

Appendix 11:

Oxidation Tests on U_3Si_2 , UN and UO_2 Pellets in
Synthetic Air

Overview of Properties and Performance of Uranium-Silicide Compounds for Light Water Reactor Applications

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INTRODUCTION

The uranium-silicon binary system possesses a range of compounds that have been historically investigated and utilized to a limited extent as nuclear reactor fuels. Of the multiple compounds, U_3Si and U_3Si_2 are most familiar; their high uranium densities have made them an intriguing choice for incorporation into composite plate fuels in research reactors and other low power core redesigns where retained neutronic performance was desired at lower enrichments [1]. This increased uranium density compared with uranium dioxide (UO_2) has made them attractive to a new generation of nuclear fuels research driven by the renewed push for accident-tolerant light water reactor (LWR) fuels. A higher uranium density may motivate incorporation of U-Si phases into composite fuels that utilize secondary phases with the goal of increasing coping time during a cladding breach before fission products and/or actinides are released. Additionally, development of fuels containing higher uranium densities than those of reference UO_2 could facilitate utilization of alternative cladding materials that offer improved high temperature performance than zirconium alloys but incur neutronic penalties.

Surveys of the existing property databases of candidate U-Si compounds revealed that very little is known of even the more common uranium silicides with respect to their thermophysical and thermodynamic performance. The absence of such data challenges development of potential fuel forms or modeling of reactor operation under hypothesized core loadings that include U-Si fuel forms. Furthermore, consideration of potential off-normal scenarios requires even more specific knowledge of the thermodynamic stability and reaction kinetics of U-Si compounds when they are exposed to diverse stimuli such as oxidizing environments or prolonged contact with cladding materials. The literature is largely devoid of any information on these critical details necessary to hypothesize the performance of U-Si compounds as LWR fuels.

An experimental campaign was undertaken at Los Alamos National Laboratory in 2012 in order to provide this data and facilitate evaluation of the potential of U-Si compounds for LWR applications. In the case of the uranium-rich U_3Si and U_3Si_2 compounds that have seen more extensive service as research reactor fuels, this work

focused on a more critical evaluation of their thermophysical properties to temperatures near their melting points. These compounds have seen limited characterization at temperatures low relative to those anticipated of an LWR fuel, but even here appreciable scatter is present [2]. Lesser-studied compounds such as USi and U_3Si_5 have received virtually no attention from previous researchers regarding their thermal conductivity, heat capacity, and thermal expansion as a function of temperature. Accurate knowledge of these properties is essential to modeling of heat transport in reactor systems.

The renewed focus on accident tolerance has also emphasized consideration of the off-normal performance of materials in nuclear reactor systems. The dominant focus has been understanding evolutions expected during a loss of coolant accident (LOCA). During a breach of cladding (brought about by a LOCA, cladding defect introduced during manufacturing, or failure during long term storage), the fuel will be exposed to high temperatures and water vapor. The potential availability of oxygen, hydrogen, or nitrogen may also dictate behavior. Aside from low temperature U_3Si studies [3], no attention has been given to understanding the oxidation kinetics of U-Si compounds under such environments at high temperature. Experimental investigation of these aspects of thermodynamic stability has also been undertaken for each of the four U-Si compounds.

Finally, exploratory studies of other factors critical to LWR deployment of U-Si compounds have begun. The compatibility of these compounds with both conventional nuclear fuels (i.e. UO_2 and UN) and other oxidation resistant materials at high temperature will be discussed. Stability of solid fission product silicide compounds (opposed to the more familiar oxides) will be presented with respect to high burnup applications. Finally, issues and potential solutions encountered during scaling of techniques employed for fabrication of high-purity uranium-silicides in the laboratory (10^{-2} kg) to the test irradiation environment (10 kg), and finally to possible commercial use (10^6 kg) will be examined.

METHODOLOGY

Characterization of the properties of U-Si compounds first required synthesis of high purity material for each of the compositions. The four compounds targeted for

investigation in this work were U_3Si , U_3Si_2 , USi , and U_3Si_5 . Although additional silicon-rich U-Si compounds do exist, it was desired to limit the investigation to these four in order to retain U-densities above or reasonably near those of UO_2 . Arc melting was used to produce all materials investigated here. Depleted uranium metal and an excess of silicon (necessary to account for volatilization in the molten state) were combined in the arc melter and melted multiple times in order to maximize homogenization. The buttons of each material were then solutionized at roughly 80% of each compound's melting point for 50-80 hours in gettered argon atmospheres. Gettered argon ($P_{O_2} < 10^{-16}$ atm) was found necessary; even ultra-high purity argon ($P_{O_2} \approx 10^{-6}$ atm) was observed to quickly oxidize the materials at moderate temperatures. Solutionization at high temperature was found necessary to eliminate second phases resulting from the peritectic transformations encountered upon cooling from the melt.

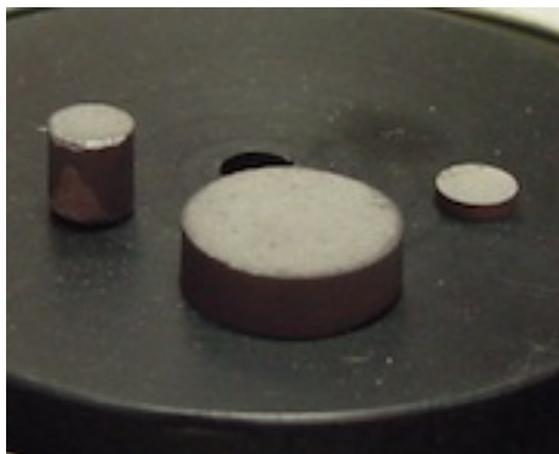


Fig. 1. Photograph of U_3Si_5 pellets produced using powder metallurgy route. The large center pellet is roughly 10 mm in diameter.

Processing of starting materials produced as described above into forms sufficient for thermal analysis and oxidation studies varied depending on the specific compound. U_3Si was found to possess ductility comparable to a metal. As such, it was possible to machine specimens of U_3Si using common fabrication techniques. The other three compounds were far more brittle and dictated use of powder metallurgy techniques. The heat-treated U_3Si_2 , USi , and U_3Si_5 buttons were first milled into a fine powder and then pressed into the necessary cylindrical geometries. Sintering was performed in gettered argon atmospheres. The precise conditions varied between U_3Si_2 , USi , and U_3Si_5 , but required 24-48 hour isothermal holds at temperatures similar to those employed in the heat treatment steps. The

fabrication routes used were found to result in materials in excess of 96% the theoretical density of the compounds and substantially free of second phases. Figure 1 shows a photograph of U_3Si_5 pellets fabricated for thermophysical property measurements.

Thermophysical property measurement of all four U-Si compositions was performed to approximately 100 K below the melting point. Thermal expansion was measured using dilatometry, the specific heat capacity was determined using differential scanning calorimetry and the ratio method, and the thermal diffusivity was measured using laser flash analysis. The thermal conductivity of each sample was calculated by taking the product of the temperature-dependent density, the specific heat capacity, and the thermal diffusivity. All measurements were again made under flowing gettered argon.

Finally, the oxidation and other relevant reactions were measured using thermogravimetric analysis. This technique provides the weight change of a sample *in situ* during exposure to controlled atmospheres at elevated temperatures. Samples of each compound were placed on platforms or shallow crucibles and heated to various test temperatures under gettered argon. After the temperature profile was switched to an isotherm at the desired point, the test atmosphere was introduced to the system and the sample's response recorded. The test atmospheres included oxygen, water vapor, hydrogen, nitrogen, and varying partial pressures of the above.

RESULTS

The thermophysical properties determined for the four U-Si compounds as a function of temperature provide data vital for consideration of their use in LWR applications. In the case of U_3Si and U_3Si_2 , fair agreement was found with the limited low temperature data as illustrated in Figure 2. In addition to the data itself, verification of the high temperature behavior of the materials was possible. The existence of a high temperature phase transformation within U_3Si has been disputed historically [4], but was clearly visible in all data obtained in this study.

The oxidation behavior of the U-Si compounds was found to be quite poor, even when compared to other ceramic nuclear fuels generally considered to have inferior resistance to oxidation. As mentioned previously, property measurement at temperatures above roughly 800K required very low partial pressures of oxygen to avoid severe degradation. This effect is shown even more dramatically in Figure 3, where the response of U_3Si_2 and U_3Si_5 to synthetic air is plotted against that of UN and UO_2 . This measurement was made during dynamic heating at 2.5 K/min in order to illustrate the approximate

temperature where severe oxidation begins to occur for the four materials. Figure 3 shows that both U_3Si_2 and U_3Si_5 begin oxidizing at the lowest temperature of the four materials. Both U_3Si_2 and UN experience extreme exothermic oxidation reactions (observable as the ducktail when the data is plotted against temperature).

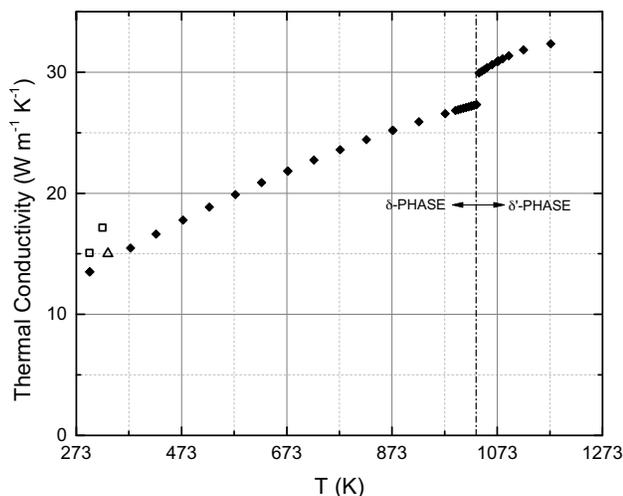


Figure 2. Thermal conductivity of U_3Si measured in this study (black diamonds) compared to available literature values (open markers).

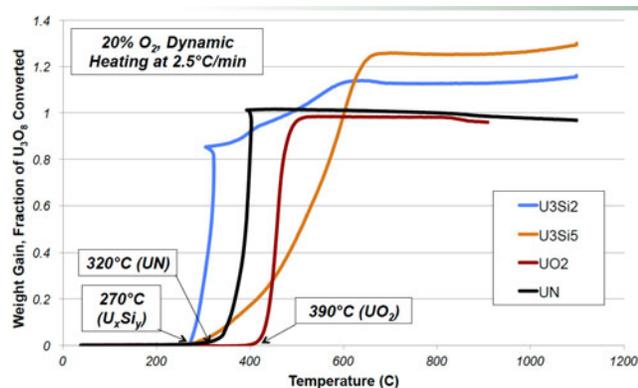


Figure 3. Comparison of the oxidation of U_3Si_2 and U_3Si_5 in synthetic air compared with UO_2 and UN. Oxidation data is expressed in terms of conversion to U_3O_8 ; the silicide compounds exceed unity on this scale as their conversion is to U_3O_8 and SiO_2 .

Kinetic data describing the oxidation and resulting structure of these compounds will be presented and discussed. These results are important not only in considering possible service in water vapor containing environments, but also in evaluating the feasibility of fabrication on an industrial scale. Analogous studies executed in high nitrogen and hydrogen environments will also be summarized. Discussion will conclude with preliminary experimental results that address the stability of U-Si compounds as a component of the larger fuel-

cladding system where the thermochemical stimuli under consideration expand considerably.

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