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# Anisotropy in the thermal expansion of uranium silicide measured by neutron diffraction

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## Abstract

In-situ neutron diffraction patterns were collected for a sample of as-cast  $U_3Si_2$  during heating to 1600°C. Anomalous changes were observed above 1000°C, including the formation of a new diffraction peak not belonging to  $P4/mbm$   $U_3Si_2$ , unequal changes in the peak intensities and onset of anisotropic lattice expansion. The large data-set enabled derivation of a function-fitted isotropic thermal expansion coefficient to high precision, in close agreement with previous dilatometry results but reducing linearly with temperature over the studied interval. Anisotropy in the instantaneous lattice thermal expansion

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corresponded to anomalies reported by White, *et al.* (2015) at a similar temperature.

## **Keywords**

accident tolerant fuel; in-situ neutron diffraction; thermal expansion; uranium silicide; phase transformation

Uranium Silicide ( $U_3Si_2$ ) is of interest as a candidate for accident tolerant fuel[1,2] (ATF) due to its high uranium density ( $11.3 \text{ gm/cm}^3$ ), high thermal conductivity ( $\sim 20 \text{ W/mK}$  at  $600 \text{ }^\circ\text{C}$ ) [3] and reasonable melting point ( $1662 \text{ }^\circ\text{C}$ ), when stoichiometric [4]. These advantages mean that assemblies fueled with  $U_3Si_2$  can be designed to operate cooler (reducing fission gas release [5] and PCMI [6]) for longer residence times, at potentially lower U-235 enrichment levels compared to the industry standard,  $UO_2$ . There are safety benefits under normal and accident conditions, as well as overall savings in fuel cycle costs.

$U_3Si_2$  has been modelled using density functional theory methods[7] and is expected to be stable from room temperature to the melting point[8], without transformations in the solid state[9]. However recent thermal expansion measurements by dilatometry[3] observed a variation in the instantaneous thermal expansion coefficient between  $900^\circ\text{C}$  and  $1000^\circ\text{C}$ , during heating to  $1500^\circ\text{C}$ . As thermal expansion is structure-sensitive this may indicate a structural transition. The thermal expansion coefficient also dictates the density

of the material at a given temperature, which the calculation of thermal conductivity is dependent upon[3]. Both thermal conductivity and thermal expansion are pivotal input parameters for all fuel performance codes. Thermal expansion coefficients may be readily calculated from diffraction-measured lattice parameters under in-situ heating [10,11]. Moreover, trends in lattice strain identify phase transformations[12,13] and composition changes[14,15].

$U_3Si_2$  was manufactured by arc melting metallic natural uranium and pure silicon in an argon atmosphere [16,17]. Pure silicon was obtained from AlfaAesar and metallic uranium from Materials Science Corporation. Impurity analysis was performed using inductively coupled plasma optical emission spectrometry. Oxygen and nitrogen impurity levels were measured in a LECO TC436DR, and carbon in a LECO series CS440. The initial charge contained less than 100 ppm oxygen, and 400 ppm carbon. Other minor impurities such as nickel, calcium, zinc were found to be less than 25 ppm. Samples were prepared using 7.8 wt. % silicon [17], a slight hyperstoichiometric content to suppress the formation of  $U_3Si$  [3] and to compensate for silicon loss during melting. The buttons were melted three times, turning between melts, followed by five additional melts to promote homogeneity within the castings.

Metallography (Olympus PMG3) in the etched condition (70/30 mixture 80% acetic acid and 65% nitric acid [18,19]), shown in Fig. 1a, revealed long, columnar grains the order of 100  $\mu m$  long and 10  $\mu m$  wide, typical of rapid cooling following arc melting. SEM/EDS (XL-30 Field Emission ESEM) reveals minor amounts of U-met and  $U_3Si$  phase, which appear “brighter” than the

surrounding  $U_3Si_2$  matrix in Fig. 1b. Pores and  $UO_2$  inclusions appear black and dark grey, respectively. Image analysis of such micrographs verified a largely homogeneous melt consisting of (by volume) 99.4%  $U_3Si_2$ , 0.1%  $U/U_3Si+U_3Si_2$ , 0.1%  $UO_2$ , and 0.4% porosity, consistent with density and inert fusion measurements.

The sample was placed in an alumina tube with a closed end. The tube was flushed with ultra high purity (99.999%) argon three times in an enclosed, argon-filled glove bag, and sealed at the top end. The sealed tube was moved to the neutron instrument and installed in a ILL-type niobium element vacuum furnace.

Diffraction patterns were collected on the 'Wombat' high intensity powder diffractometer[20]. The sample was oscillated around the vertical axis by  $\pm 15^\circ$  to improve an otherwise 'spotty' Debye-Scherrer ring pattern caused by the cast silicide grains[21]. Temperature was ramped from ambient to  $1600^\circ C$  at  $5^\circ C$  per minute heating rate. Instrument parameters were refined using a NIST  $LaB_6$  standard.

The graphical abstract shows all of the diffraction patterns from ambient to  $1600^\circ C$  as a colour map[13], where diffraction intensity is scaled to colour, and x and y axes are Q and temperature, respectively. Figure 2 shows the diffraction pattern and refinement models for data collected at  $1305^\circ C$ , corresponding to a slice through the colour map along a horizontal line at  $y=T=1305^\circ C$ . Peaks from the  $Al_2O_3$  tube,  $U_3Si_2$  sample and the Nb heating element 110 peak are visible, as well as an unmatched peak that is observed above  $900^\circ C$  (arrow on

Fig. 2). This extra peak is also shown clearly by the enlargement subfigure in the graphical abstract. The  $\text{Al}_2\text{O}_3$  phase was fit using a true Rietveld model where intensities are fixed by the structure factor calculation with an assumed random texture. For the  $\text{U}_3\text{Si}_2$  phase, peak intensities calculated in this way did not fit the observations, likely due to significant texturing in the cast sample.  $\text{U}_3\text{Si}_2$  peaks were therefore fit with arbitrary intensities, using the Le Bail model [22]. While most  $\text{U}_3\text{Si}_2$  peaks form doublets with the  $\text{Al}_2\text{O}_3$ , the diffraction model for this phase is constrained between the background function and the well known  $\text{Al}_2\text{O}_3$  peaks. Refinement constraints were progressively relaxed over four successive optimizations to refine scale parameters, lattice parameters and peak shape for crystal size and microstrain. The  $\text{Al}_2\text{O}_3$  Debye-Waller, 'B' factors were fixed throughout and isotropic. Parameters for each pattern were refined independently. The  $\text{U}_3\text{Si}_2$  lattice parameters at ambient temperature, obtained from a line fit to initial 50 data points are  $a = 7.324(3) \text{ \AA}$  and  $c = 3.882(2) \text{ \AA}$ , within 0.09% and 0.47% of previously reported  $\text{U}_3\text{Si}_2$  lattice parameters [23].  $\text{Al}_2\text{O}_3$  lattice parameters  $a$  and  $c$  concur with the literature [11] within 0.08% and 0.13%.

A total of 312 patterns were obtained and refined in batch mode [24,25] to track lattice parameters and peak intensities throughout heating. The peaks progressively shift to lower  $Q$  through thermal expansion. This is shown by off-vertical slant in the lines formed by high intensity peaks in the graphical abstract. Figure 3 shows thermal strain  $\Delta L/L_0$  for  $\text{U}_3\text{Si}_2$  lattice parameters. The  $\text{U}_3\text{Si}_2$   $a$  parameter initially follows a constant expansion but the gradient of these points reduces at an intermediate temperature, signifying a change in derivative

$$\alpha_a(T) = \frac{1}{\Delta T} \frac{\Delta a}{a_0}. \quad \text{Eqn. 1}$$

This and, similarly,  $\alpha_c(T)$  are calculated from linear regression of the Fig. 3 strain points in a moving-window 150°C wide. The result is the shaded regions in Fig.

4. Around 1000°C, from an initial isotropic  $\alpha \cong 1.7 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ ,  $\alpha_a(T)$  reduces to  $\sim 1.0 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  and  $\alpha_c(T)$  increases to  $\sim 2.0 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$

The true volumetric thermal expansion coefficient  $\beta$  and corresponding true isotropic linear thermal expansion coefficient  $\alpha$  are defined as linear functions of temperature by:

$$\beta(T) = 3\alpha(T) = \frac{1}{V} \frac{dV}{dT} = b_0 + b_1 T \quad \text{Eqn. 2}$$

Integration between limits  $V_0$  and  $V_0 + \Delta V$  provides a fitting function that was used to find the polynomial constants for  $\beta(T)$ . These are  $b_0 = 6.2929(21) \times 10^{-5}$ ,  $b_1 = -2.1760(15) \times 10^{-8}$  and are represented by the curve/line in Figures 3 and 4. Fig. 4 includes the thermal expansion data points from White *et al.* [3].

The change in  $\alpha_a$  coincides with the appearance of a new peak, which does not belong to the  $P4/mbm$  space group attributed to  $\text{U}_3\text{Si}_2$ [26,27]. It is marked with an arrow in Fig. 2. Its intensity is tracked in Fig. 5 along with three clearly

resolved  $U_3Si_2$  peaks. Because B-factors were fixed, all peak intensities would appear to reduce smoothly with increasing temperature, and so have been normalised to the  $Al_2O_3$  012 peak as an approximate correction for this effect. Coinciding with growth of the new peak, the  $U_3Si_2$  002 and to a lesser extent 201 peaks begin a clear reduction in intensity around 900-1000°C. Meanwhile 111 intensity remains constant.

Many of the  $U_3Si_2$  diffraction peaks reduce in intensity with increasing temperature, including when compared to the  $Al_2O_3$  peaks, which served as an internal standard to make an approximate correction for Debye-Waller factor. A simple explanation for the new peak would be formation of a new phase. An oxide produced through reaction of any available oxygen (from the gas or  $Al_2O_3$  tube) would be one candidate. In air,  $U_3Si_2$  oxidizes to  $U_3O_8$  and  $UO_2$  [28]. However the new diffraction peak does not coincide with any peak positions of  $UO_2$  [29] or  $U_3O_8$  [30], including when adjusting lattice parameters for thermal expansion [10,31]. To the uranium side of  $U_3Si_2$  intermetallic in the U-Si phase diagram [8],  $U_3Si$  decomposes in a peritectoid reaction at 930°C to  $U_3Si_2$  and  $\gamma$ -phase uranium metal (BCC,  $a = 3.48 \text{ \AA}$ ) [32]. The d-spacing of the new diffraction peak is close to the 110 peak of  $\gamma$ -uranium, which could indicate decomposition of  $U/U_3Si+U_3Si_2$  regions to  $\gamma$ -U+ $U_3Si_2$ . The peritectoid temperature also matches the onset of changes in the diffraction patterns. The general reduction in  $U_3Si_2$  peak intensities would support a transformation that reduced the fraction of this phase; concurrent reorientation could account for the relative changes in  $U_3Si_2$  peak intensity. However if  $\gamma$ -uranium has formed, it must then melt. Yet the new peak is still observed well beyond 1135°C, the

liquidus for  $\gamma$ -uranium and it is doubtful that the measured, sub-0.1% fraction of Si-substoichiometric phases could account for such an observable effect. We therefore hesitate to advance a microstructural explanation for this peak.

Neutron diffraction is a bulk analysis technique because neutrons diffract from the whole sample volume. Formation of any new phase by surface oxidation or other causes does not affect the thermal expansion observations central to this experiment, which are based on lattice parameters measured from clearly identified  $U_3Si_2$  peaks. Our fitted results for  $\alpha(T)$  (lines, Fig. 3 & Fig. 4) match those of Ref. [3] within the reported standard error (points, Fig. 4) in the range 350-1010 °C. At lower temperatures we have measured a higher coefficient and vice versa, a trend clearly following the unit cell volume (Fig. 3). To enable comparison with early results [33–35] an average expansion coefficient [36] for a prescribed temperature range may be derived from Eqn. (2):

$$\alpha_{av} = [\exp(\frac{b_0}{3}(T - T_0) + \frac{b_1}{6}(T^2 - T_0^2)) - 1] / (T - T_0) \quad \text{Eqn. 3}$$

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Among these, most recent is  $1.73 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  [33] for 100-880°C with cast  $U_3Si_2$ , only 1% off  $1.75 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  calculated by Eqn. 3.

In sintered  $U_3Si_2$ ,  $\alpha_{av}$  measured from 25 or 20 °C was observed variously to increase [34] from  $1.35$  to  $1.50 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  over the 200 to 1200 °C range and to decrease from  $1.55$  to  $1.46 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  over the 200 to 950 °C range [35]. By comparison our  $\alpha_{av}$  for this range is higher and does not drop below minimum  $1.67 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  at 1200 °C. Comparing  $\alpha_{av}$  [33–35] to  $\alpha(T)$  can appear favorable (as in White, et al. [3] who assumed fixed  $\alpha$  over the temperature range) but is

not strictly valid if  $\alpha(T)$  is variable [36]. If calculated from a linear  $\alpha(T)$  function based on the points of Ref. [3] in Fig. 4, ( $b_0=5.32 \times 10^{-5}$ ,  $b_1 = -8.04 \times 10^{-09}$ ), then the derived  $\alpha_{av}(T)$  are, as for our results, also significantly higher than the older[34,35], reducing from  $1.76 \times 10^{-5}$  to  $1.62 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$  over the 50 - 1200  $^\circ\text{C}$  range.

Our new measurements concur with the observation of White, *et al.* of unexplained but significant variations in  $\alpha(T)$  around 1000 $^\circ\text{C}$ . They also provide a possible explanation, which is that this temperature coincides with the onset of anisotropic thermal expansion in  $\text{U}_3\text{Si}_2$ . Agreement of unit cell volume expansion with the two most recent linear expansion results[3,33] shows that the overall isotropic thermal expansion in a polycrystal is not affected by this. However, given the observed anisotropy, significant thermal stresses must exist in the polycrystal for this to occur. The relaxation of thermal stresses by plastic deformation will affect dilatometry results and may affect the long term material performance in thermal cycling conditions. Asserting  $\beta(T)=3\alpha(T)$  for an anisotropic material is valid only for a randomly oriented polycrystal. In a textured sample overall thermal expansion would still be anisotropic, possibly explaining the observed variations including  $\alpha_{av}(T)$  of opposite gradient [34,35].

At high temperatures, configurational entropy effects allow greater defect concentrations to be accommodated within a material. Recent modelling work identified a possible high temperature phase field above 800 $^\circ\text{C}$  where  $\text{U}_3\text{Si}_2$

diverged from a line compound and may permit small changes in stoichiometry [4]. The experimentally measured aspect ratio of the unit cell in intermetallics is sensitive to variations from stoichiometry [14] and the diverging thermal expansion rates in the *a* and *c* axes observed here above 1000 °C describe a corresponding increase in the tetragonal *c/a* ratio. Entry into this newly predicted phase field on reheating, accompanied by changes in Si defect concentration is therefore one explanation for changes in thermal expansion and, if site occupancies are also affected, also for changes in relative peak intensity.

A change in atomic positions would explain changes of U<sub>3</sub>Si<sub>2</sub> peak intensities, thermal expansion and the new diffraction peak. The room temperature structure of U<sub>3</sub>Si<sub>2</sub> was first reported as *P4/mbm* [26] and later confirmed both experimentally [27][23] and by modelling [7,37]. However the original work on the structure of U<sub>3</sub>Si<sub>2</sub> [26] alludes to an uncertainty over the space group as either *P4/mmm* or *P4/mbm* noting that for *P4/mbm* *00l* is always present but *h0l* is absent if *h* is odd. The new peak is observed close to the expected position of a *P4/mmm* 300 reflection, which at 1305°C is at  $Q=2.52\text{\AA}^{-1}$ , consistent with its position in Fig. 2.

## Conclusions

The linear, isotropic averaged thermal expansion coefficient in U<sub>3</sub>Si<sub>2</sub> measured by in-situ neutron diffraction is well described by a line  $\alpha(T) = 2.10 \times 10^{-5} - 7.25 \times 10^{-9} \times T \text{ } ^\circ\text{C}^{-1}$ , supporting, and adding precision to, two most recent measurements, but giving somewhat higher average expansion,  $\alpha_{av}$  than older

estimates. Above 1000°C thermal expansion becomes anisotropic with reduced expansion in the *a*-axis and increased expansion in the *c*-axis, coinciding with previously observed anomalies in the thermal expansion at this temperature. This could be caused by a change in defect concentrations, or cell atomic positions and space group from *P4/mbm* to *P4/mmm*. Given the implication that anisotropy leads to thermal stresses in a polycrystal this needs to be investigated further in relation to use of U<sub>3</sub>Si<sub>2</sub> as an accident tolerant fuel.

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## Figure Captions

Figure 1: (a) Optical micrograph and (b) backscattered electron SEM micrograph of as-cast  $\text{U}_3\text{Si}_2$  sample material.

Figure 2: Neutron diffraction pattern and Rietveld/Le Bail refinement models for  $\text{U}_3\text{Si}_2$  in an  $\text{Al}_2\text{O}_3$  tube at 1305 °C.

Figure 3: Thermal strain in  $\text{U}_3\text{Si}_2$  *a* and *c* lattice parameters and in cell volume (data for *c* and *v* are offset from *a*).

Figure 4: Linear thermal expansion coefficients of  $U_3Si_2$  calculated from local derivative of thermal strain and from fitting Eqn. 2 to volumetric thermal strain. Data points from [3]. Height of shading and thickness of line is their standard error. The line is  $\alpha(T) = 2.10 \times 10^{-5} - 7.25 \times 10^{-9} \times T$ .

Figure 5: Normalized intensity of selected  $U_3Si_2$  diffraction peaks and of the unidentified peak marked by the arrow in Figure 1; shaded area heights indicate standard error; (for b&w: series/legend order in y direction corresponds at 1000°C).