OXIDATION OF CARBIDES INCLUDING CARBIDE NUCLEAR FUELS

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Distinctive Theme 1
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Bristol

Overview

The understanding of the OXIDATION mechanism in carbide spent nuclear fuels is of prior importance

DISPOSAL/REPROCESSING

ACCIDENT SCENARIOS

http://www.world-nuclear-news.org/ENF-Triso_fuel_triumphs_at_extreme_temperatures-2609137.html

Oxidation of carbide fuel can be performed in several oxidizing environments

CARBIDE SPENT FUEL
UC / (U.Pu)C

$$UC + \begin{matrix} O_2 \\ CO_2/H_2O \end{matrix} \xrightarrow{ZrC} \begin{matrix} U_3O_8 \\ UO_2 \end{matrix}$$

MIXED OXIDE POWDER FOR REPROCESSING

CARBIDE MATERIAL USED IN NUCLEAR FUEL APPLICATIONS

OXIDATION OF CARBIDES INCLUDING CARBIDE NUCLEAR FUELS

In situ monitoring of Zirconium Carbide oxidation (800 - 1200˚C) using a high temperature environmental SEM

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Introduction

Zirconium Carbide

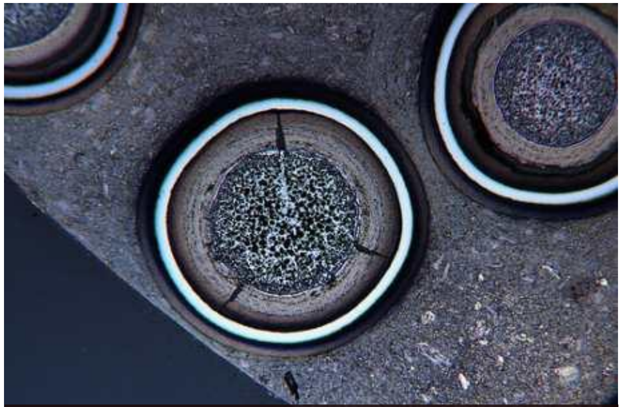
•Extremely high melting point (around 3500 ˚C)

•High thermal conductivity (35 W/m · K at 1000 ˚C)

•High hardness and high neutron transparency

These properties make ZrC a candidate for use in extreme environment applications such as hypersonic vehicles and as coating materials in nuclear fuels.

However a drawback of this material is its low resistance towards **oxidation**.



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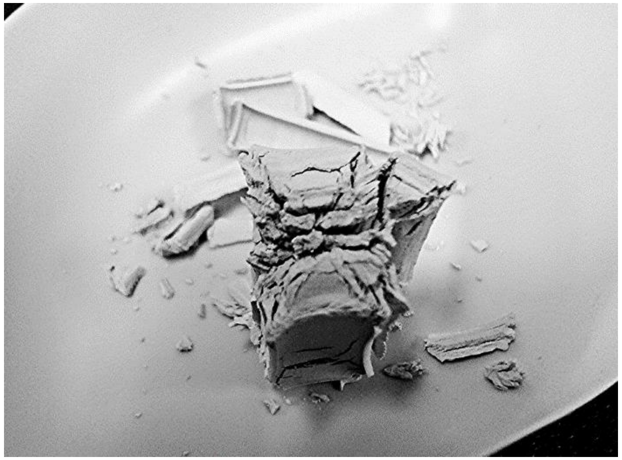

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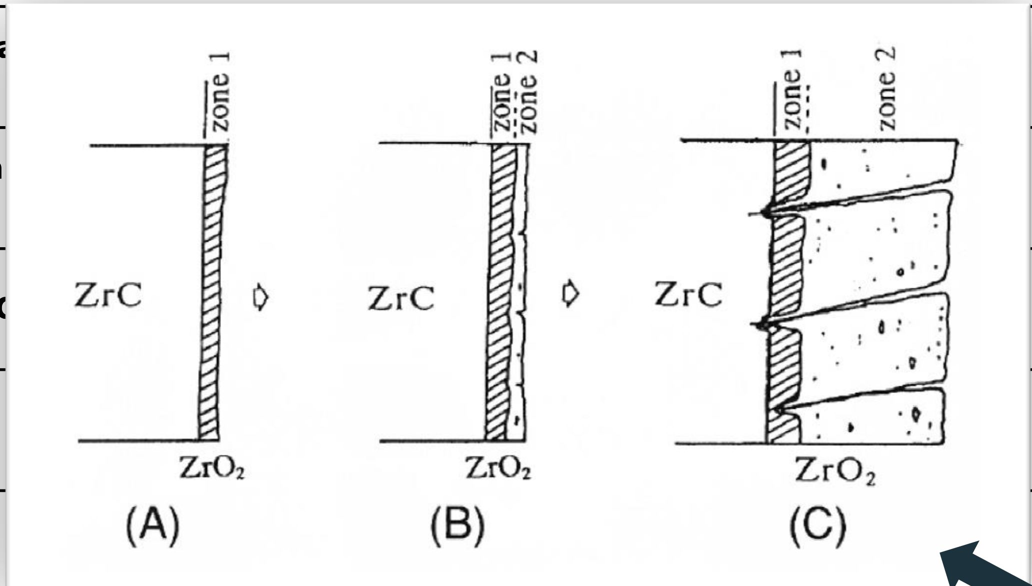
Literature Overview

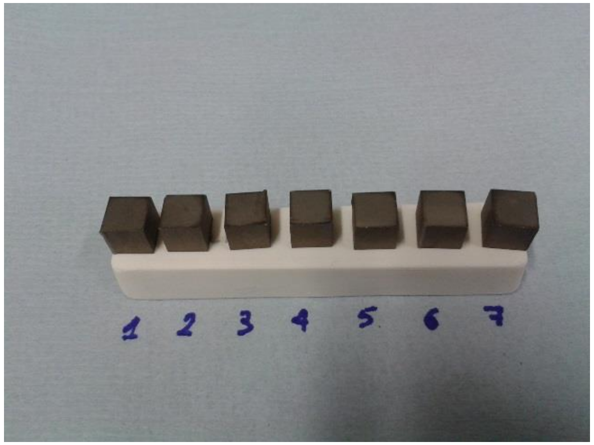
Starting materia ZrC	Reference
Electron beam melted ZrC	Kuriakose and Margrave (1964)
Commercial Zr(	Shimada et al. (1990)
ZrC powder	Rama rao and Venugopal (1994)
Zone floated single crystal $ZrC_{0.97}$	Shimada et al. (1995)

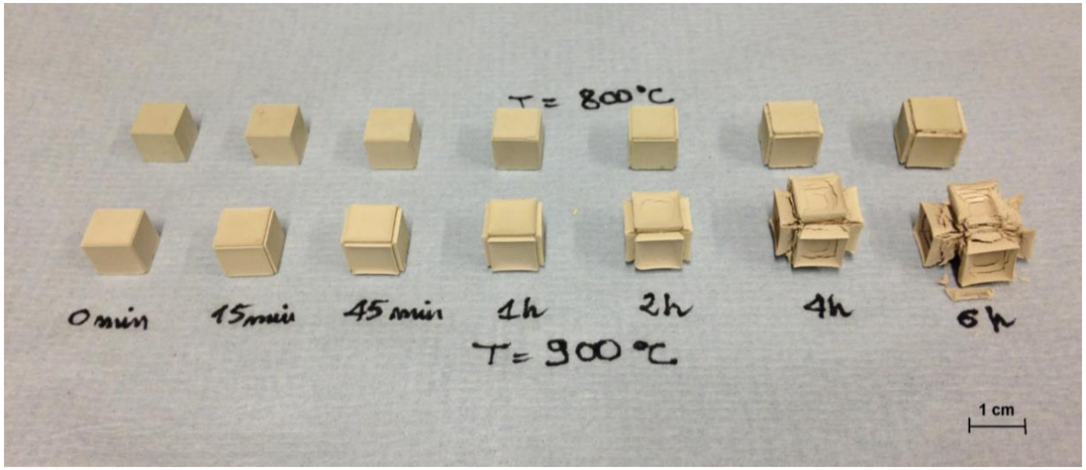


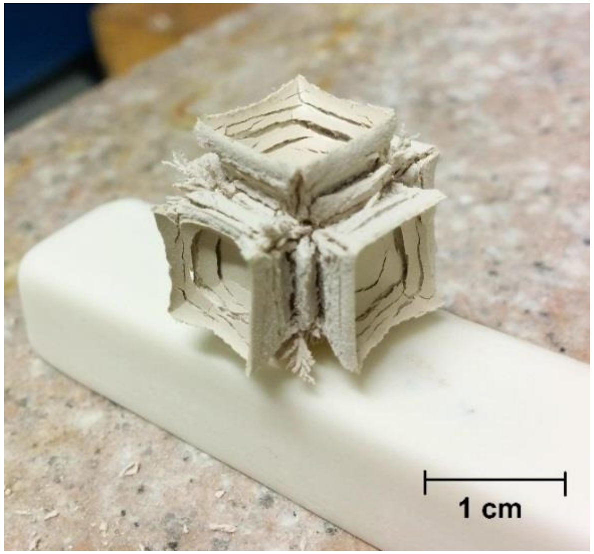
Literature controversy → Systematic study required to get full understanding of mechanism of ZrC oxidation

Production and oxidation experiments

- ZrC commercial powder hot pressed at 2000˚C for 1h
- Oxidation on specimens performed in a chamber lift furnace at 800 – 900 - 1000 ⁰C with quenching to follow different stages of the oxidation
- Oxidation develops into a Maltese Cross shape forms







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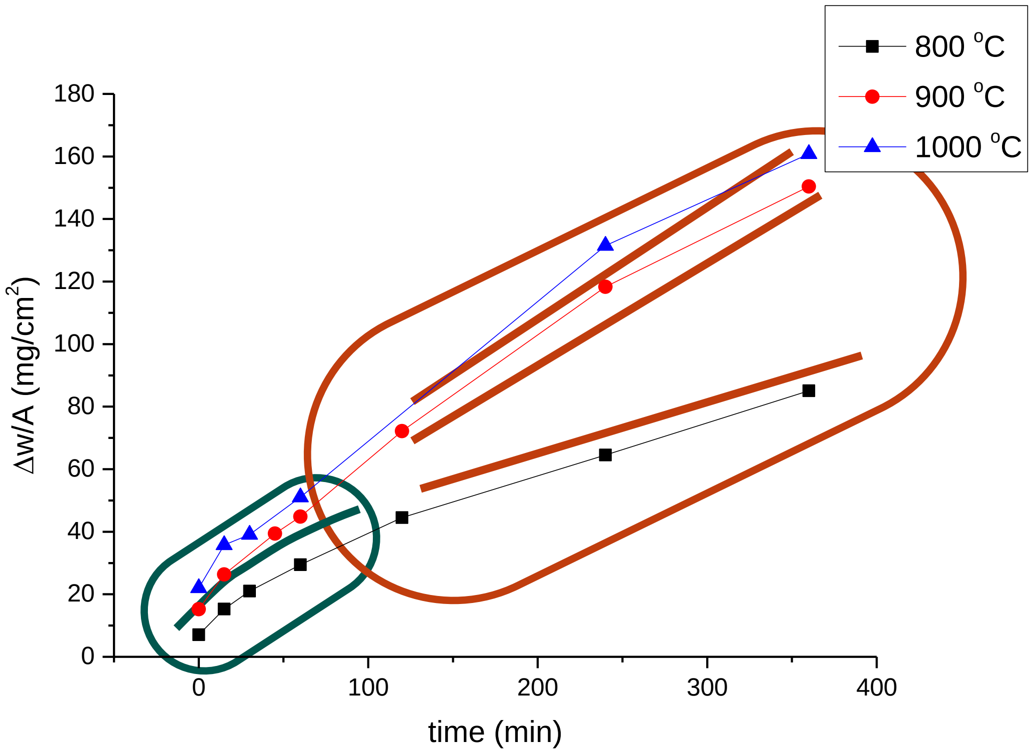
Kinetic Analysis

Mass gain normalized per surface area vs time shows a complex kinetics better described with a PARALINEAR fitting

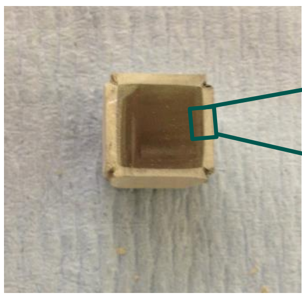
PARAbolic **LINEAR**



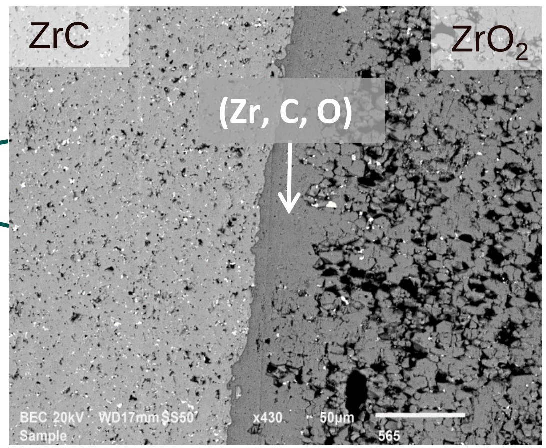
How to take into account the volume expansion and deformation?
Difficulties to fit ZrC oxidation against a simple model.

Microscale approach : SIMS-FIB

Chemical analysis at the cross section of not fully oxidized specimens

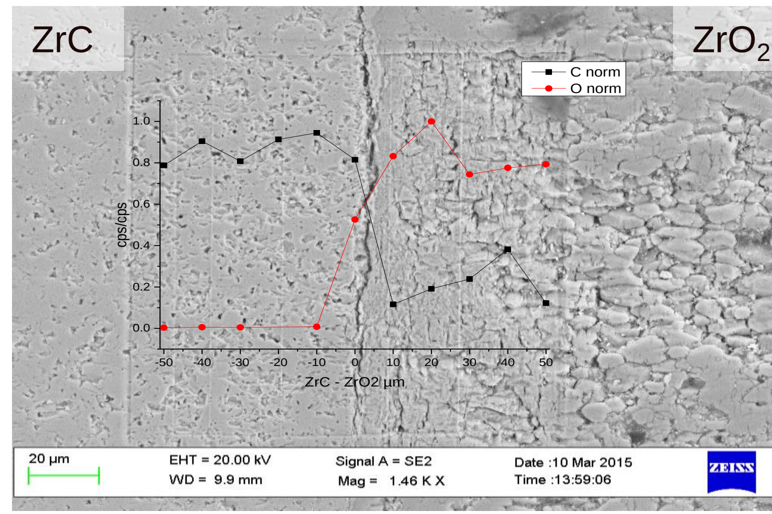


SEM+EDX



Dense interface separates the carbide and the oxide. EDX shows the presence of carbon and oxygen

FIB+SIMS



Surface analysis across the sputtered interface layer: compositional analysis of carbon and oxygen

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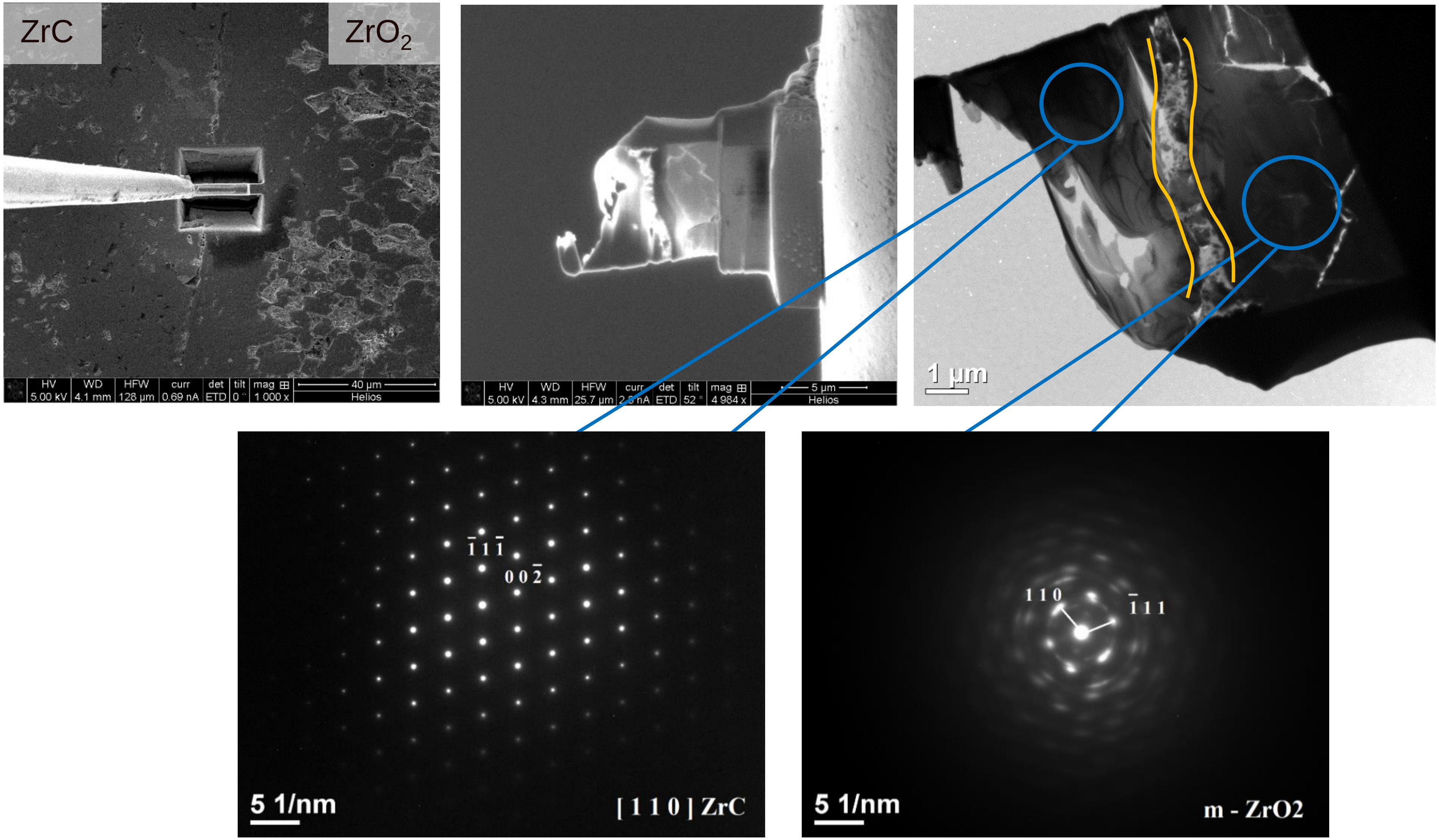
Nanoscale approach : TEM



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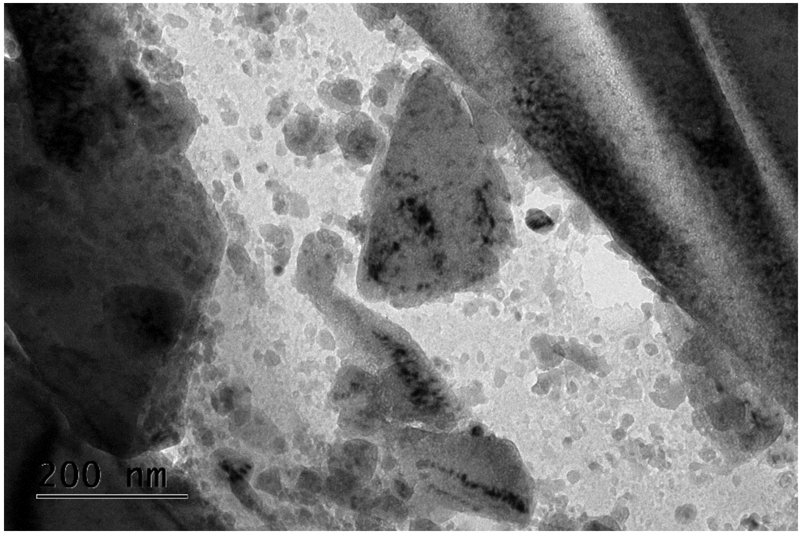
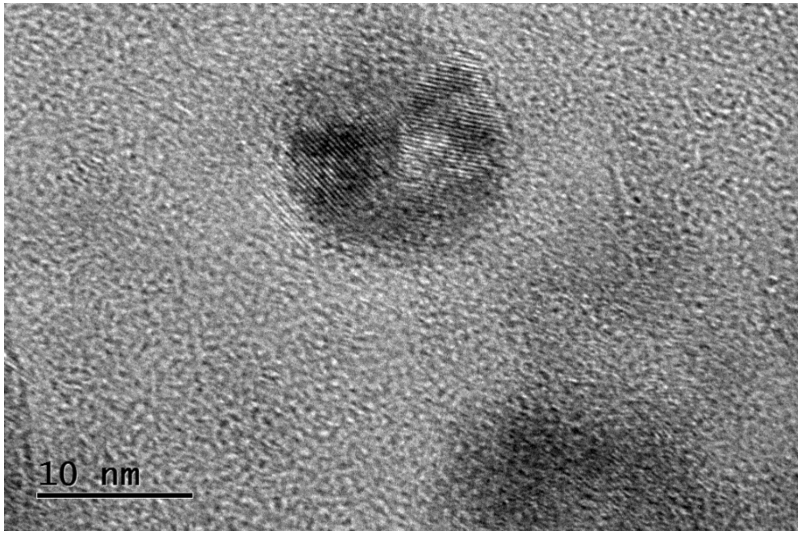
Nanoscale approach : HRTEM

The interface that separates the carbide area with the oxide is further analysed at a HRTEM. This a few microns thick intermediate layer is primarily made of amorphous carbon and zirconia nanocrytals (<5nm).





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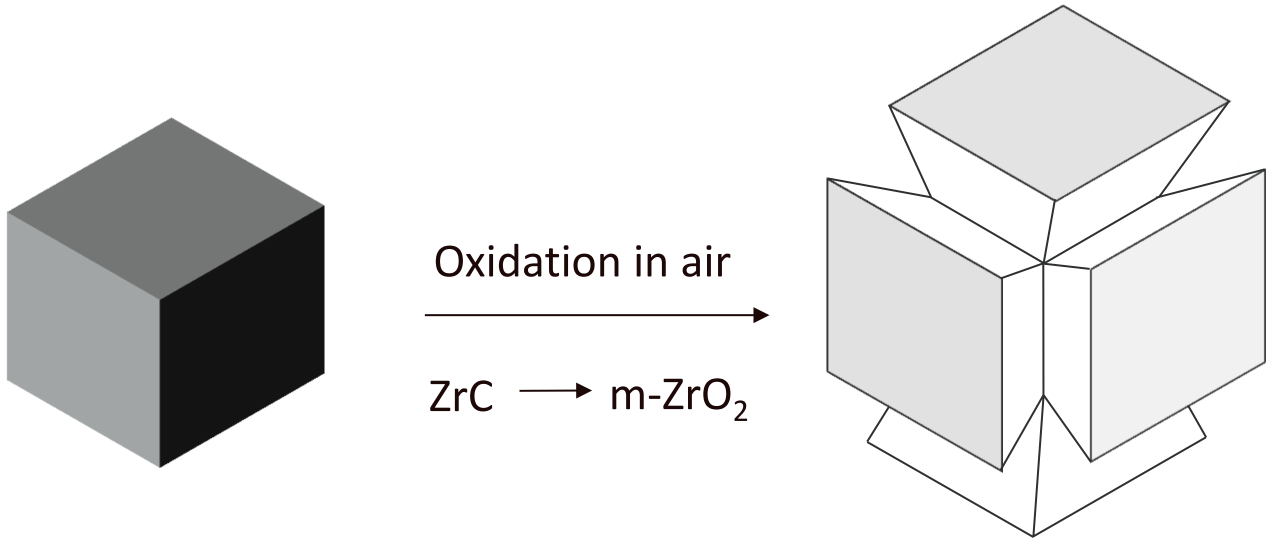
Considerations

What is the mechanism behind this characteristic volume expansion?

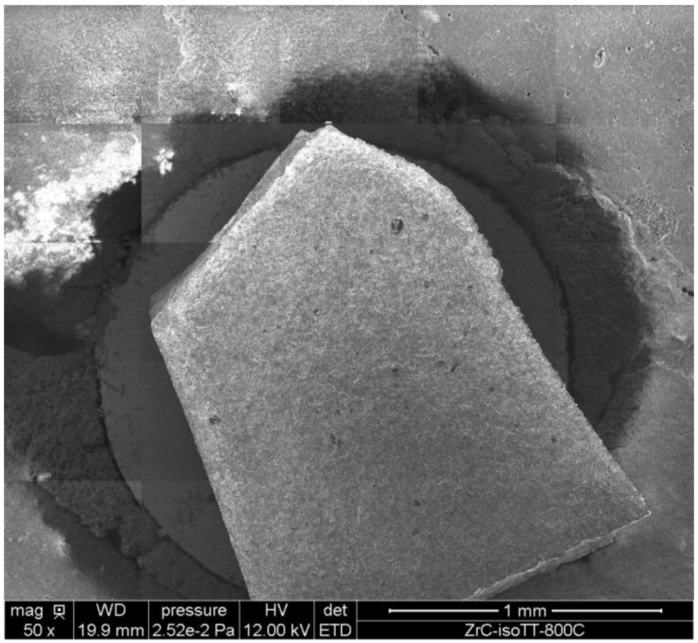


Volume expansion due to transformation in crystal structure

$ZrC \rightarrow m\text{-}ZrO_2$ $\Delta V = (V_{m\text{-}ZrO2} - V_{ZrC}) / V_{ZrC} = 36\%$

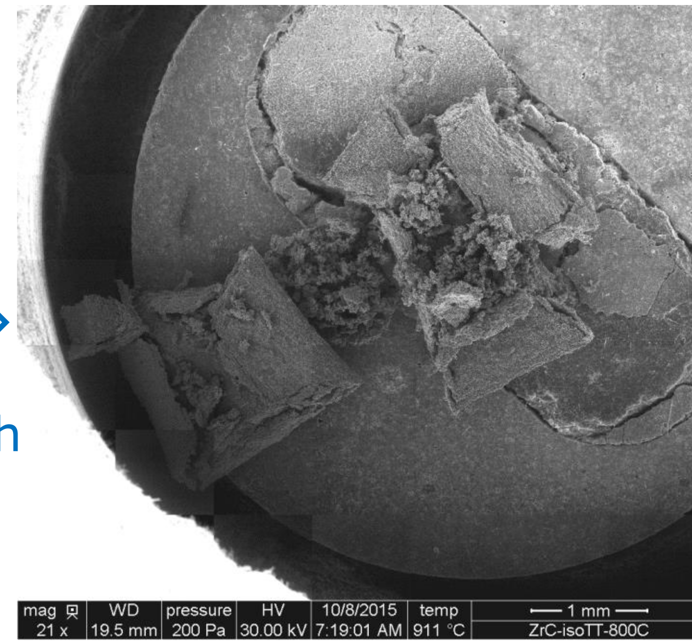
In situ experiments

All previous analysis have been performed on samples cooled down at room temperature.
To further investigate the oxidation mechanism and Maltese Cross formation, in situ experiments are performed in a HT-ESEM.



2 mbar O_2

800°C - 18h



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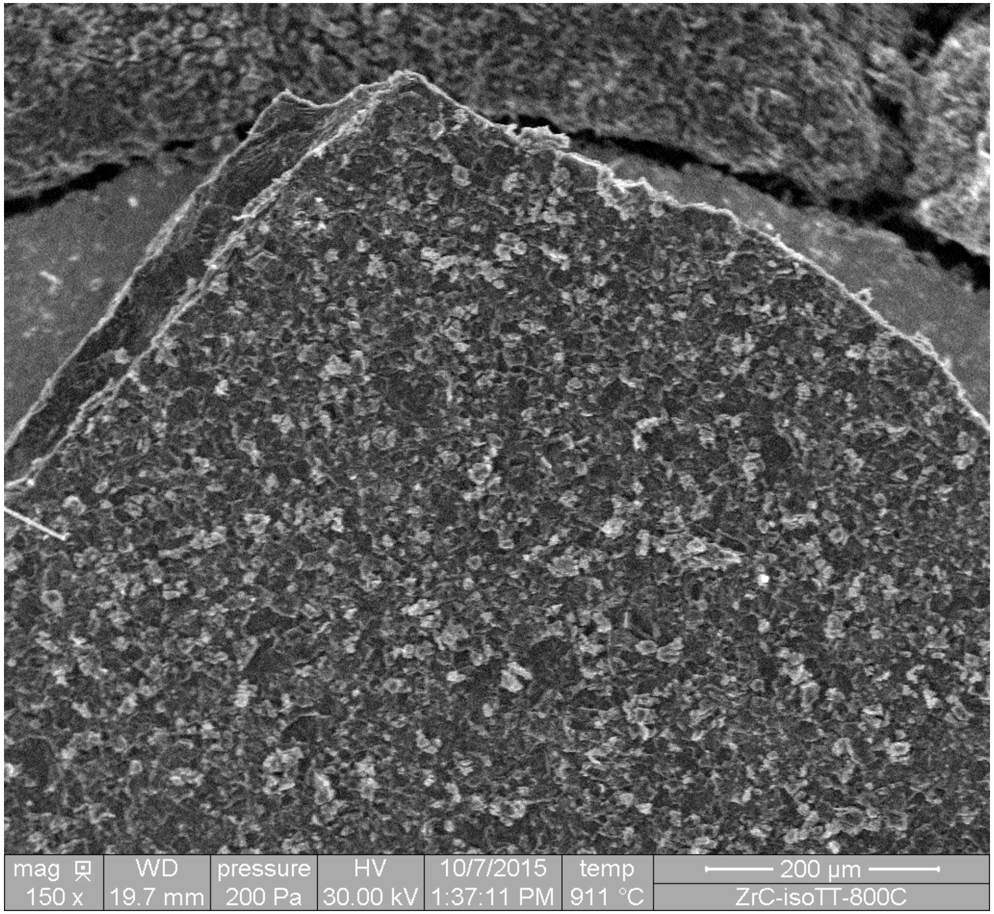
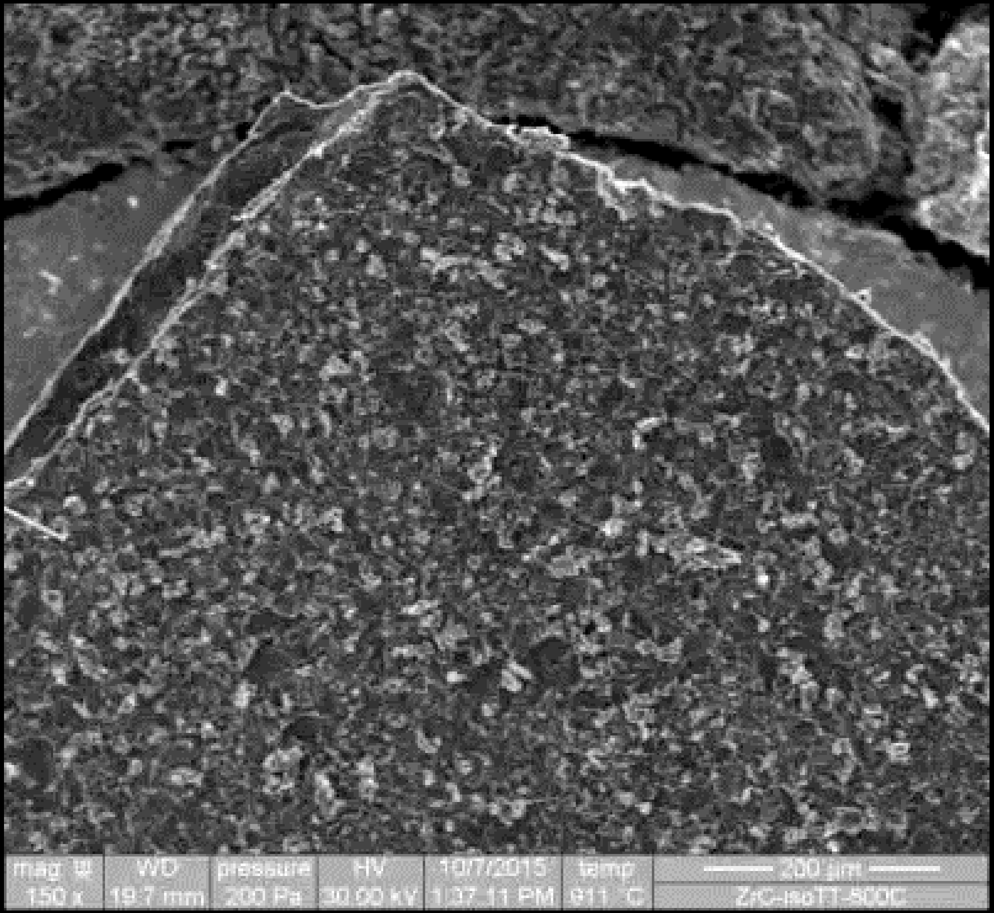
Oxidation of ZrC in a HT-ESEM

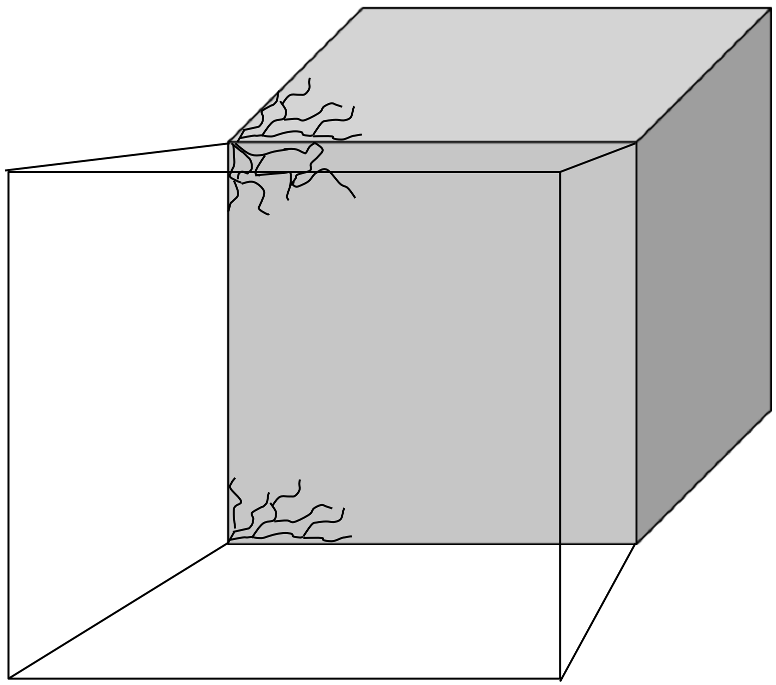


ZrC oxidation in a HT-ESEM



Maltese Cross Formation

The formation of the Maltese Cross seems to be attributed to cracks formation at edges and borders



CRACKS PROPAGATION AT EDGES

⇩

INCREASE OF REACTIVE SURFACE

⇩

FURTHER OXIDATION IN THIS AREA

Crack formation phenomenon:
Is this due to stresses attributed to thermal expansion? Or just volume expansion?

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Conclusions

- Oxidation of ZrC has been investigated through a hierarchical level of analysis :

MACROSCALE Optically / HT-ESEM	→	MICROSCALE SEM / FIB-SIMS	→	NANOSCALE TEM / HRTEM
Maltese cross		*ZrC – ZrO_2 Interface*		*ZrO_2 nanoclusters*

- The interface region where the oxidation reaction occurs has been identified by SEM / FIB – SIMS, its characterization has been performed via TEM

- The formation of the Maltese Cross is found to be directly related to severe cracks formation at the edges and border of the sample in the early stages of the oxidation

- Investigations on the nature of the cracks formation will be done via FEM analysis in order to understand if these are thermal expansion or volumetric expansion related

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Thanks for your attention !

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