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Oxidation of Hot Pressed Zirconium Carbide between 800 – 1000 ˚C

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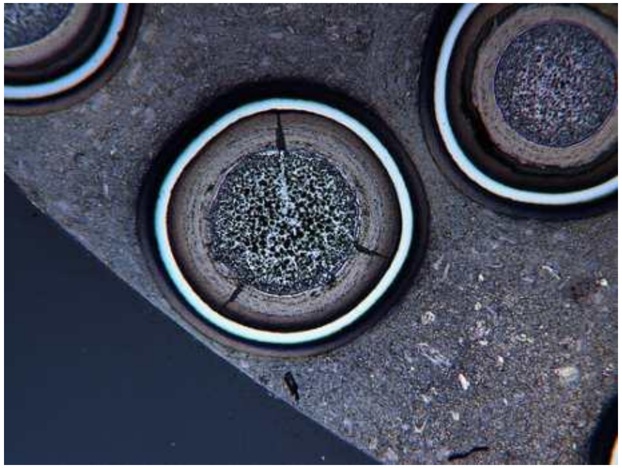
Introduction

Zirconium Carbide has
- **extremely high melting point (3420 ˚C)**
- **high thermal conductivity (35 W/m · K at 1000 ˚C)**
- **good stability at high temperature and under vacuum**

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.



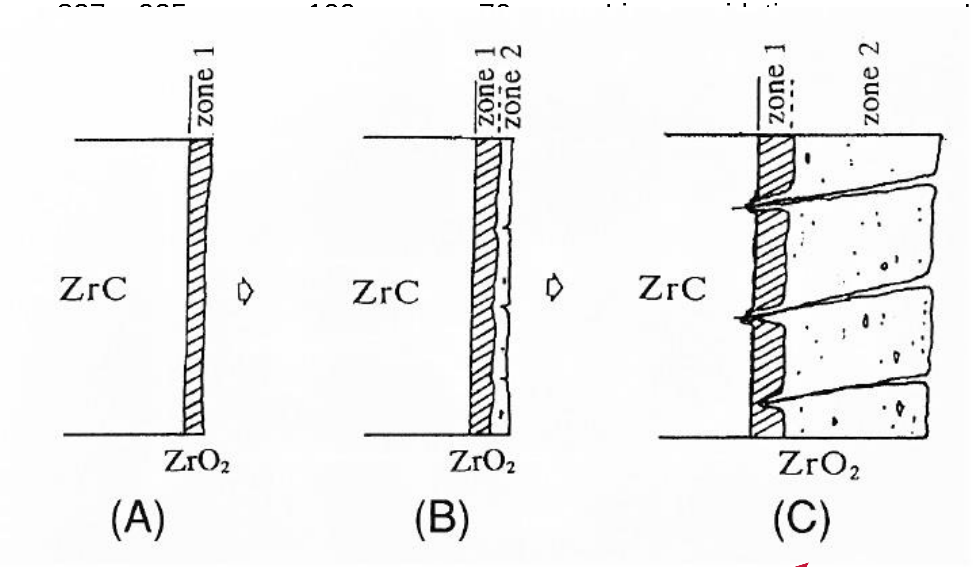
Microscopic cross-section of Triso fuel particles (Image: INL)
http://www.world-nuclear-news.org/ENF-Triso_fuel_triumphs_at_extreme_temperatures-2609137.html

ZrC
carbide coating material in TRISO particle

Its oxidation behaviour can affect the integrity of the material in case of an accident

Previous ZrC oxidation studies

Starting material ZrC	Range of T (K)	O_2 pressure (kPa)	E_a (kJ/mol)	Kinetic data	Ref
Electron beam melted ZrC (99.5% pure)					…iakose and …argrave (1964)
Zone refined bars (11.2%C)					…erkowitz (1967)
Hot pressed cylindrical ZrC (0.1% excess C)					…ch and Pugach (1973)
Commercial ZrC					…mada et al. (1990)
ZrC powder		20	110	mechanistic …	…ma rao and …enugopal (1994)
Zone floated single crystal $ZrC_{0.97}$	873 - 1773	0.02 - 2	-	Oxide carbide interface observations	Shimada et al. (1995)



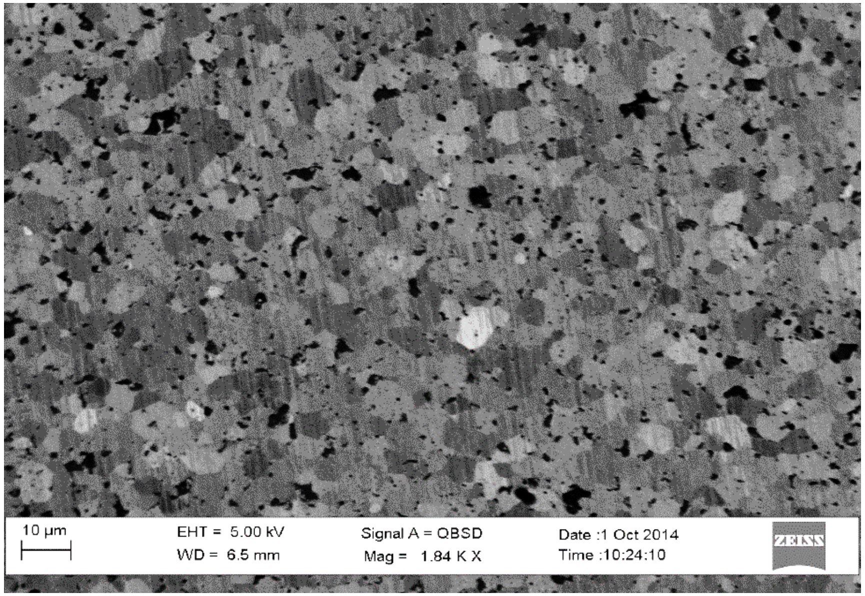
Literature controversy → **Systematic study required to get full understanding of mechanism of ZrC oxidation**

Production of ZrC pellets

Sample	Atm.	Temperature (ºC)	Dwell time (h)	Pressure (MPa)	Dimensions: diameter – height (mm)	Density (g/cm^3)	Relative Density (%)	Mean grain size (µm)
Batch - 1	Ar	1850 10(ºC/min)	1	50	40 - 5	6,39	96.2	3 - 8
Batch - 2	Ar	2000 10(ºC/min)	1	50	40 - 10	6.59	-	-

Chemical analysis using combustion analysers on crushed and ground hot pressed samples:

Zr 0.48 % atomic
C 0.47 % atomic
O 0.03 % atomic
N 0.01 % atomic



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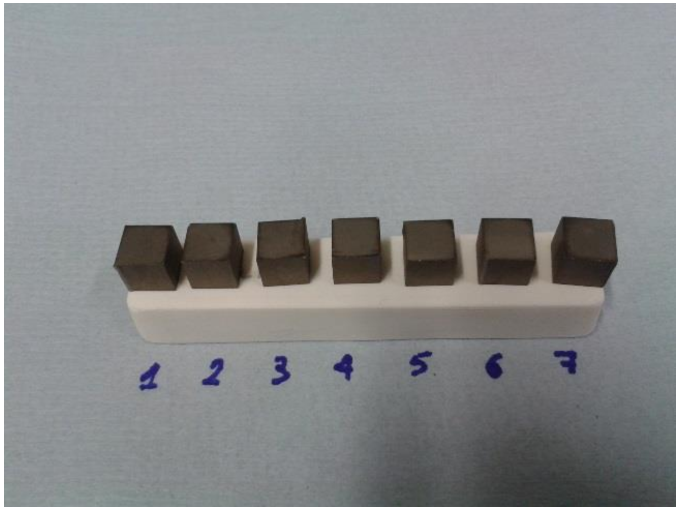
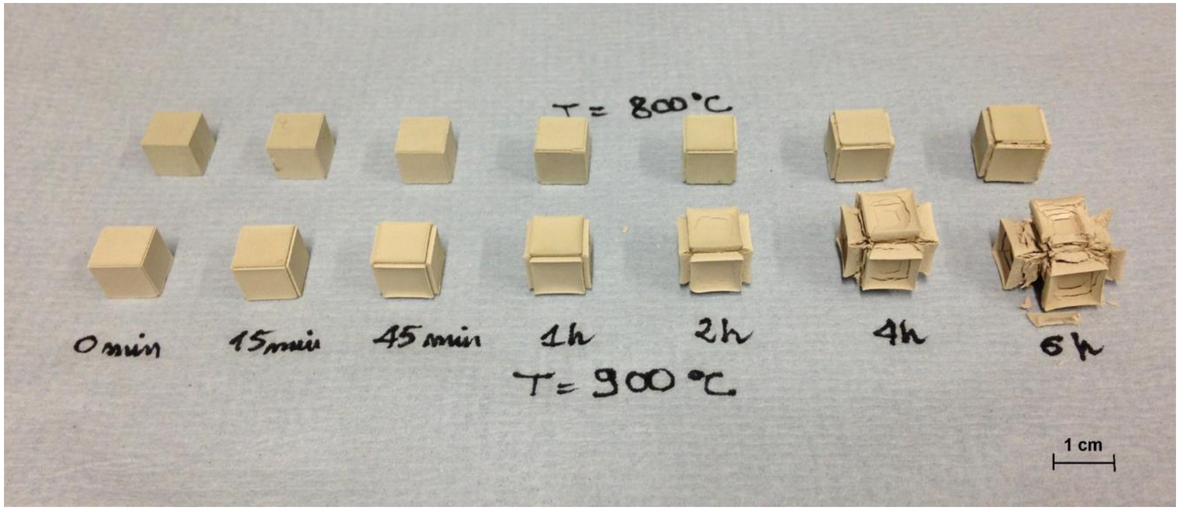
Oxidation of ZrC pellets: chamber lift furnace experiments

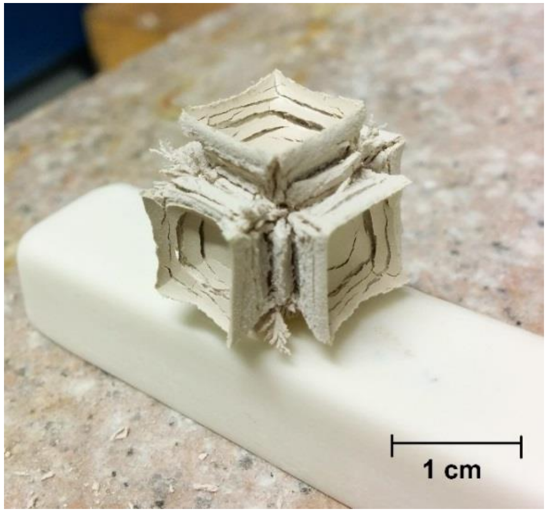




Oxidation performed at 800 – 900 - 1000 ^{0}C
(quenching at 0 – 15 – 45 – 60 – 120 – 240 – 360)

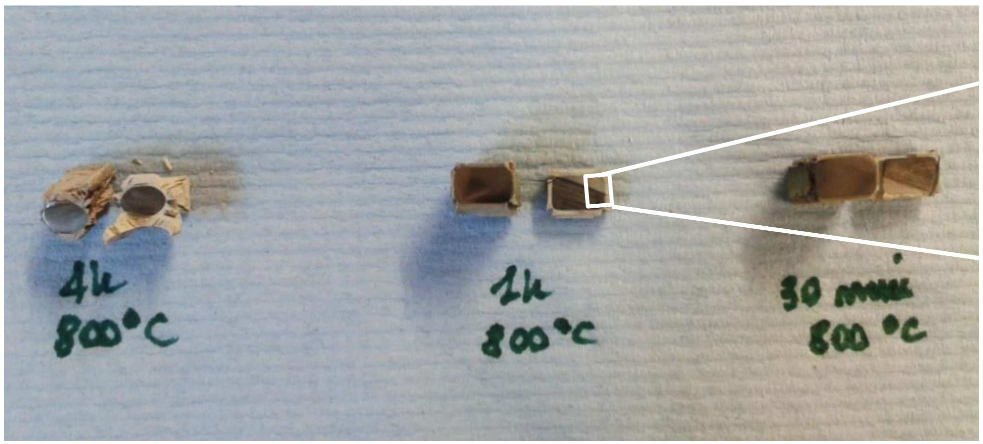
Fully developed Maltese Cross shape forms

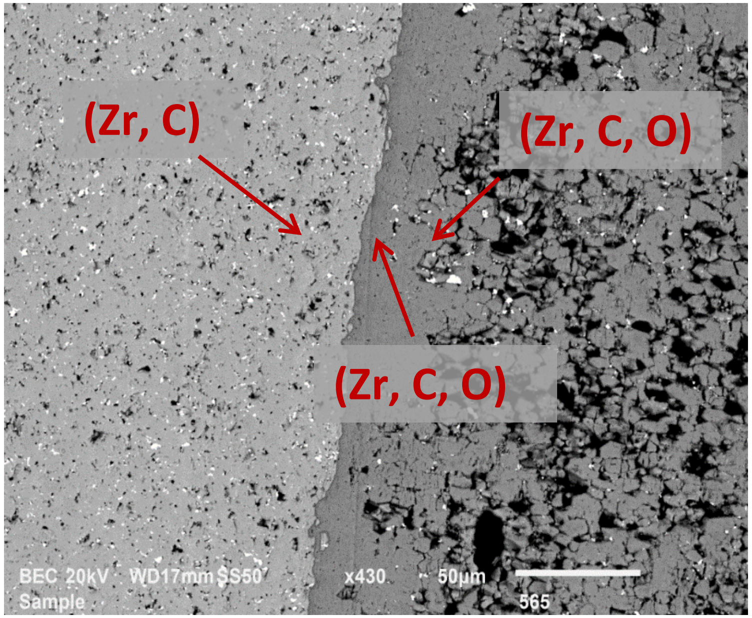
What is the mechanism of reaction causing this characteristic volume expansion?



Oxidation of ZrC pellets: furnace experiments

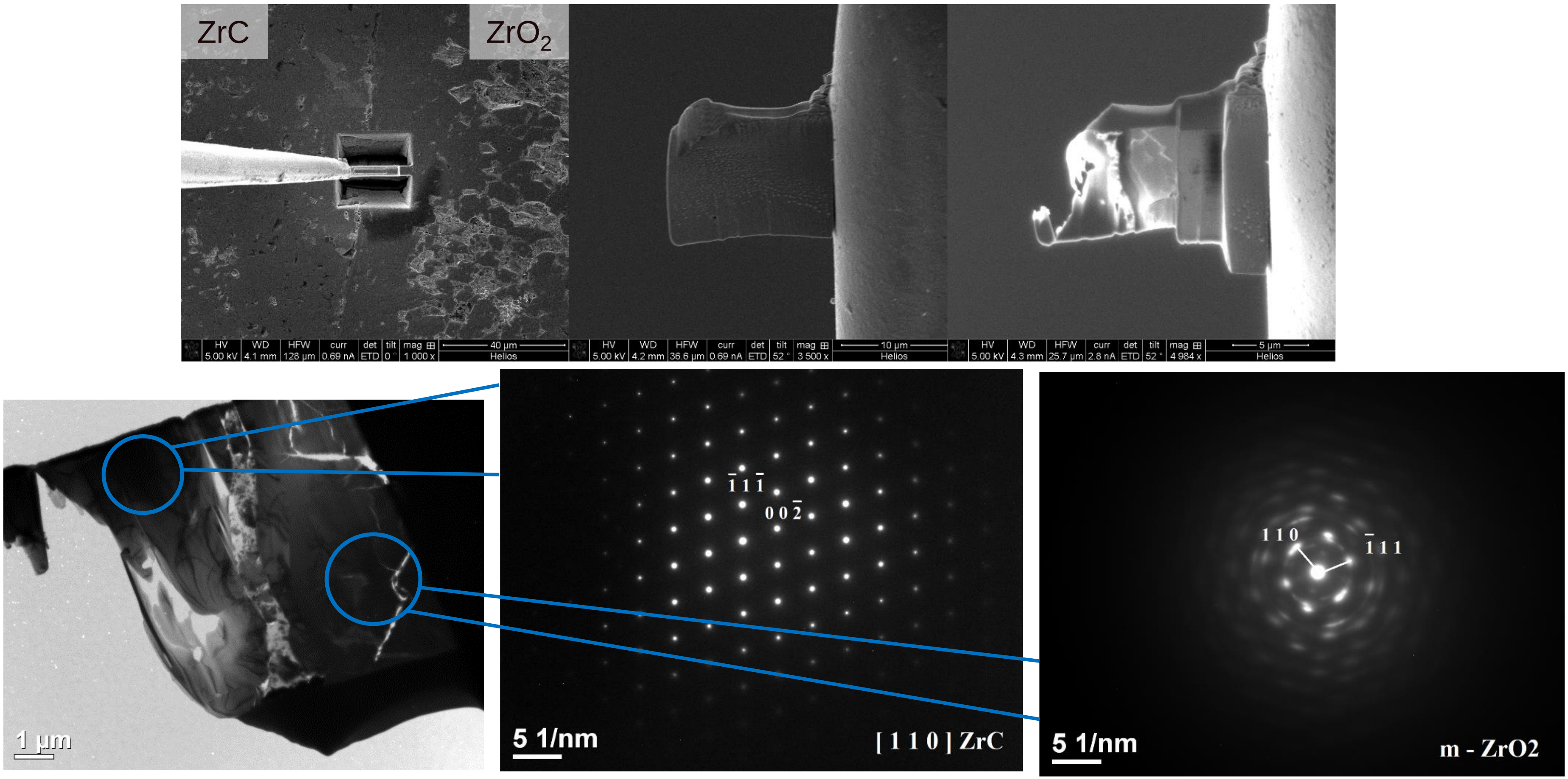
Furnace oxidation at 800 ^{o}C





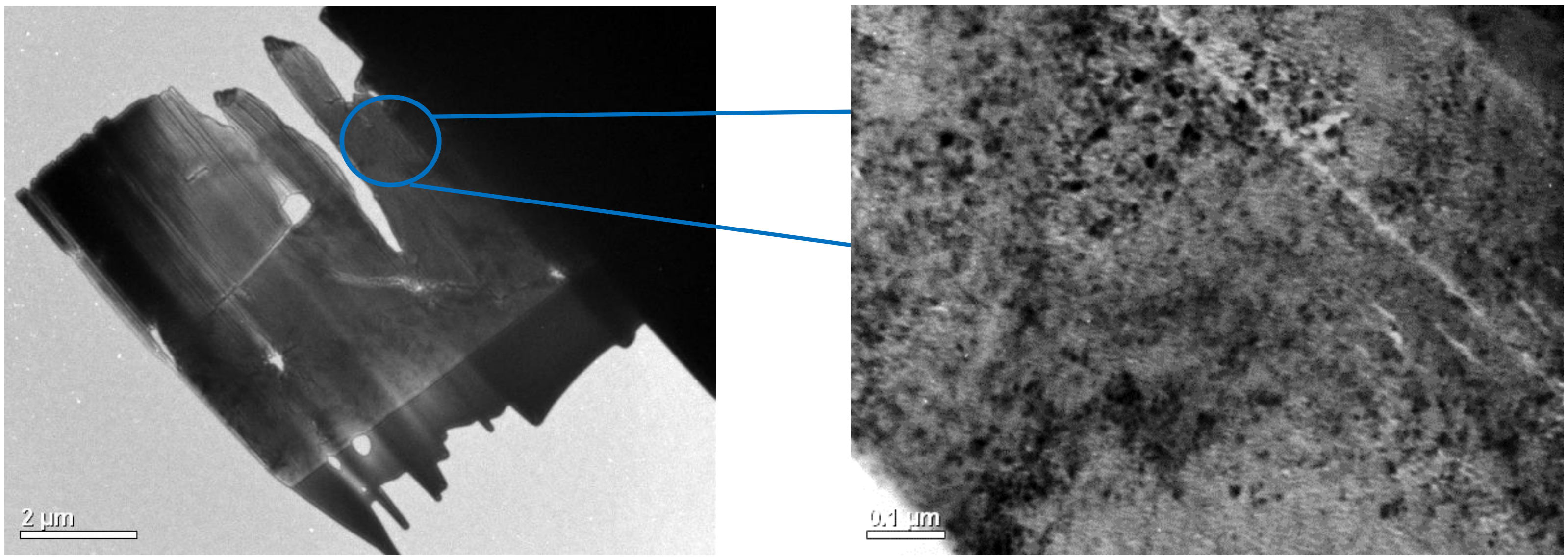
Cross sectional SEM reveals dense pore - free interface

TEM analysis on interface: sample oxidized 1h at 800ºC



SAED pattern suggests monoclinic zirconia at the interface

TEM analysis on interface: sample oxidized 1h at 800ºC



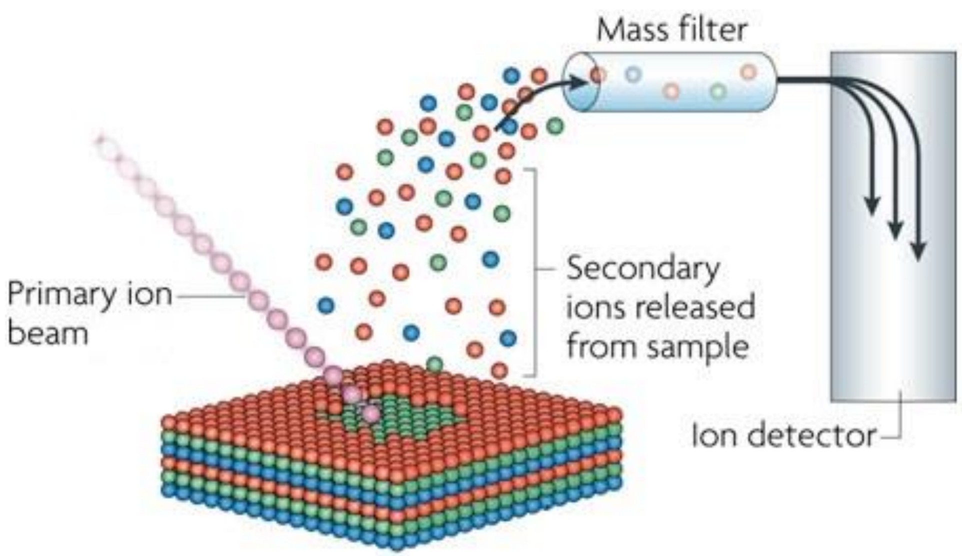
TEM specimen taken from ZrC – ZrO_2 interface, bright field images reveal nanoclusters which may be the start of the oxidation process

Principle of Focused Ion Beam - Secondary Ion Mass Spectrometry (FIB - SIMS)

PRIMARY ION BEAM
Gallium liquid metal ion source

SECONDARY IONS
sputtered from the surface are collected and sent to the detector

The focused beam (Ga+) can be used for IMAGING of the surface or for MILLING

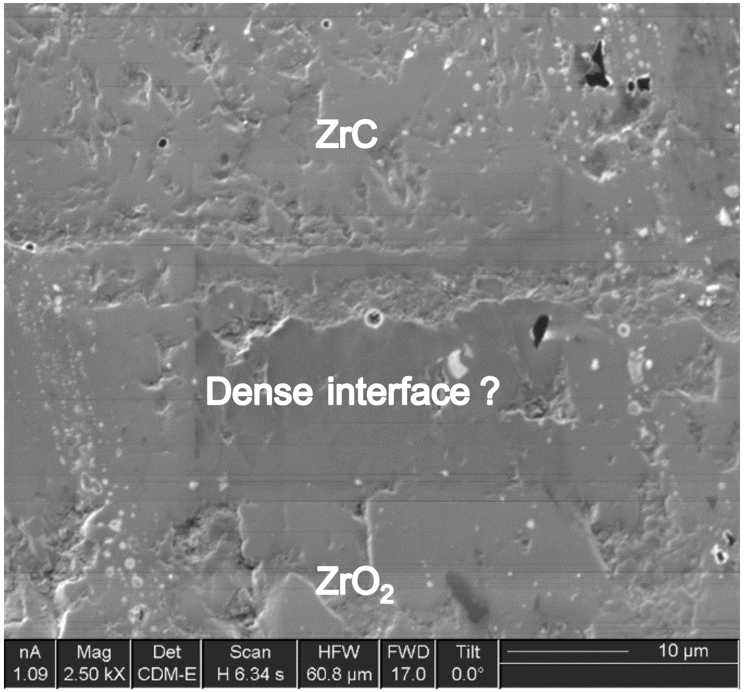


Secondary Ion Mass Spectrometry
http://www.nature.com/nrmicro/journal/v5/n9/fig_tab/nrmicro1714_F2.html

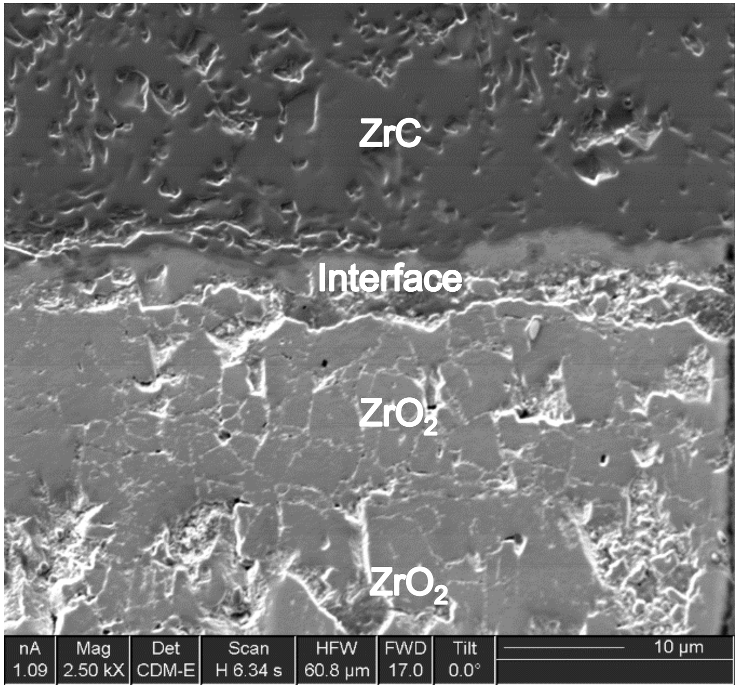
SIMS detector
measure the mass to charge ratio (m/z) of ions giving the COMPOSITION of the sample

FIB sputtering analysis : sample oxidized 1h at 800ºC

SE image of ground and polished surface

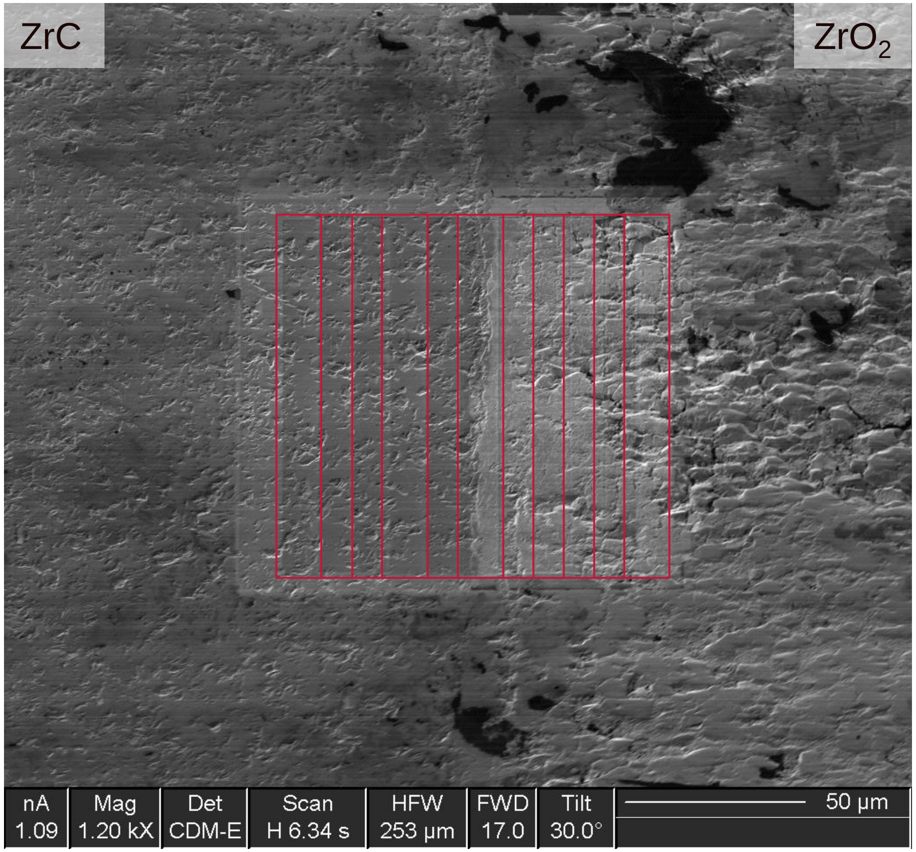


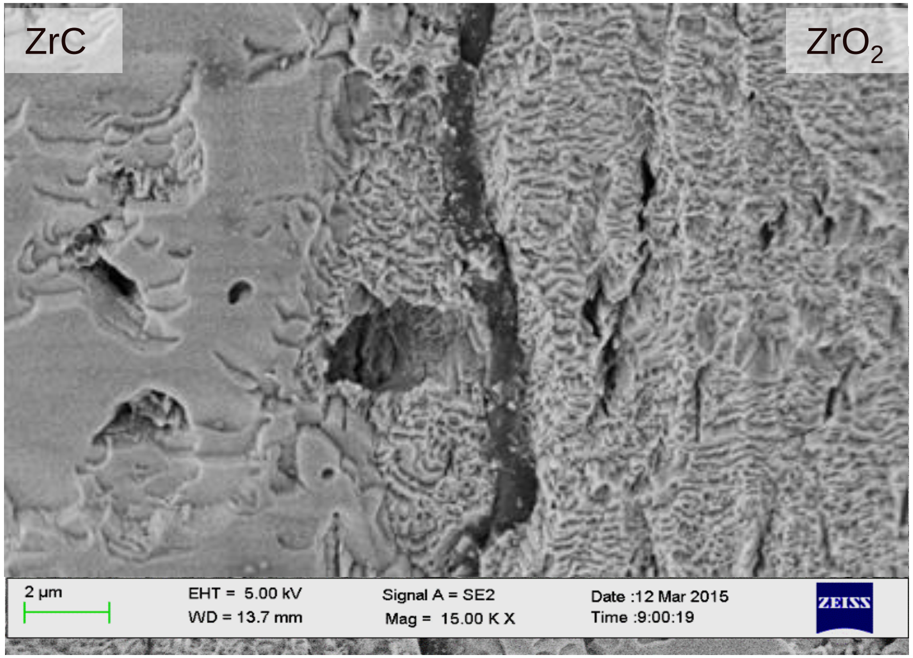
SE image after FIB sputtering



FIB milling has enhanced the morphology of the interface.

SIMS - FIB characterization : sample oxidized 1h at 800ºC





SIMS analysis on a clean surface (sputtered via FIB), the chemical composition of these 11 regions have been analysed via FIB – SIMS and EDX

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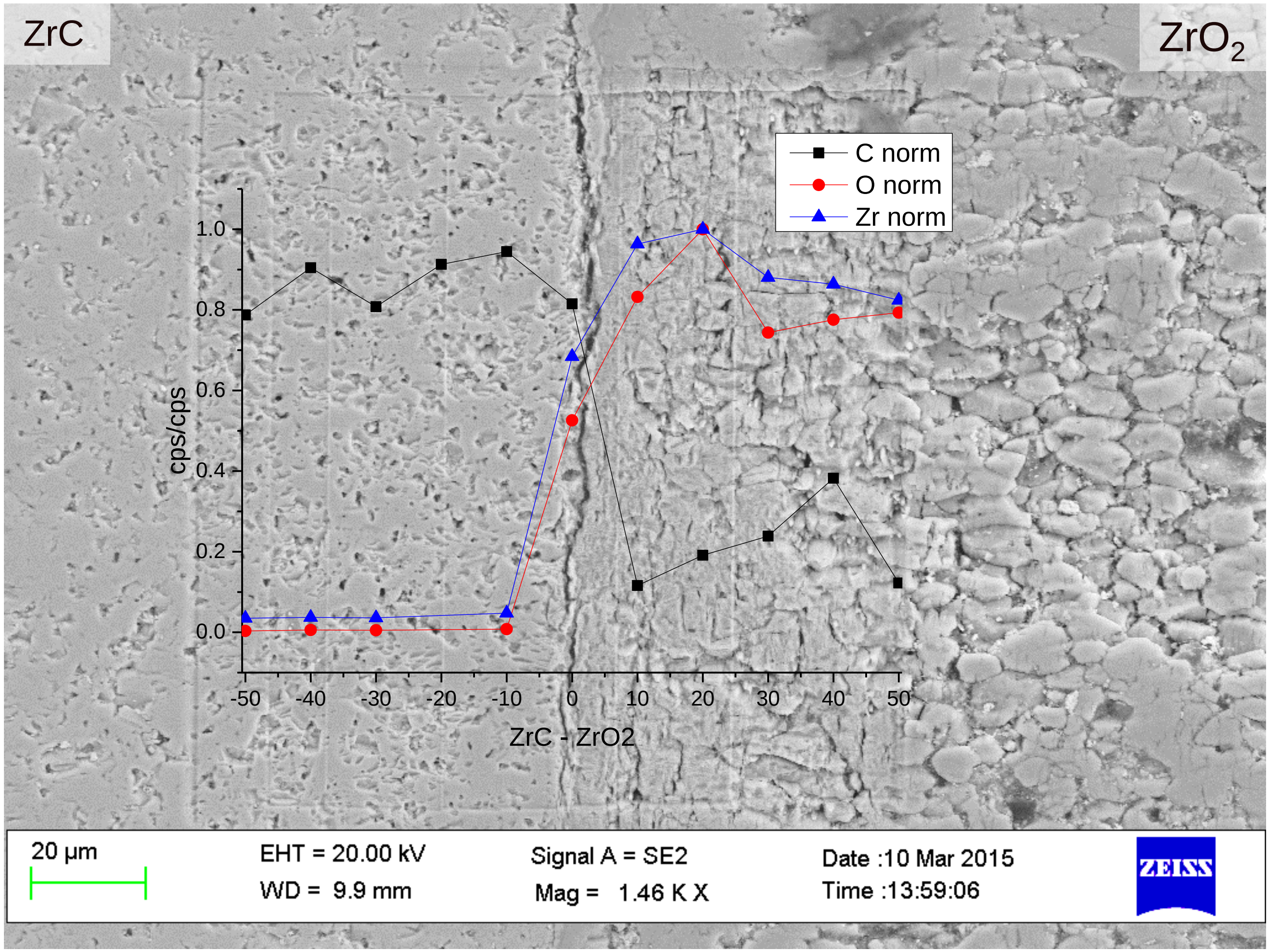
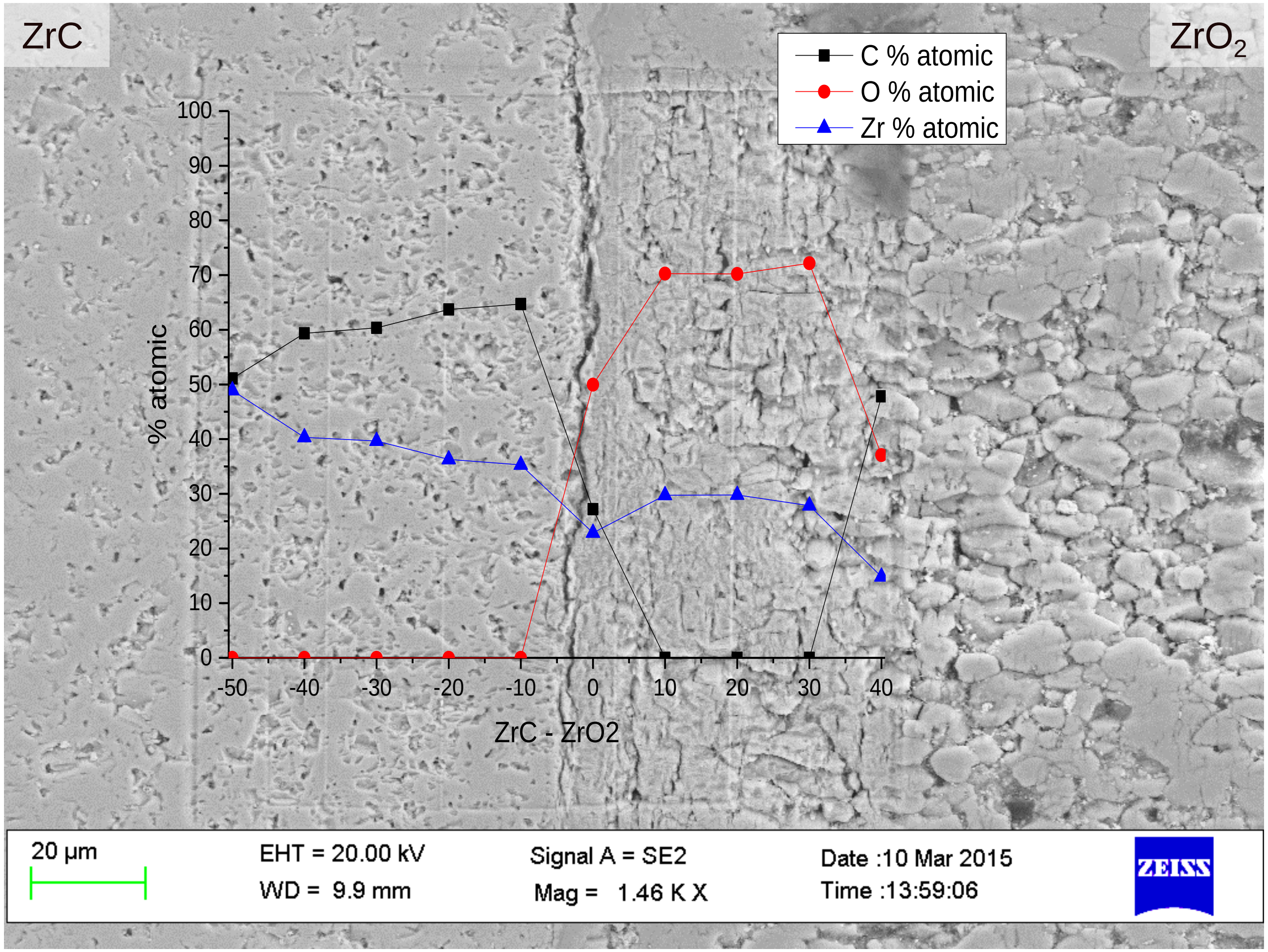
SIMS - FIB characterization : sample oxidized 1h at 800ºC



Compositional analysis of the interface Normalized signals of Carbon – Oxygen and Zirconium Secondary Ions

EDX analysis on FIB milled area : sample oxidized 1h at 800ºC



Compositional analysis of the interface Carbon – Oxygen and Zirconium atomic %

Conclusions

- The ***oxidation of ZrC*** has been investigated through a hierarchical level of analysis :

MACROSCALE optically	→	MICROSCALE SEM / FIB	→	NANOSCALE TEM
Maltese cross		*ZrC – ZrO_2 Interface*		*m – ZrO_2 Oxide Clusters*

- The ***interface region*** where the oxidation reaction occurs has been identified by FIB – SIMS and SEM and its characterization is ongoing via TEM.

- No evidence for an oxycarbide intermediate phase is reported, evidence of clustering of small oxide particles is shown near the interface.

- The driving force for the ***volume expansion*** seems to be the zirconium diffusion towards the oxide region.

Acknowledgements

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