The Effect of Aluminum Additions on the Oxidation Resistance of U_3Si_2

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Abstract

The effect of aluminum additions to U_3Si_2 is investigated as a means to improve the oxidation resistance of this nuclear fuel form. Four U-Si-Al compositions have been synthesized and characterized using scanning electron microscopy, energy dispersive spectroscopy, and x-ray diffraction. The onsets of breakaway oxidation are identified in air thermal ramp tests using thermogravimetric analysis. The final oxidation products following 1000°C air exposure are identified using x-ray diffraction and compared to those of UO_2 and U metal oxidized in the same manner. Thermogravimetric data acquired in this study indicates that increasing amounts of Al in U_3Si_2 further delays the onset of breakaway oxidation, providing enhanced oxidation resistance in air. Al_2O_3 formation on $\text{U}_3\text{Al}_2\text{Si}_3$ is observed following a heat treatment performed at 500 °C in air, demonstrating the potential of Al additions to improve the oxidation resistance of U_3Si_2 .

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1. Introduction

The U-Si system presents multiple candidate nuclear fuel compounds, including U_3Si , U_3Si_2 , USi , and U_3Si_5 . All provide increased thermal conductivity compared to conventional oxide fuel.[1–4] U_3Si_2 is receiving the most attention for deployment as a drop-in fuel form to improve the performance of commercial light water reactors due primarily to its increased U density compared to reference UO_2 , improved thermal conductivity, and limited but demonstrated record of satisfactory service as a nuclear fuel. However, it is susceptible to oxidation. Existing data suggests that U_3Si_2 would be, at best, neutral to UO_2 and provide no additional accident tolerance with respect to oxidation resistance.[5–8]

Small additions of alloying elements can increase the oxidation tolerance of many materials. For example, Cr and Al are often added to steels to retard degradation in oxidizing atmospheres by forming oxide scales that act as diffusion barriers to continued oxidation. UO_2 formation is thermodynamically favored over SiO_2 in U_3Si_2 and leads to the eventual pulverization of the compound.[8] An alloying element which would oxidize preferentially to U and yield a passivating oxide could delay UO_2 formation and potentially delay the onset of breakaway oxidation which inevitably leads to rapid pulverization.

An Ellingham Diagram, shown in Figure 1, was constructed to elucidate potential alloying additions to the U-Si systems that would preferentially oxidize relative to U.[9] The change in Gibbs Free Energy (ΔG) for Al to form Al_2O_3 is more negative than that for U to form UO_2 below 600°C . Given the well known ability of Al_2O_3 to act as a passivating oxide such that base material remains shielded from the oxidizing specie, Al was chosen as an initial elemental addition for study of its effect on oxidation of U_3Si_2 . This work presents the results of initial investigations of the ability of dilute Al additions to forestall breakaway oxidation in U_3Si_2 .

2. Background

U-Si-Al fuel forms have been explored in the past. The primary applications were dispersion/plate fuel concepts, in which U_3Si , U_3Si_2 , and/or UAl_2 were distributed in an Al plate.[10, 11] Through a series of experimental efforts which included high temperature annealing, oxidation, and diffusion couple tests, it was found that non-equilibrium compositions of U-Si-Al (e.g. $\text{U}_3(\text{Si},\text{Al})$) resulted in multi-phase composites after high temperature exposure.[12, 13] However, some reports indicate that these phases swelled less than U_3Si under irradiation and displayed little to no cracking during post irradiation examination.[14, 15] In addition, the UAl_2 phase was reported to more readily accommodate fission product gases such as Kr and Xe, making it less prone to fission gas swelling when compared to non-equilibrium composition U_3AlSi . [16] Boiling water corrosion tests were performed on a single non-equilibrium composition. The researchers exposed the candidate plate fuel to boiling water for several hours and then monitored the water bath for increased radioactivity following exposure. No increased activity was detected in the water bath following the experiment; oxidation behavior was not investigated.[10]

The ternary phase diagram for the U-Si-Al system has been investigated to limited extent.[17] The $\text{U}_3\text{Al}_2\text{Si}_3$ equilibrium compound with a U density of 7.45 g/cm^3 provides a similar fissile density to U_3Si_5 (7.57 g/cm^3) and U_3O_8 (7.28 g/cm^3). Referring to the published phase diagram reproduced in Figure 2, the compound labeled $\text{U}_3\text{Al}_2\text{Si}_3$ does not correspond to such a composition. Rather, this composition should be U_2AlSi_2 . $\text{U}_3\text{Al}_2\text{Si}_3$ is calculated to be on the line between U_2AlSi_2 and UAlSi . This discrepancy in the phase diagram makes it difficult to discern if $\text{U}_3\text{Al}_2\text{Si}_3$ is truly an equilibrium compound. Rogi *et al* do not address this inconsistency in the study used to assemble this part of the phase diagram.[18] Nevertheless, $\text{U}_3\text{Al}_2\text{Si}_3$ (i.e. a composition corresponding to $\text{U}_{.375}\text{Al}_{.25}\text{Si}_{.375}$) is studied here as the upper bound for Al additions to U_3Si_2 with the goal of forming Al_2O_3 to provide a passive oxide layer while retaining a U density amenable to service as a nuclear reactor fuel.

The maximum solubility of Al (1.8 at% at 900°C) within a U-Si matrix was chosen to set the lower limit of Al addition.[17] Therefore the low-doped Al composition investigated here incorporates 1.8 at% Al and is nominally

⁶⁵ $\text{U}_3\text{Al}_{0.09}\text{Si}_{1.91}$.¹ Two intermediate compositions, $\text{U}_3\text{Si}_2\text{Al}_{1.25}$ and $\text{U}_3\text{Si}_2\text{Al}_{0.75}$,
⁶⁶ are also synthesized to conclude the present study.

¹Each composition is normalized to three moles U for consistency, however these should not necessarily be interpreted as single phase structures.

3. Experimental

3.1. Material Preparation

Each composition was synthesized by arc melting of the pure metals. A tri-arc furnace (Centorr Vacuum Industries, Nashua, NH, USA) was used. The starting partial pressure of O_2 (pO_2) for each melt was $<10^{-12}$ parts per million (ppm) as verified by the O_2 sensors located on both the inlet and exhaust of the system. An internal Ti getter, maintained in the molten state during synthesis of all compositions, reduced the pO_2 to $<10^{-19}$ ppm on the exhaust of the arc melter. $U_3Al_2Si_3$ and $U_3Si_2 + 1.8 \text{ at}\%Al$ were synthesized via arc melting uranium metal discs (approx. 99.5% pure) that were ground to remove surface oxide and weighed. Silicon metal pieces (Cerac 99.999% pure, 3-6 mm pieces) and aluminum wire (Alfa Aesar 99.999% pure, 1 mm diameter) were sectioned and weighed to match the projected wt% necessary to synthesize the target compositions according to the U weight in each button. For each composition investigated here, the arc melted button was melted and flipped five times to homogenize the chemical composition of the melt.

In order to minimize oxide contamination during synthesis of the $U_3Si_2Al_{0.75}$ and $U_3Si_2Al_{1.25}$ compositions, the arc melter was placed in an Ar glove box with pO_2 and $pH_2O < 0.1$ ppm. The same Si and Al stocks were used in this arc melt, and U metal rods (99.9+% purity, AeroJet Rocketdyne, Jonesborough, TN, USA) were ground to remove surface oxides. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis performed by MCL Inc. revealed no contamination by rare earth or transition metals greater than either the detection limits or $10 \mu\text{g/g}$.

Material loss during arc melting can cause compositional error. One can determine the likely cause of this mass loss is either splintering of the button on cooling or volatilization of Al or Si. Table 1 reports the target compositions along with the resulting stoichiometries assuming all of the mass loss is due to Al volatilization, which is the most conservative estimate of compositional error. This uncertainty should not affect the results of assessing relative increases in Al content to the oxidation resistance of U_3Si_2 . However, when arc melting equilibrium compositions, either additional Al and Si should be included prior to melt to compensate for the anticipated loss, or a melt process should be devised to avoid volatilization. Si volatilization has been observed in the synthesis of U-Si compounds in the past where additional Si was incorporated in the melt.[1–4]

104 3.2. Compositional Analysis

105 X-ray diffraction (XRD) and scanning electron microscopy (SEM) anal-
106 ysis were used to determine compositional purity and phase identification
107 for each of the as-melted compositions. No additional solutionization heat
108 treatments or metallurgical processing were employed for any of these com-
109 positions prior to analysis and measurement. The samples used in both the
110 SEM characterization and oxidation testing were fracture pieces from the as
111 melted buttons, and the material used for XRD analysis was ground from
112 button fragments.

113 XRD was employed to analyze the ground, as-melted buttons using a
114 Bruker XRD (D2 Phaser, Bruker AXS, Madison, WI, USA). The samples
115 were prepared in an Ar glove box and encapsulated to avoid oxidation. A
116 two theta range of 10-90°, 0.01° step size, and 2 s dwell time were used for
117 all samples. XRD analysis of the resulting oxides following oxidation testing
118 used the same parameters.

119 A Phenom ProX SEM (Phenom-World, Phoenix, Arizona, USA) equipped
120 with a backscatter electron detector and energy dispersive spectrometer (EDS)
121 was used to image and analyze the as melted compositions. Three button
122 fragments were potted in epoxy and ground/polished to 3 μm using a com-
123 bination of SiC grinding discs and diamond suspension for each as-melted
124 composition. A backscatter detector was used to image the phase contrast
125 in each sample.

126 3.3. Thermogravimetric Analysis

127 The mass of each fracture sample was measured in an Ar glove box us-
128 ing a balance (Mettler-Toledo, Columbus, Ohio) calibrated to ± 0.1 mg. The
129 sample was placed in an Al_2O_3 crucible. A commercial simultaneous ther-
130 mal analyzer (STA 449 F3, Netzsch Instruments, Selb, Germany) was used
131 to measure the mass gain during thermal ramp oxidation tests. A thermo-
132 couple calibration was performed using Ni, Au, Ag, Al, and Zn melt point
133 standards (6.223.5-91.3, Netzsch, Selb, Germany) prior to this experimental
134 effort, and both the thermocouple correction and a baseline correction file
135 were incorporated in each oxidation test using the Netzsch software. The
136 compositions were ramped in a synthetic air atmosphere (80% Ar, 20% O_2)
137 at 5 $^\circ\text{C}/\text{min}$ to 1100 $^\circ\text{C}$, held for 15 min, and then cooled at 20 $^\circ\text{C}/\text{min}$ in a
138 manner used previously to study oxidation of U-Si compounds.[8]

139 4. Results and Discussion

140 4.1. Compositional Analysis

141 The XRD diffraction pattern for the ground, as-melted $\text{U}_3\text{Si}_2 + 1.8\text{at}\%\text{Al}$
142 button is displayed in Figure 3. The collected XRD pattern is in good agree-
143 ment with the reference U_3Si_2 pattern, however there are discrepancies that
144 were not resolved during phase analysis when compared to other silicide and
145 aluminide phases. The peak heights at higher angle, $2\theta > 50^\circ$, are inconsis-
146 tent with the reference pattern relative intensities. This could be due to a
147 secondary phase formed on cooling, which was identified in SEM analysis, or
148 lattice augmentations caused by the aluminum addition.

149 Multiple phases were identified in the $\text{U}_3\text{Si}_2\text{Al}_{0.75}$ composition, which is to
150 be expected for this non-equilibrium composition. It is composed primarily
151 of U_3Si_2 with some Al containing phases as displayed in Figure 3.

152 $\text{U}_3\text{Si}_2\text{Al}_{1.25}$ was also identified as multiphase, which is again to be ex-
153 pected for this non-equilibrium composition. It is composed primarily of
154 U_3Si_2 and $\text{U}_3\text{Al}_2\text{Si}_3$ with some unidentified phase present as displayed in
155 Figure 3.

156 Lastly, Figure 3 displays the x-ray diffraction pattern for the as melted
157 $\text{U}_3\text{Al}_2\text{Si}_3$ composition. Though there is good agreement with the reference
158 pattern for $\text{U}_3\text{Al}_2\text{Si}_3$, there are also a number of peaks which match an Al-
159 rich, Si-poor phase, $\text{U}(\text{Si}_{0.44}\text{Al}_{1.56})$. In addition there are three small, uniden-
160 tified peaks at $2\theta = 27, 30$, and 35° .

161 Characteristic SEM micrographs of these four compositions are displayed
162 in Figure 4. The secondary phases which have segregated in each of these
163 compositions may have done so upon cooling during the arc melting process.
164 While each of these compositions have multiple phases, the $\text{U}_3\text{Al}_2\text{Si}_3$ compo-
165 sition is comprised of primarily two phases in agreement with the XRD data
166 displayed in Figure 3. $\text{U}_3\text{Si}_2 + 1.8\text{at}\%\text{Al}$ appears mostly single phase in
167 Figure 4, with only a small amount of phase segregation. The two secondary
168 phases identified were only found together during SEM analysis. These ap-
169 peared as a lighter and darker phase, the darker being an Al-rich and the
170 lighter a U-rich phase. This is also characteristic of phase segregation dur-
171 ing cooling. The two intermediate compositions have at least three phases
172 present as observed in SEM analysis, and while two phases contain all three
173 of the elemental constituents per the XRD analysis, it is likely that the mi-
174 nor phases are U-Si or U-Al binary compounds. EDS analysis was able to
175 identify Si and Al-rich areas, however no area was found totally devoid of all

three elements; this is thought to be due to the interaction volume during EDS analysis.

A solutionization heat treatment could prove beneficial in homogenizing two of these compositions from multiphase to single phase. It is reported that 1.8at% Al should be soluble in U_3Si_2 at 900°C, though it may have segregated on cooling. Also it is reported that $U_3Al_2Si_3$ is an equilibrium compound although uncertainty exists as discussed earlier. Therefore, using a heat treatment to allow homogenization of the secondary phases present in these two samples could result in a single phase material, where the rapid and nonuniform (the outer portions of the button tend to cool first) cooling of the arc melting process caused segregation. Phase segregation should not affect the results of the present study which investigates the relative oxidation resistance of U-Si-Al compositions with increasing Al content.

4.2. Thermogravimetric Analysis

Table 1 presents the calculated onsets of breakaway oxidation as identified by the Netzsch Proteus software and the terminal oxidation, which is the percentage mass gain measured following oxidation.[8] Figure 5 displays the thermograms used to calculate the onsets of breakaway oxidation. This data is normalized to the theoretical mass gain expected for each composition assuming U_3O_8 , SiO_2 , and Al_2O_3 are the final oxidation products. The shoulder present in the TG data for U_3Si_2 and $U_3Si_2 + 1/8at\%$ Al is characteristic of U-Si oxidation.[8] The terminal oxidation mass gain of each compositions falls short of the theoretical maximum for all U-Si-Al compositions tested here, though a plateau is reached for each sample. It should be noted that U_3Si_2 without Al addition suffers breakaway oxidation and pulverization at a temperature comparable to UO_2 during air oxidation. However these screening test atmospheres are not representative of either reactor operation or design basis accident conditions. Steam and autoclave testing are still necessary to understand how they will behave in an environment more characteristic of normal operating occurrences (e.g. 'leaker') or an off-normal reactor scenario.

Figure 5 and Table 1 indicate that the onset of breakaway oxidation is further delayed by increasing Al content. However, given the multiphase nature of the intermediate compositions, $U_3Si_2Al_{0.75/1.25}$, it is possible to capture more of one phase in a TG sample than another. The delayed onsets reported here were reproduced during testing within the error of this

212 technique, which has been shown to be minimally sensitive to ramp rate and
213 sample geometry.[8]

214 4.3. X-Ray Diffraction Analysis of Oxidation products

215 X-ray diffraction patterns for the oxide products formed during thermal
216 ramp oxidation of these compositions compared to U metal are displayed in
217 Figure 6. The primary phase present is U_3O_8 with a small amount of UO_2 .
218 This is typical of air oxidation of U-Si compounds.[8] Since U metal accounts
219 for approximately 90% of the weight percent, it is expected that U_3O_8 would
220 dominate the final oxidation product of these compositions. Si and Al oxida-
221 tion products were not identified in this analysis; however the lack of Si/ SiO_2
222 appears to be characteristic of these types of oxidation test.[8, 7] Al_2O_3 was
223 identified in cross sectional SEM analysis of a partially oxidized $\text{U}_3\text{Al}_2\text{Si}_3$
224 sample, indicating that XRD is not an exhaustive method of analysis to
225 identify the products formed during oxidation of these materials.

226 4.4. Scanning Electron Microscopy analysis of Oxide formation

227 The cross sectioned and polished surface of the as-melted $\text{U}_3\text{Al}_2\text{Si}_3$ com-
228 position is displayed in the left image of Figure 7. This composition proved
229 to be multi-phased, primarily $\text{U}_3\text{Al}_2\text{Si}_3$ with some Al and Si containing sec-
230 ondary phase. The oxidized surface of this sample is displayed in the right
231 image of Figure 7 following a 500°C isothermal oxidation heat treatment.

232 The sample was potted in epoxy, cross sectioned, and polished. Dur-
233 ing SEM investigation, EDS was utilized as a qualitative elemental analysis
234 method; no elemental standards were employed, and therefore the result-
235 ing elemental analysis cannot be quantified. It was observed that only Al
236 and O are located on the outer surface and along cracks, which propagated
237 throughout the button fragment. The oxide identified is likely Al_2O_3 . The
238 SEM analysis is displayed along with an EDS map in Figure 8. The Al_2O_3
239 layer appears to be fairly uniform in thickness throughout the sample edges
240 and cracked portions. U is not mapped here since it dominates throughout
241 the EDS map.

242 The presence of Al along the cracks of the button fragment demonstrates
243 that Al_2O_3 has indeed formed preferentially to UO_2 . In previous investiga-
244 tions, UO_2 was identified along the edges and cracks of button fragments.
245 UO_2 is known to be a non-passivating oxide, readily allowing the diffusion of
246 oxygen through the oxide layer, resulting in further oxidation of the material

247 and eventual pulverization.[8] It is likely that the preferential formation of
248 Al_2O_3 is the cause of the delay in the onset of breakaway oxidation.

249 The heat treatment used to form the Al_2O_3 layer was repeated and the
250 isothermal hold at 500°C was continued until the sample reached its ter-
251 minal oxidation. The resulting material was a pulverized oxide. Therefore
252 the layer formed under these conditions is not fully passivating, however the
253 preferential formation of Al_2O_3 indicates that engineering a protective layer
254 is feasible. It is possible that Al_2O_3 is not coarsening at 500°C , and a higher
255 temperature oxidation treatment is necessary to produce a passivating sur-
256 face layer on the U-Si-Al composition.

257 5. Conclusions

258 The effect of Al additions on oxidation resistance of U_3Si_2 has been inves-
259 tigated. Thermogravimetric analysis has indicated that increasing amounts
260 of Al in U_3Si_2 further delays the onset of breakaway oxidation in air. Scanning
261 electron microscopy paired with energy dispersive spectroscopy has revealed
262 that an Al_2O_3 layer forms at 500°C . Though this layer was not found to be
263 passivating in this study, it demonstrates the potential for this approach to
264 increase the oxidation resistance of U_3Si_2 . Further work is necessary to assess
265 if a passivating layer can be formed on these materials.

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Table 1: Summary of oxidation results

Sample	Composition assuming Al volatilization	Onset of breakaway oxidation °C	Terminal oxidation % Mass Gain
U metal		495	18 (18*)
UO ₂		455	4(4*)
U ₃ Si ₂		384	21(25*)
U ₃ Si _{1.91} Al _{0.09}	U ₃ Si _{1.92} Al _{0.12} **	415	21(25*)
U ₃ Si ₂ Al _{0.75}	U ₃ Si ₂ Al _{0.46}	466	21(26*)
U ₃ Si ₂ Al _{1.25}	U ₃ Si ₂ Al _{1.17}	523	23(27*)
U ₃ Al ₂ Si ₃	U ₃ Al ₂ Si ₃	670	25(32*)

340 *Theoretical % mass gain assuming final oxidation products are U₃O₈,
341 SiO₂ and Al₂O₃

342 **Additional Al an Si were incorporated in the initial charge; therefore
343 accounting for the mass loss during arc melting results in an excess of Al in
344 this composition.

Figure 1: Ellingham diagram from relevant oxides for U-Si oxidation.

Figure 2: Phase diagram for the U-Si-Al system[17, 18] with the compositions investigated here and labeled along with the error associated with the arc melting process.

Figure 3: X-ray diffraction patterns of the as melted U-Si-Al composition. All but the $\text{U}_3\text{Si}_2 + 1.8\text{at.\% Al}$ is multiphase.[19–21]

Figure 4: Cross-section backscatter SEM micrographs for the as melted U-Si-Al compositions.

Figure 5: Thermogravimetric data plotted as the fraction of theoretical maximum mass gain for U metal, UO₂, U₃Si₂, U₃Si₂+ 1.8at% Al, U₃Si₂Al_{0.75}, U₃Si₂Al_{1.25}, and U₃Al₂Si₃ during synthetic air ramp oxidation testing showing a delay in the breakaway oxidation onset with the inclusion of Al.

Figure 6: XRD pattern for the oxide products formed during ramp oxidation testing for U metal, U_3Si_2 ,^[8] $U_3Si_2Al_{0.75}$, $U_3Si_2Al_{1.25}$,²¹ and $U_3Al_2Si_3$.^[22, 23]

Figure 7: Micrographs of the as-melted $\text{U}_3\text{Al}_2\text{Si}_3$, equilibrium composition (left) and the oxidized surface (right) following 500°C exposure to synthetic air

Figure 8: Cross-sectional micrograph of the oxidized $\text{U}_3\text{Al}_2\text{Si}_3$, equilibrium composition (left) and EDS maps of the selected area (middle and right) which display Al_2O_3 formation along the edges of the sample and along cracks