Oxidation Behavior of U-Si Compounds in Air from 25-1000°C

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Abstract

The air oxidation behavior of U_3Si_2 , USi , and U_3Si_5 is studied from room temperature to 1000°C. The onsets of breakaway oxidation for each compound are identified during synthetic air ramps to 1000°C using thermogravimetric analysis. Isothermal air oxidation tests are performed below and above the breakaway oxidation onset to discern the oxidation kinetic behavior of these candidate accident tolerant fuel forms. Uranium metal is tested in the same manner to provide a reference for the oxidation behavior. Thermogravimetric, x-ray diffraction, and scanning electron microscopy analysis are presented here along with a discussion of the oxidation behavior of these materials and the impact of the lack of oxidation resistance to their deployment as accident tolerant nuclear fuels.

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1. Introduction

Uranium silicide compounds are of current interest as candidate light water reactor (LWR) fuels due to their high thermal conductivities compared to reference uranium dioxide (UO_2). Two uranium silicide compounds, U_3Si and U_3Si_2 , contain uranium densities superior to UO_2 , and have been of the most extensive historic interest. However, the low melt point of U_3Si coupled with its understood limitations due to amorphization and swelling[1] have limited its consideration as a nuclear fuel. The majority of recent interest has been focused on U_3Si_2 due to the above properties coupled with demonstrated irradiation history, but USi and U_3Si_5 have also received initial consideration.[2]

Use of a U-Si compound as an LWR fuel constituent requires acceptable minimum performance across a number of areas. The unirradiated thermal conductivity advantages of each of the above compounds have been verified relative to UO_2 . [3–6] However, a large number of basic properties remain unknown. One fundamental behavior of high importance to many avenues of nuclear fuel performance is the susceptibility of a nuclear fuel compound to oxidation. In the absence of either thermodynamic inertness or formation of a passivating oxide layer, oxidation generally results in physical pulverization of material due to the volume change induced by chemical and structural accommodation of oxygen or oxidizing specie.[7] Oxidation may be tolerable if limited in extent, but failure of a nuclear fuel form to retain structural integrity is a clear detriment.[8]

The concern posed by oxidation of a candidate nuclear fuel depends upon the result of chemical and structural incorporation of oxygen into the native structure, the temperature range that the above evolutions are observed to occur, and the kinetics that govern the reaction. Such data is inadequate or wholly absent from the literature for the U-Si compounds of interest, preventing informed assessment of the challenge presented by deployment of U_3Si_2 , USi , or U_3Si_5 as a commercial LWR fuel. The present work was conceived to address this inadequacy and provide an initial assessment of the oxidation behavior of these compounds.

2. Background

The majority of studies that assessed the oxidation resistance of the U-Si system were performed in the 1950s and 1970s. Silicides are typically arc

melted from the pure metals, though historically little data is provided to indicate purity of the resulting materials.[9, 10] Previous efforts used primarily x-ray diffraction (XRD) to analyze the source material and the oxidation products. Some studies do not state source material purity or phase analysis and rather provide times and temperatures of disintegration of the U-Si compounds.[9] Earliest investigations concluded that U_3Si , U_3Si_2 , and USi would disintegrate in air exposure at or above 400°C in under 7.5 hr.[9] Snyder *et al* state that uranium and uranium alloys oxidize per Equation 1.[10] The power-law oxidation behavior indicates that the silicides oxidize linearly ($n=1$), parabolically ($n=.5$), etc for a given set of conditions.[10] Observing USi , U_3Si_2 , USi_2 and USi_3 oxidation in air from 150 - 400°C the authors reported the formation of a spalling oxide (U_3O_8) and an adherent oxide film (UO_2). The oxide remained adhered to the surface up to 400°C . No SiO_2 was identified in this study. The authors concluded that USi displayed linear oxidation kinetics at 150 and 300°C and USi_3 , USi_2 , and U_3Si_2 displayed parabolic kinetics up to 400°C .[10]

$$w = kt^n \tag{1}$$

Koenig completed a more focused observation of U_3Si_2 and reported that it displayed minimal oxidation at 100°C in air, parabolic oxidation kinetics at 200°C , and rapid oxidation leading to full disintegration to powder of both as-cast and heat treated forms at temperatures as low as 315°C .[11]

U_3Si became the primary uranium silicide of interest in the 1970's for nuclear fuel applications due to its higher uranium density compared to the other silicide compounds. Its corrosion behavior in oxygen, water vapor, and hydrogen containing atmospheres was studied by Feraday.[12] Feraday reports that a black, spalled oxide identified as U_3O_8 was formed during air exposures of U_3Si from 350 - 550°C at durations of 45 min to 28 h. Also reported is the formation of an adherent UO_2 layer. No UO_2 was identified in the spalled oxide. No Si or SiO_2 was identified in this study. It was suspected that an amorphous phase formed, which could not be detected by XRD.[12]

Finally, the kinetics of U_3Si oxidation were measured in a thermogravimetric analyzer (TGA) from 250 - 400°C and were reported to be linear with the formation of U_3O_8 , UO_2 and U_2O_5 in air.[13] Little is reported regarding the oxidation mechanism of the compounds investigated. One study utilizing x-ray photoelectron spectroscopy (XPS) to investigate room temperature oxidation of U-Si compounds in increasing oxygen levels states that there is

evidence of simultaneous oxidation of both U and Si, forming a combined oxide.[14] However the only reported ternary oxide USiO_4 will decompose to UO_2 and SiO_2 at 400-500°C.[12, 15]

The data pertaining to the oxidation of U-Si compounds is therefore limited and primarily entails ex-situ analysis of oxidation products of starting materials of unknown phase purity. As the majority of these preliminary studies performed thermal ramp oxidation testing in air/oxygen containing atmospheres,[9–12] this study will also use ramp oxidation testing to dynamically identify the onsets of oxidation in various U-Si compounds in comparison to U metal using TGA. U_3Si oxidation is not reported here, as it has been studied previously[9, 12, 13] and U_3Si is of limited interest as a nuclear fuel due to the aforementioned shortcomings.

3. Experimental

3.1. Material Preparation

The U-Si compounds were synthesized via arc melting of the pure metal constituents in an Ar atmosphere using a titanium getter to remove O_2 contamination. Both sintered monolithic samples and as-melted button fragments of U_3Si_5 , USi , and U_3Si_2 were oxidized in this study. The preparation methodology, resulting phase purity and microstructure of the U_3Si_5 , USi , and U_3Si_2 match those presented in previous investigations.[4–6] In addition, U metal was included as a baseline. Uranium metal used in this study (Aero-Jet Rocketdyne, Jonesborough, TN) was prepared before oxidation testing by hand grinding using SiC metallography paper and cleaned with DI water to remove surface contamination.

3.2. Thermal Analysis

The mass of each fractured or monolithic sample was measured in an Ar glove box ($\text{O}_2 < 30$ ppm and $\text{H}_2\text{O} < 0.1$ ppm) using a balance (Mettler-Toledo, Columbus, Ohio) calibrated to 0.1 mg. The sample was placed in an Al_2O_3 crucible. A commercial simultaneous thermal analyzer (STA 449 F3, Netzsch Instruments, Selb, Germany) was used to measure the mass gain during both ramp and isothermal oxidation testing. The sample in the Al_2O_3 crucible was loaded onto the STA stem/thermocouple. A thermocouple calibration was performed using Ni, Au, Ag, Al, and Zn melt point standards prior to this experimental effort and both the thermocouple correction and a baseline correction file were incorporated in each oxidation test using the Netzsch

software.[16] Percent mass gain is recorded and reported here rather than the mass gain normalized to surface area (e.g. mg/cm^2) due to the irregular shape of the button fragments. The effect of oxidizing an as melted button fragment as opposed to a sintered monolithic sample is outlined in the Discussion section of this study. This comparison was included due to the customary use of arc melting as the primary means of synthesizing novel intermetallic compounds for initial experimental characterization. Although use of powder metallurgy methods for production of regular geometries is possible and has been demonstrated for these systems,[4–6] processing and sintering to obtain high-density regular geometries represents significant effort. A more simple route to sample preparation is desirable if only initial or screening properties are necessary.

3.2.1. Ramp Oxidation Testing

Each of the materials under investigation was exposed to a synthetic air atmosphere (80% Ar, 20% O_2) at a flow rate of 100 sccm, the temperature was ramped at $5^\circ\text{C}/\text{min}$ to 1100°C furnace temperature ($T \approx 1000^\circ\text{C}$ at the sample), held for 1 hour, and then cooled at $20^\circ\text{C}/\text{min}$. The STA has the ability to control the ramp by either a furnace or sample thermocouple. Due to the strongly exothermic reaction which occurs at the onset of breakaway oxidation, controlling the thermal ramp with the sample thermocouple can lead to TGA signals which are difficult to analyze and extract the true onset temperature due to the systems compensation for a measured over temperature condition. Therefore, the furnace thermocouple was used to control the ramp rate. The ramp data presented is the sample thermocouple reading for each furnace controlled ramp. The percentage mass change is recorded for each material. The onset of breakaway oxidation is defined here as the onset of the exothermic transition in the c-DTA (calculated-Differential Thermal Analysis) curve calculated by the Proteus software Version 6.1.[16] Figure 1 depicts an example of a typical mass gain and c-DTA onset. The onset of breakaway oxidation is defined here as the intersection of the extrapolated baseline and tangent line to the exothermic peak of the reaction as identified in the c-DTA calculation.

The onset of breakaway oxidation is then used to determine the two isothermal test temperatures for each material. The first isotherm is performed 50°C below the onset to observe the oxidation kinetics for each composition at a temperature sufficiently below the point of rapid oxidation and the second at 25°C above the onset for 2 hours to characterize the oxidation

products following rapid oxidation of each material.

3.2.2. Isothermal Oxidation Testing

Each isothermal oxidation test was controlled by the sample thermocouple. The button fragments were ramped in an Ar atmosphere ($O_2 < 1\text{ppm}$) to the isothermal test temperature and held for 15 minutes for thermal equilibration, before introduction of synthetic air. The total flow rate remained consistent with the ramp testing at either 100 sccm Ar or synthetic air throughout the thermal profile. The percentage mass change is recorded for each material. The dwell time for the isothermal tests performed below the onset of breakaway oxidation was 10 h. The dwell time for the isothermal tests performed above the onset of breakaway oxidation was 2 h. Table 1 provides the temperature, dwell time, and results summary for each of the thermal analysis tests.

3.3. Post Oxidation Analysis

3.3.1. X-Ray Diffraction

XRD was employed to analyze oxidation products using a Bruker XRD (D2 Phaser, Bruker AXS, Madison, WI, USA). The resulting material from each test was homogenized using a mortar and pestle and scanned over a two theta range of $10\text{-}90^\circ$, using a 0.02° step size and 5 s dwell time.

3.3.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to characterize both the as oxidized, surface oxide formed on the monolithic samples following isothermal oxidation as well as the cross-section of the oxidized samples. A Phenom ProX SEM (Phenom World, Eindhoven, Netherlands) equipped with a backscatter detector was used for the microscopy analysis presented here. Specimens for SEM were prepared in the STA. Isothermal holds were optimized to retain the pellet integrity and produce an oxide layer thick enough to image with this technique. The samples were coated with 15 nm of Pt/Pd when necessary for imaging. The as oxidized surfaces typically did not require coating. The accelerating voltage during imaging was varied from 5-15 kV to best image the secondary phases present. Energy dispersive spectroscopy (EDS) was utilized to identify the corrosion products formed. EDS was performed with an accelerating voltage of 15kV. These results are considered qualitative as elemental standards were not used to calibrate the detector for O, Si, and U content.

4. Results

A comprehensive summary of both the mass gain due to oxidation of the U-Si compounds following thermal ramp testing and isothermal air exposure along with the phases identified in the resulting oxidation products by XRD can be found in Table 1.

4.1. Ramp Oxidation

4.1.1. Thermal Analysis

The thermograms for the ramp oxidation test for U_3Si_5 , USi , U_3Si_2 in comparison with U metal and UO_2 are displayed in Figure 2. Each of the silicide compounds initially display sharp onsets of breakaway oxidation, where UO_2 and U metal are more gradual. The terminal oxidation of each silicide is below the theoretical maximum mass gain due to oxidation (oxidation to U_3O_8 and SiO_2) indicating either unoxidized metal remains or volatilization has occurred. The onset of breakaway oxidation for each ramp as calculated using the method described previously for each compound is U_3Si_5 -185°C, USi -390°C, U_3Si_2 -384°C, UO_2 -455°C, and U-495°C. The resulting oxidation product for each material tested was a pulverized, black powder.

4.1.2. XRD

Figure 3 displays the XRD patterns for the oxidation products of each composition following the air atmosphere, thermal ramp exposures to 1100°C. Only the main peaks are identified for each reference compound. All peaks were identified for this material. U_3O_8 is the primary oxidation product identified in each scan with a small amount of either UO_2 or U_4O_9 present, which agrees well with previous studies of U and U-Si oxidation at these elevated temperatures.[10, 12, 17–24] U_3Si_5 displays evidence of either Si or U_4O_9 , however the primary peaks for these phases are convoluted. This will be discussed further in later sections.

4.2. Isothermal testing 50° C Below the Calculated Breakaway Oxidation Onset

4.2.1. Thermal Analysis

Figure 4 displays the isothermal oxidation trends at 50°C below the breakaway oxidation onset for each composition. Uranium metal reaches its theoretical maximum mass gain due to oxidation, though at a slightly delayed rate. The kinetics for the U metal oxidation are primarily linear

during isothermal testing, however the elevated temperature (445°C) could cause more rapid kinetics than have been reported previously.[17] U_3Si_5 , USi , and U_3Si_2 display more gradual oxidation than observed in the ramp testing, though it is neither linear nor parabolic as reported in previous papers.[10, 11, 13] More discussion of the kinetic behavior of the U-Si compounds oxidation below their rapid oxidation onset will follow in a later section.

4.2.2. XRD

Figure 5 displays the XRD patterns of the oxidation products for each composition following isothermal exposures in air at 50°C below the calculated onset of breakaway oxidation. Only the main peaks are identified for each reference compound. All peaks were identified for this material. U_3O_8 is the primary oxidation product identified for U metal with a small amount of either UO_2 or U_4O_9 present, which agrees well with previous studies of U oxidation.[17] In addition to UO_2 , USi_3 is also present in the USi and U_3Si_2 oxidation products below the oxidation onset temperature. U_3Si_5 ($\text{USi}_{1.67}$) remains the primary phase following oxidation. However even at this low a temperature, USi_3 and UO_2 are present following air exposure for 10 h.

4.3. Isothermal testing 25°C Above the Calculated Breakaway Oxidation onset

4.3.1. Thermal Analysis

Figure 6 displays the isothermal oxidation trends of the 25°C above the breakaway oxidation onset exposures. U metal reaches its theoretical maximum mass gain due to oxidation at a more rapid rate than either the ramp or lower temperature isothermal exposure. The kinetics for the U metal oxidation are primarily linear during isothermal testing. U_3Si_5 , USi , and U_3Si_2 display more rapid/linear oxidation than observed in the ramp testing; however none reach their theoretical maximum mass gain due to oxidation. It is assumed that oxidation would continue parabolically until the theoretical limit is reached.

4.3.2. XRD

Figure 7 displays the XRD patterns of the oxidation products of each composition following the air isothermal exposures at 25°C above the calculated onset of breakaway oxidation. Only the main peaks are identified for

each reference compound. Unidentified peaks are indicated with blue triangles. U_3O_8 is the primary oxidation product identified for U metal with a small amount of either UO_2 or U_4O_9 present, similar to the ramp testing XRD results. USi and U_3Si_2 contain significantly more U_3O_8 than other specimens tested below the onset. In addition to UO_2 , USi_3 is also present in the USi and U_3Si_2 corrosion products above the oxidation onset temperature. The primary component of the above onset temperature (135°C) air exposure of U_3Si_5 is the remaining U_3Si_5 matrix following oxidation. However even at this temperature (210°C) with limited kinetics USi_3 , U_3O_8 , and UO_2 are present following air exposure for 2 h as well as unidentified peaks at approximately 22.5, 23.2, 53.5, and 67.5° .

4.4. Microscopy Analysis of the Oxide Formation

Figure 8 displays the surface of the as oxidized monolithic samples. U_3Si_2 formed a relatively uniform surface oxide with varying textures as shown in Figure 8a. USi formed a more porous oxide as shown in Figure 8b. The porosity of the oxide layer is likely due to the low density starting monolith (80% theoretical density). Lastly, U_3Si_5 showed a relatively uniform oxide which displays both intra- and inter-granular cracking in Figure 8c. This cracking is hypothesized here as the cause of the low temperature oxidation onset of this material. U metal was also oxidized in this manner to produce a microscopy sample. The U_3O_8 layer spalled during testing, leaving only a thin surface layer of UO_2 . It is not displayed here.

Figure 9 displays the cross-sectional microscopy of these oxidized materials. EDS was performed on each of these samples. The granular oxide phase centered in Figure 9a is identified as U_3O_8 using EDS, where the more uniform phase is hypothesized to be UO_2 . The EDS spectra is reported in Figure 10. The ratio of weight percents calculated by Phenom EDS software for O/U in Spots 2 and 3 correspond to 0.087 and .126 respectively. This result is in agreement with previous studies which report the formation of an adherent UO_2 layer and spalling U_3O_8 powder. Also visible in Figure 9a are subsurface oxidation products likely due to cracking in the sample as a result of the oxide growth.

Unlike U_3Si_2 , both USi and U_3Si_5 display more silicide phase segregation following oxidation, as displayed in Figure 9b and c respectively. A Si-rich phase is identified in the dark inner region of the oxidized U_3Si_5 sample, indicating that the U is oxidizing, which segregates Si into the bulk of the sample.

5. Discussion

5.1. Sensitivity of the Test Technique to Initial Sample Form

Arc melted button fragments were used for the majority of the oxidation testing presented here. This is a convenient way to test novel compounds, though these sample types are prone to cracking and can lack homogenization. To assess whether this is a sound technique for sample preparation capable of attaining reliable and reproducible results, a monolithic, sintered pellet of U_3Si_5 (95% theoretical density) was oxidized using the same ramp parameters. Figure 11 displays the trends for both button fragment and pellet oxidation. The onsets were within 50°C , though more gradual in the case of the pellet. The button fragment proved to be the more conservative (lower T onset) for all silicides tested, and was within 50°C of the pellet onset for USi and U_3Si_2 as well.

Also displayed in Figure 11 is the sensitivity of this testing technique to ramp rate. U_3Si_2 button fragments were ramped at 3 different rates to determine the effect to the onset temperature. The more rapid ramp rates lead to a slightly delayed onset, with less rapid oxidation following the onset of breakaway oxidation.

Due to the sensitivities of this technique, the onsets of each composition should be considered approximate and not absolute. However, no delay of more than 100°C was observed by parameter manipulation in air, and it is sufficient to say that these materials will rapidly oxidize at temperatures above 400°C in air.

5.2. Kinetics of oxidation below the onset of breakaway oxidation temperature

The authors concur with previous studies of uranium silicide oxidation that UO_2 is the first oxide to form on the surface.[12, 10] The subsequent oxidation of UO_2 drives the oxidation kinetics presented here. For oxidation above the calculated onset, the oxidation front is assumed to progress linearly until the majority of U is oxidized. Oxidation must either terminate or progress very slowly as no silicide tested here reached its theoretical maximum of mass gain due to oxidation, however no Si or SiO_2 was definitively identified.

Each silicide oxidation trend below the calculated onset fit a logistic (sigmoidal) trend, rather than the linear and parabolic kinetics presented previously.[10–13] UO_2 is documented to oxidize sigmoidally below 400°C .[18,

17, 25, 26] The sigmoidal behavior in UO_2 oxidation in air is linked to the two step process which terminates at U_3O_8 presented below.[17, 20]

Each of the 50°C below-onset experiments was performed below 400°C, and the sigmoidal behavior depicted in Figure 12 could purely be attributed to the oxidation kinetics of UO_2 in this temperature range.

Additionally, the authors note that these materials are prone to cracking. U_3Si_5 is particularly prone to cracking upon cooling during the arc melting process due to a phase transition at 450°C.[5] Oxidation of the exposed surface area along cracks that propagate into the bulk of the silicide is hypothesized here to be the leading cause for the early breakaway oxidation onset in U_3Si_5 . It is possible that alloying methods that improve the toughness of these materials may result in increased resistance to oxidation even if the additives do not contribute to the oxidation mechanism itself.

5.3. Oxide phases formed during testing

The change in Gibbs free energies for the reactions forming UO_2 and SiO_2 from the pure metals as well as reactions for oxidation of U_3Si_2 at 400°C normalized per mol O_2 are provided in Equations 3-7.[27, 28]

Thermodynamically, UO_2 is the more stable oxide under these conditions when compared with SiO_2 . The experimental work presented here indicates that UO_2 preferentially forms, thereby inhibiting the formation of a passivating SiO_2 layer for each silicide compound. The ΔG for the formation of UO_2 is more negative than SiO_2 for the entire temperature range tested here. Uranium is known to oxidize first to UO_2 , then UO_2 subsequently oxidizes to $\text{U}_3\text{O}_7/\text{U}_4\text{O}_9$ and terminates at U_3O_8 in air below 400°C.[17, 20] Therefore,

it is not surprising that U_3O_8 is the primary oxidation product for each of these materials following the high temperature ramps. The secondary phase in the ramp data for the silicides is identified as primarily UO_2 . An XRD pattern centered around the primary indexed U oxide peaks is shown in Figure 13. U_3Si_5 displays a splitting of peaks, indicative of two secondary phases present. However, U_4O_9 , U_3O_7 , UO_2 , and Si metal each have primary peaks in this narrow range. These phases are possible following oxidation of these materials, so additional characterization is necessary to definitively assign one over others.

While Equations 3 and 6 show that oxidation of uranium is thermodynamically preferred to oxidation of silicon in O_2 atmospheres for all temperatures studied, SiO_2 formation remains probable from a thermodynamic standpoint under all conditions evaluated here. Characterization of oxidized U-Si compounds as performed here did not produce evidence of SiO_2 . It should also be noted that in the oxidation of U_3Si_2 in O_2 , the oxidation of only U and not Si is thermodynamically more stable than SiO_2 formation by itself or simultaneously with UO_2 formation. Experimentally this work provides evidence of a Si-rich phase in partially oxidized U-Si compounds (See Figure 9), characteristic of Si metal being rejected into the bulk of the sample while UO_2 is formed during oxidation. These analyses do not preclude its presence at levels and distributions either too fine to be detected using SEM, or as an amorphous phase undetectable through XRD. The results of this work do show that, regardless of whether small amounts of SiO_2 are present, it neither prevents breakaway oxidation nor pellet pulverization. The preferential formation of UO_2 displayed in Equations 4,5, and 7 for U_3Si_2 oxidation is also the case for USi and U_3Si_5 .

USi and U_3Si_2 display similar onsets of oxidation. U_3Si_5 displays a particularly low onset of breakaway oxidation, likely due to oxidation along microcracks formed during cooling of the arc melt. This cracking in U_3Si_5 is not unique to the as arc melted samples tested here; it has also been observed in pellets prepared by powder metallurgical methods.[5] The 450°C phase transition U_3Si_5 encounters is the likely source of the microcracking, and therefore, this fuel candidate presents significant challenges to deployment and storage.

6. Conclusions

The oxidation kinetics of U_3Si_2 , USi , and U_3Si_5 both below and above the break away oxidation onset follow the well defined oxidation dynamics of U oxidation. U_3Si_2 and USi display later onsets of breakaway oxidation compared to U_3Si_5 . U_3Si_5 exhibits an early breakaway oxidation onset (185°C) which the authors attribute to oxidation progression through the intra- and inter-granular cracks. The results of this study demonstrate that preferential oxidation of U will dominate the response of the U-Si compounds investigated under oxidizing conditions. Oxidation of Si will not occur before the formation of UO_2 . This reaction leads to pulverization of all compounds tested.

U_3Si_2 and USi suffer breakaway oxidation and pulverization at a temperature comparable to UO_2 during air oxidation. However, highly oxidizing atmospheres are not representative of either reactor operation or design basis accident conditions. Further investigations are necessary to assess U-Si fuel behavior under representative LWR coolant conditions, steam, and steam-hydrogen atmospheres to provide additional insights into the candidacy of these compounds as LWR fuels. Si performance in steam and water containing atmospheres is necessary; though the air oxidation results presented in this study indicate that U-Si fuel forms could degrade under these conditions.

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Table 1: Summary of oxidation results

Material	Test Type	Temperature (°C)	Dwell time (h)	Terminal oxidation (%)	Calculated Onset (°C)	Primary Phases & Secondary Phases Identified via XRD
U ₃ Si ₅	Ramp	1100	1	24 (33*)	185	U ₃ O ₈ , U ₄ O ₉ , UO ₂ , Si
U ₃ Si ₅	Isotherm	135	10	2	N/A	U ₃ Si ₅ , USi ₃ , UO ₂ , U ₃ O ₈
U ₃ Si ₅	Isotherm	210	2	2	N/A	U ₃ Si ₅ , Si, U ₃ O ₈ UO ₂ , USi ₃ , U ₄ O ₉
USi	Ramp	1100	1	23 (28*)	390	U ₃ O ₈ , UO ₂
USi	Isotherm	340	10	17	N/A	U ₃ O ₈ , USi ₃ , UO ₂
USi	Isotherm	415	2	18	N/A	U ₃ O ₈ , USi ₃ , UO ₂
U ₃ Si ₂	Ramp	1100	1	21 (25*)	384	U ₃ O ₈ , UO ₂
U ₃ Si ₂	Isotherm	350	10	16	N/A	UO ₂ , USi ₃ , U ₃ O ₈
U ₃ Si ₂	Isotherm	425	2	18	N/A	U ₃ O ₈ , USi ₃ , UO ₂
UO ₂	Ramp	1100	1	4 (4*)	455	U ₃ O ₈
U metal	Ramp	1100	1	18 (18*)	495	U ₃ O ₈ , UO ₂
U metal	Isotherm	445	10	18	N/A	U ₃ O ₈ , UO ₂
U metal	Isotherm	520	2	18	N/A	U ₃ O ₈ , UO ₂

*Theoretical maximum mass gain due to oxidation, assuming U₃O₈ and SiO₂ are the terminal oxidation product.

Figure 1: U_3Si_2 breakaway oxidation onset calculation using the extrapolated onset of the c-DTA curve as calculated by the Netzsch Proteus software.

Figure 2: Thermograms of the synthetic air, 5°C/min ramp oxidation of U-Si compositions, U metal, and UO₂.

Figure 3: XRD patterns of the oxidation products following ramp oxidation to 1100°C.

Figure 4: Isothermal oxidation of U-Si compositions and reference U metal in synthetic air at 50°C below the calculated onset of breakaway oxidation for each composition.

Figure 5: XRD patterns of the oxidation products of U-Si compounds and U metal following 10 hour isothermal air oxidation at 50°C below the calculated onset of breakaway oxidation.

Figure 6: Isothermal oxidation of U-Si compositions and reference U metal in synthetic air at 25°C above the calculated onset of breakaway oxidation for each composition.

Figure 7: XRD patterns of the oxidation products of U-Si compounds and U metal following isothermal air oxidation at 25°C above the calculated onset of breakaway oxidation. The blue circles indicate unidentified peaks in the diffraction pattern.

Figure 8: SEM backscatter micrographs of the as formed surface oxide of a) U_3Si_2 at 300°C, b) USi at 250°C, and c) U_3Si_5 at 275°C

Figure 9: SEM backscatter micrographs of the cross section of a) U_3Si_2 oxidized at 275°C, b) USi oxidized at 250°C, and c) U_3Si_5 oxidized at 317°C. The USi and U_3Si_5 samples did not retain their structure; imaged is a cross section of the remaining oxidation product.

Figure 10: Energy dispersive spectroscopy spectra for the points identified in the U_3Si_2 cross section presented in Figure 9a.

Figure 11: Thermograms depicting the sensitivity of these onset measurements to the sample geometry/form and ramp rate.

Figure 12: Oxidation curve for the 50°C below the breakaway oxidation onset isotherm of U_3Si_2 with a logistic function fit. Also plotted is the 25°C above the breakaway oxidation onset isothermal trend.

Figure 13: XRD patterns for oxidation products of U_xSi_y following a thermal ramp to 1000°C in synthetic air where the data is centered around the primary oxide phases, indicating that Si and U_4O_9 are challenging to discriminate using this method.