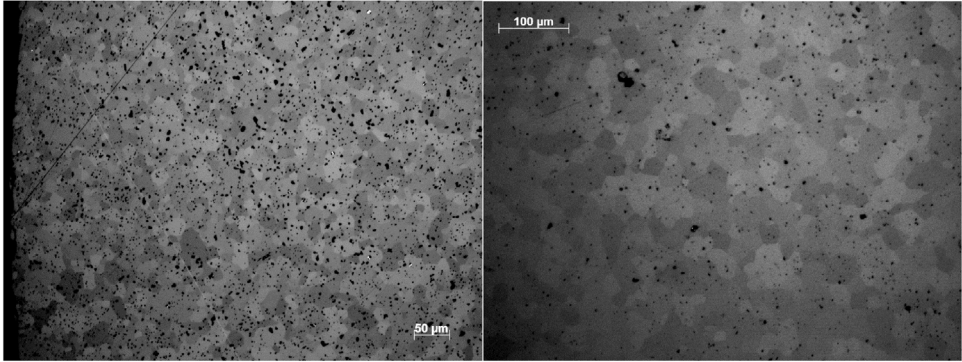


Fig. 6. a) Polarized optical image of pellet with average grain size of 23 μm , sintered under vacuum; b) Polarized optical image of pellet with average grain size of about 30 μm , sintered under Ar.

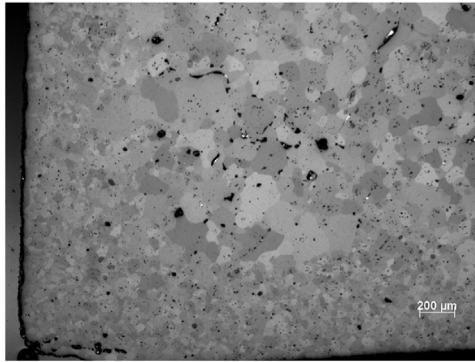


Fig. 7. Polarized optical image of a pellet with non-uniform texture; fine grain microstructure on edge (grain size about 28 μm), coarse grain structure in center (grain size about 107 μm).

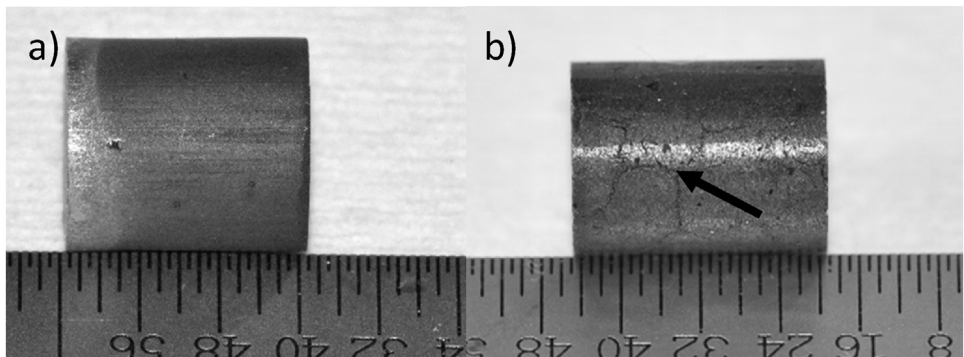


Fig. 8. a) Sintered pellet prior to centerless grinding; b) sintered pellet after centerless grinding exhibiting machining induced surface fissures.

Grain growth brought on by the aforementioned conditions has been remedied by sintering pellets in a larger furnace and under an inert (Ar) atmosphere (Fig. 6b).

Mechanical properties

In light of the observed surface fissures and microstructure discussed in the previous section, structural integrity of the pellets was a concern. Industry partners have indicated that pellets need to withstand a compressive force of about 100 MPa during the rod loading process. If pellets fracture during the loading process, this could introduce unwanted fragments in the rod leading to potentially adverse FCMI (Fuel Cladding Mechanical Interaction) during irradiation. Thus, pellets were subjected to compression testing.

Pellets with and without surface fissures were subjected to compression testing. Each pellet was compressed with a strain rate of 0.100 mm/min at room temperature, with compressive strengths ranging from 29.14 MPa to 186 MPa (Table 1). The lowest compressive strength (Pellet 1459-v: 29.14 MPa) was due to the pellet having faces out of parallel.

Phase purity

Pellets fabricated for the ATF-1 irradiation had an U_3Si_2 purity between 84 and 88% with USi between 8 and 13%, and UO_2 between 2 and 4% [2]. However, for the ATF-2 fabrication the phase purity improved significantly—through XRD and SEM image analysis [7], a greater than 94% U_3Si_2 phase was observed. The primary minor phases present were UO_2 (1–2%) and USi (4–5%), other minor phases were significantly less than 1%, Fig. 9 shows XRD patterns for a few select pellet batches. The peaks have been identified with markers indicating U_3Si_2 or UO_2 peaks; no USi, U_3Si or uranium carbides were observed in these patterns. Peak splitting and broadening (approximately 33.5, 34.6, and 35.7 2-theta) was observed, possibly due to interstitial carbon atoms straining the U_3Si_2 crystal lattice [8], or the presence of a strain mismatch caused by the heterogeneous microstructure [6]. Further investigation is needed to determine the cause of the peak splitting and broadening. The oxide phase present in the pellets was likely due to native oxide growth on the surface and powder aging in the glovebox [9]. Thus, if powder is not pressed into green pellets and sintered within a few days of the last powder fabrication step, oxygen content of the pellet will increase.

Pellets were also subjected to light element analysis. A LECO OH836 O&H Analyzer was used to quantify the hydrogen and oxygen content [10], and an ELTRA CS800 and ON900 were used to quantify the carbon and nitrogen content. The average, for 12 samples, hydrogen, oxygen, carbon, and nitrogen content were—0.932 ppm H_2 (High: 1.65, Low: 0.194) 3010 ppm O_2 (High: 4250, Low: 2060) 2084 ppm C (High: 3392, Low: 1497); 96.6 ppm N_2 (High: 427, Low: 0.0).

Conclusion

High purity uranium silicide, U_3Si_2 , fuel pellets have been fabricated by arc melting a stoichiometric ratio of uranium and silicon. Through the stoichiometric fabrication, a fabrication method has been established which significantly decreases the presence of USi in the fuel pellet; in essence dropping the USi impurity from about 10% to less than 5%. In light of recent corrosion results

Table 1
Compressive strength of pellets.

Pellet Identification	Compressive strength [MPa]
1475-pp {Surface fissures}	154
1437-n {Surface fissures}	96
1459-v{Surface fissures}	29
1496-s{Surface fissures}	96
1405-j {No surface fissures}	160
1425-d {No surface fissures}	186

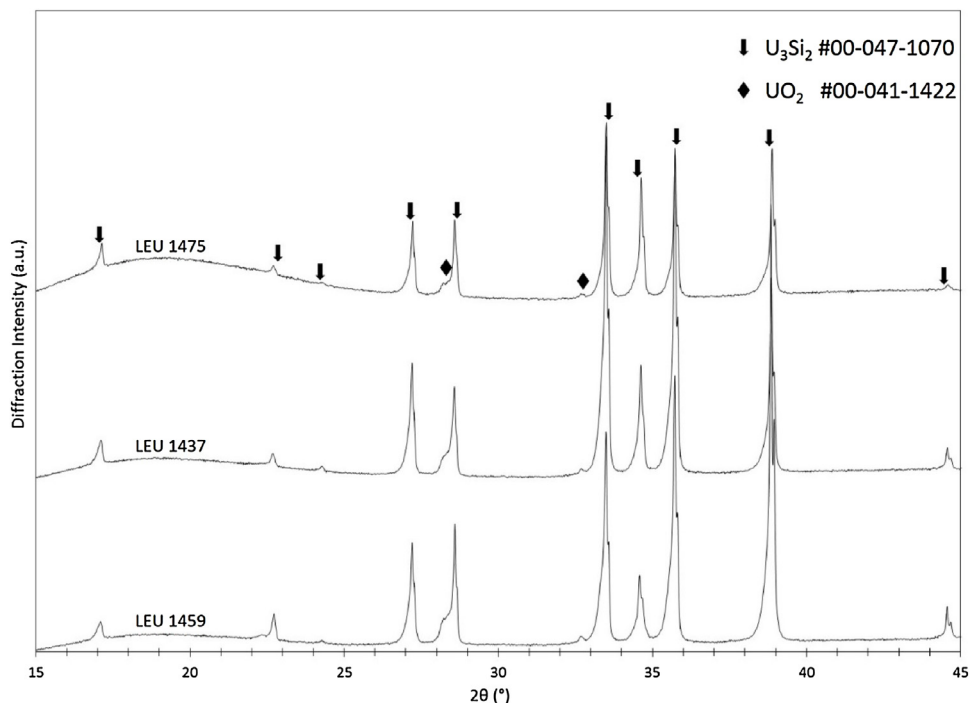


Fig. 9. XRD pattern for 3 pellet batches. In the observed data, U_3Si_2 (00-047-1070) and UO_2 (00-041-1422) peaks have been identified.

[3], the use of pure U_3Si_2 fuel pellets in an LWR is uncertain. However, this fabrication method will be used to produce U_3Si_2 fuels pellets for an upcoming lead test rod experiment with Westinghouse Electric Company, and can be utilized to fabricate material for corrosion resistant composites.

Further work is underway to develop a high uranium density fuel pellet that is corrosion resistant above 350 °C, and investigate the cause of the peak splitting and broadening seen in the XRD plots.

Disclosure statement

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