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A thermal conductivity model for U-Si compounds

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1. Introduction

U_3Si_2 is a candidate for accident tolerant nuclear fuel being developed as an alternative to UO_2 in commercial light water reactors (LWRs). One of its main benefits compared to UO_2 is higher thermal conductivity that increases with temperature. This increase is contrary to UO_2, for which the thermal conductivity decreases with temperature. The reason for the difference is the electronic origin of thermal conductivity in U_3Si_2, as compared to the phonon mechanism responsible for thermal transport in UO_2. The phonon thermal conductivity in UO_2 is unusually low for a fluorite oxide due to the strong interaction with the spins in the paramagnetic phase.

The thermal conductivity of U_3Si_2 as well as other U-Si compounds has been measured experimentally [1-4]. However, for fuel performance simulations it is also critical to model the degradation of the thermal conductivity due to damage and microstructure evolution caused by the reactor environment (irradiation and high temperature). For UO_2 this reduction is substantial and it has been the topic of extensive NEAMS research resulting in several publications [5, 6]. There are no data or models for the evolution of the U_3Si_2 thermal conductivity under irradiation. We know that the intrinsic thermal conductivities of UO_2 (semi-conductor) and U_3Si_2 (metal) are very different, and we do not necessarily expect the dependence on damage to be the same either, which could present another advantage for the silicide fuel. In this report we summarize the first step in developing a model for the thermal conductivity of U-Si compounds with the goal of capturing the effect of damage in U_3Si_2. Next year, we will focus on lattice damage. We will also attempt to assess the impact of fission gas bubbles.

2. Fitting procedure of the model

For binary alloys the thermal conductivity K can be written as [7]:

$$K = \frac{1}{w_e + \rho_0 / LT} \quad (1)$$

Here w_e is the intrinsic thermal resistivity, and ρ_0 is the residual electrical resistivity. L is the Lorentz number, 0.02443 ($W\mu\Omega/K^2$), which gives the ratio between thermal conductivity and electrical conductivity, and T is temperature.

The residual electrical resistivity is induced by impurity scattering of electrons. It is 0 for an ideal pure metal, but for any real material it is a function of impurity concentration. For a random alloy ρ_0 follows the Nordheim rule by:

$$\rho_0 = a_0 c(1-c) \quad (2)$$

with a_0 being a material-specific constant and c the impurity concentration.

It has been shown that for U based binary actinide alloys, the second order term needs to be included for an accurate description [8], which gives

$$\rho_0 = c(1-c)(a_0 + b_0(c^2 - (1-c)^2)) \quad (3)$$

with b_0 being another material-specific parameter. It is not yet clear if this more complicated model is required to represent the conductivity of binary uranium alloys involving non-f-elements (Si). Nevertheless, we have applied Eq. (3) in order to capture the subtleties of the uranium f electrons. Equation (3) implicitly assumes that the U-Si compounds acts as a random solution, which is not strictly correct since they are ordered compounds. Nevertheless, this relation will be used in the present assessment and it is considered to be an adequate first approximation. Re-writing equation (1) with equation (3) gives:

$$K(c) = \frac{1/w_e}{1 + c(1-c)(a_0 + b_0(c^2 - (1-c)^2))/LTw_e} \quad (4)$$

using

$$L_1 = a_0 / LTw_e$$
$$L_2 = b_0 / LTw_e \quad (5)$$

equation (4) becomes:

$$K(c) = \frac{1/w_e}{1 + c(1-c)(L_1 + L_2(c^2 - (1-c)^2))} \quad (6)$$

The intrinsic thermal resistivity (w_e) is a consequence of the interaction between electrons and phonons. It is usually obtained as a weighted average of the conductivity for the pure elements. Eq. (6) can be re-written as

$$K(c) = \frac{(1-c)/w_e^U + c/w_e^{Si}}{1 + c(1-c)(L_1 + L_2(c^2 - (1-c)^2))} \quad (7)$$

With c being the Si concentration, and the conductivities of U and Si being $1/w_e^U$ and

$1/w_e^{Si}$, respectively. The uranium term contributes much more to thermal conductivity than the silicon term, because of the low electrical conductivity of silicon [9]. This is also supported by our density functional theory (DFT) calculations, showing that the region around the Fermi energy is dominated by uranium states for all U-Si compounds, specifically from uranium f electrons. However, at high temperature there is a small but non-negligible silicon contribution. The weighted average of the intrinsic conductivities in Equation (7) is consistent with analysis of the electronic density of state (DOS) obtained by density functional theory calculations. As shown in Fig. 1, the DOS of electrons decreases linearly as Si content increases.

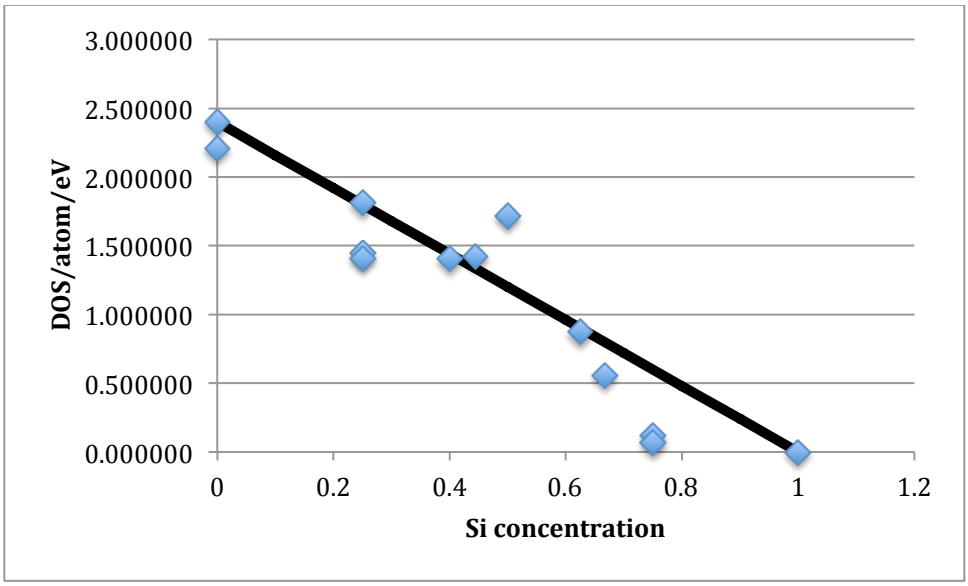

Fig. 1: Electronic density of states in U-Si compounds as a function of Si content. The black line is to guide the reading. From left to right the U-Si compounds are: U, U_3Si, U_3Si_2, USi, U_3Si_5, Si.

To fit equation (7), we use the data for U given by Ho et al. [10], where the measurements were done for high purity polycrystalline U from 12K to 1200 K. The data was fitted using a second order polynomial and extended to 1800K to fit the high temperature region. For Si, we use the results from Glassbrenner et al. [9]. As in uranium silicides the thermal conductivity is dominated by the electrical contribution, only the electrical component of Si thermal conductivity is included here.

The first step of the fitting is to get w_e as a function of temperature. It is found that for both U and Si, the exponential decay function can be used to actually reproduce the thermal conductivity well:

$$w_e = m_0 + m_1 \exp(-(T - T_0)/T_1) + m_2 \exp(-(T - T_0)/T_2) \quad (8)$$

The parameters used in equation (8) are listed in Table I. The form of this equation does not necessarily have a strong physical basis, but for the present purpose only the ability to represent the data is important since no extrapolation beyond the known data ranges will be attempted.

Table 1: Parameters used to fit the intrinsic thermal resistivity of U and Si.

Parameters	m_0	m_1	m_2	T_0	T_1	T_2
U	0.00448	0.0089	0.03267	0	500.76917	1555.4716
Si	0.08303	29.152	3.88841	645	87.48315	252.19318

After fitting the pure element conductivities, the experimental data reported recently for U_3Si_2 [2] and U_3Si_5 [3] are used to fit the parameters L_1 and L_2.

Please note that both parameters are temperature dependent, and they can actually be solved analytically using equation (7) at each given temperature provided that the experimental data are available. In the fitting, again we first fit the experimental data using a second order polynomial. For U_3Si_5 only data with temperature above 670K are used to avoid the data obtained for a defective phase at low temperature [3], where scattering of electrons by lattice defects further lowers the conductivity. Then we solve equation (7) for L_1 and L_2 every 50K in the temperature range from 300K to 1800K. For convenience, these two parameters are further fitted using 5th order polynomials as functions of temperature T by:

$$L_1 = 6.0959 - 0.01457\times T + 1.75527\times10^{-5}\times T^2 - 1.13428\times10^{-8}\times T^3 + 4.05139\times10^{-12}\times T^4 - 6.04924\times10^{-16}\times T^5$$

$$L_2 = -1.82488 + 0.01487\times T - 2.92953\times10^{-5}\times T^2 + 2.68933\times10^{-8}\times T^3 - 1.15846\times10^{-11}\times T^4 + 1.90712\times10^{-15}\times T^5 \quad (9)$$

We note that this extends the original relation in equation (5). In future work we will retain equation (5) in the fit of the experimental U_3Si_2 and U_3Si_5 data. Therefore, for uranium silicide with a certain Si concentration, the thermal conductivity at a given temperature T can be calculated using equation (7) with the parameters given by equation (8) and (9). In Fig. 2, the fitted results and the original data used in fitting are plotted. The model reproduces the experimental data very well except for the low temperature region of U_3Si_5 [3], where the data was not included in the fitting. It was suggested that a phase transformation occurred with a highly defective phase formed when the temperature was decreased below 670K. The lattice defects scatter electrons and further lower the conductivity, resulting an abrupt drop in the curve. Such a scattering effect is not included in equation (7). However, at even lower temperature when the phase approaches defect free, good agreement can be seen between the model and previous experiments.

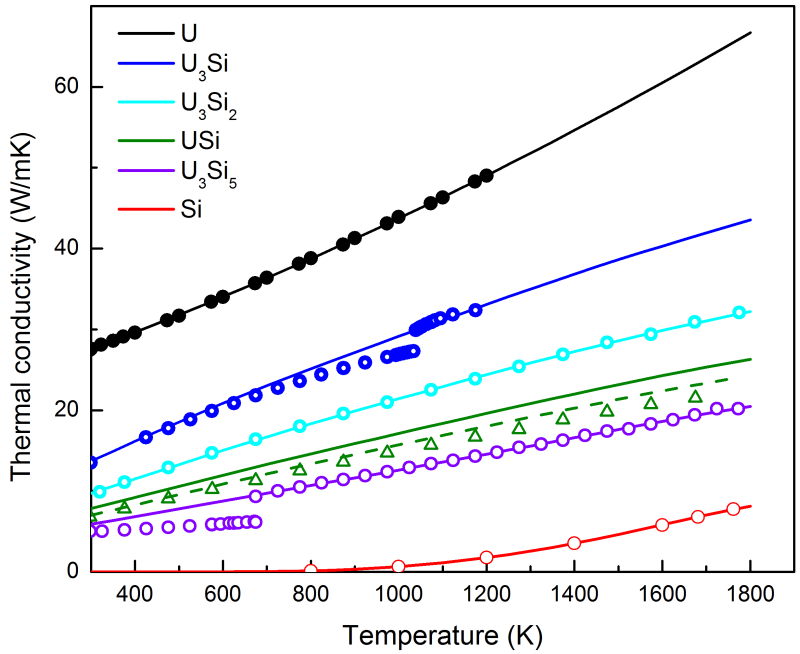

Fig. 2 Thermal conductivities of U, U_3Si, U_3Si_2, USi, U_3Si_5 and Si as functions of temperature. The solid curves are the model predictions using equation (7), and the symbols are experimental data. For Si only electrical contribution is plotted here.

To further test the applicability of the model, the conductivities of U_3Si and USi are calculated and compared with the results from recent experiments [1, 4]. It is very encouraging to see that overall, the model agrees well with experimental measurements for U_3Si, as shown in Fig. 2. In particular, in the low and high temperature regions, the model prediction is almost right on top of the experimental data. Some discrepancy is noticed at about 1070K, where a phase transformation occurs. For USi, the model prediction by equation (7) (solid green curve) is higher than the experimental results. It has been suggested in the experiments that the USi sample could be non-stoichiometric, $U_{34}Si_{34.5}$ instead of USi, with 1 of the 70 Si sites not occupied, and contain secondary phases such as UO_2 and U_3Si_5. To account for the effect of Si vacancies, we follow Martin et al. [11] by assuming extra resistivity induced by lattice defects:

$$\Delta\rho = c_i\rho_i + c_v\rho_v \qquad (10)$$

and the corrected conductivity of USi is given by:

$$K^* = LT/(\rho_0 + \Delta\rho) = LT/(LT/K_0 + \Delta\rho) \qquad (11)$$

Here c_i (c_v) and ρ_i (ρ_v) are the concentration and resistivity of interstitial (vacancy), and K_0 is the conductivity for stoichiometric USi as given by equation (7). However, for USi no data exist for resistivities of interstitial and vacancy. Here, we take the data for U Frenkel pairs, ρ_{FP}, 22 μΩm [12], and further assume that $\rho_i = \rho_v = \rho_{FP}/2$. To account for the effect of secondary phases, another reduction of 3.2% as suggested in White et al. [4] is included. The corrected conductivity of USi (dash green curve in Fig. 2) agrees very well with the experimental measurements. While these results are promising, the treatment in equations (10) and (11), and the parameters used

will be further examined in the future. Moreover, no temperature dependence is considered for resistivities of vacancy and interstitial. Nevertheless, the excellent agreement between the model and experimental data suggests that the model based on Si concentration (thus impurity scattering) is suitable to describe thermal conductivity of U-Si compounds. More importantly, the treatment in equation (10) and (11) show a promising way of considering irradiation induced lattice defects.

2. Discussions

The current model is based on the assumption that for uranium silicides, the thermal transport is dominated by the electronic contribution. The heat transport by phonons (lattice vibration) is assumed to be negligible. This assumption is supported by the nearly linear increasing conductivities of U_3Si, U_3Si_2 and U_3Si_5 over temperature. The good agreements between the model predictions and experimental measurements also suggest the validity of the assumptions made here.

The effect of crystal structure is also assumed to be negligible here since in the model the conductivity depends only on temperature and composition. The Nordheim-like rule applied in this study strictly relies on a random distribution of elements on the same lattice, which is not fulfilled for the U-Si series of compounds but our results indicate that this deviation is small and the Nordheim-like rule seems to capture the behavior well. As can be seen from the experiments, discontinuities occur at the points of phase transformation for U_3Si and U_3Si_5, suggesting possible effect of crystal phases. Similar abrupt change has been observed in the electrical resistivity of uranium too [13]. Although the changes induced by phase transformation are noticeable, they are not substantial relative to the overall temperature dependence. Sometimes they are induced by the lattice defects, which appear at temperatures of phase transformation [3].

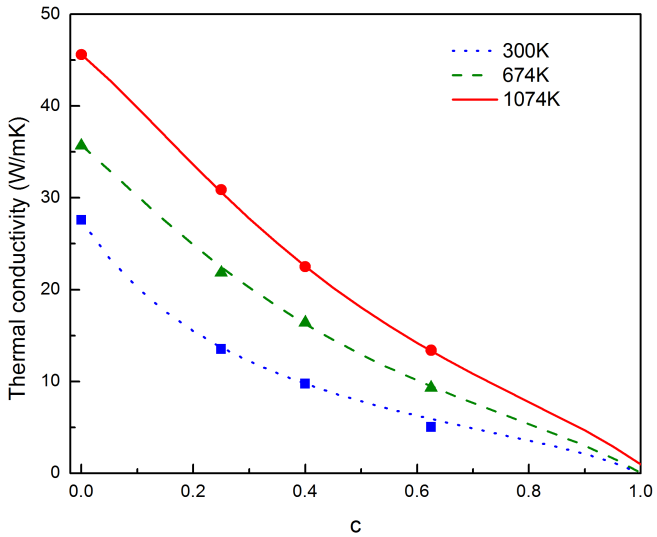

Fig. 3: Thermal conductivity of U-Si compounds as a function of Si concentration, c, at three selected temperatures. The curves are calculated using equation (7) and the

symbols are from experiments. Please note the measurement temperatures can be slightly different from the selected temperatures.

The current model is based on the conductivities of pure U and Si. For Uranium silicides, the model predicts monotonic decreasing conductivity with increasing Si concentration, c, as shown in Fig. 3. Such monotonic decrease is mainly due to the low electrical conductivity of Si and also the scattering of impurity - Si here. While under irradiation, lattice defects are generated by irradiation of neutrons and fission fragments. These lattice defects will act as an extra scattering mechanism of electrons, leading to reduction in the thermal conductivity in reference to that of fresh fuel. The scattering of lattice defect is evident from a re-plot of previous experiments of U_3Si fuel [14], where only relative conductivities with respect to that of fully dense fuel are given. To produce the data in Fig. 3, the conductivity of fully dense fuel (σ_{100} in the original paper) is calculated by

$$\sigma_{100} = LT / \rho \qquad (10)$$

Here L is the Lorentz number, 2.44×10^{-8} $W\Omega K^{-2}$, and ρ is the electrical resistivity measured in Ref. Hastings et al. [14]. It is not clear what temperature was used for the measurements. A temperature of 300 K is used to re-plot the results. After re-generating the data, the as irradiated and annealed results are further fitted using

$$\sigma(P) / \sigma_{100} = (1-P) / [1 + P(\beta - 1)] \qquad (11)$$

For as irradiated fuel, σ_{100} is 10.79884 W/mK and β is 1.51711 from the fitting. They are 13.6719 W/mK and 2.37768 respectively after annealing. Assuming that all lattice defects have been annealed out, the conductivity of fully dense fuel (13.6719 W/mK) is very close to that predicted by equation (7), 13.69431 W/mK. The difference between the as irradiated and annealed samples at zero porosity suggests the contribution of lattice defects (probably fission products too), in agreement with the increase in the electrical resistivity measured experimentally. Following the treatment of equation (11), the difference between as-irradiated and annealed results suggests that about 6.4% Frenkel pairs were annealed out. These samples experienced a rather high burn-up of 0.32 to 1.76×10^{20} fissions cm^{-3}, meaning that it is not unreasonable to think that the total defect concentration (including lattice defects and dispersed fission products) reached a few percent. Again, we note that the resistivity of Frenkel pair is taken from U, which could be different for U-Si compounds. This indicates it is likely (and highly desirable) to develop a model for radiation induced lattice defect and fission products based on equation (11). This will be our next step. The as irradiated samples in Fig. 3 were obtained for temperatures below 100°C and residual damage was quickly annealed out above 300°C. This implies that, for practical purposes of U_3Si_2 in reactor environments, most of the damage would be annealed out quickly and the thermal conductivity would only be weakly affected by the irradiation conditions. Even the reduction predicted at low temperature where annealing does not occur, is smaller than for

UO_2. All in all this leads to a smaller or even much smaller thermal conductivity reduction for U_3Si_2 than for UO_2, which provides added fuel performance benefits.

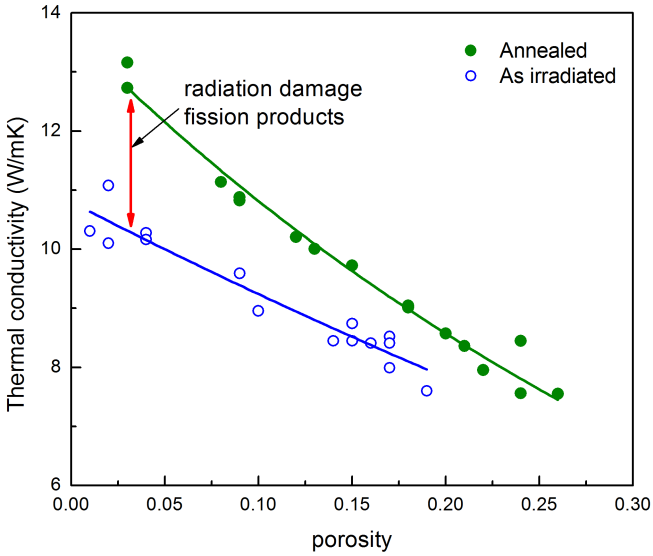

Fig. 3: Thermal conductivities of as irradiated and annealed U_3Si fuels as functions of porosity. The curves are fitted using equation (11).

In addition, the different values of β for as irradiated and annealed fuels indicate different dependence of thermal conductivity on porosity. One possible reason for this is the bubble alignment formed during annealing. The bubbles may transition from a random distribution in as irradiated fuel to a preferential grain boundary alignment after annealing. It has been shown in UO_2 fuels, grain boundary alignment of gas bubbles causes more significant reduction in thermal conductivity at the same porosity level. However, this hypothesis needs to be testified with meso-scale modeling of gas bubble evolution in silicide fuels.

In FY 17, we will extend the model to include the contribution of lattice defects. MARMOT simulations will also be done by utilizing the current model to assess the effect of gas bubbles, to address the different trends observed in as-irradiated and annealed U_3Si as shown in Fig. 3. The same model may be extended to other uranium based metal fuels such as UZr and UMo.

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