Oxidation of UC: an in-situ high temperature environmental scanning electron microscopy study

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Oxidation of UC: an \textit{in situ} high temperature environmental scanning electron microscopy study

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Uranium Carbide: a UHTC with peculiar popcorn-like transformation

UC has high melting temperature (2508 °C) and thermal conductivity (25 W/(m K) from 1150 – 2250 °C) and therefore is an UHTC.

https://www.youtube.com/watch?v=FSZd33awqQk

400 °C 10 Pa O₂

T > 177 °C *

Oxidation of UC: a key step prior immobilisation

Understanding uranium carbide (UC) oxidation is important as it is used for reprocessing or as conditioning treatment before disposal:

Proposed mechanism of UC oxidation in oxygen environment:

(1) \( UC + O_2 \rightarrow UO_2 + C \)
(2) \( C + O_2 \rightarrow CO_2 \)
(3) \( 3UO_2 + O_2 \rightarrow U_3O_8 \)
(4) \( UC + \frac{7}{3}O_2 \rightarrow \frac{1}{3}U_3O_8 + CO_2 \)

Experimental work on UC performed at NNL and ICSM

UC pellets from Dounreay oxidised @ NNL laboratories

UC pellets (CEA Cadarache) @ICSM

- Pyrophoricity Assessment
  - Small batch (mg) UC fragments
- Conversion / SSA and C% vs T
  - Medium batch (g) UC fragments and pellets
- Influence of T and PO$_2$ on oxidation and ignition
Oxide morphology vs temperature: UC fragments
SEM characterisation

Oxidation performed in air in a muffle furnace on UC fragments

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell time (h)</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>17</td>
</tr>
</tbody>
</table>

Photo of the oxide product

Secondary electron images of oxide powder
In situ high temperature oxidation of UC

The sintering of oxide seen in furnace experiments was investigated with a fixed partial pressure of 10 Pa O$_2$ from 600-900°C.
Temperature influence ($T \geq 600^\circ$C) on oxidation: oxide sintering

10 Pa $O_2$ $T = 600^\circ$C $\rightarrow$ oxidation completed in 20 minutes
Oxidation occurs all over the surface as soon as sample is in contact with oxygen

10 Pa $O_2$ $T = 800^\circ$C $\rightarrow$ oxidation not yet completed in 3 hours
Oxidation occurs at the edges first whilst the top surface appeared compact due to partial sintering of the oxide. Stress build-up promotes cracks which generate the next surfaces to oxidise.
In situ high temperature oxidation of UC

The sintering of oxide seen in furnace experiments was investigated with a fixed partial pressure of 10 Pa O₂ from 600-900°C.

Transformation from UC to UO₂ and UO₂ to U₃O₈ was investigated in atmosphere of 10-100 Pa O₂ from 450-575°C.
Image processing via Fiji ImageJ is used to get information on sample expansion, crack propagation, crack length and network during oxidation.

UC oxidation pathways

The morphological changes during transition from UC to UO$_2$ and from UC to U$_3$O$_8$ have been monitored in situ. These are characterised by two pathways: a non explosive (pathway 1) and an explosive one (pathway 2).

**Pathway 1: UC $\rightarrow$ UO$_2$**

- Sample area Crack propagation
- Crack length
- Logarithmic
- Induction time
- Time

**Pathway 2: UC $\rightarrow$ U$_3$O$_8$**

- Sample area Crack propagation
- Crack length
- Exponential
- UC ignition
- Time

Exponential law: $y = A e^{(x/t_1)}$

$t_1 > 740 \pm 49$ s

$t_1 < 470 \pm 14$ s

*In situ* UC oxidation in a HT-ESEM

\[ T = 450^\circ C \]

\[ PO_2 = 10 \text{ Pa} \]

Time = 6 h (shown in 35 seconds)
UC transformation to UO$_2$ (450 °C 10 Pa O$_2$)

Sample area expansion and crack propagation follow a similar trend comprised of: induction period, exponential area expansion and crack propagation followed by and logarithmic trend.

HRTEM analysis shows the oxide to be polycrystalline UO$_2$. 
UC oxidation in a HT-ESEM

\[ T = 450^\circ C \]
\[ \text{PO}_2 = 50 \text{ Pa} \]
\[ \text{Time} = 3 \text{ h} \text{ (shown in 23 seconds)} \]
UC transformation to $\text{U}_3\text{O}_8$ (450 °C 50 Pa $\text{O}_2$)

Sample area expansion, crack propagation crack length and number of junctions all follow an exponential trend. UC ignition is triggered by the fragmentation of the sample.

HRTEM analysis shows the oxide to be orthorhombic $\text{U}_3\text{O}_8$ and tetragonal $\text{U}_3\text{O}_7$. $\text{U}_3\text{O}_8$ transformation is triggered by ignition of UC which propagates as a SHS reaction.
Self-propagating high-temperature synthesis (SHS)

The slow motion popcorn-like explosion recorded on a sample oxidised at 575 °C in 10 Pa O₂ shows the propagation front of the SHS reaction.

The SHS reaction in this sample propagates with a speed between 150 – 500 ± 50 µm/s across the sample.
Conclusions

- *In situ* HT-ESEM study on UC oxidation reveals the influence of T and PO$_2$ on the transformation between UC to UO$_2$ and U$_3$O$_8$.
- A method for the correlation of crack propagation and sample expansion has been developed via Fiji ImageJ. Crack network is responsible for UC ignition. UC oxidises to UO$_2$ when growth factor $t_1 \geq 740 \pm 49$ s, or to U$_3$O$_8$ when $t_1 \leq 470 \pm 14$ s.
- UC ignition to U$_3$O$_8$ triggers a SHS reaction which propagates throughout the sample.
Thanks for your attention!

And special thanks to all the people at NNL, ICSM, CEA and Imperial that made this project possible!