Non-stoichiometry in U_3Si_2

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Abstract

Uranium silicides, in particular U_3Si_2 , are being explored as an advanced nuclear fuel with increased accident tolerance as well as competitive economics compared to the baseline UO_2 fuel. Here we use density functional theory calculations and thermochemical analysis to assess the stability of U_3Si_2 with respect to non-stoichiometry reactions in both the hypo- and hyper-stoichiometric regimes. We find that the degree of non-stoichiometry in U_3Si_2 is much smaller than in UO_2 and at most reaches a few percent at high temperature. Non-stoichiometry impacts fuel performance by determining whether the loss of uranium due to fission leads to a non-stoichiometric U_3Si_{2-x} phase or precipitation of a second U-Si phase. We also investigate the U_5Si_4 phase as a candidate for the equilibrium phase diagram.

Key words: accident tolerant fuel; density functional theory; stoichiometry; silicide

1. Introduction

Uranium silicides are being considered as the basis for next generation nuclear fuel, providing an increase in uranium density (U_3Si_2 has $11.3 \text{ g(U).cm}^{-3}$ compared to UO_2 with 9.7 g(U).cm^{-3} [1]), and an improved thermal conductivity (that constantly increases with temperature - the thermal conductivity can be modelled as $K=7.98+0.0051 \times T-273.15$, where T is the temperature in Kelvin [2]). Furthermore, improved mechanical performance [3] will permit alternate cladding materials to be utilized. Together these enable an accident tolerant fuel product to be feasible with respect to both materials behaviour and economy.

U_3Si_2 has a high melting point of 1938 K and therefore is straightforwardly incorporated into light-water reactor assembly geometries as pellets, permitting a large variation in temperature from pellet rim to center without melting. In comparison, the test reactor fuel U_3Si has a eutectic melting point at 1258 K after going through a decomposition to U_3Si_2 and U(m) at 1198 K [4]. The U-Si phase diagram provided by Domagala [5] highlights the phases that form, U_3Si_2 appearing as a line compound (i.e. no deviations in stoichiometry are anticipated) flanked by the U-rich U_3Si phase (with the two reported higher temperature crystal structures), γ -U metal and the Si-rich USi phase. The phase diagram of Domagala is reproduced in Figure 1 (the $\beta \rightarrow \gamma$ U_3Si

phase transition at 1048 K as reported by Remschnig et al. [6] is shown as a green dashed line).

Figure 1 - Uranium-silicon phase diagram reproduced from Domagala [5]. The U_3Si_2 phase is highlighted by a red line, the U_3Si phase by a green line and the USi phase by a blue line. The $\beta \rightarrow \gamma$ phase transition for U_3Si as reported by Remschnig et al. [6] is shown as a green dashed line.

The phase U_5Si_4 , reported by Noël et al. [7] is not included in this phase diagram as it has only recently been reported although it will be investigated here. U_5Si_4 has been reported to exhibit the hexagonal space group $P6/mmm$ and lattice parameters $a=10.468 \text{ \AA}$ and $c=3.912 \text{ \AA}$ with U occupying the 1a, 3g and 6l lattice sites with positions (0.0, 0.0, 0.0), (0.5, 0.0, 0.5) and (0.21357, 0.42714, 0.0), respectively, and Si occupying the 2d and 6k sites with positions (0.333, 0.666, 0.5) and (0.7727, 0, 0.5), respectively (all fully occupied) [8].

The current standard light water reactor fuel, uranium dioxide, can accommodate significant excess oxygen (forming UO_{2+x}) from low temperatures [9] [10]. This permits uranium to undergo fission without significant fuel degradation/modification throughout its life in a reactor – although fission product secondary phases form in the matrix [11], by and large, it behaves similarly throughout life in a reactor (e.g. no severe volume and thermo-mechanical changes are

observed due to a phase change). There are, however, subtle changes to the diffusion constants with changes in stoichiometry [12] [13], as well as melting temperature variation and fission product accommodation mechanisms [14], due to changes in defect equilibria. It is important to know whether U_3Si_2 will behave in a similar manner, or if, as the uranium content of the fuel is reduced over life-time in reactor, new uranium silicide phases form (most probably the $\text{USi}/\text{U}_5\text{Si}_4$ phases). Equally, it is important to know from a manufacturing standpoint whether or not excessive secondary phase formation is expected for either Si rich or U rich compositions, allowing a more targeted reliable microstructure to be designed.

Previous experimental work has highlighted that in U-rich compositions U_3Si or U metal phases form [15] [16] [17] and in U-poor stoichiometries, USi is reported to form as a secondary phase [1] [17]. The degree to which the U_3Si_2 phase exhibited non-stoichiometry was not reported in these investigations. Finally, the stability of U_5Si_4 with respect to U_3Si_2 and USi is investigated further in this study.

2. Methodology

Recent theoretical work by Noordhoek et al. [18] has been carried out to identify a reliable method to simulate U-Si compounds. It was shown that the use of an on-site Coulombic correction (GGA+U) method [19] was vital to predict the experimentally observed phases as structurally and thermodynamically stable. A +U value of 1.5eV was suggested as appropriate and is therefore used throughout this work (it is expected that further tuning of this U parameter will occur in subsequent works, although the impact on the calculations is expected to be minimal). Recent work by Wang et al. has also investigated U_3Si_2 using a similar methodology [21]. Here, the Vienna Ab-initio Simulation Package (VASP) [20] [21] [22] was employed, using Projected Augmented Wave potentials provided with the GGA exchange correlation. $2\times 2\times 2$ supercells of tetragonal U_3Si_2 [23] [24] were constructed that contain a total of 80 lattice sites. A $3\times 3\times 3$ Monkhorst-pack k -point mesh was implemented and the mesh was appropriately scaled for calculations of other systems. All defect calculations were performed without any prescribed symmetry. The total energy (electronic) convergence criterion was set to at least 10^{-4} eV and the force criteria for the geometry optimization was converged to at least 10^{-2} eV/Å. A cut-off energy of 400 eV was employed for all calculations and the Methfessel-Paxton smearing method used with an energy of 0.2 eV. Calculations were performed with a cut-off energy of up to 500 eV for a few cases, which confirmed that the impact on defect energies and non-stoichiometry is small. The low temperature $Fmmm$ U_3Si structure reported by Kimmel et al. [25] and the $Pbnm$ symmetry USi structure reported by Zachariasen [24] were assumed. When modelling U metal, both the low temperature α -phase and the high temperature γ -phase were considered. The experimentally observed difference in enthalpy between the α -phase and γ -phase of U metal (estimated to be 0.101 eV from [26]) was used to compute the energy of the γ -phase as it is known that the BCC γ -phase is dynamically unstable when using static DFT methods (giving a larger difference in enthalpy of 0.271 eV).

The following intrinsic defects were considered in U_3Si_2 : vacancies on the Si site (4g) and the two symmetrically distinct U sites (the 2a and 4h sites); substitutional defects on the same sites and three symmetrically distinct interstitial sites with fractional coordinates (0.0, 0.0, 0.5), (0.319,

0.181, 0.0) and (0.611, 0.111, 0.5). The U (0.611, 0.111, 0.5) interstitial was observed to spontaneously form a split geometry, orientated in a [110] direction, which is also the lowest energy structure for the U interstitial. Both the U and Si (0.319, 0.181, 0.0) interstitials are high in energy and the Si interstitial was found to relax to the (0.0, 0.0, 0.5) site. The Si (0.0, 0.0, 0.5) was found to be the lowest energy Si interstitial defect. The U (0.611, 0.111, 0.5) interstitial also reconfigures, but towards the low energy split interstitial structure. Si substitution for U is most favourable on the 2a site, which also hosts the most stable uranium vacancy.

3. Results

To understand the potential for stoichiometry deviation in U_3Si_2 , reactions 1-12 are considered (in Kröger-Vink notation [27]). As the U_3Si_2 system is metallic, charge balancing of defects to maintain charge neutrality is not required:

Excess Si from USi:

Excess Si from U_5Si_4 :

Excess U (from U_3Si):

Excess U (from U metal):

Two sets of reactions are considered for excess U as the phase diagram shows two regimes for hypo-stoichiometry (with respect to Si) – a $U_3Si_2+U_3Si$ regime (both β and γ symmetries) at low temperatures and a $U_3Si_2 + U$ metal at higher temperatures. Reactions in the excess Si regime have been carried out with respect to both USi and U_5Si_4 . In all sets of reactions with excess Si and excess U, each of the reactions is normalized to the added compound USi , U_5Si_4 , U or U_3Si . All of the predicted enthalpies for reactions 1-12 are summarized in Table 1.

Table 1 – Summary of reaction enthalpies for each intrinsic defect and reaction that permits a deviation in stoichiometry in U_3Si_2 . For reactions where multiple defect positions are available, the most stable case is used to calculate the reaction enthalpies.

Deviation type	Defect type	Reaction #	Detail	Enthalpy (eV)
Excess Si from USi	Interstitial	1	–	0.19
	Vacancy	2	–	0.68
	Substitutional	3	–	0.16
Excess Si from U_5Si_4	Interstitial	4	–	0.40
	Vacancy	5	–	1.38
	Substitutional	6	–	0.35
Excess U from U_3Si	Interstitial	7	From α - U_3Si	0.77
	Interstitial	7	From β - U_3Si	0.77
	Interstitial	7	From γ - U_3Si	0.72
	Vacancy	8	From α - U_3Si	1.59
	Vacancy	8	From β - U_3Si	1.59
	Vacancy	8	From γ - U_3Si	1.54
	Substitutional	9	From α - U_3Si	0.35
	Substitutional	9	From β - U_3Si	0.35
	Substitutional	9	From γ - U_3Si	0.31
Excess U from $U(m)$	Interstitial	10	From α - U	0.51
	Interstitial	10	From γ - U	0.41
	Vacancy	11	From α - U	1.06
	Vacancy	11	From γ - U	0.96
	Substitutional	12	From α - U	0.24
	Substitutional	12	From γ - U	0.14

3.1 Excess Si in U_3Si_2

Equations 1-6 provide mechanisms that accommodate excess silicon in the U_3Si_2 lattice by forming an interstitial, vacancy or substitutional defect, respectively. In turn, the reactions are predicted to proceed with energies of 0.19eV, 0.68eV and 0.16eV, respectively, for USi and 0.40eV, 1.38eV and 0.35eV, respectively for U_5Si_4 . With respect to USi , both the interstitial formation mechanism and the substitutional mechanism have sufficiently low reaction energies to allow some excess Si accommodation (once configurational entropy is included, which here will be accomplished via the mass action analysis). As both mechanisms have similar energies, the interstitial and substitutional defects are expected to co-exist in a Si-rich lattice.

Assuming an excess of USi , the dominant (0.0, 0.0, 0.5) interstitial concentration can be quantitatively assessed by the mass action [28, 29] equation corresponding to equation 1.

$$S_{ii} = \exp(-0.19 \text{ eV} \times 3kT) \quad (13)$$

This yields a concentration of 2.52×10^{-2} at 1800 K. The (0.0, 0.0, 0.5) interstitial has a multiplicity of 2 in the unit cell for U_3Si_2 and therefore there is one 2b interstitial per U_3Si_2 unit (as there are two U_3Si_2 units per unit cell). The deviation associated with the (0.0, 0.0, 0.5) Si interstitial defect at 1800 K is therefore $[Si]/([Si]+[U]) = (2 + 2.52 \times 10^{-2})/(2 + 2.52 \times 10^{-2} + 3) = 0.40301$ – the stoichiometric ratio – or simply $U_3Si_{2.0252}$. Similarly, the dominant Si substitutional defect (on the 2a site) concentration can be assessed by the mass action equation:

$$SiU = \exp(-0.16 \text{ eV} \times 5kT) \quad (14)$$

This yields a smaller concentration of 5.43×10^{-3} at 1800 K. The deviation in stoichiometry as a result of this defect can be computed by multiplying the calculated concentration by 1 (as there is one 2a site per unit of U_3Si_2) and then adding this concentration to 2 and dividing the total by 5 plus the defect concentration ($[Si]/([U]+[Si]) = 0.40065$). The deviations from stoichiometry due to all considered defects can be summed to provide a total variation in stoichiometry. For example, at 1800 K, the maximum deviation in stoichiometry in U_3Si_2 is $[Si]/([U]+[Si]) = 0.40415$ (or $U_3Si_{2.035}$).

Before the variation in stoichiometry of U_3Si_2 in the presence of U_5Si_4 is assessed, the stability of the system with respect to USi and U_3Si_2 is investigated to identify whether U_5Si_4 is stable or not. This can be determined by considering the following reaction:

which, we calculate, requires an energy of 0.02eV to proceed. Thus, the U_5Si_4 phase is predicted to be stable with respect to the two bounding phases although it should be noted that practically, this small energy could be negated by entropic effects or small variations in the energy associated with the methods [19]. Despite the small energy, as the reaction is predicted to be favourable this phase will be considered to judge the potential deviation in stoichiometry for U_3Si_2 in the presence of U_5Si_4 . It should also be noted that U_5Si_4 has only been observed experimentally on one occasion [7].

In a similar manner to USi, when considering the U_5Si_4 phase, the interstitial and substitutional defects are the two preferential mechanisms by which excess Si is accommodated in U_3Si_2 . Via mass action equations the concentration of Si interstitials and Si substitutional defects can be estimated by the following equations:

$$Sii = \exp(-0.40 \text{ eV} \times 32kT) \quad (16)$$

$$SiU = \exp(-0.35 \text{ eV} \times 52kT) \quad (17)$$

At 1800K the concentration of the dominant Si interstitial defects and dominant Si substitutional defects are computed to be 2.02×10^{-2} and 3.77×10^{-3} . The conversion of concentrations to deviation in total stoichiometry is the same as for USi. The total deviation in stoichiometry at 1800 K, for example, is $[Si]/([U]+[Si]) = 0.403215$ (or $U_3Si_{2.027}$).

As all defect concentrations from equations 13, 14, 16 and 17 yield very low concentrations of excess silicon at room temperature, the predictions are consistent with the line compound currently reported in the literature. Even at a typical LWR reactor operating temperature of 700K, the maximum concentrations with respect to the U_5Si_4 phase are 4.41×10^{-5} and 5.881×10^{-7} for the dominant interstitial and substitutional mechanisms, respectively.

3.2 Excess U in U_3Si_2

Equations 7-9 provide basic mechanisms that offer excess uranium accommodation in the U_3Si_2 structure in the presence of excess U_3Si . Again, interstitial, vacancy and substitutional defects are investigated. The enthalpies for the reactions described by equations 7-9 are 0.77eV, 1.59eV and 0.35eV, respectively for both *Fmmm* α - U_3Si and *I4/mmm* β - U_3Si . Reactions from the high temperature *Pm3m* γ - U_3Si structure yield similar energies, only reducing each of these values to 0.72eV, 1.54eV and 0.31eV, respectively. Reactions 10-12 also provide a mechanism for excess U accommodation (relating to temperatures >775°C in Figure 1). These reactions yield energies of 0.51eV, 1.06eV and 0.24eV from α -U metal (reduced by 0.10eV when γ -U metal is considered).

At 1250K (when the excess U phase is γ -U metal), the concentration of substitutional defects (onto the Si site) can again be assessed through mass action from equation 18:

$$U_{Si} = \exp(-0.14 \text{ eV} \times 52kT) \quad (18)$$

which provides a concentration of 4.13×10^{-2} substitutional defects. The deviation in stoichiometry associated with this defect is $[U]/([U]+[Si]) = 0.3899$ (or $U_3Si_{1.917}$). The concentration of interstitial defects that would form as a result of the reaction provided in equation 7:

$$U_i = \exp(-0.51 \text{ eV}/kT) \quad (19)$$

The concentration of the dominant U interstitial defect in U_3Si_2 at 1250 K is computed to be 2.18×10^{-2} . As this interstitial takes the form of a split interstitial across a Si site (with a multiplicity of 4), the deviation of stoichiometry associated with this interstitial can be computed by multiplying the concentration by 2 and adding this value to 3, then divide the result by the sum of 5 and the concentration of interstitials (again multiplied by 2). This results in a deviation in stoichiometry associated with this U interstitial as $[U]/([U]+[Si]) = 0.6035$ or $[Si]/([U]+[Si]) = 0.3965$.

At a typical reactor operating temperature of 700 K, the excess uranium phase is observed to be β - U_3Si . The concentration of substitutional defects at this temperature is predicted to be 5.41×10^{-5} while the concentration of the most favourable interstitial defects at this temperature is predicted to be only 2.07×10^{-4} . The calculated maximum deviation in stoichiometry with excess U at 700 K is calculated to be $[Si]/([U]+[Si]) = 0.3999$, in essence this equates to a stoichiometric compound.

3.3 Predicted phase field for stoichiometry deviations in U_3Si_2

All of the defects considered have been translated into defect concentrations, which in turn are converted to deviations in stoichiometry allowing a phase field to be predicted, providing an update to the U_3Si_2 section reported in Figure 1. All possible defects at relevant temperatures are considered and their effect on the stoichiometry computed. The values do not take into account temperature dependent variations in the Gibbs free energy apart from the configurational entropy associated with the defects. To maintain the Gibbs phase rule, it is necessary to account of other forms of entropy such as vibrational entropy and as such a scaling has been put in place at phase transitions to ensure a coherent boundary.

Figure 2 illustrates the predicted phase field using the calculated variations in stoichiometry. The stoichiometry variation on the Si rich portion of the phase field considers both the deviation when U_5Si_4 is treated as the reference state (solid red line) and USi (dashed red line). It can be seen that the difference in behaviour when considering either U_5Si_4 or USi as the Si-rich phase is small.

Blue dashed lines have been placed for transitions that have not been calculated in this work and were taken from Figure 1. Also included in Figure 2 is the expected position of the U_5Si_4 phase, which is not included in Figure 1. The melting point and effect on the solidus has been set to the values of USi as the phase field for this stoichiometry has not been studied in detail.

A typical centre-line temperature (980K) and outer pellet temperature (800K) [3] are reported as dashed green lines. In this temperature range, the U_3Si_2 phase is predicted to exhibit only very small deviations from the stoichiometric composition: the maximum Si rich composition is predicted to correspond to $U_3Si_{2.0005}$ with reference to U_5Si_4 (the values are similarly small with regards to excess Si in the presence of USi : $U_3Si_{2.0007}$) and the maximum Si poor composition is predicted to be $U_3Si_{1.999}$. This is consistent with the phase being described as a line compound. At higher temperatures, possibly reached during manufacture, the potential stoichiometry range increases: the maximum Si rich composition occurs at approximately 1840K is $U_3Si_{2.018}$ with respect to U_5Si_4 ($U_3Si_{2.023}$ with respect to USi) and the maximum Si poor composition occurs at approximately 1260K with a predicted composition of $U_3Si_{1.982}$.

Figure 2 - Predicted phase field for U_3Si_2 from mass action analysis of the defect concentrations. The red lines show the extent of deviation in stoichiometry of U_3Si_2 (the dashed red line considering USi instead of U_5Si_4 as the Si-rich reference phase). Dashed blue lines indicate portions of the phase diagram not calculated in this work. Green lines show typical centre-line and outer pellet temperatures for the U_3Si_2 pellet (from [3]).

4. Discussion

Figure 2 can be used to optimize the fabrication of a stoichiometric U_3Si_2 form and highlights the necessity for a distinctly stoichiometric mixture to be used, avoiding potential U_3Si secondary phase formation at operating temperatures, which is known to induce swelling and melts at a significantly lower temperature [30].

The proposed phase diagram can also be used to suggest how the material will behave during burnup. Low and moderate burnups of 1-5% FIMA (fissions per initial heavy metal atom) are likely to lead to the formation of a secondary (Si rich) phase that may impact in-reactor processes such as amorphisation [31] [32], fission product accommodation [31] [33], swelling [3] [34], thermal conductivity [35, 36] and fission gas distribution [33] [37]. Specifically relating to fission gas distribution, it is possible that any secondary phases of $\text{U}_5\text{Si}_4/\text{USi}$ that precipitate due to burnup induced variations in stoichiometry, may act as multiple nucleation sites for fission gas

bubbles. If these precipitates reside as intra-granular inclusions, their formation may contribute to the highly dense fission gas bubble microstructure observed experimentally [34] [38].

To improve behaviour related to burnup effects, dopants/alloying additions may be used to modify a specific materials property, for example, extending the degree to which the material can accommodate changes in stoichiometry. This is important because increased retention of fission gases coupled with the formation of U_5Si_4 /USi may have a negative effect on the swelling of U_3Si_2 , increasing forces that the pellet exerts on the fuel cladding. The pellet-cladding mechanical interaction (PCMI) needs to be considered fully for LWR fuel applications.

5. Conclusion

We have shown the line compound description of U_3Si_2 is valid for operating conditions of U_3Si_2 as a pellet and that Si-rich precipitates are expected to form as a consequence of fuel burnup (whether U_5Si_4 or USi). Additionally, very little excess U can be accommodated in U_3Si_2 at fuel operating temperatures without promoting the formation of the U_3Si phase. The U_3Si phase is reported to induce poor fuel behaviour under irradiation, including run-away swelling due to bubble coalescence. At higher temperatures expected during manufacture of U_3Si_2 pellets, the range of non-stoichiometry is much larger (between $U_3Si_{1.982}$ and $U_3Si_{2.018}$), predicted here by considering the possible upper limit for defect concentrations in the material. We have performed calculations that corroborate some experimental evidence that the phase with stoichiometry U_5Si_4 is stable, although the formation energy with respect to neighbouring phases is very small. The impact on the change in stoichiometry when considering U_5Si_4 instead of USi as the Si-rich reference phase is negligible at operating temperatures.

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Minor stoichiometry deviation in U_3Si_2 at high temperatures (red zone shows extent) predicted.
 U_3Si_2 predicted to act as line compound at light water reactor fuel operating temperatures.
 U_5Si_4 formation indicated as possible excess Si compound.