Journal of Nuclear Materials 507 (2018) 44–49

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Enthalpy of formation of U_3Si_2: A high-temperature drop calorimetry study

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HIGHLIGHTS

- The standard enthalpy of formation of U_3Si_2 is determined to be −33.2 kJ/mol·at.% using high-temperature drop calorimetry.
- TGA/XRD measurements indicate that U_3Si_2 decomposes into U_3O_8 and amorphous SiO_2 at high temperature under O_2 atmosphere.
- This study lays the basis for thermodynamic studies of other U-Si compounds whose enthalpies of formation are not available.

ARTICLE INFO

Article history:
Received 14 March 2018
Received in revised form
17 April 2018
Accepted 18 April 2018
Available online 21 April 2018

Keywords:
Uranium silicide
High temperature drop calorimetry
Enthalpy of formation

ABSTRACT

U_3Si_2 is presently receiving consideration as a high density light water reactor fuel. A reliable knowledge of the formation enthalpy of U_3Si_2 not only helps study the thermal stability but also facilitate the modeling efforts by serving as a benchmark parameter for thermodynamic calculations of phase equilibria at high temperatures. Previous high temperature thermal analysis on U_3Si_2 laid the basis for us to conduct two types of high-temperature drop calorimetric measurements to determine its enthalpy of formation: oxide-melt drop-solution calorimetry and transposed temperature drop calorimetry, from which the results obtained are consistent. The determined standard enthalpy of formation of U_3Si_2 per mole atom, -33.2 ± 3.1 kJ/mol•at.%, is in good agreement with previously reported values obtained by other techniques. Our drop calorimetry methods will be used for thermodynamic studies of other U-Si compounds whose enthalpies of formation are not available.

1. Introduction

Uranium silicide compounds are of considerable interest in nuclear industry as an alternative to uranium dioxide (UO_2). The primary advantages of U-Si compounds compared to UO_2 are higher thermal conductivities at operating temperatures. The U-Si compounds typically considered as either monolithic or composite constituents include U_3Si, U_3Si_2, USi, and U_3Si_5 [1–6]; the U-rich compositions U_3Si and U_3Si_2 are more favored for nuclear fuel applications, as they possess higher uranium densities than UO_2. In particular, U_3Si_2 has received the majority of recent attention due to its relatively high melting point (1938 K) and enhanced resistance to radiation-induced amorphization and swelling [7–10].

These advantages have motivated several experimental and computational studies on the phase equilibria, thermal properties and high temperature stability of U_3Si_2 [2,5,11–17]. In particular, White et al., Wood et al., and Johnson et al. studied the thermal decomposition of U_3Si_2 in synthetic air on heating to ~973 K [2,5,15]. Previously, there were only two experimental studies on its standard enthalpy of formation (ΔH°_f), where the standard state is defined as 1 atm and 298.15 K. Alcock and Grieveson obtained a ΔH°_f value of -36.0 ± 3.3 kJ/mol·at.% from vapor pressure measurements using a silicon implemented Knudsen cell [18]. Gross et al. reported the ΔH°_f of U_3Si_2 to be -33.9 ± 0.4 kJ/mol·at.% measured using a bomb type calorimeter [19], though the result was obtained by reacting two large quantities of metallic U (12 g) and Si (0.9 g) in a sealed chamber and was therefore subject to slow

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https://doi.org/10.1016/j.jnucmat.2018.04.032

and perhaps incomplete reactions.

In this study, we determined the $\Delta H^{\circ}{}_{f}$ of U_3Si_2 using two different drop calorimetry methods (drop solution calorimetry and transposed temperature drop calorimetry) with an isoperibol type Twin-Calvet high-temperature calorimeter, which provides a higher detection accuracy yet on much smaller samples (~5 mg). The two approaches yielded similar values of $\Delta H^{\circ}{}_{f}$ that are consistent with previously reported experimental and calculated results [13,18–20].

2. Experimental methods

2.1. Sample synthesis

U_3Si_2 was synthesized by arc melting 12.12 g of pure metallic U and Si with an excess of 0.1 wt % Si using a tri-arc furnace (Centorr Vacuum Industries, Nashua, NH, USA) with the same methodology previously described by White et al. [2]. The U metal had 31 wppm C impurity, with no other detectable impurities as determined by inductively couple mass spectroscopy. Silicon metal was 99.999% pure that was procured from a commercial vendor (Alfa Aesar, USA) and had no detectable impurities.

2.2. X-ray diffraction

Phase purity was determined via X-ray diffraction (XRD) using a Bruker D2 Phaser diffractometer (Bruker, Wisconsin, USA). Approximately 100 mg of U_3Si_2 powder was prepared inside an Ar inert glove box with <30 ppm O_2 using an Al_2O_3 mortar and pestle from the as-prepared U_3Si_2 ingot. The powder was subsequently secured with vacuum grease to a low background acrylate-domed holder which maintained an inert atmosphere during the measurement on the benchtop XRD unit. The polymer dome was also equipped with an air scatter shield to minimize the background contribution from the polymer dome. Each measurement was collected with a scan step of 0.01° while dwelling for 4 s at each interval. Analysis of the XRD data was conducted with the Bruker DIFFRAC.SUITE EVA software package using the ICDD PDF-2 database.

2.3. Scanning electron microscopy

A retrieved sample from the transposed temperature drop calorimetric experiments (see below) was examined by scanning electron microscopy (SEM). A FEL XL30 FEG SEM/Orientation Imaging Microscopy System equipped with a backscatter detector was used. The specimen was coated with gold for SEM imaging. The accelerating voltage used was 5 keV for better visualizing the formed oxide products during the calorimetric experiments.

2.4. Thermogravimetric analysis

Samples for thermogravimetric analysis (TGA) were prepared from the arc-melted ingot in the same Ar glove box line described above. The ingot was fractured using an Al_2O_3 mortar and pestle and a particle sample of 10–15 mg was collected in order to be more comparable to the drop calorimetry studies (see below). Specimens were loaded into a 3.4 mL Al_2O_3 crucible and then placed into a STA449 F3 Jupiter (Netzsch Instruments, Selb, Germany) for subsequent analysis. The instrument was purged three times to replace the atmosphere with $O_2(g)$, which flowed through the system at 100 mL/min throughout the duration of the measurement. A profile was chosen to emulate the drop calorimetry experiment by heating the specimen at 25 K/min to 988 K, which was then held for 1 h.

2.5. High temperature drop calorimetry

High-temperature oxide-melt drop-solution calorimetry and high-temperature transposed drop calorimetry were conducted using a commercial Tian-Calvet twin microcalorimeter, Setaram Alexsys-800, at Los Alamos National Laboratory [21,22]. U_3Si_2 samples for calorimetry were prepared in the form of chunks (~5 mg each) in an Ar glovebox. Each chunk was dropped from room temperature into the calorimeter chamber at 973 K where a silica-glass crucible contained either *i*) a molten solvent (~15 g of sodium molybdate ($3Na_2O\cdot4MoO_3$) saturated with ~100 mg amorphous silica) with O_2 gas being continuously bubbled through the melt at 5 mL/min in the case of the oxide-melt drop-solution experiment, or *ii*) no solvent for the transposed drop experiment. In both cases, O_2 gas was flushed at ~100 mL/min through the calorimeter chamber to maintain a constant oxidizing gas environment [23]. Due to the low solubility of silica/silicon in the $3Na_2O\cdot4MoO_3$ melt, where only small amounts of SiO_2/Si would dissolve and generate inconsistent heats of solution [24], the molten solvent was pre-saturated with amorphous silica prior to experiments to prevent further dissolution of Si/SiO_2. In this case, thermal outputs by Si from U_3Si_2 exclude the dissolution effect (only the heat content, decomposition and oxidation). The $3Na_2O\cdot4MoO_3$ pre-saturation method has been demonstrated to exert no other impacts on elements other than Si and can yield reliable thermodynamic data for Si-containing materials [24,25]. Complete dissolution of uranium-containing compounds such as oxides, uranates and silicates were confirmed in this solvent, and their formation enthalpies were obtained accordingly [25–30]. Derivation of the enthalpies of formation of U_3Si_2 were done by constructing different thermochemical cycles (Tables 1 and 2) using the drop enthalpy values obtained from these two types of calorimetric experiments based on different reactions that U_3Si_2 underwent in the calorimeter chamber. A detailed description of the calorimetric techniques and their applications to thermodynamic studies of other materials such as nuclear waste form phases can be found elsewhere [31–33].

3. Results and discussion

The phase purity of our synthesized U_3Si_2 sample was confirmed by XRD (referenced by PDF # 47–1070, Fig. 1-a). To check whether the sample can be dissolved in molten $3Na_2O\cdot4MoO_3$ solvent, we performed a furnace test where a piece of sample (~5 mg) was dropped into the solvent contained in a silica-glass crucible at 973 K. A full dissolution of U_3Si_2 was confirmed by visualizing a clear melt through the transparent crucible after 10 min. In addition, the high temperature behavior of U_3Si_2 in an $O_2(g)$ environment exhibits breakaway oxidation at ~657 K, shown in Fig. 2, which is comparable to oxidation in synthetic air from Wood et al. [5]. Thus, we anticipate that U_3Si_2 undergoes high-temperature oxidation and dissolution upon dropping into the $3Na_2O\cdot4MoO_3$ under flowing oxygen at 973 K. Uranium oxides can be well dissolved in $3Na_2O\cdot4MoO_3$ melt and fully oxidized to a hexavalent state [31]. On the other hand, the other thermally decomposed product of U_3Si_2, silica, has a low solubility in the pre-saturated solvent at 973 K [24,25] and thus remains in the tetravalent state. Therefore, U^{6+} and Si^{4+} as the final states of U_3Si_2 in the molten solvent results from the following reaction that occurred in the calorimeter:

$$U_3Si_{2(s,\ 298\ K)} + 13/2\ O_{2(g,\ 973\ K)} \rightarrow 3\ UO_{3(sln,\ 973\ K)} + 2\ SiO_{2(s,\ 973\ K)} \quad (1)$$

from which the heat of drop solution (ΔH_{ds}) was obtained to be −5366.20 ± 133.71 kJ/mol (Table 1), where 133.71 kJ/mol is the standard deviation of the average value (−5366.20 kJ/mol) based