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

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Centre for Nuclear Engineering

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

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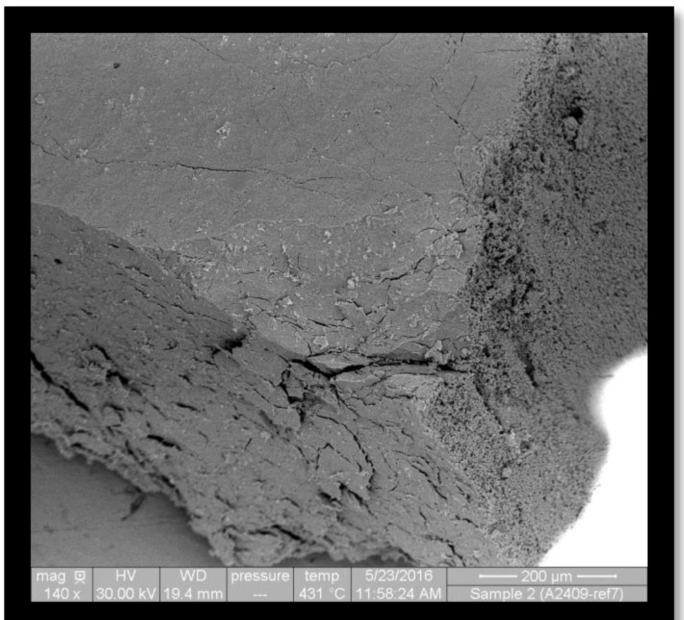
EPSRC Engineering and Physical Sciences Research Council

Uranium Carbide: a UHTC with peculiar popcorn-like transformation

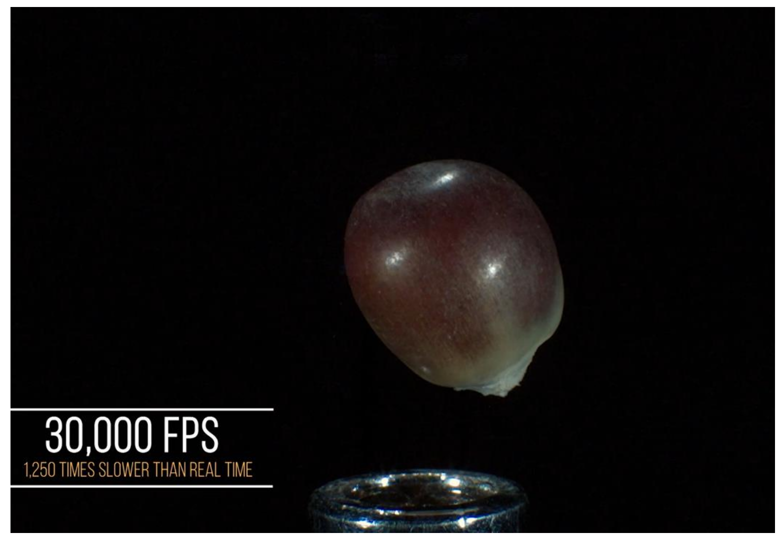
UC has high melting temperature (2508 ^{o}C) and thermal conductivity (25 W/(m K) from 1150 – 2250 ^{o}C) and therefore is an UHTC.

Uranium carbide



400 ^{o}C 10 Pa O_2

Corn



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

T > 177 ^{o} C *

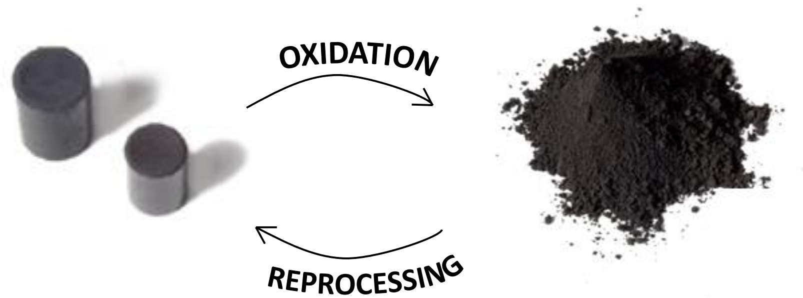
* Hoseney, R C; Zeleznak, K; Abdelrahman, A,"Mechanism of popcorn popping", Journal of Cereal Science, 43-52, 1983,

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 :

DISPOSAL/REPROCESSING

UC
(U,Pu)C



UO_2/U_3O_8
$(U,Pu)O_2$

Proposed mechanism of UC oxidation in oxygen environment:

$$UC \xrightarrow{O_2/\ AIR} U_3O_8$$

$$(1)\ UC + O2 \rightarrow UO_2 + C$$

$$(2)\ C + O_2 \rightarrow CO_2$$

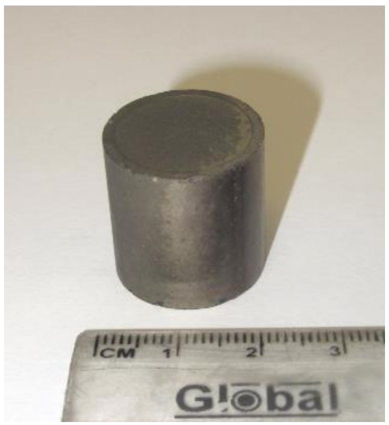
$$(3)\ 3UO_2 + O_2 \rightarrow U_3O_8$$

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

* Iyer, V. S. et al. "Oxidation behavior of carbide fuels". *Nucl. Technol.* 91, 388–393 (1990).

Experimental work on UC performed at NNL and ICSM

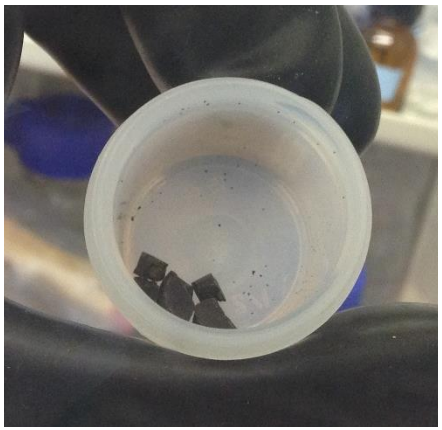
UC pellets from Dounreay oxidised @ NNL laboratories



Depleted UC pellet

- ❑ **Pyrophoricity Assessment**
  Small batch (mg) UC fragments
- ❑ **Conversion / SSA and C% vs T**
  Medium batch (g) UC fragments and pellets

UC pellets (CEA Cadarache) @ICSM



- ❑ **Influence of T and PO_2 on oxidation and ignition**

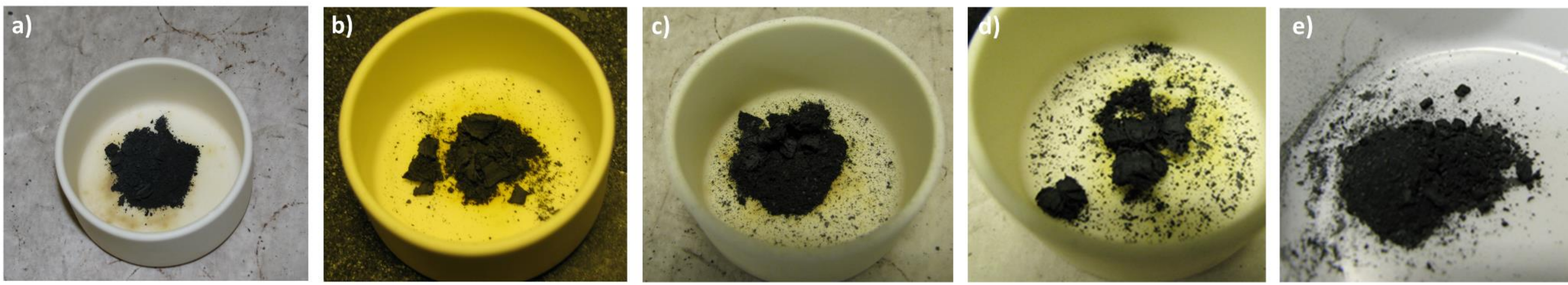
Oxide morphology vs temperature: UC fragments

SEM characterisation

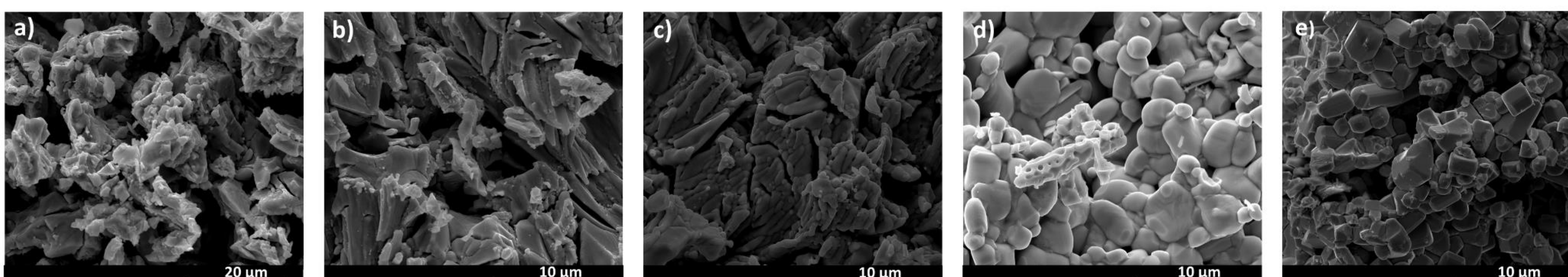
Oxidation performed in air in a muffle furnace on UC fragments

T (°C)	600	700	800	900	900
Dwell time (h)	4	4	4	4	17

Photo of the oxide product

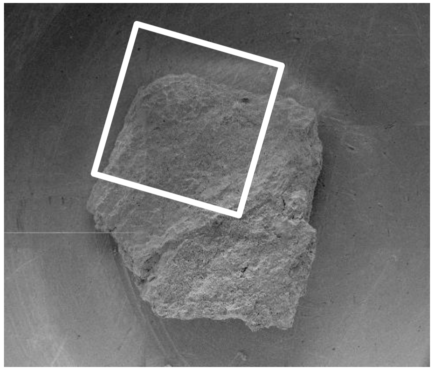


Secondary electron images of oxide powder

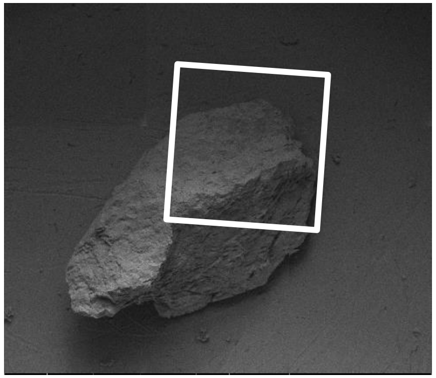


In situ high temperature oxidation of UC

The sintering of oxide seen in furnace experiments was investigated with a fixed partial pressure of 10 Pa O_2 from 600-900°C



10 Pa O_2 600 °C

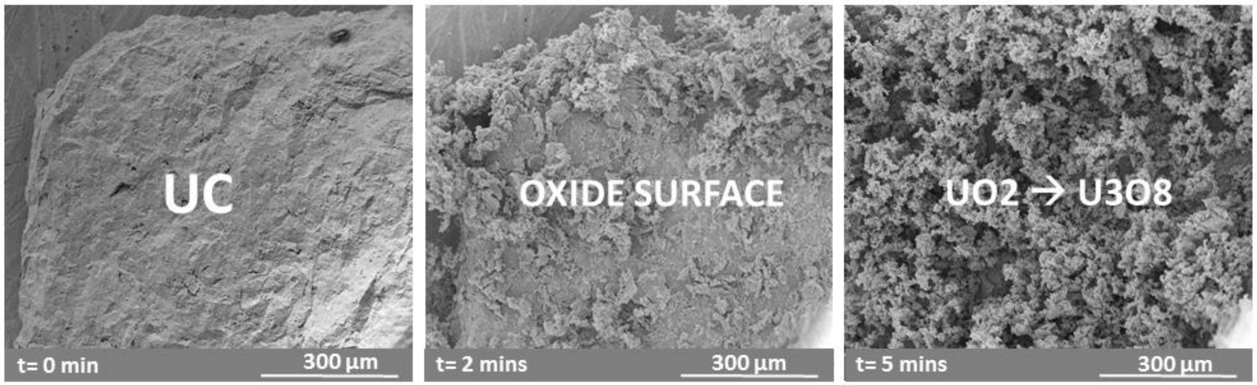


10 Pa O_2 800 °C

Temperature influence (T≥ 600°C) on oxidation: oxide sintering

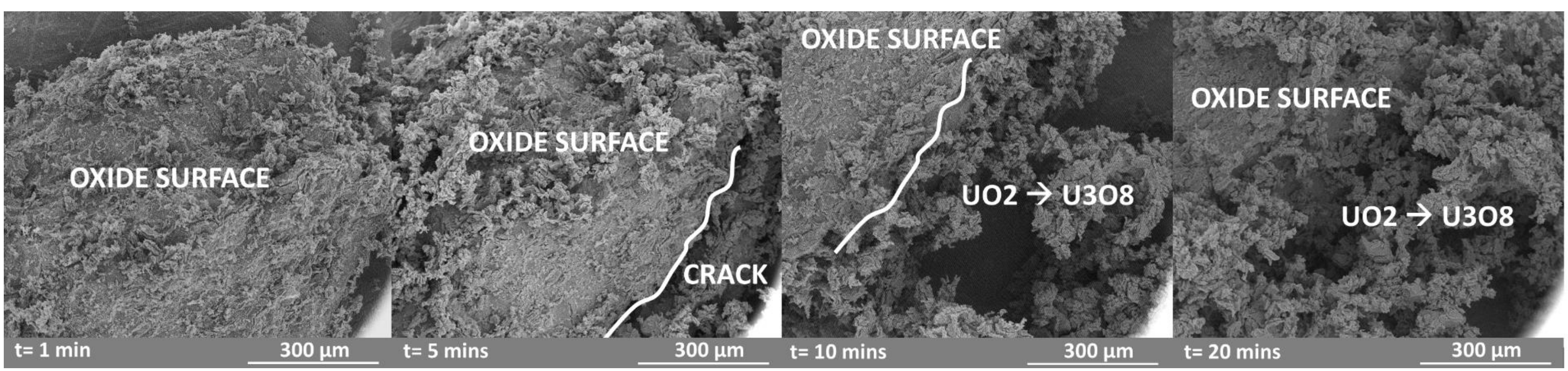
10 Pa O_2 T = 600°C → oxidation completed in 20 minutes

Oxidation occurs all over the surface as soon as sample is in contact with oxygen



10 Pa O_2 T = 800°C → 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

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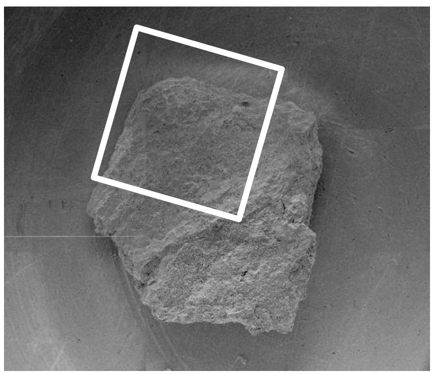
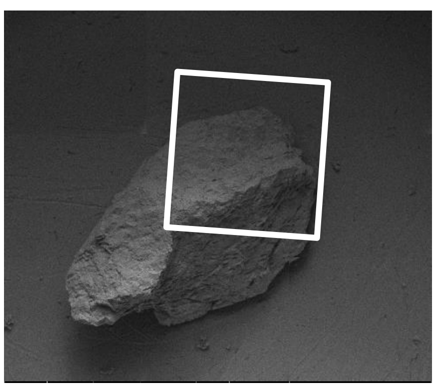
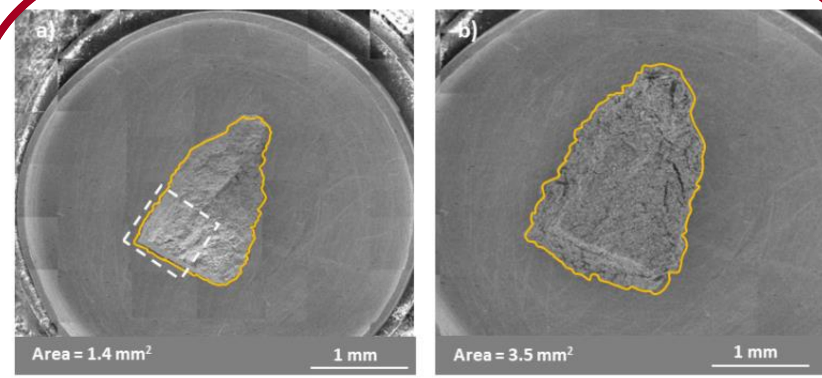


10 Pa O_2 600 °C

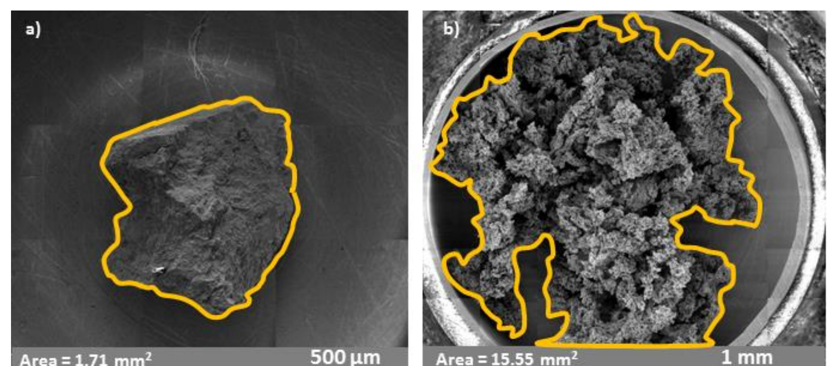


10 Pa O_2 800 °C

Transformation from UC to UO_2 and UO_2 to U_3O_8 was investigated in atmosphere of 10-100 Pa O_2 from 450-575°C



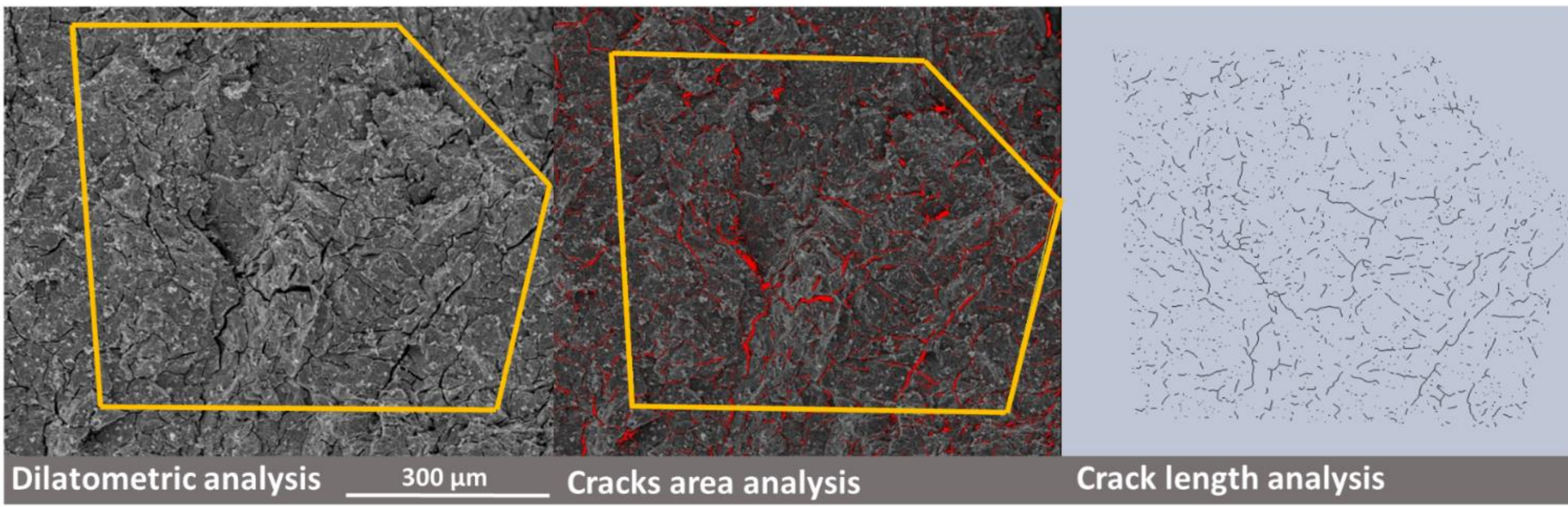
10 Pa O_2 450 °C



50 Pa O_2 450 °C

Image analysis techniques: sample area expansion and crack propagation

Image processing via Fiji ImageJ is used to get information on sample expansion, crack propagation, crack length and network during oxidation.

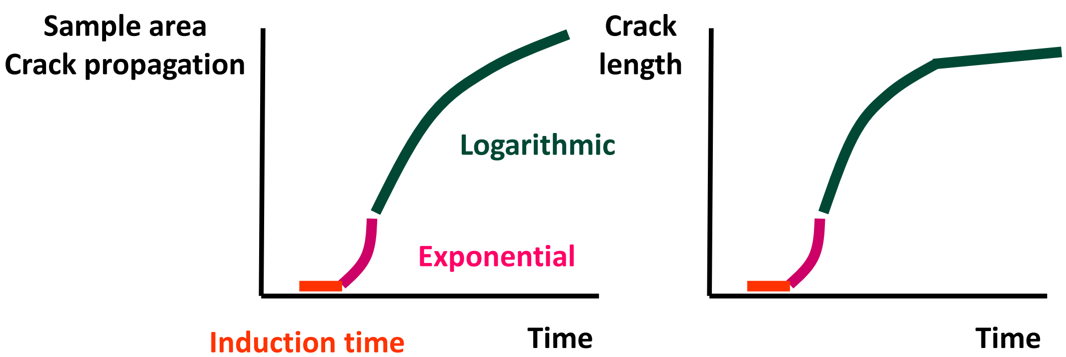


* Gasparrini, C et al. "Oxidation of UC: an *in situ* high temperature environmental scanning electron microscopy study". *J Nucl Mat*, 494, 127-137, (2017)

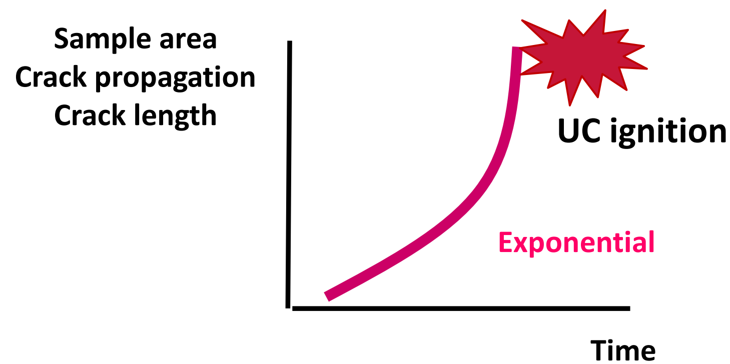
UC oxidation pathways

The morphological changes during transition from UC to UO_2 and from UC to U_3O_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 → UO_2



Pathway 2: UC → U_3O_8



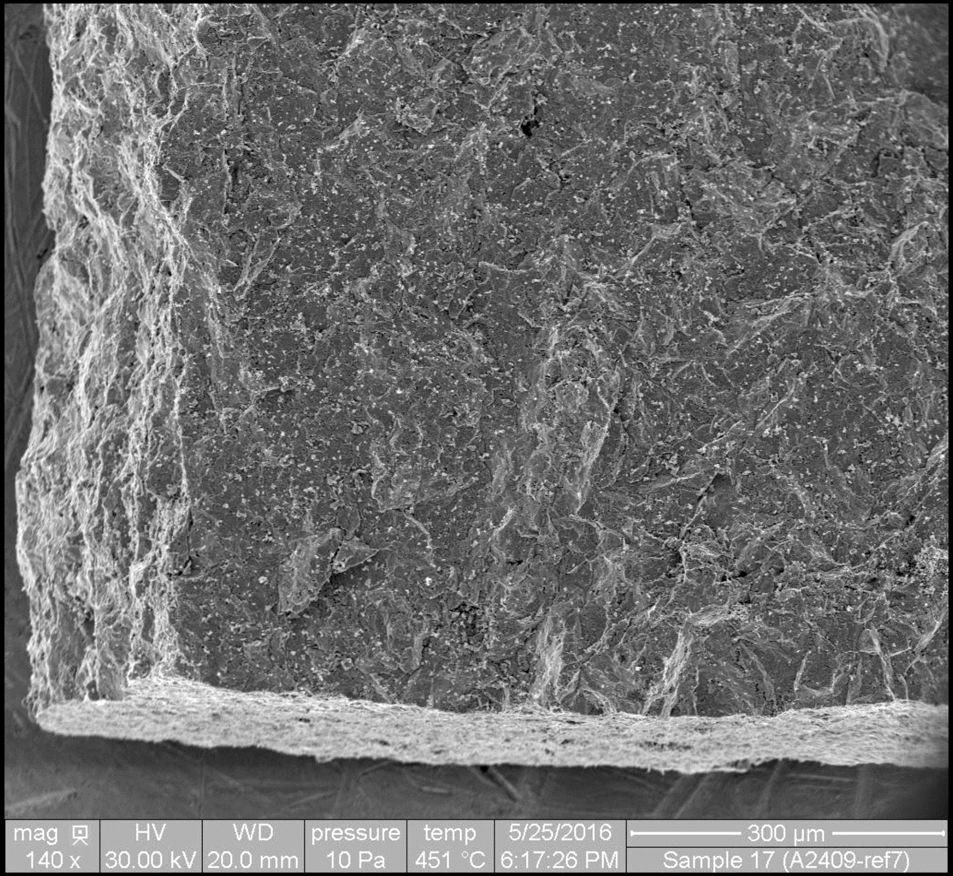
t_1 > 740 ± 49 s

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

t_1 < 470 ± 14 s

* Gasparrini, C et al. "Oxidation of UC: an *in situ* high temperature environmental scanning electron microscopy study". *J Nucl Mat*, 494, 127-137, (2017)

In situ UC oxidation in a HT-ESEM

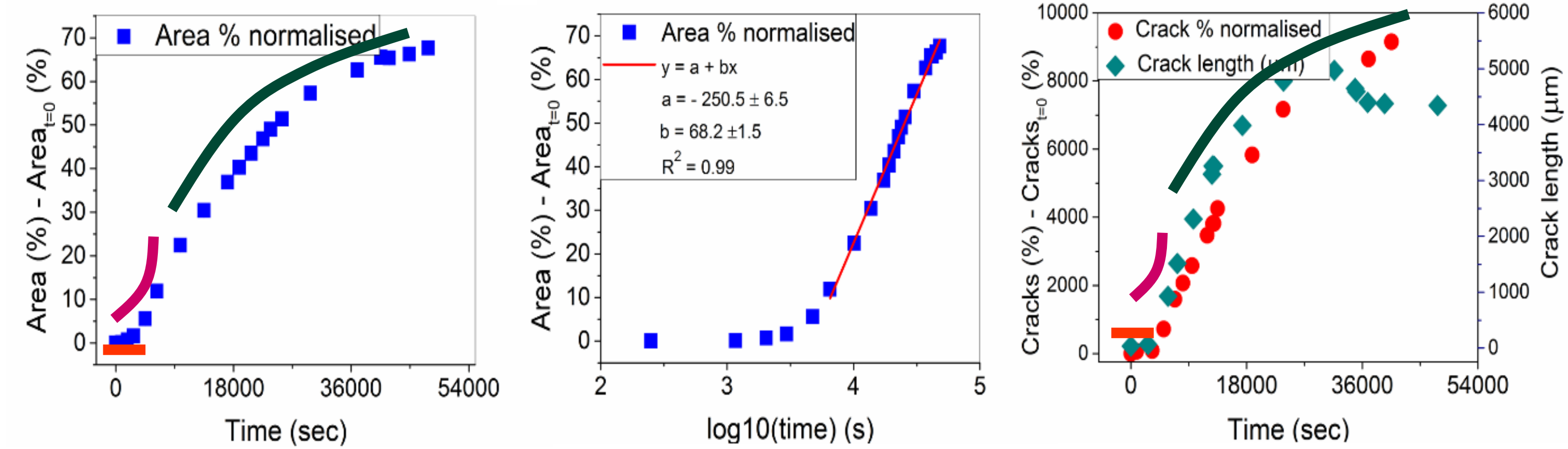


T = 450˚C

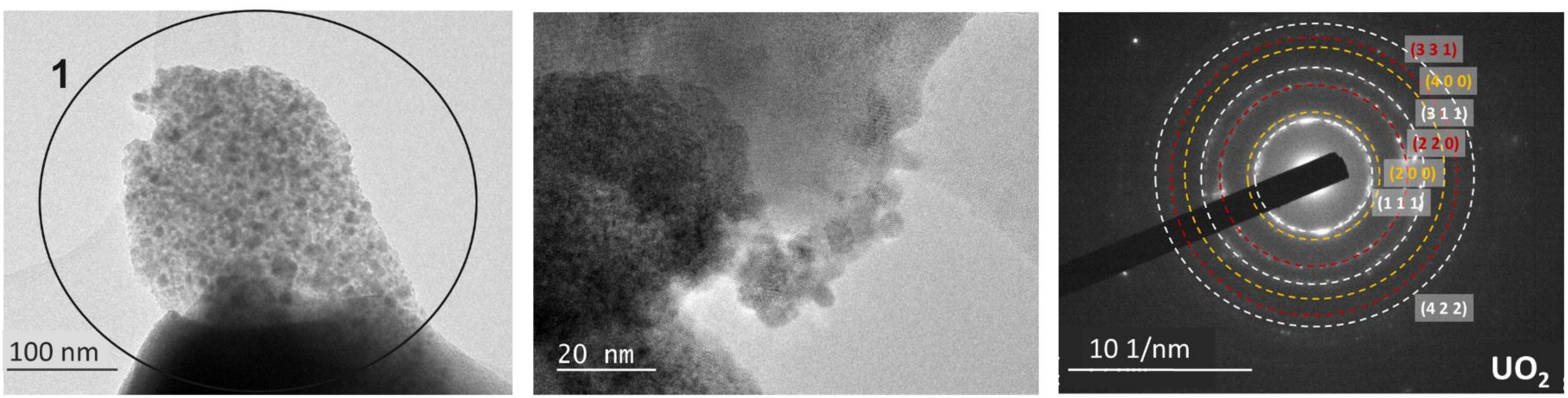
PO_2 = 10 Pa

Time = 6 h (shown in 35 seconds)

UC transformation to UO_2 (450 ^{o}C 10 Pa O_2)

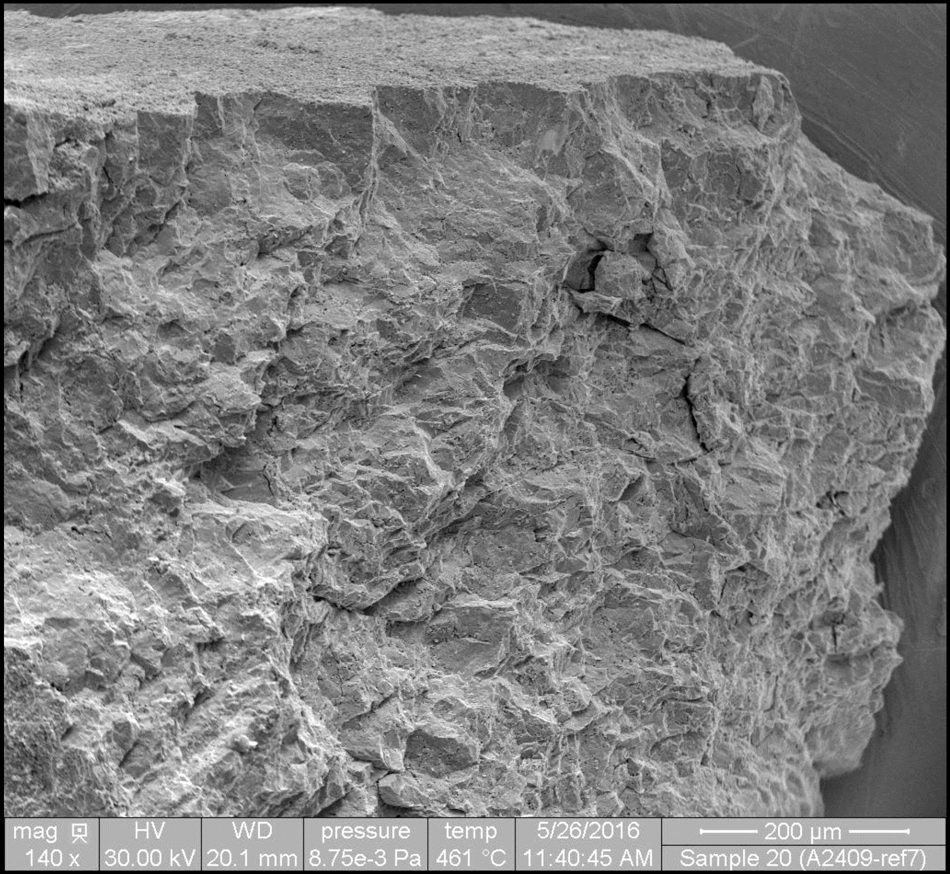


Sample area expansion and crack propagation follow a similar trend comprised of: induction period, exponential area expansion and crack propagation followed by and logarithmic trend.



HRTEM analysis shows the oxide to be polycrystalline UO_2

UC oxidation in a HT-ESEM

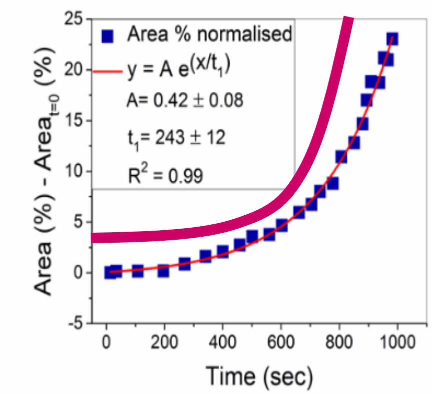


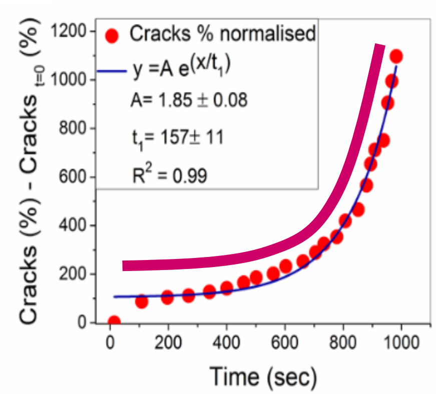
T = 450˚C

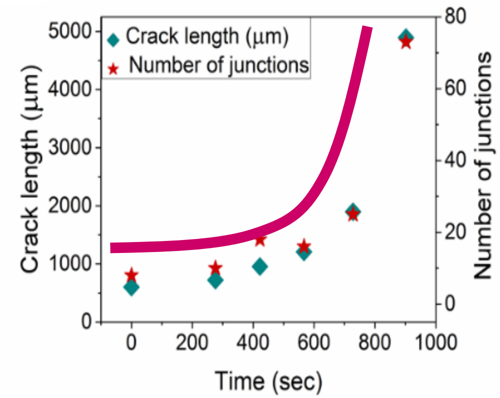
PO_2 = 50 Pa

Time = 3 h (shown in 23 seconds)

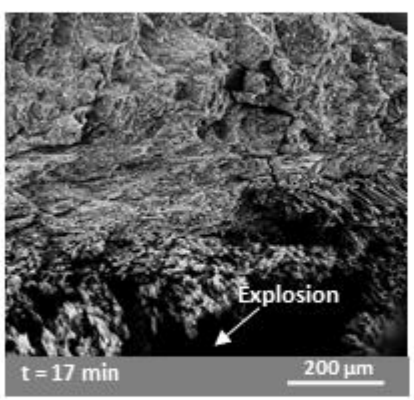
UC transformation to U_3O_8 (450 ^oC 50 Pa O_2)

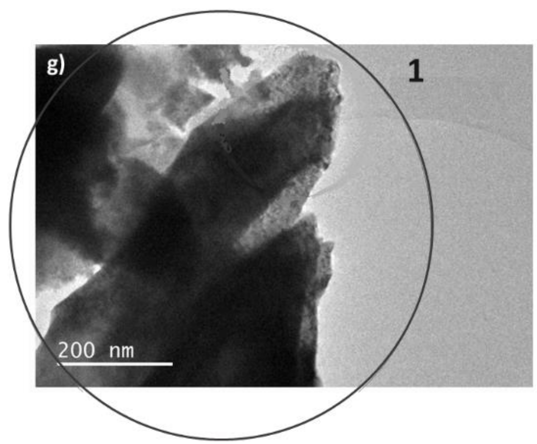


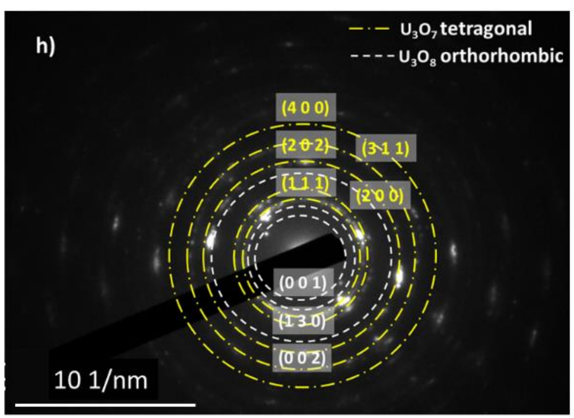




Sample area expansion, crack propagation crack length and number of junctions all follow an exponential trend. UC ignition is triggered by the fragmentation of the sample.



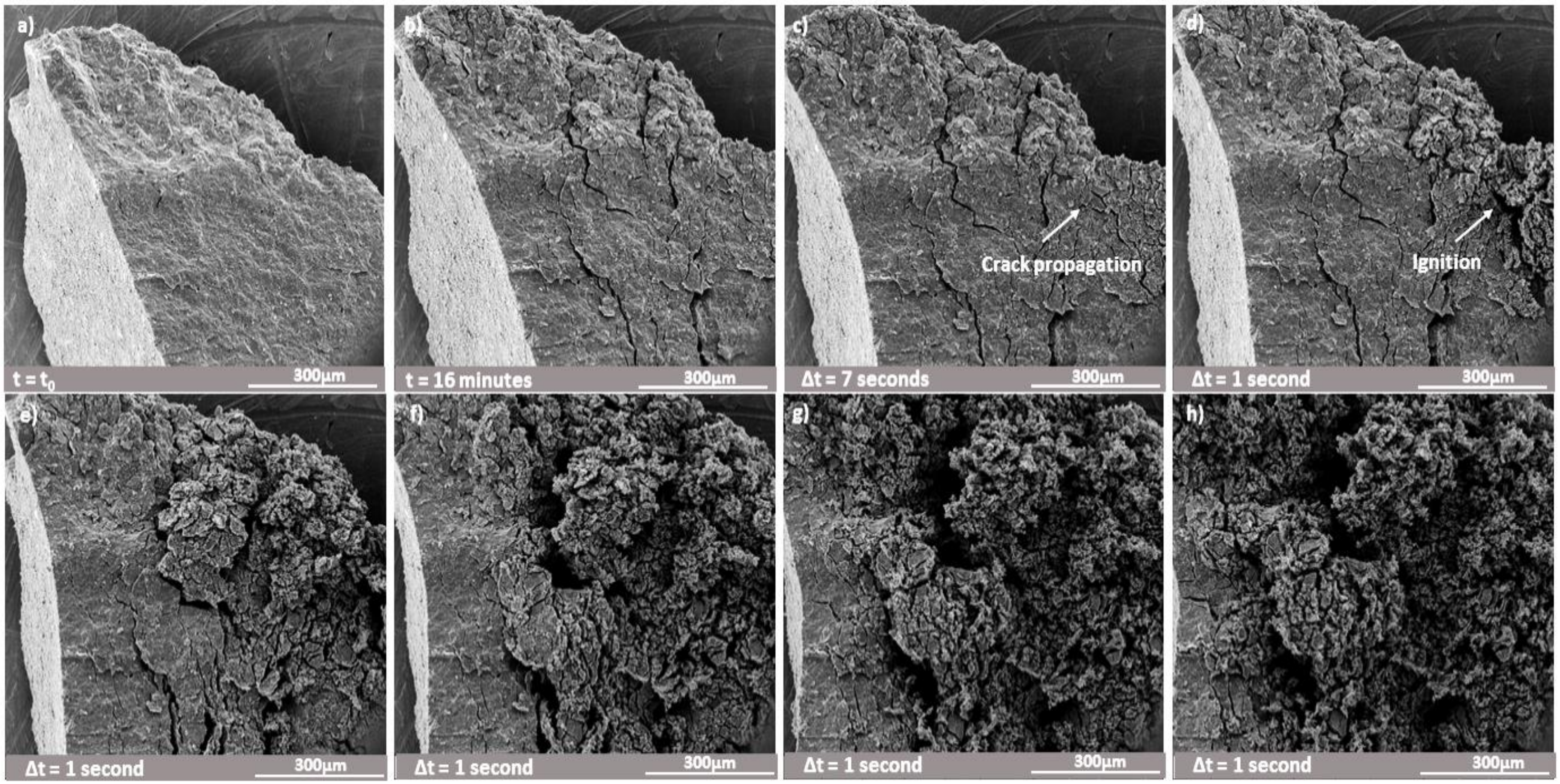




HRTEM analysis shows the oxide to be orthorhombic U_3O_8 and tetragonal U_3O_7 . U_3O_8 transformation is triggered by ignition of UC which propagates as a SHS reaction.

Self-propagating high-temperature synthesis (SHS)

The slow motion popcorn-like explosion recorded on a sample oxidised at 575 °C in 10 Pa O_2 shows the propagation front of the SHS reaction.

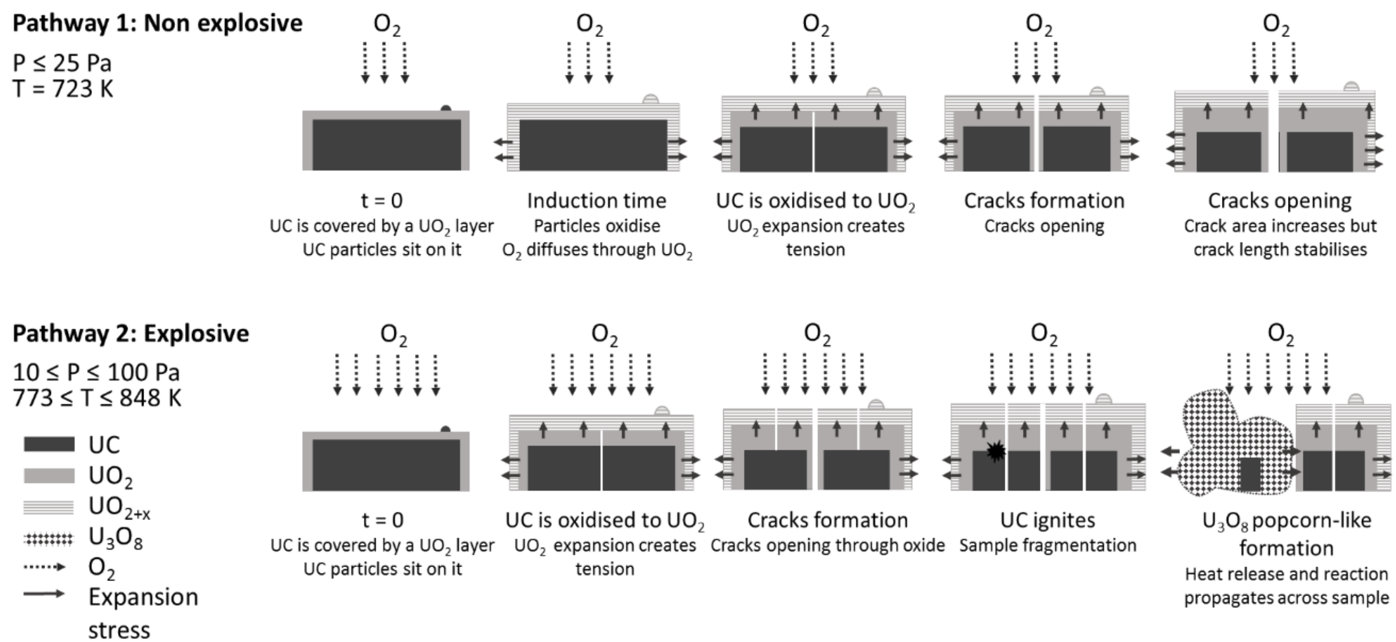


The SHS reaction in this sample propagates with a speed between 150 – 500 ± 50 μm/s across the sample.

Conclusions

UC → UO_2

UC → U_3O_8



- *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_3O_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_3O_8 when $t_1 \leq 470 \pm 14$ s.
- UC ignition to U_3O_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 !

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