Thermophysical properties of urania-zirconia \((U,Zr)O_2\) mixed oxides by molecular dynamics

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Abstract

Molecular dynamics simulations were used to investigate the thermophysical properties of \((U,Zr)O_2\) between 300 K and 3500 K. For compositions with \(<25\%\) \(UO_2\) the tetragonal phase is stable and beyond 25\% the cubic fluorite phase becomes stable for all temperatures. Thermal expansion, heat capacity and thermal conductivity have been predicted. The addition of \(ZrO_2\) to \(UO_2\) causes a reduction in thermal conductivity however this effect decreases with increased temperature and becomes insignificant beyond 1000 K. Thermal expansion of \((U,Zr)O_2\) mixtures with \(>25\%\) \(UO_2\), which are in the cubic fluorite phase, is similar to that of \(UO_2\). A superionic transition is observed in cubic \((U,Zr)O_2\) at temperatures between 1500 K and 3000 K, occurring at progressively lower temperatures with increasing \(ZrO_2\) content. The heat capacity of these mixed oxides increases from 80 J/mol.K up to 130 J/mol.K at temperatures relevant to accident conditions, possibly retarding temperature increase in fuels with a significant pellet-clad bonding layer.

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1. Introduction

Light water reactors (LWRs) predominantly utilise \(UO_2\) pellets as fuel \([1]\). \(UO_2\) fuel pellets are often clad in zirconium based alloys to protect the fuel and to prevent radionuclides from being released into the coolant \([1]\). Zirconium alloys have been used as cladding materials since the early 1950s as they are corrosion resistant in water and have a small neutron absorption cross section \([1]\).

Pellet cladding interaction (PCI) is a phenomenon found in nuclear reactors in which the fuel becomes mechanically and/or chemically bonded with its cladding material. PCIs affect the structural stability of both the fuel and the cladding, sometimes leading to the detrimental failure of the cladding \([2]\). When the cladding bonds with the fuel pellets a layer is formed that is composed of a solid solution of \(UO_2\) and \(ZrO_2\) in the full range of possible compositions across the layer \([3]\). PCIs are attributed with \(<1\%\) of cladding failure in pressurised water reactors and \(<9\%\) in boiling water reactors \([2]\). Failures induced by PCI occur in a small fraction of fuel rods, however, the chemical bonding occurs in the majority of commercial fuel rods \([4–6]\).

The root cause of pellet clad bonding is oxidation of \(Zr\) caused by iodide (\(I^–\)) build-up in the pellet-cladding gap \([4–6]\). The initial formation of \(ZrO_2\) allows a bond to form between the \(UO_2\) fuel pellets and \(Zr\) alloy cladding. The stresses applied to the pellet-clad bonding layer during cooling or power ramps can lead to radial stresses on the pellet-clad bond, resulting in cracks \([4–6]\). Cracks are known to lead to an increase in iodide concentration at the cladding interface, which further exacerbates and accelerates the production of pellet-clad bonding \([6]\).

Fuel burnup has risen from 15 GWD/t in the 1950s to over 50 GWD/t currently \([7,8]\). The incidence of pellet-clad bonding increases with burnup until, at 50 GWD/t, all fuel rods exhibit a chemical bonding between the fuel and cladding \([3,9,10]\). Beyond this, the \(ZrO_2\) continues to leach into the fuel pellet and increases the thickness of the mixed oxide layer \([3,9,10]\). Reactor operators are attempting to reach higher burnups and are utilising fuel performance codes to simulate burnups over 100 GWD/t \([11]\). As the layer increases in thickness with burnup it becomes more important to the overall heat transfer coefficient with increased burnup. Burnup is currently on the cusp of permanent bonding, and as such the PCI bonding layer has not received the attention that perhaps it
deserves. The continued increase in burnup makes it prudent to investigate how this layer will affect the thermodynamics of nuclear fuel.

ZrO₂ exhibits several crystal structures depending on temperature and pressure. At atmospheric pressure, ZrO₂ is found in the monoclinic phase up to ~1420K, followed by the tetragonal phase to ~2620K and then the cubic phase until melting [12]. Cubic and tetragonal ZrO₂ are often stabilised using trivalent cations, of which Y₂O₃ is the most common, where ~2% Y₂O₃ is required for tetragonal stabilisation and ~8% is required for cubic stabilisation [13,14]. However, when looking at tetravalent dopants, such as CeO₂, it takes ~25% to stabilise ZrO₂ in the cubic phase [15,16].

ZrO₂ found in the pellet-clad bonding layers has been shown to be either cubic or tetragonally stabilised at room temperature, where, under out of pile conditions, the monoclinic phase is observed [12]. As burnup increases the tetragonal ZrO₂ is gradually replaced by cubic ZrO₂ and beyond 30GWD/t practically all ZrO₂ is cubic [3,9,10,17]. This stabilisation of both the cubic and tetragonal phases in nuclear fuel is due to a combination of factors including radiation damage, fission product dopants, accommodation of U in solid solution and stress induced stabilisation [9].

Past research on (U,Zr)O₂ has focussed on the phase diagram of the pellet-clad bonding material [18–22]. However, the thermophysical properties are still not well understood. Knowledge of thermal conductivity and heat capacity are useful in that they can be used to increase the accuracy of fuel centreline temperatures and heat transfer predictions [23,24]. Thermal expansion can be used to gauge how changes in temperature have the potential to cause cracking of fuel pellets at the pellet-clad interface. Mixed oxides sometimes have a minima in the melting point that is below both end members which could lead to localised melting at temperatures lower than expected [25].

Superionic conductivity is another phenomenon of interest that has been found to occur in UO₂ as well as several other actinide oxides [25–30]. ZrO₂ is often used with dopants to create higher temperature superionic conductors, [31–34]. UO₂ is known to have a superionic transition at around 75% of its melting temperature [26–30,35]. Similarly, ZrO₂ undergoes a superionic transition at temperatures above 2500 K [31,33]. The effects that the addition of ZrO₂ to UO₂ will have on the superionic conductivity is explored in the current work.

The properties of the pellet-clad bonding layer are not currently accounted for in fuel performance codes [23,24]. This is partly due to the unavailability of data. In subsequent sections the thermophysical properties of cubic (U,Zr)O₂ are investigated along with those of tetragonal ZrO₂ using molecular dynamics (MD) simulations.

2. Methodology

2.1. Potential form

The Cooper-Rushton-Grimes (CRG) potential set, including interactions between Zr-O, Zr-Zr and Zr-U, were used for these simulations [29,36]. The CRG potential was chosen as it accurately reproduces the experimentally derived thermal expansion, bulk modulus and melting points of UO₂ and several mixed oxides containing UO₂ [29,30,35,37,38]. The CRG potential combines a pair potential with the embedded atom method (EAM) as per equation (1) [29,39]. This gives the potential energy of an atom i, Eᵢ, Tables 1 and 2 contain the potential parameters used in all simulations taken from Cooper et al. and Liu et al. [29,36].

### Table 1

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Aᵢ,j (eV)</th>
<th>φᵢ,j</th>
<th>Cᵢ,j (eVÅ²)</th>
<th>Dᵢ,j (eV)</th>
<th>φᵢ,M</th>
<th>r₀ (Å)</th>
<th>T₀ (Å⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>Zr - Zr</td>
<td>18600</td>
<td>0.2747</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr - O</td>
<td>18600</td>
<td>0.2907</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr - U</td>
<td>18600</td>
<td>0.2517</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr - O</td>
<td>448.779</td>
<td>0.3878</td>
<td>0.0</td>
<td>0.6608</td>
<td>2.058</td>
<td>2.381</td>
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</tr>
<tr>
<td>Zr - O</td>
<td>1147.471</td>
<td>0.3224</td>
<td>0.0</td>
<td>1.2269</td>
<td>1.4482</td>
<td>1.998</td>
<td></td>
</tr>
<tr>
<td>O - O</td>
<td>830.283</td>
<td>0.3529</td>
<td>3.8843</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

**Table 2**

<table>
<thead>
<tr>
<th>Species</th>
<th>Cᵥᵢ (eVÅ⁻²)</th>
<th>nᵢ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>1.806</td>
<td>3450.995</td>
</tr>
<tr>
<td>Zr</td>
<td>1.597</td>
<td>1188.786</td>
</tr>
<tr>
<td>O</td>
<td>0.690</td>
<td>106.856</td>
</tr>
</tbody>
</table>

\[
Eᵢ = \frac{1}{2} ∑_{j} φᵢ,j(rᵢ,j) - Cᵢ √ ∑_{j} δᵢ,j(rᵢ,j)
\]

### 2.2. Simulation parameters

For all equilibrium simulations a Nosé-Hoover barostat and thermostat were used with the NPT (isothermal-isobaric) ensemble. The timestep, thermostat and barostat relaxation times were set to 2 fs, 0.1 ps and 0.5 ps, respectively. These values have been used widely in previous work that used the CRG potential [29,30,35,37,40]. Simulations were conducted for ZrO₂, (Zr₀.₇₅,U₀.₂₅)O₂, (Zr₀.₅₀,U₀.₅₀)O₂, (Zr₀.₂₅,U₀.₇₅)O₂ and UO₂.

#### 2.2.1. Thermal expansion and heat capacity

Thermal expansion and heat capacity simulations were conducted for each composition. The tetragonal ZrO₂ P4/2/mmc unit cell was repeated 12 times in each orthogonal direction to create a 12 × 12 × 12 supercell (10368 atoms) [41]. All other structures consisted of a 10 × 10 × 10 supercell (12000 atoms) of the cubic fluorite structure Fm₃m [42].

Mixed oxide compositions were generated by randomly substituting U for Zr on cation sites. Due to the large number of atoms only one random arrangement of atoms was used for each composition. Previous work showed there to be minimal deviation between several random structures using 12000 atoms [30,35]. The pellet-clad layer is subject to continued ballistic intermixing during in-reactor operations and consequently no ordering is expected on the cation sublattice. This is in agreement with the TEM observations of Nogita et al. on the pellet-clad bonding layer of 48 GWD/t BWR samples [43]. Each supercell was heated from 300 K to 3500 K in 25 K increments. Each step consisted of a 20 ps ramp followed by a 20 ps equilibration. All results were calculated by taking the average over the final 4 ps of each equilibration step.

The cubic a lattice parameter was determined by taking the average of the unit cell length in the x, y and z directions. Similarly for the tetragonal structure the a lattice parameter was calculated from the average of the x and y simulation box dimensions, while the c parameter was taken from the z direction only. The thermal expansion coefficient (αᵥ) was determined, for isotropic materials, as \( \alphaᵥ = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right) = 3αᵢ = ∑_{i} \frac{1}{c_i} \left( \frac{\partial c_i}{\partial T} \right) \) where V is volume [44]. For the
tetragonal structure the thermal expansion components in the $a$ and $c$ directions were calculated separately and the volumetric thermal expansion, $\alpha_V$, was approximated as the trace of the tensor; $\alpha_V = 2\alpha_{11} + \alpha_{13}$ [44]. The derivative of the enthalpy increment as a function of temperature, $H(T) - H(T_0)$, can be used to determine the specific heat capacity, $C_p = 1/2 \left( \frac{\partial H}{\partial T} \right)$, where $n$ is the number of moles. For both heat capacity and thermal expansion the derivatives were calculated by taking a 3-point average before and after each point ($\pm 25 \text{ K}$, $50 \text{ K}$ and $\pm 75 \text{ K}$) and using this in a central derivative.

2.3. Thermal conductivity

Thermal conductivity simulations utilised non-equilibrium molecular dynamics. The Müller-Plathe reverse perturbation method was utilised here [45]. This method involves swapping the kinetic energies of particles at the end of the supercell with those in the centre to generate a thermal gradient in the system. These simulations began by ramping to the desired temperature over a period of 20 ps followed by a 20 ps equilibration in an NPT ensemble. Following this an NVE ensemble (isochoric-isenthalpic) is used over a period of 5 ns, during which the Müller-Plathe function is used. 5 ns was used as it ensured that the thermal conductivity and heat flux had converged, see supplementary materials.

Thermal conductivity, $k_i$, is then calculated as per equations (2) and (3), where $j_i$ is the heat flux, $q_i$ is the energy that has been transferred between atoms, $L_i$ is the supercell length in the $i$ direction, $A$ is the area of the supercell, $\Delta T$ is the thermal gradient and $t$ is the simulation time. As the centre of the box is the point to which energy is transferred the thermal gradient acts over two halves ($\frac{t}{2}$) and acts over twice the area ($2A$).

$$k_i = j_i \left( \frac{L_i}{2\Delta T} \right)$$  \hspace{1cm} (2)

$$j_i = q_i \left( \frac{1}{2A} \right)$$  \hspace{1cm} (3)

Bulk thermal conductivity was calculated by extrapolating from the thermal conductivity for several supercell sizes. This was done for a $5 \times 5 \times 20$, a $5 \times 5 \times 40$ and a $5 \times 5 \times 60$ supercell for each composition. The bulk value was determined by fitting a straight line to $\frac{1}{k}$ as a function of $\frac{1}{L_i}$ and extrapolating to an infinite cell, see supplementary materials for details. For tetragonal $\text{ZrO}_2$ the thermal conductivity was calculated in the $a$ and $c$ directions.

3. Results and discussion

Upon modelling the pure $\text{ZrO}_2$ phases it appears that the Zr-O CRG potential correctly predicts the tetragonal phase of $\text{ZrO}_2$, however, fails to predict the monoclinic and cubic phases, unless dopants are introduced. The inability to model the monoclinic phase was reported previously and is attributed to the centrosymmetric form of the potential [36]. Previous work observed a tetragonal to cubic phase transition, but, when we were attempting to simulate the cubic phase, the structure collapsed into a parasitic symmetric form of the potential [36]. Previous work observed a monoclinic phase was reported previously and is attributed to the centro-symmetric form of the potential [36].

The presence of an early-onset superionic transition in Zr-rich (U,Zr)O2 is further evidenced by examining the O-O pairwise radial distribution function of (U0.25,Zr0.75)O2, shown in Fig. 3a. It is
apparent that there is a loss of all peaks beyond the first nearest neighbour above 1500 K, consistent with disorder in the oxygen sublattice. Additionally, Fig. 3b shows that the cation sites maintain structure at the superionic transition temperature and above, with peak broadening due to increased thermal vibrations. This analysis of the superionic transition can not be done for pure ZrO₂ as the potential is unable to predict the cubic phase without the addition of dopants.

3.2. Heat capacity and melting point

The predicted specific heat capacity as a function of temperature for each composition can be seen in Fig. 4. Heat capacity increases linearly and approximately equally with temperature for all compositions below 1700 K. The predicted heat capacity for both UO₂ and ZrO₂ show good agreement with the literature [27,52–55]. The predictions do not replicate the peak caused by the monoclinic to tetragonal transition that occurs at ~1470 K in ZrO₂. (U₀.25,Zr₀.75)O₂, (U₀.50,Zr₀.50)O₂, (U₀.75,Zr₀.25)O₂ and UO₂ exhibit a steep increase in the heat capacity at 1800 K, 2000 K, 2300 K and 2500 K respectively. This correlates with the previously mentioned superionic transition temperatures. Higher concentrations of UO₂ exhibit a shift in superionic transition peaks towards higher temperatures. The increased heat capacity at the superionic transition temperature, seen in Fig. 4, is due to the increase in concentration of defects being created in the oxygen sublattice [27,30,35].

At operating temperatures the heat capacity is fairly constant for all compositions examined here. However, under accident conditions the sharp increases in heat capacity of the Zr-rich (U,Zr)O₂ mixtures at lower temperatures than for UO₂ could result in delayed heating of fuel containing a permanently bonded (U,Zr)O₂ layer compared to fresh fuel. This suggests that high burnup fuels, > 50 GWd/t, which contains the greatest fraction of (U,Zr)O₂ layer has
an inherent mechanism to delay temperature increases in fuel during accident scenarios. This may partly compensate for the reduced thermal conductivity of high burnup microstructures.

3.3. Thermal conductivity

The thermal conductivity of UO$_2$ and (U,Zr)O$_2$ are shown in Fig. 5a and for ZrO$_2$ in Fig. 5b. MD alone tends to overestimate thermal conductivity at low temperatures as it doesn’t include spin-phonon scattering contributions [56]. However, at high temperature these become negligible, and a good agreement between MD and experiments is observed at temperatures exceeding 1000 K [27,37,56]. Differences between this work and earlier work using the CRG potential to determine thermal conductivity of UO$_2$, at low temperatures, are attributed to differing cell sizes used to determine the bulk values. The largest supercell used by Cooper et al. was 10$^3$ x 10$^3$ x 60 compared to the 5$^3$ x 5$^3$ x 60 supercell used here. This had a marked effect at room temperature but came within uncertainty bounds of the current and previous work.

The thermal conductivity of zirconia, Fig. 5b, shows a similar trend seen in UO$_2$, where predicted thermal conductivity of ZrO$_2$ deviates from experimentally derived results for YSZ at low temperatures [57,58]. Accounting for phonon-spin scattering would result in improved accuracy of thermal conductivity predictions as seen by Cooper et al. [56]. The lower thermal conductivity in the z direction could be a function of the anharmonicity of phonon scattering found in tetragonal ZrO$_2$ [59]. Where the composition of (U,Zr)O$_2$ contains >25% UO$_2$ the thermal conductivities are similar to those of UO$_2$. At typical cladding interface temperatures ~ 625 K the bonding layer would have a negligible impact on the thermal conductivity of the fuel compared to fresh fuel.

At burnups less than 30 GWd/t, where ZrO$_2$ remains tetragonal, our predictions show a limited difference between ZrO$_2$ and the mixed oxides. The effect of differences in the thermal conductivities would have little impact on overall heat transfer. The mixed oxide layer has similar predicted thermal conductivity to that of the fuel. In fact, due to bonding, the thermal conductivity would likely be better than in fresh fuel as the bonding layer has significantly higher thermal conductivity than the He and fission product gases, if the inclusion of cracks are ignored [60]. It is, however, recommended to include the formations of ZrO$_2$ and the (U,Zr)O$_2$ with distinct thermal properties in a gap evolution model used by fuel performance codes, mainly due to the thermal degradation caused by tetragonal ZrO$_2$. Table 3 contains predicted properties of (U,Zr)O$_2$ at standard temperature and pressure along with selected literature values for comparison. The uncertainty in the results is the standard deviation over the averaging window (final 4 ps per temperature step).

4. Conclusion

Thermophysical properties of urania-zirconia mixed oxides

Table 3

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$</th>
<th>$c$</th>
<th>$\alpha_a$</th>
<th>$C_p$</th>
<th>$k_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>3.613 ± 0.002</td>
<td>5.214 ± 0.002</td>
<td>9.59 ± 0.11</td>
<td>77.3 ± 0.9</td>
<td>6.0</td>
</tr>
<tr>
<td>ZrO$_2$ Exp. (3.596)$^a$</td>
<td>(5.177)$^a$</td>
<td>(9.72)$^a$</td>
<td>(60.4)$^a$</td>
<td>(3.1)$^a$</td>
<td></td>
</tr>
<tr>
<td>U$<em>{0.25}$Zr$</em>{0.75}$</td>
<td>5.228 ± 0.001</td>
<td>9.66 ± 0.10</td>
<td>77.4 ± 0.7</td>
<td>9.37</td>
<td></td>
</tr>
<tr>
<td>U$<em>{0.50}$Zr$</em>{0.50}$</td>
<td>5.312 ± 0.001</td>
<td>9.75 ± 0.10</td>
<td>77.0 ± 0.7</td>
<td>10.77</td>
<td></td>
</tr>
<tr>
<td>U$<em>{0.75}$Zr$</em>{0.25}$</td>
<td>5.394 ± 0.001</td>
<td>9.87 ± 0.10</td>
<td>76.4 ± 0.8</td>
<td>12.57</td>
<td></td>
</tr>
<tr>
<td>UO$_2$</td>
<td>5.469 ± 0.001</td>
<td>10.16 ± 0.11</td>
<td>76.9 ± 0.8</td>
<td>21.04</td>
<td></td>
</tr>
<tr>
<td>UO$_2$ Exp. (5.468)$^b$</td>
<td>(10.56)$^b$</td>
<td>(75.0)$^b$</td>
<td>(7.59)$^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a – Lutterotti et al. [61].
b – Terblanche et al. [49].
c – Tojo et al. [55].
d – Hasselman et al. [62].
e – Fink [27].
have been modelled using MD. The simulations predict the properties of the end members with a high degree of accuracy, including the lattice parameter, heat capacity and thermal conductivity. Following this, the properties of mixed (U,Zr)O₂, which are commonly found in high burnup nuclear fuels, have been predicted.

At temperatures below 1800 K, the predicted thermal expansion coefficient of tetragonal ZrO₂ is lower than that of all compositions of cubic (U,Zr)O₂. The cubic (U,Zr)O₂ mixtures have very similar thermal expansion to that of UO₂ until they reach their superionic transition temperature. The results indicate that adding ZrO₂ to UO₂ causes a shift in the superionic transition to lower temperatures, similar to that of UO₂, especially beyond 1000 K. The formation of tetragonal ZrO₂, associated with burnups <30 GWD/t, does not impede heat transfer. However, at temperatures close to room temperature the formation of cubic (U,Zr)O₂ compounds, associated with high burn-up, results in a reduction in thermal conductivity compared to either end member, with this difference reducing as temperature increases.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnucmat.2019.151876.

Data availability

The raw and processed data required to reproduce these findings are available to download from https://doi.org/10.26190/5d1d47a9eb76f.

References


