DE LA RECHERCHE À L'INDUSTRIE

Experimental contribution to the corium thermodynamic modelling

A. QUAINI
C. GUÉNEAU
T. ALPETTAZ
S. GOSSÉ

CEA Saclay – DEN / DANS / DPC / SCCME /
Laboratory on Modeling, Thermodynamics and Thermochemistry

Dario MANARA
P. LAJARGE
D. BOTTOMLEY

European Commission, Institute for Transuranium Elements

E. BRACKX
R. DOMENGER
A. CHOCARD

CEA Marcoule – DEN / DTEC / SGCS /
Laboratory of Metallography and Chemical Analysis

Fiqiri HODAJ

SIMAP – UMR CNRS 5266, INP Grenoble-UJF

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FRAMEWORK / CORIUM THERMODYNAMICS

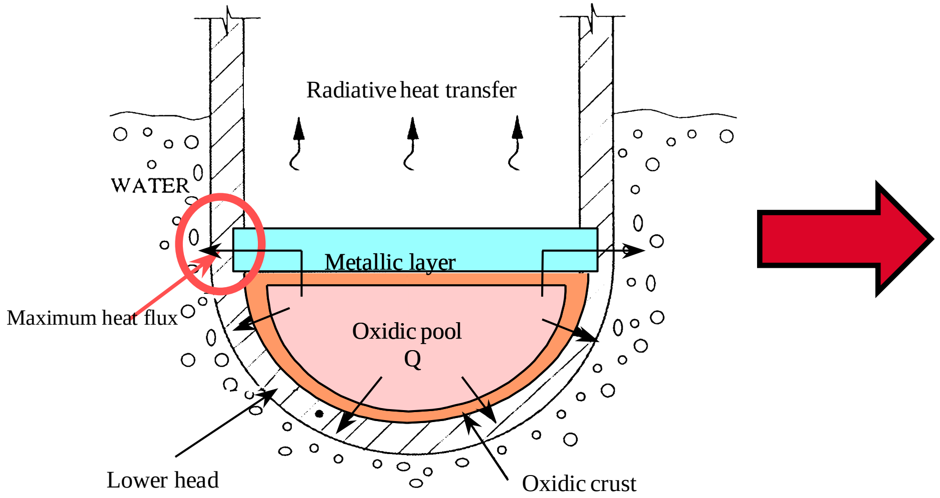
Severe accident in a PWR:

→ **Interaction UO_2 + Zircaloy + stainless steel + Inconel + neutronic absorber + FPs**

U-(Pu)-Zr-O-Fe-Cr-Ni-Ag-Cd-In-B_4C-FPs → In vessel corium

→ **U-Pu-Zr-Fe-O system is selected as the prototypic in-vessel corium**

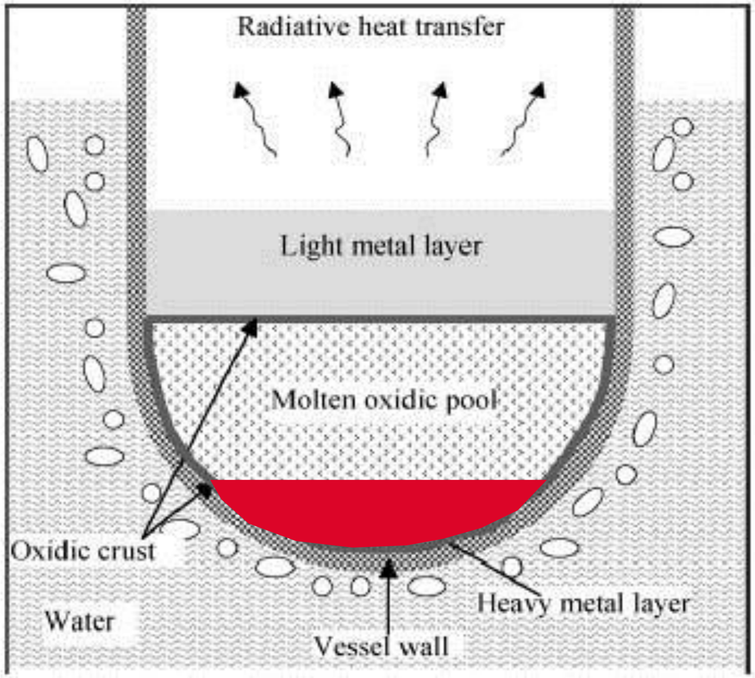
Key point: <u>miscibility gap in the in-vessel corium system liquid phase</u>

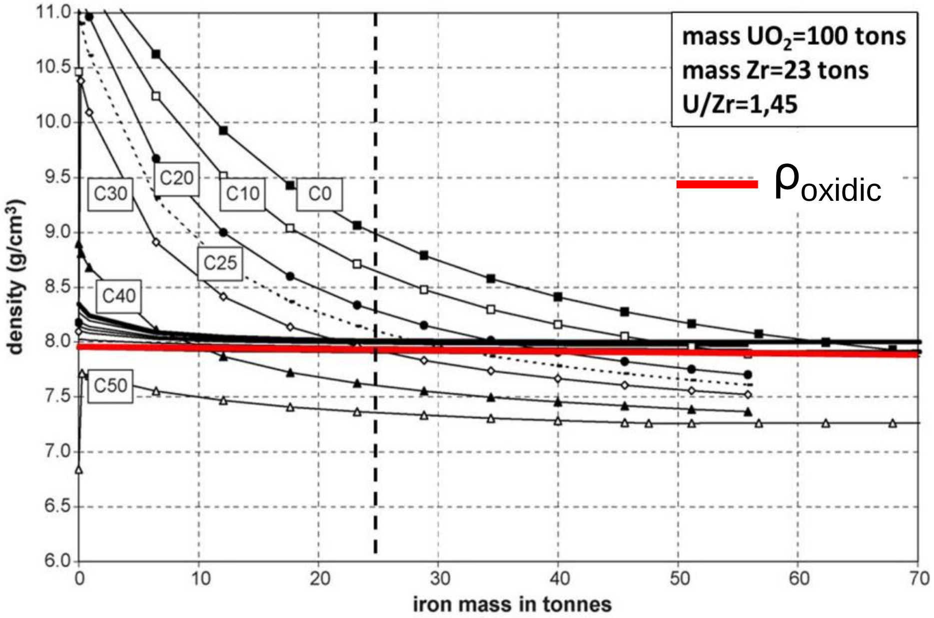


Configuration of the molten in-vessel corium

FRAMEWORK / CORIUM THERMODYNAMICS

Miscibility gap → stratification of the molten pool





Seiler et al. (2007)

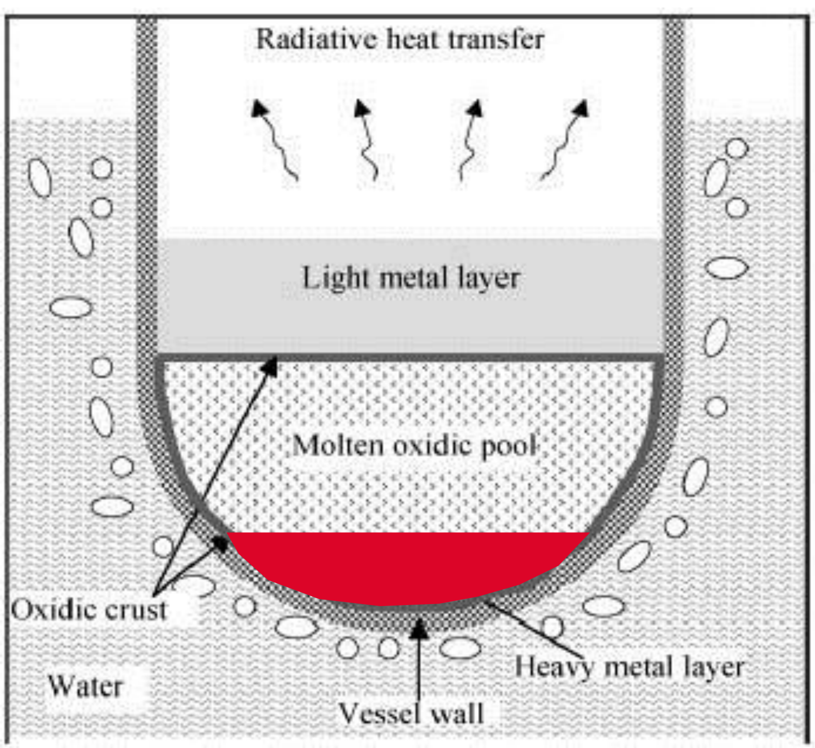
Degree of oxidation of zirconium
U/Zr ratio
Amount of molten steel

Heavy metal layer forms below the oxidic pool

→ **Enhanced focusing effect**
→ **Loss of the reactor vessel barrier**

FRAMEWORK / CORIUM THERMODYNAMICS

In-vessel corium configuration due to density inversion $\rho_{heavy\ metal} > \rho_{oxidic}$



Thermodynamics

- Composition and density of the metallic and oxidic phases

Thermo-hydraulics

- Heat flux in the molten pool

coupling

Thermodynamics
Thermo-hydraulics

Minimum mass of steel needed to maintain the heat flux below the critical heat for loosing the vessel

Calculation performed at the thermodynamic equilibrium

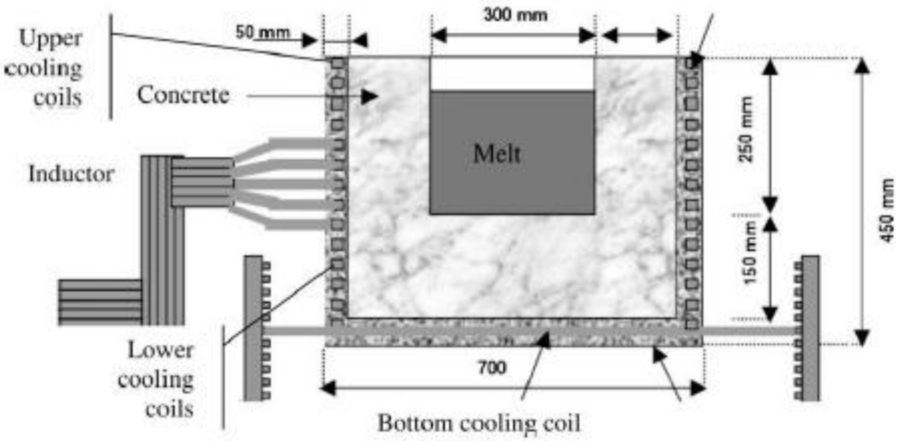
FRAMEWORK / MCCI THERMODYNAMICS

Ex-vessel stage of a severe accident → Interaction in-vessel corium - concrete

- High temperature concrete decomposition
- Gas bubbles agitation
- Formation of several phases
- Metals oxidation
- Concrete ablation
- …

➡ Severe accident experiments → **Phenomenology of the accident**

➡ Severe accident codes → **Design of the reactor, mitigation actions**



VULCANO facility, Journeau et al. (2003)

Thermo-physical properties of the in-vessel corium + concrete system are of paramount importance
→ **U(Pu)-Zr-Fe-Al-Ca-Si-O**

APPROACH

Experimental

- Identification of in-vessel some corium key-systems
  → U-Zr-O
  → Fe-Zr-O
  → Fe-U-O
  → U-Zr-Fe-O
  → UO_2-PuO_2-ZrO_2

Thermodynamic modelling – CALPHAD method (on going)

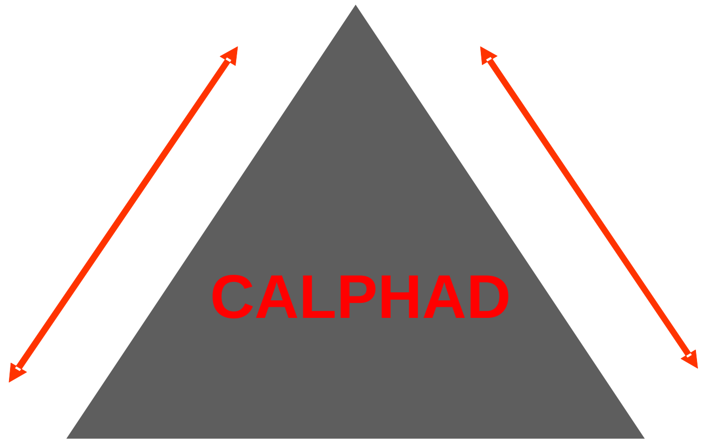
- U-Zr-O-Fe
- U-Pu-Zr-O

- **Solidification path calculation applied to experimented composition**

  → in vessel corium : UO_2-ZrO_2-Zr-Fe
  → ex-vessel corium : UO_2-ZrO_2-Al_2O_3-CaO-SiO_2

APPROACH - THE CALPHAD METHOD

Critical analysis of experimental data



Experimental data acquisition

ΔH_f, Cp(T), H(T)-H(298K) ➪ Calorimetry, D.S.C.
Phase diagrams ➪ heat treatments, D.T.A.
Activities ➪ H.T.M.S., e.m.f.
ΔH (0 K) ➪ ab-initio calculations

Thermodynamic modelling

Optimization
(Code **Thermo-Calc**)

Thermodynamic database
G (phases) = f (T,x) @ P=1 atm

Minimization of G(system)
(Codes Thermo-Calc, FACTSAGE, Gemini …)

Thermodynamic properties
Phase diagrams ….

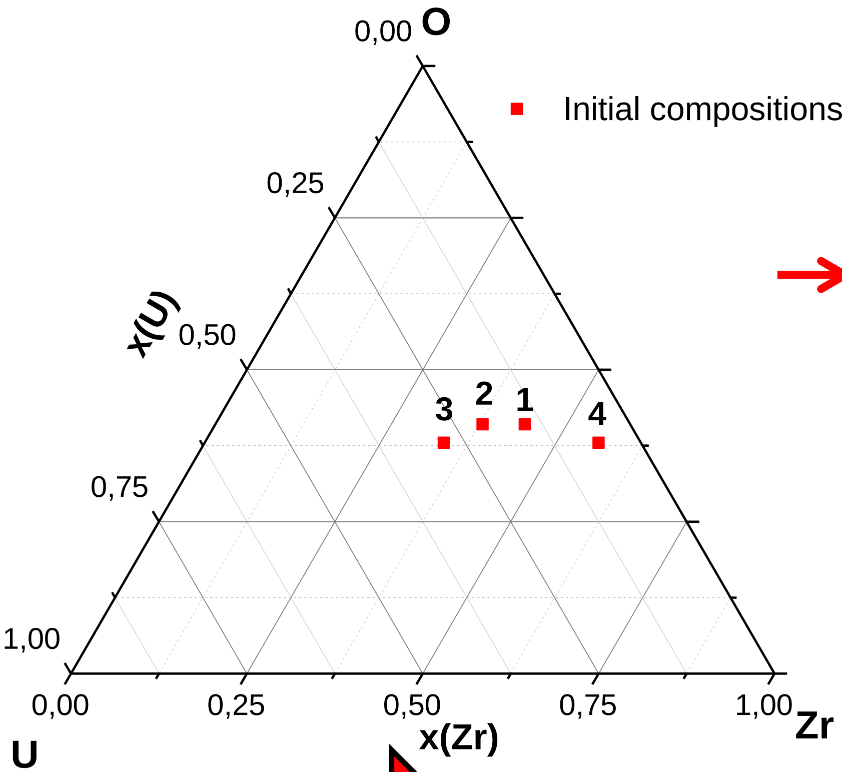
EXPERIMENTAL RESULTS

→ U-Zr-O

→ UO_2 – PuO_2 – ZrO_2

→ EX-VESSEL CORIUM

EXPERIMENTAL RESULTS – U-Zr-O SYSTEM



# sample	at % U	at % Zr	at % O
Sample 1	15	44	41
Sample 2	21	38	41
Sample 3	28	34	38
Sample 4	6	56	38

Starting materials:
- metallic Zr
- ZrO_2 powder
- metallic U

W-crucible

→ Interaction at the sample / crucible interface

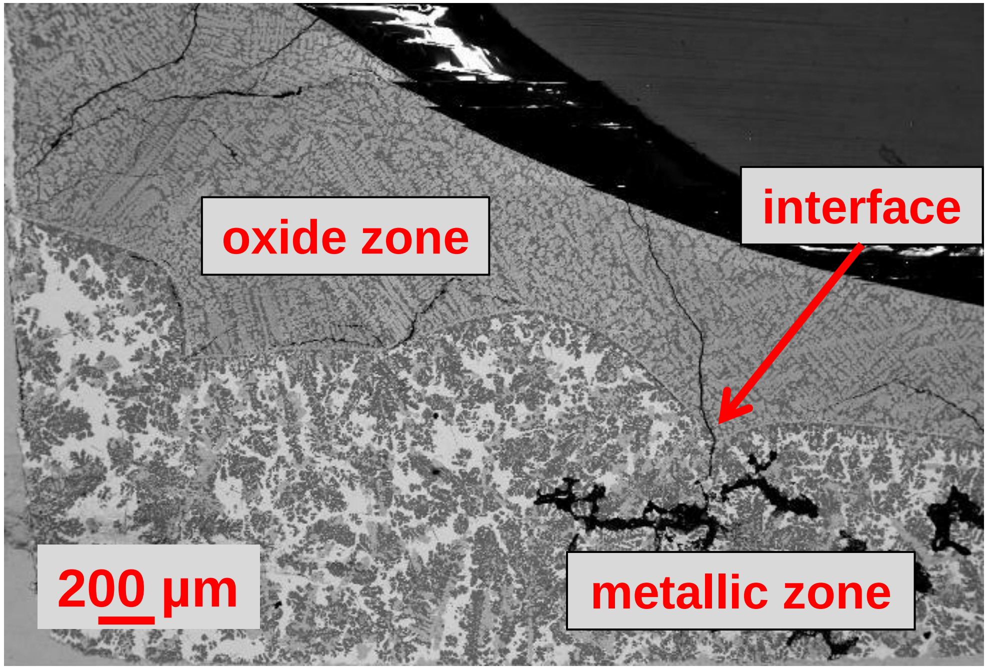
Heat treatment @ 2550 K for 45 minutes → QUENCHING

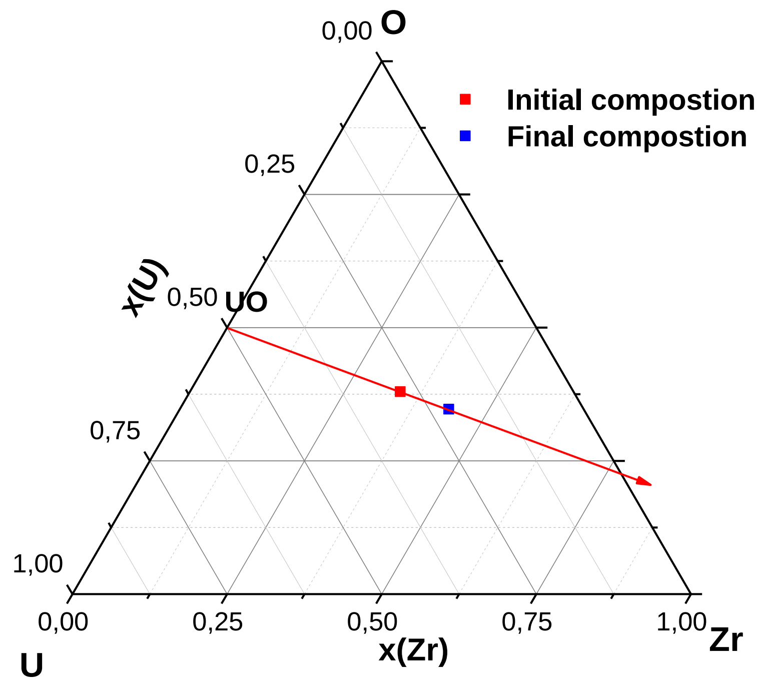
SEM/EDS analyses + WDS analyses

!! Final compositions ≠ Initial compositions → volatile species UO

EXPERIMENTAL RESULTS – U-Zr-O SYSTEM

Sample 3 – $U_{28}Zr_{34}O_{38}$ (initial composition)





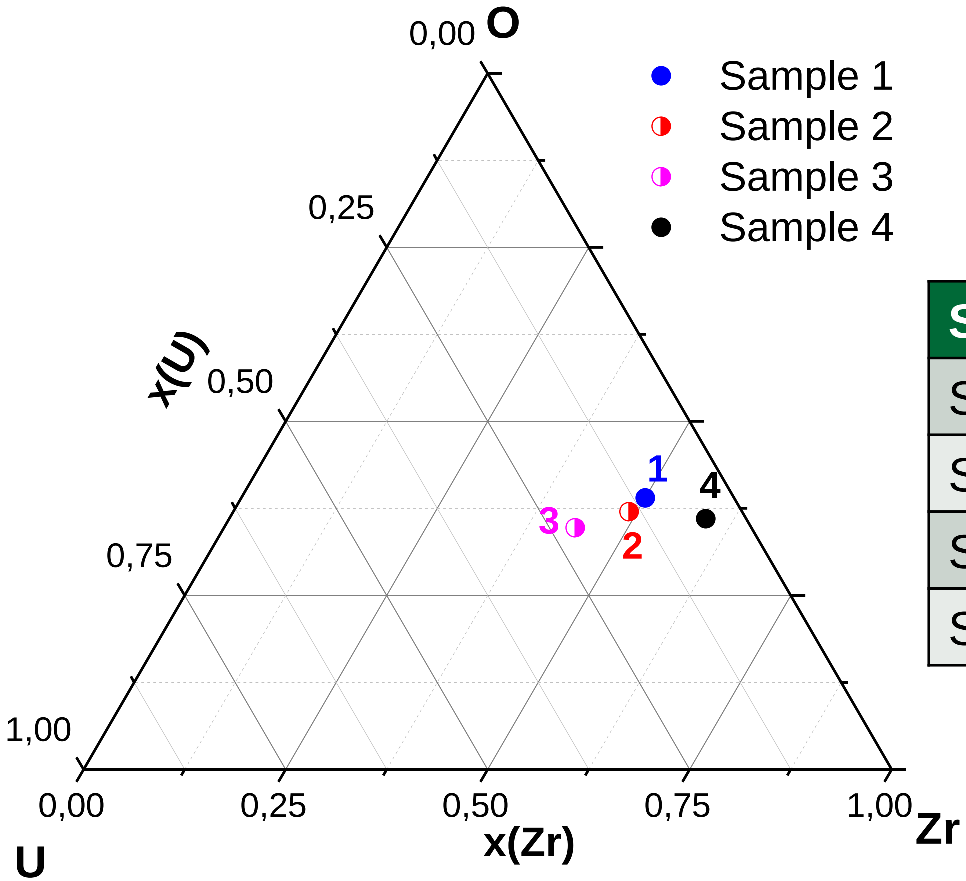
SUMMARY U-Zr-O

- **Miscibility gap** was observed in two samples (2 & 3)

→ **metallic** and **oxide** liquids in equilibrium at 2550 K

→ Tie-lines for the thermodynamic modelling

- The remaining samples, at 2550 K were in an homogeneous liquid state



Sample	Experimental observation
Sample 1	Liquid
Sample 2	Two Liquids : OX + MET
Sample 3	Two Liquids : OX + MET
Sample 4	Liquid

EXPERIMENTAL RESULTS

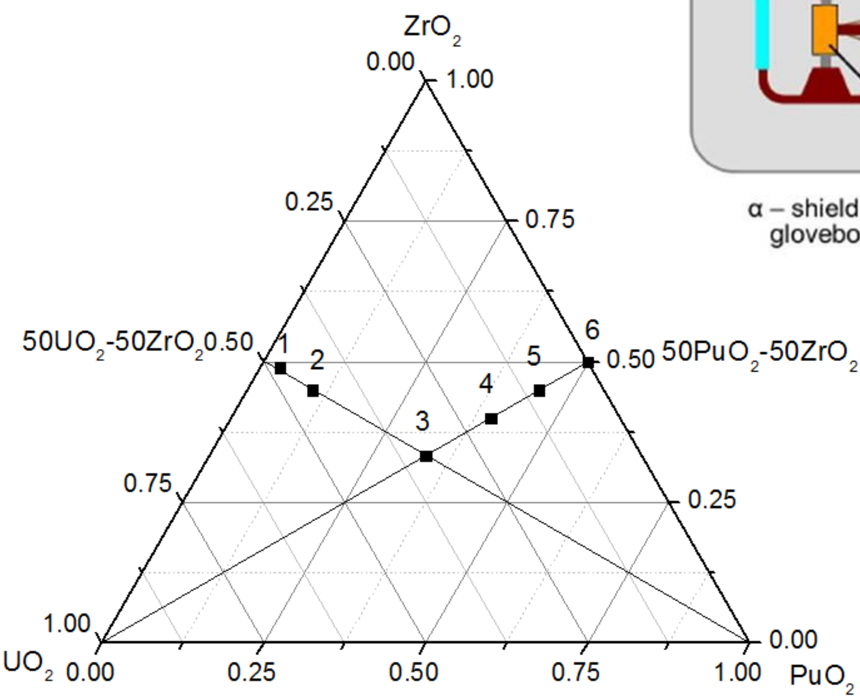
→ U-Zr-O

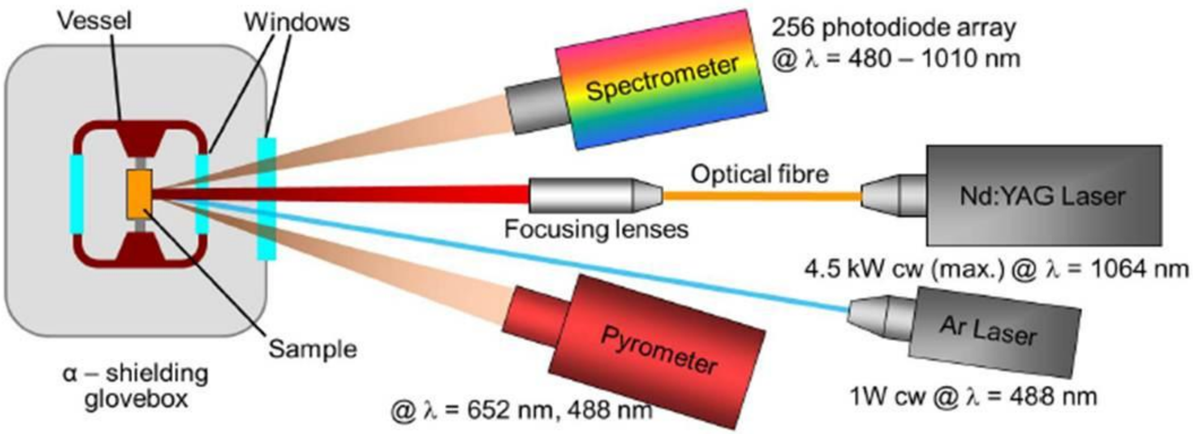
→ UO_2 – PuO_2 – ZrO_2

→ EX-VESSEL CORIUM

EXPERIMENTAL RESULTS UO_2 – PuO_2 – ZrO_2

Six composition within the pseudo-ternary UO_2 – PuO_2 – ZrO_2

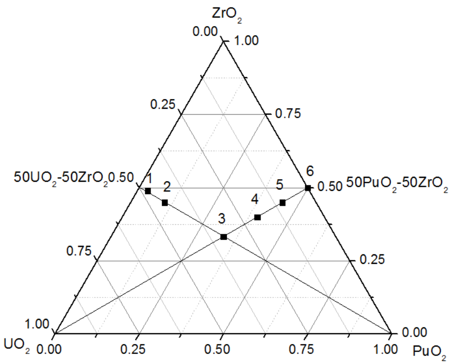




Böhler et al. J Alloy Comp 2014

Sample	mol% UO_2	mol% PuO_2	mol% ZrO_2
1 U48P3Z49	48	3	49
2 U45P10Z45	45	10	45
3 U33P33Z33	33	33	33
4 U20P40Z40	20	40	40
5 U10P45Z45	10	45	45
6 P50Z50	0	50	50

EXPERIMENTAL RESULTS UO_2 – PuO_2 – ZrO_2



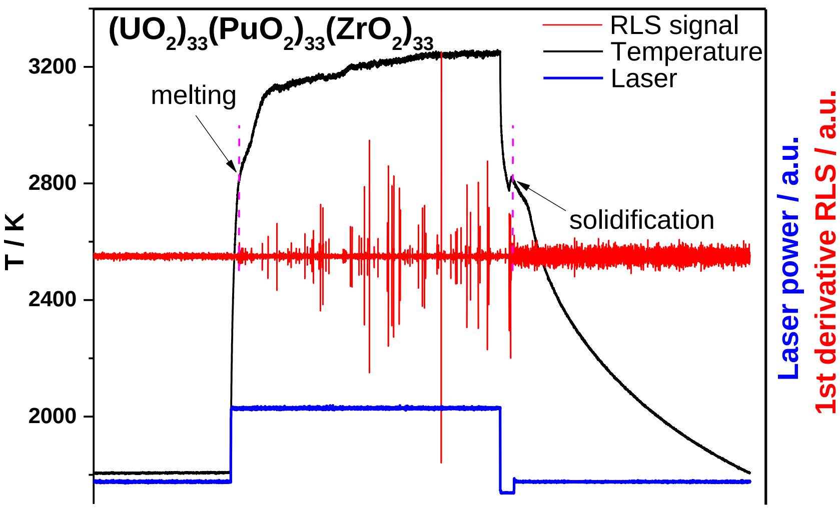
RLS : Reflected Light Signal

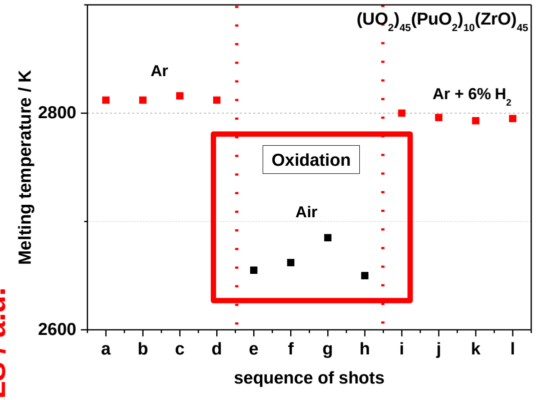
heating stage: estimation of the **melting temperature**

cooling stage: solidification temperature

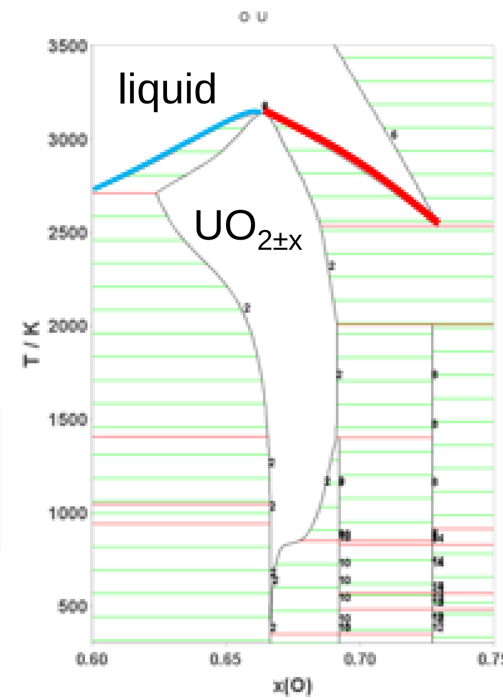
Strong effect of the experimental atmosphere on the melting results

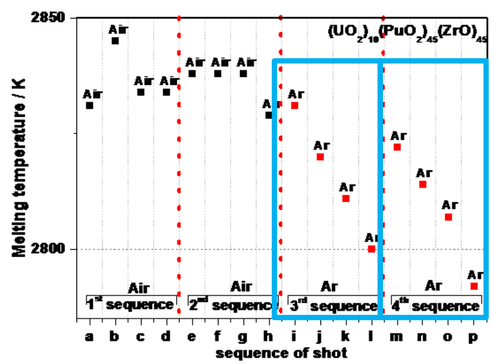
→ **Oxygen potential** is paramount for the comprehension of the high temperature behavior of actinide oxides





UO_2-rich sample





UO_2-poor sample

EXPERIMENTAL RESULTS

→ U-ZR-O

→ UO_2 – PUO_2 – ZRO_2

→ $\boxed{\text{EX-VESSEL CORIUM}}$

EX-VESSEL CORIUM

Prototypic ex-vessel corium system: **UO_2-ZrO_2-Al_2O_3-CaO-SiO_2**

- 2 compositions calculated by TOLBIAC-ICB code (A. Boulin, LPMA CEA Cadarache)

CORIUM_1: 80 tons UO_2 + 20 tons ZrO_2 + limestone concrete
CORIUM_2: 80 tons UO_2 + 20 tons ZrO_2 + siliceous concrete

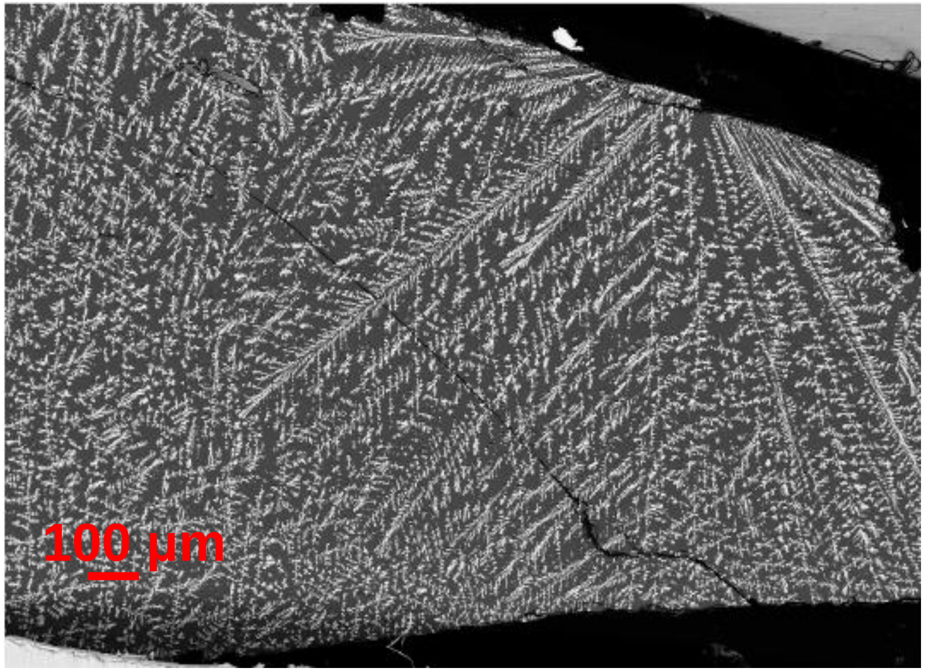
Composition of the liquid pool after 24h of MCCI

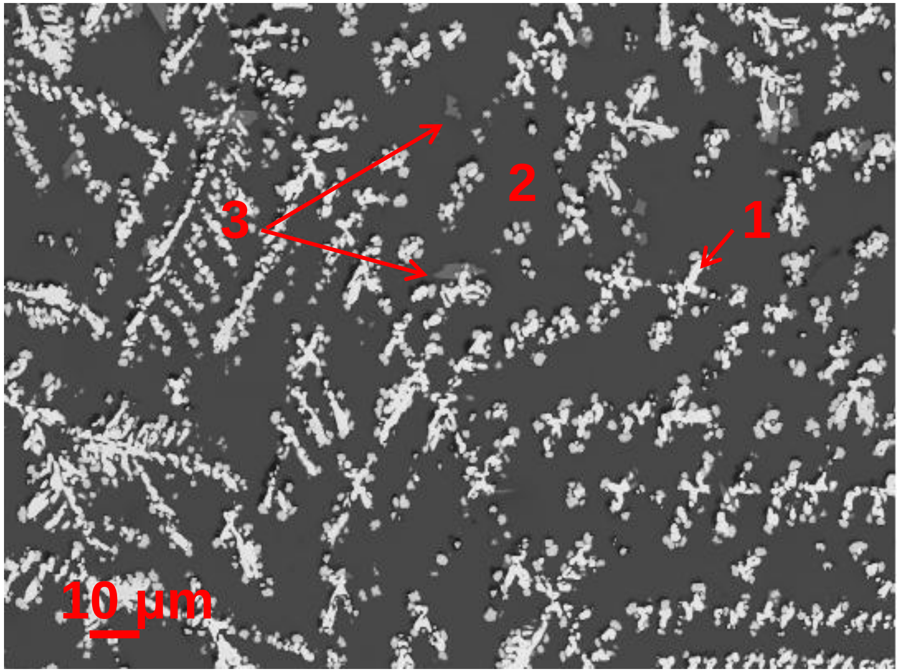
wt%	CORIUM_1	CORIUM_2
Al_2O_3	1,8	2,1
CaO	32,4	11,0
SiO_2	24,6	64,0
UO_2	30,8	15,4
ZrO_2	10,4	7,8

Heat treatment at 2530 K for 30 minutes → quenching

CORIUM 1

In-vessel corium + limestone concrete



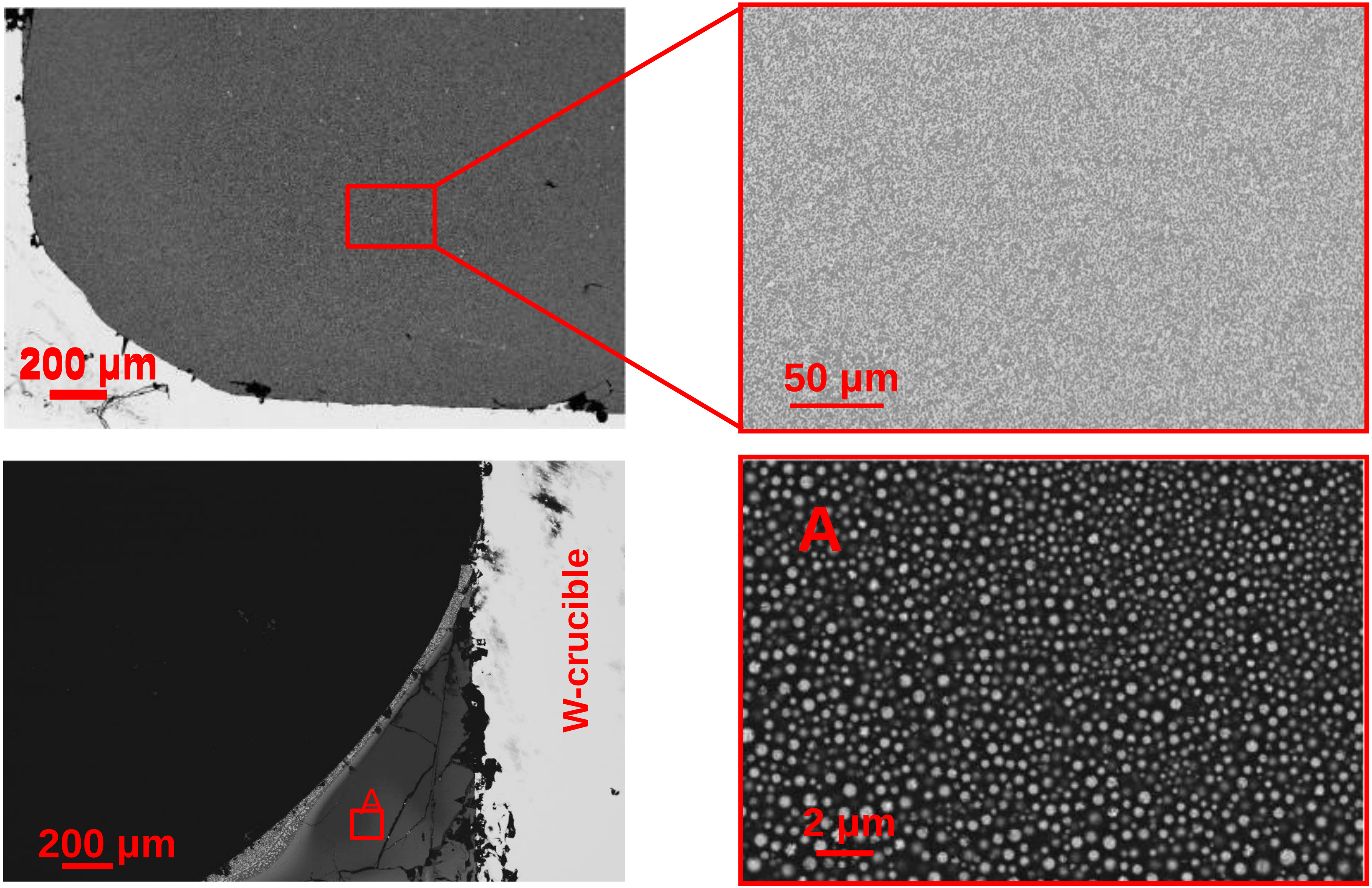


WDS results in atomic percent

	Phase	Al	Ca	Si	U	Zr	O	
1	White phase	/	2,6	/	22,3	6,7	68,4	$(U,Zr,Ca)O_2$
2	Dark phase	1,5	20,5	16,9	traces	1,0	59,8	Quenched liquid
3	Minor grey phase	traces	21	13,6	traces	4,5	59,3	$Ca_3Si_2O_7$

CORIUM 2

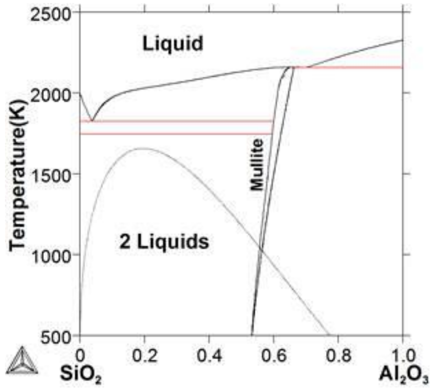
In-vessel corium + siliceous concrete

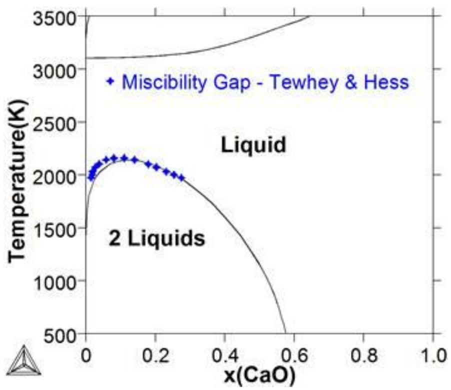


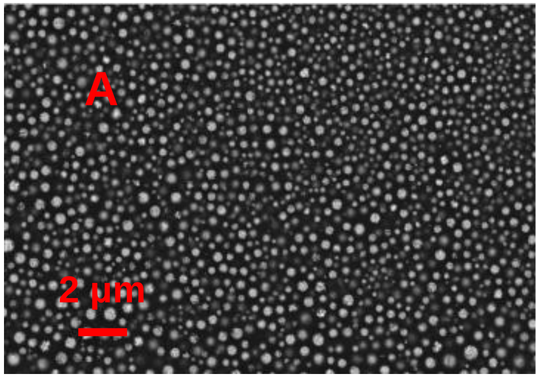
SUMMARY EX-VESSEL CORIUM

Simulated solidification of two ex-vessel corium samples from 2530 K
- **Limestone concrete**
- **Siliceous concrete**

Miscibility gap was probably observed in CORIUM 2 sample
- A minor amorphous phase with small droplets was observed: **SiO_2-rich phase**







Metastable liquid immiscibility in SiO_2-containing systems

Further analyses are needed to confirm these assumption (on going at the LMAC, CEA Marcoule)

The thermodynamic calculation with the TAF-ID database will help to interpret the experimental results

ATTILHA SETUP

DEVELOPMENT AND PERSPECTIVES

ATTILHA SETUP

Advanced **T**emperature and **Th**ermodynamics **I**nvestigation by a **L**aser **H**eating **A**pproach

Development of a versatile experimental setup on the same idea of the ITU's one

ATTILHA allows both

- Aerodynamic levitation
- Containerless measurements

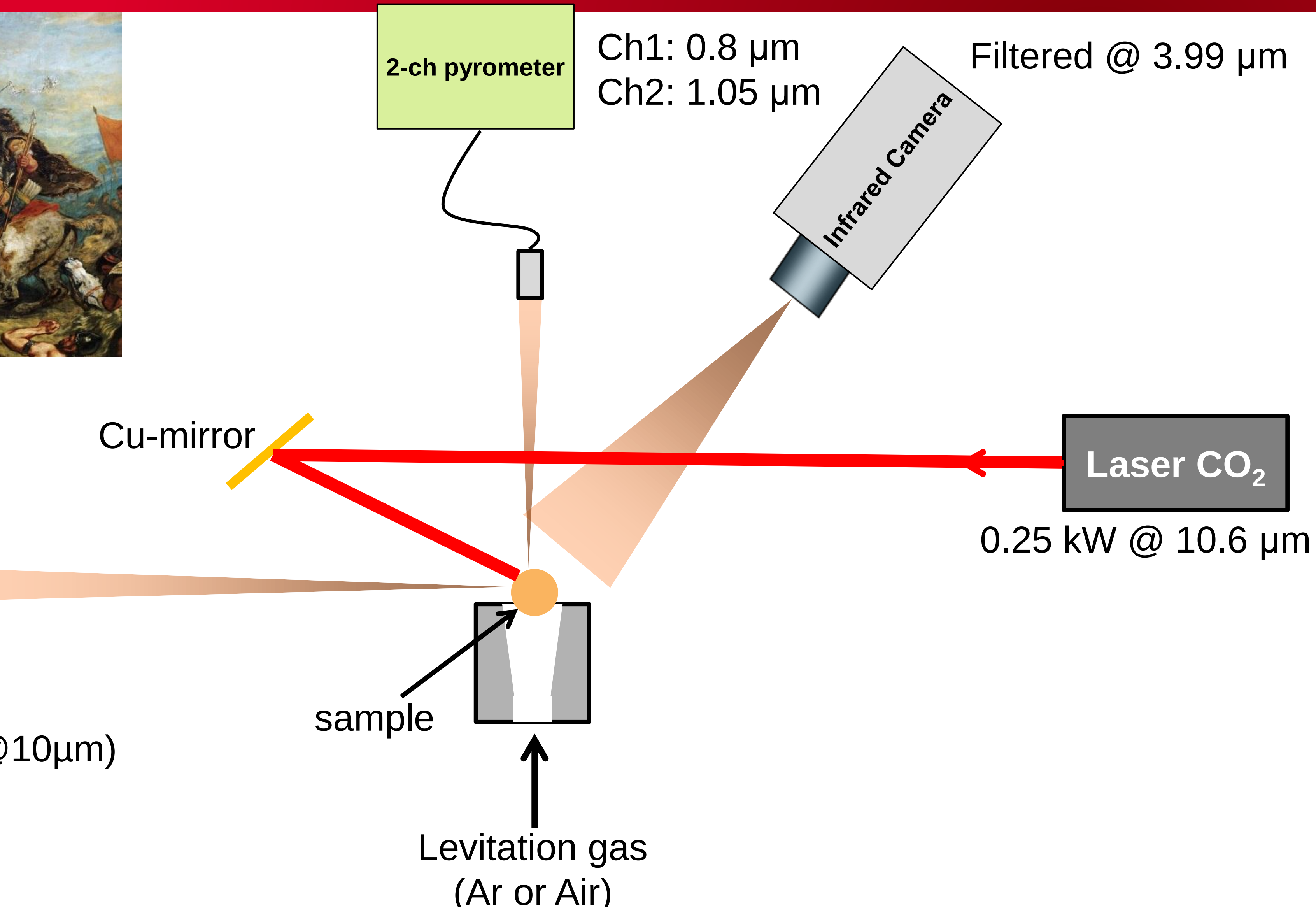
↓

High temperature data (T>2000 °C) are needed in the framework of the thermodynamic description of the corium system

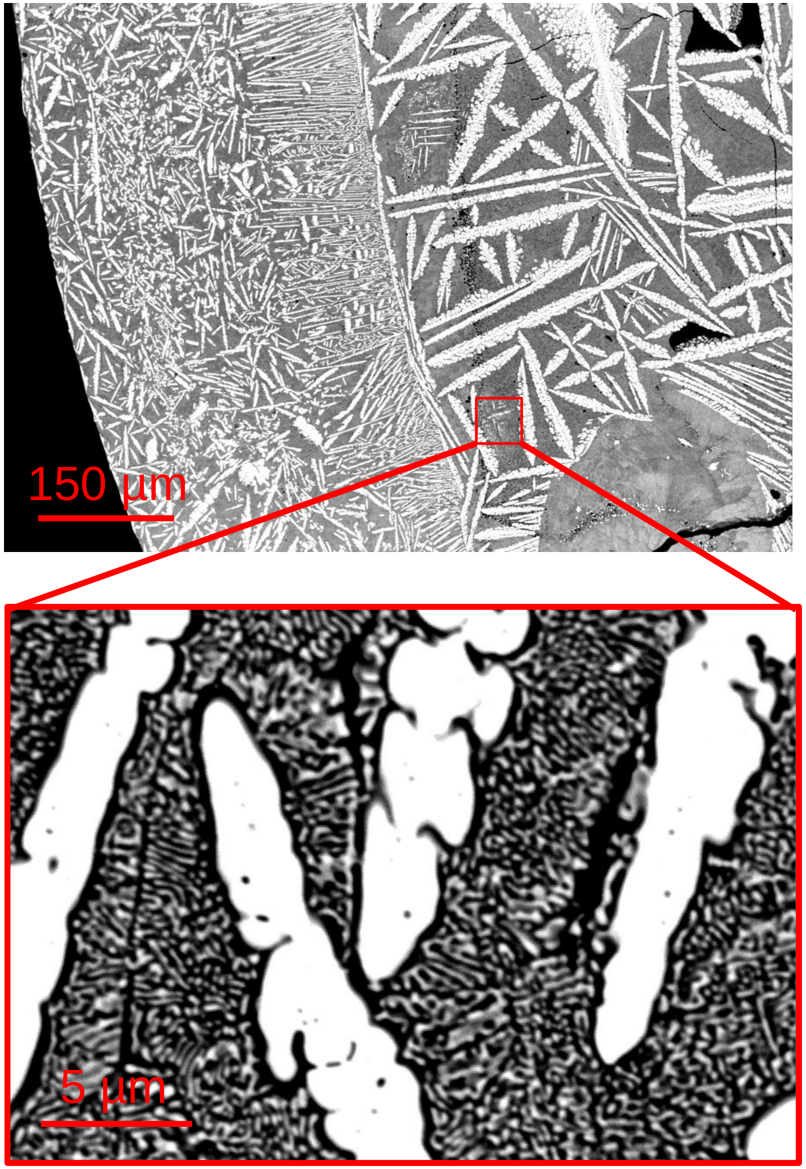
↓

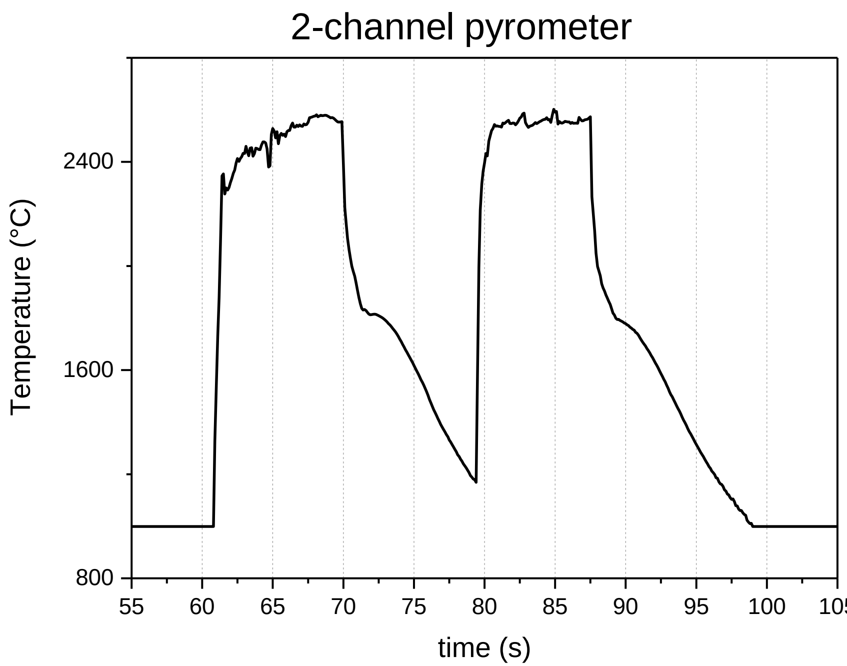
Transition temperatures (liquidus, solidus, eutectic)
Characterisation of samples "inside" a miscibility gap

ATTILHA SETUP



Al_2O_3-HfO_2 EUTECTIC





- Liquidus temperature was not detected → decrease integration time ≈10 ms

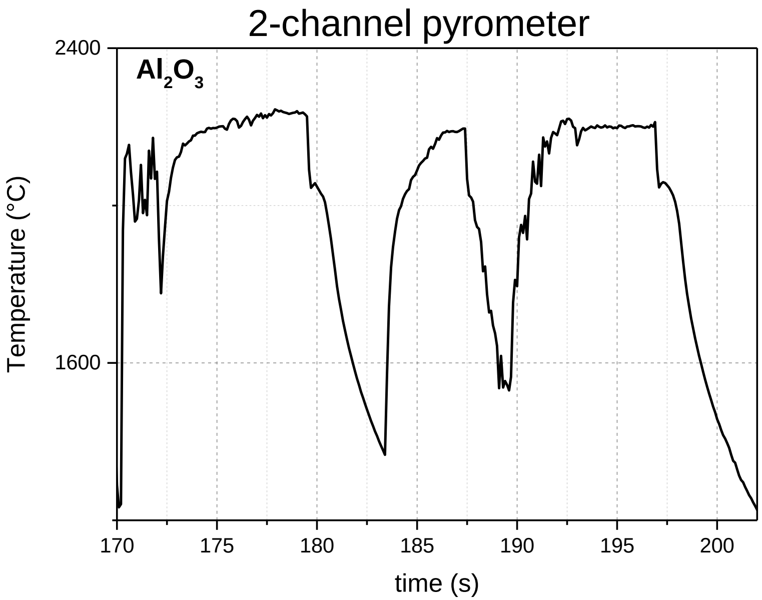
SUMMARY ATTILHA

Preliminary test on

- pure compounds (Al_2O_3, HfO_2, ZrO_2)

$T_{melting}$ (Al_2O_3)= 2057±15 °C

- Eutectics Al_2O_3-HfO_2 and Al_2O_3-ZrO_2



Perspectives

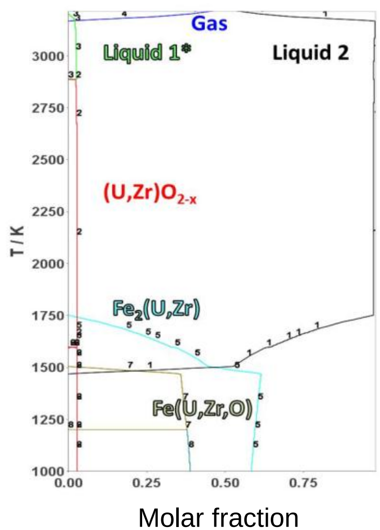
- Add the MCT detector (calibration on going)
- Add the Infrared camera

➡ Temperature detection (pyrometer and MCT detector)
Spatial melting and solidification behaviour of the sample (IR camera)

CONCLUSIONS AND PERSPECTIVES

Modeling

U-Pu-Zr-Fe-O



Solidification paths calculation →

Corium + concrete thermodynamic model

Thermodynamics – thermo-hydraulics coupling

→ Severe accident codes accuracy

Experiments

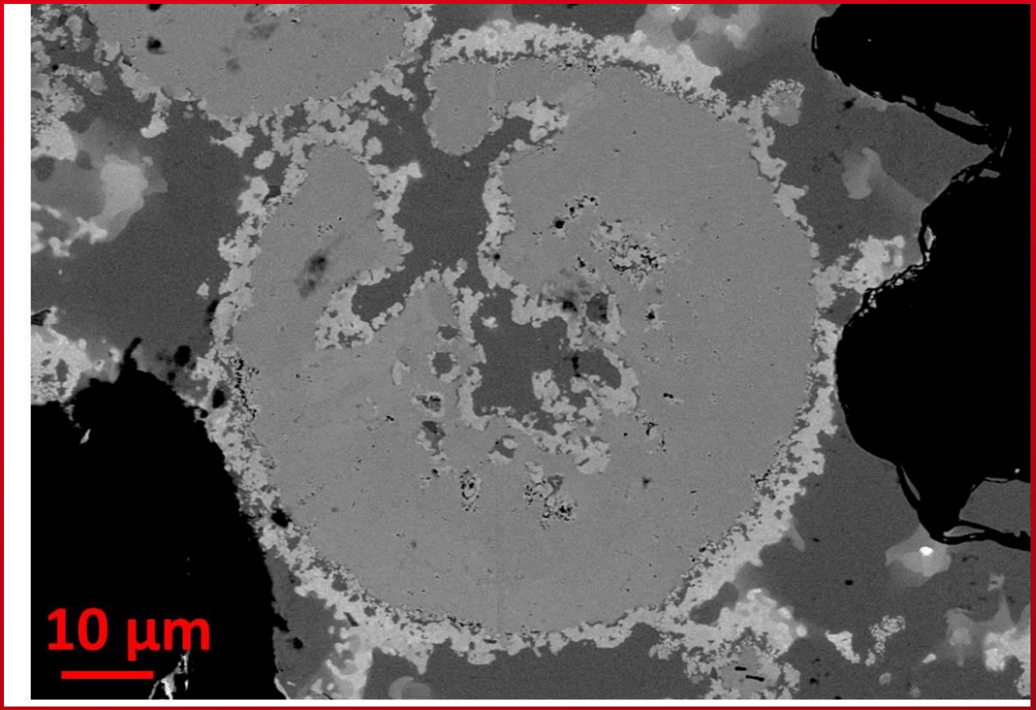
- Heat treatment : **U-Zr-O** system @ 2550 K
- Laser heating : **UO_2-PuO_2-ZrO_2**
- Arc furnace : **U-Zr-Fe-O** (in-vessel corium)
- Laser heating : **Fe-Zr-O** and **U-Zr-O**

interpretation of microstructures

- **ATTILHA setup**
- **Interaction corium / concrete**

  → UO_2-ZrO_2-Al_2O_3-CaO-SiO_2

THANKS FOR YOUR ATTENTION



Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 21 70| F. +33 (0)1 69 08 92 21

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'Energie Nucléaire
Département de Physico-Chimie
SCCME
Laboratoire de Modélisation
Thermodynamique et Thermochimie
CEA de Saclay