

DE LA RECHERCHE À L'INDUSTRIE

cea den

Experimental study and thermodynamic modelling of corium mixtures – Application to severe accidents in Pressurized Water Reactors

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Context

Issues

- MOx / oxidised cladding interaction
- Miscibility gap in the in-vessel corium liquid
- Corium / concrete interaction
- State of the art

Objective and approach

Methods and tools

- CALPHAD
- Experimental techniques

Results

- U-Zr-O and U-Zr-O-Fe
- $\text{UO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$

Development of ATTILHA

Conclusions and perspectives

Out of nominal functioning may lead to a nuclear accident



Severe accident (SA): the normal functioning of the nuclear power plant is not re-established

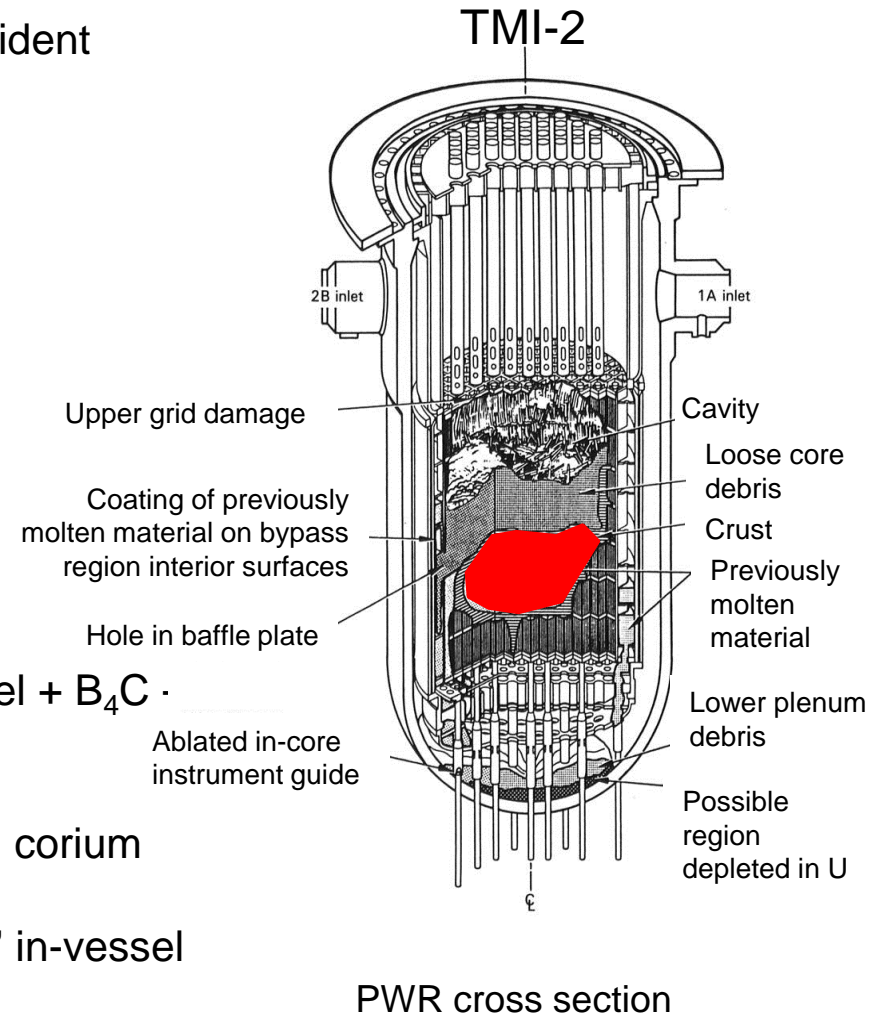


Fusion of the core and internal structure

→ Interaction MOx + Zircaloy + stainless steel + Inconel + B₄C -
FPs

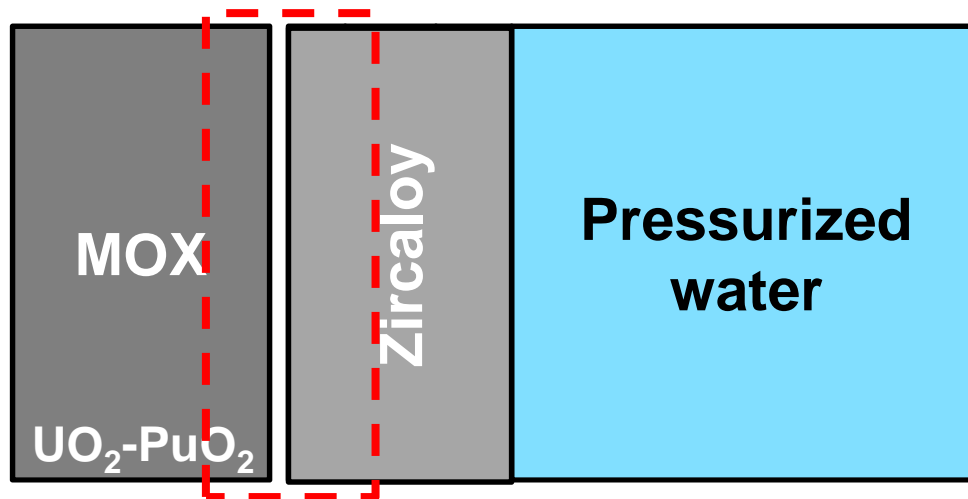
U(Pu)-Zr-O-Fe-Cr-Ni-Ag-Cd-In-B-C-FPs → In vessel corium

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



During **normal functioning** of a PWR → ZrO_2 forms at the inner and at the outer surface of the Zircaloy cladding

Accidental scenario: MOx fuel + oxidised cladding when interacting with the metallic structures and the reactor vessel



Effect of PuO_2 → MOx fuels

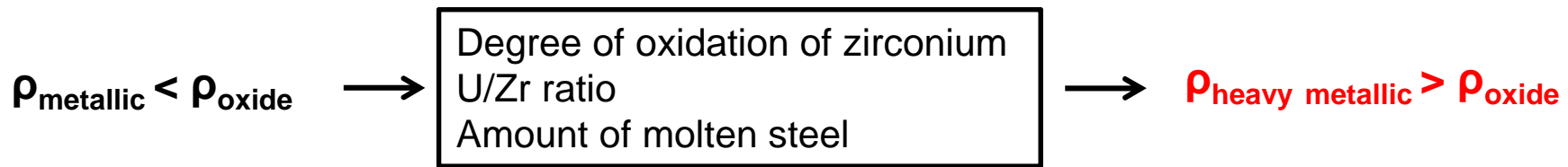
Melting behaviour of the U-Pu-Zr-O system

→ $UO_2 - PuO_2 - ZrO_2$ → Experimental data are rare

Experimental data on Pu-containing systems →

Thermodynamics of the U-Pu-Zr-Fe-O prototypic in-vessel corium

Key point: miscibility gap (MG) in the in-vessel corium system liquid phase



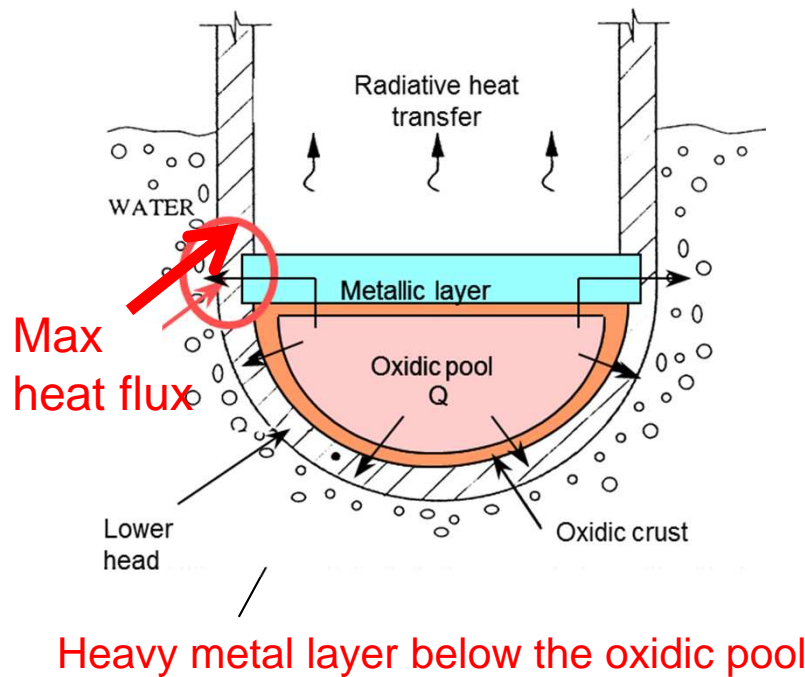
Thickness of metallic layer ↓

- Enhanced focusing effect
- Failure of the reactor vessel

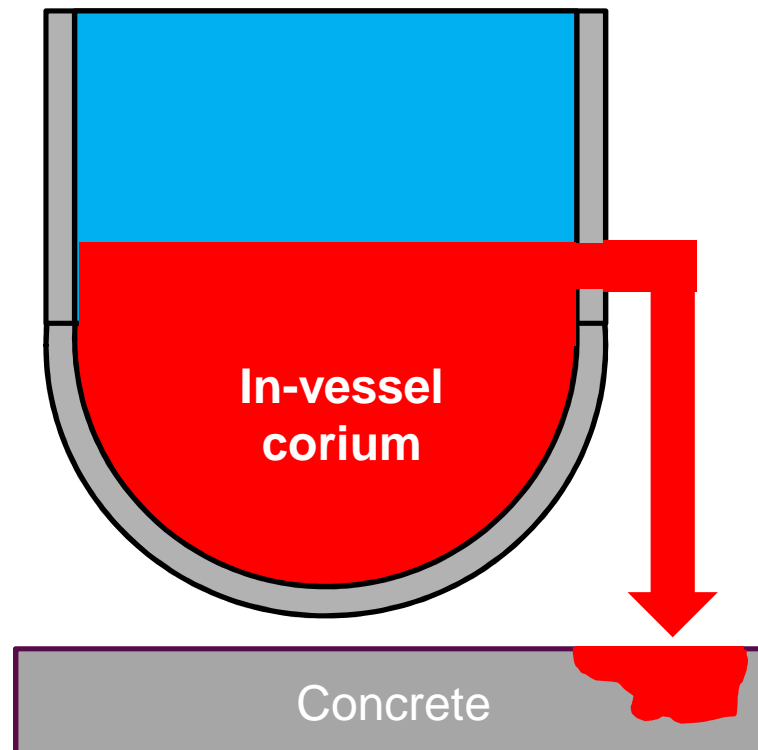
Existent database: NUCLEA, TAF-ID
Developed starting from a limited number of experimental data



New knowledge of the system are needed in the MG metallic and oxide (U, Zr, Fe) and T_{liquidus} and T_{solidus} are paramount for density calculations
Re-criticality → concentration of fissile material



Ex-vessel scenario
→ Reactor steel vessel failure



- ➔ Large scale experiments → Phenomenology of the severe accident
- ➔ Severe accident codes → Design of the reactor
→ Mitigation actions

Data from large scale experiments: out-of-equilibrium transformations
due to thermal and composition gradients

No standard composition exists for the concrete (except for the EPR concept)

The thermo-physical properties of the corium-concrete system are paramount for
the comprehension and the modelling of the interaction corium/concrete



**Thermochemical data (T_{solidus} , T_{liquidus})
are needed**

MOx / oxidised cladding interaction

→ $\text{UO}_2\text{-PuO}_2\text{-ZrO}_2$: NO EXPERIMENTAL DATA

Miscibility Gap in the in-vessel corium liquid phase

→ U-Zr-O-(Fe) : isothermal data

ISABEL1 at CEA: two tie-lines in the U-Zr-O and U-Zr-O-Fe systems

MASCA project: T and composition gradients

Corium / concrete interaction

→ Large scale experiments:

VULCANO at CEA Cadarache

MOCKA at KIT

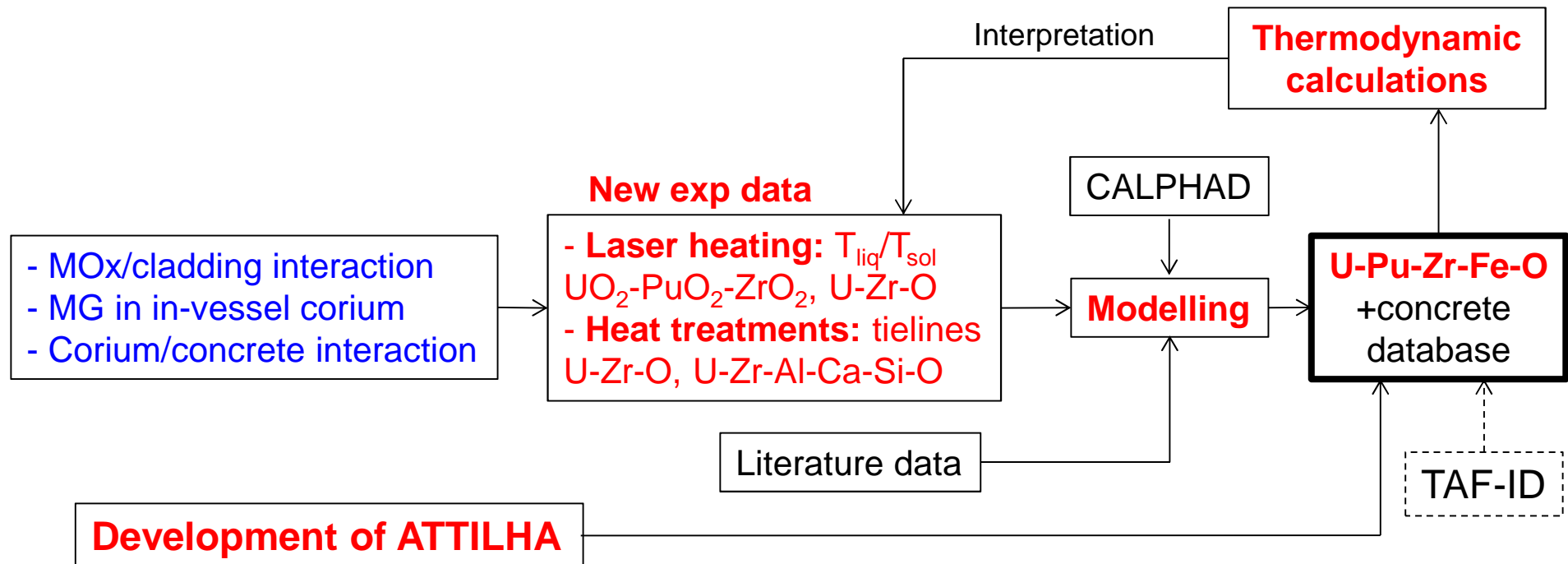
COTELS



Large temperature and
composition gradients

OBJECTIVE

Improve the thermodynamic models of the in-vessel and ex-vessel corium systems



OBJECTIVE of the development of ATILHA

New experimental setup for the investigation of complex mixtures at very high temperature ($T > 2300$ K)

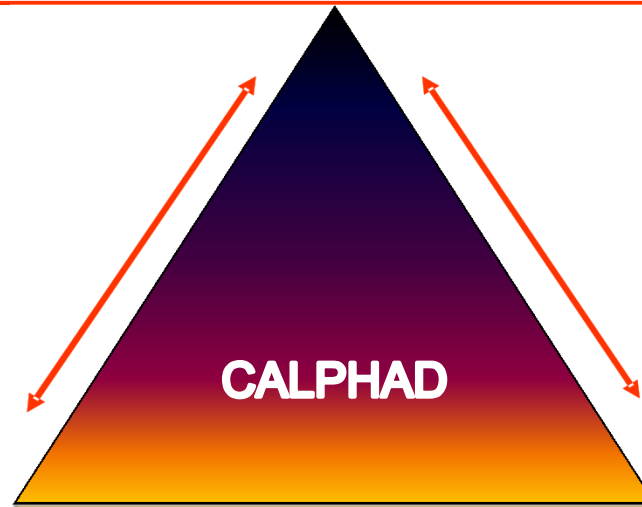
Minimisation of the Gibbs energy of the system

$$\min(G) = \min\left(\sum_{\alpha} n^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha} \text{ or } y_k^{(l,\alpha)})\right)$$

n=number of mole of phase α
 x=molar fraction of i in α
 y=site fraction

Critical analysis of experimental data

Prediction of higher order systems behaviour by extrapolation from lower order systems



Synergic approach

Experiments \longleftrightarrow Calculations

Experimental data acquisition

Thermodynamic data \Rightarrow Calorimetry, D.S.C.
 Phase diagrams \Rightarrow Heat treatments, D.T.A.

Thermodynamic modelling

Optimization
 (Code Thermo-Calc)

Thermodynamic database

$G(\text{phases}) = f(T, x) @ P=1 \text{ atm}$

Minimization of G(system)
 (Code Thermo-Calc)

Thermodynamic properties

Phase diagrams

Application calculations

Thermal analysis → Transition temperatures (T_{liquidus} , T_{solidus} , T_{eutectic})

Laser heating setup (ITU)

Manara et al., Rev. Sci. Instrum. 2008

Isothermal measurements → tie-lines, equilibrium phases

Joule effect furnace (W-resistor) : $T_{\text{max}} \sim 2600$ K

Rare experimental setup for very high temperature measurements ($T > 2300$ K)

Actinide containing systems

Interaction sample / crucible

Thermocouples are not adapted → optical monitoring of the temperature



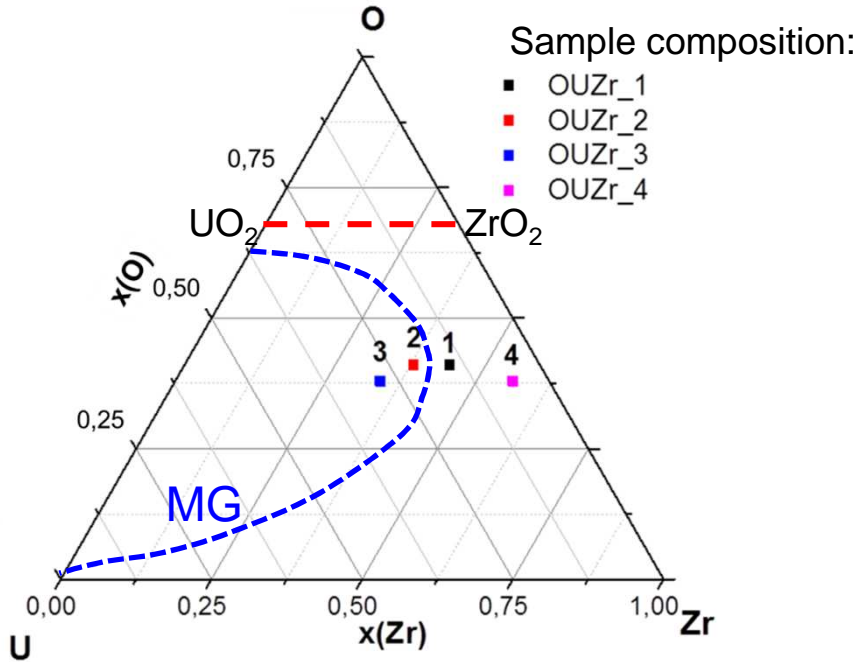
Development of the ATTILHA setup

U-Zr-O and U-Zr-O-Fe systems

→ Experimental results: U-Zr-O

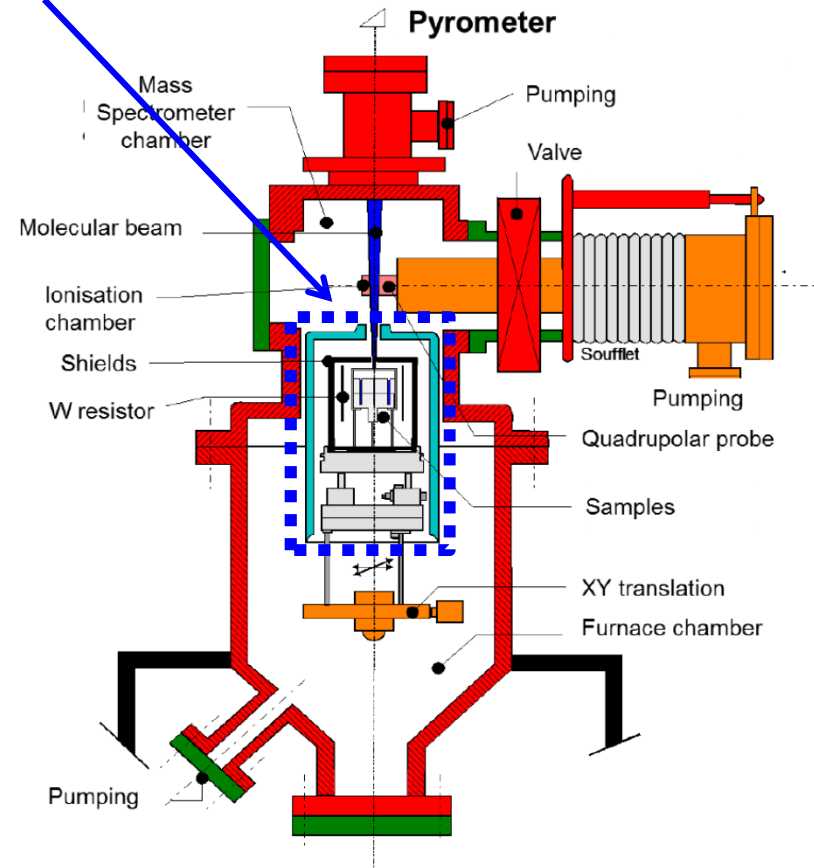
→ Calculations: U-Zr-O and U-Zr-Fe-O

→ Summary



- Starting materials: U, Zr, ZrO₂ (in-situ fabrication)
- W crucible

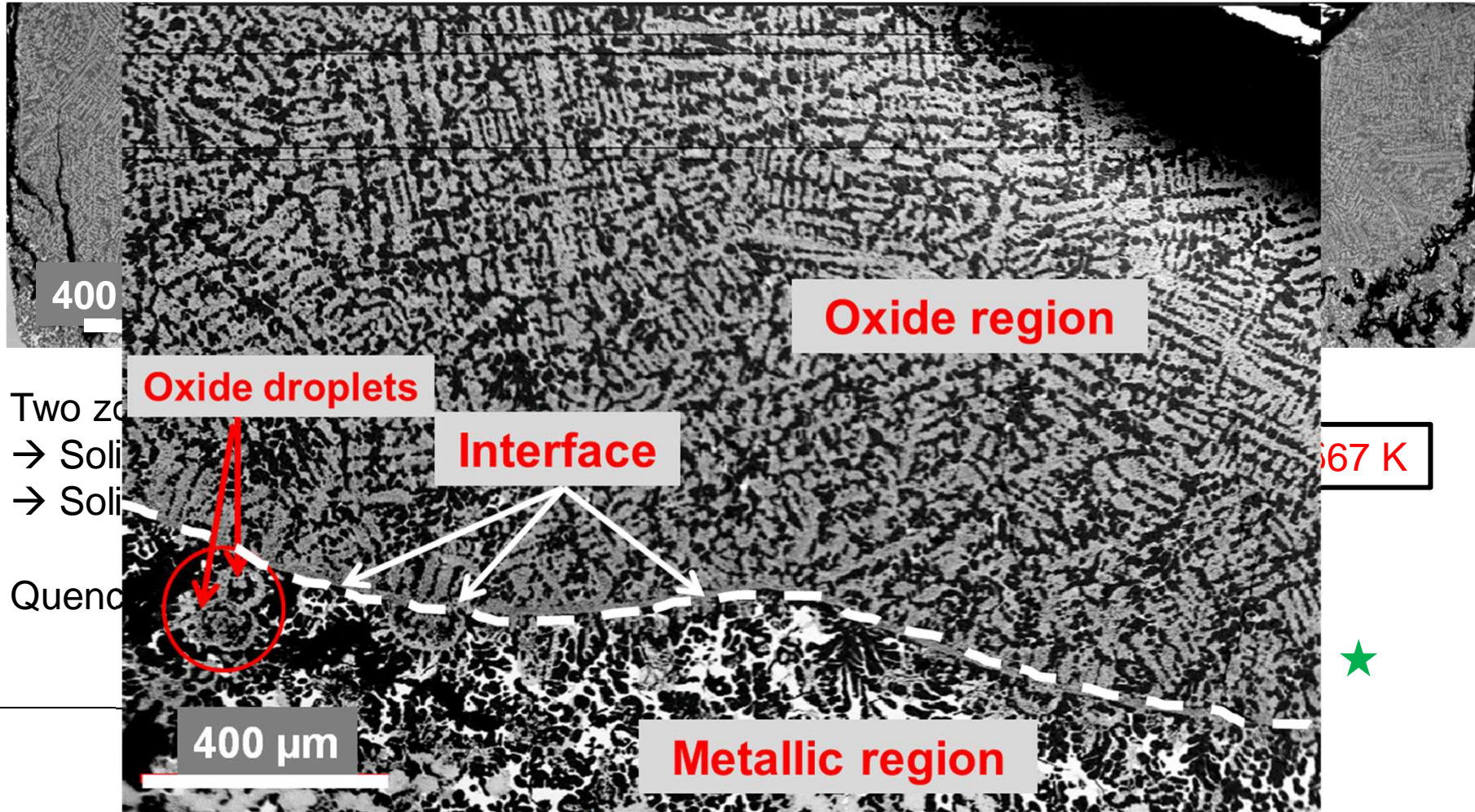
Joule effect furnace
Secondary vacuum



Heat treatment at 2567 K for 45 minutes

SEM-EDS/WDS analyses at LMAC, CEA Marcoule

OUZr_2 and OUZr_3 → Miscibility gap



Liquid 1 (met) : $O_{0.302}U_{0.162}Zr_{0.536}$ ★

Liquid 2 (ox) : $O_{0.460}U_{0.139}Zr_{0.401}$ ★

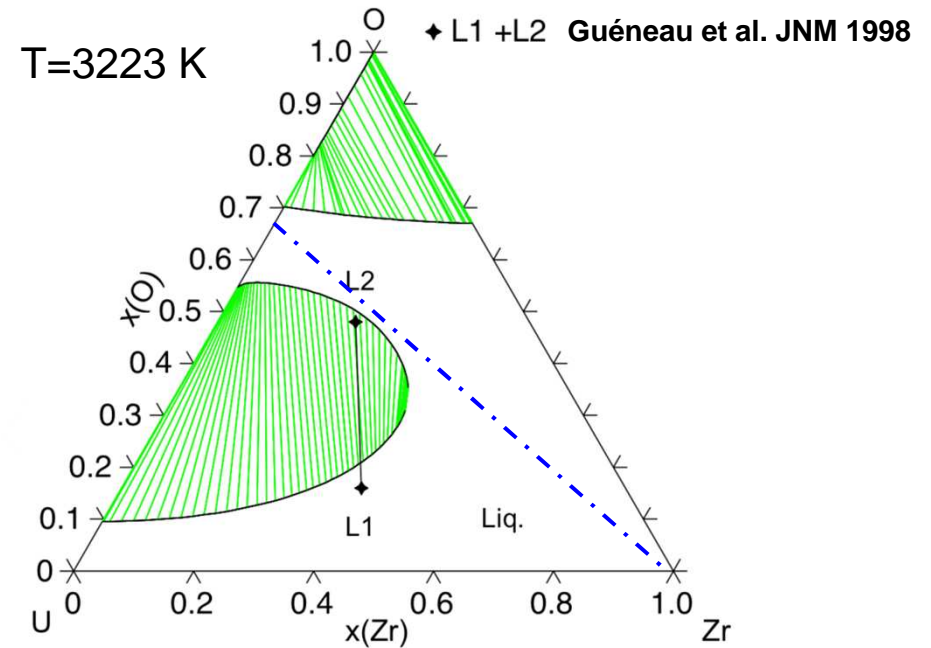
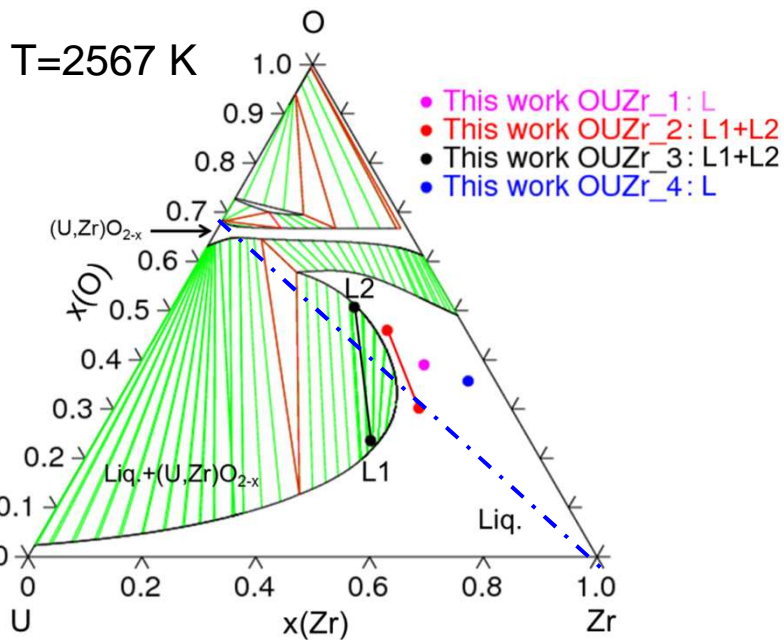
U-Zr-O and U-Zr-O-Fe systems

→ Experimental results: U-Zr-O

→ Calculations: U-Zr-O and U-Zr-Fe-O

→ Summary

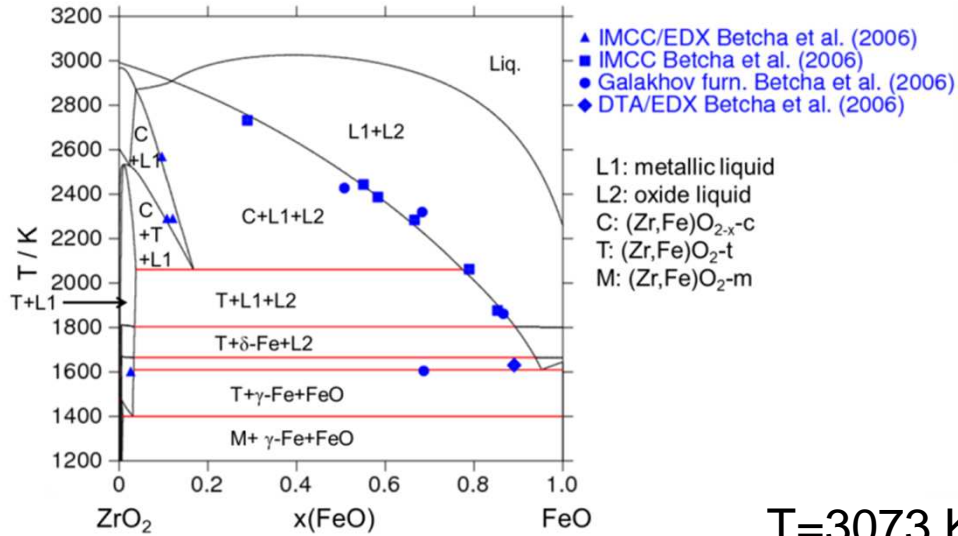
Calculated isothermal sections



Comments:

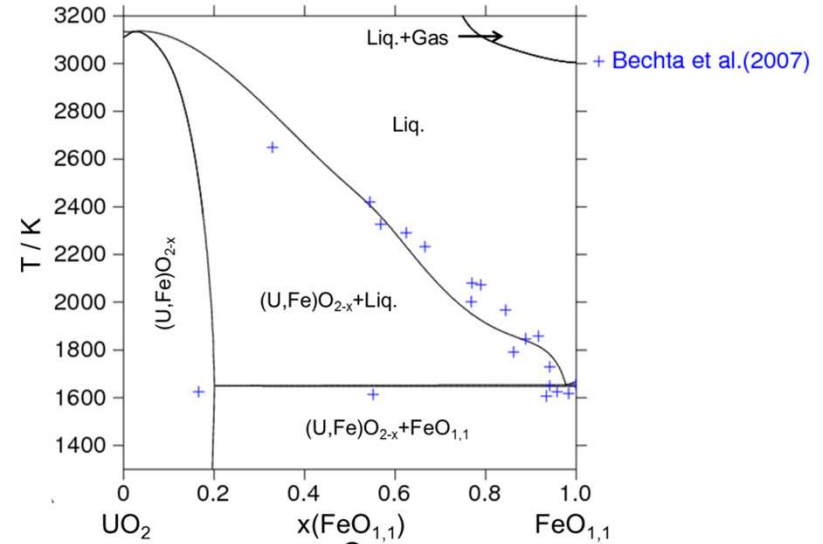
- Reassessment of the U-Zr-O system
- Tie-lines at 2567 K → **improvement of the description of the miscibility gap in the liquid phase**
- Good agreement between calculations and experimental results
- MG exists between ~2450 K and ~3100 K along the **UO₂-Zr section**

Fe-Zr-O



T=3073 K

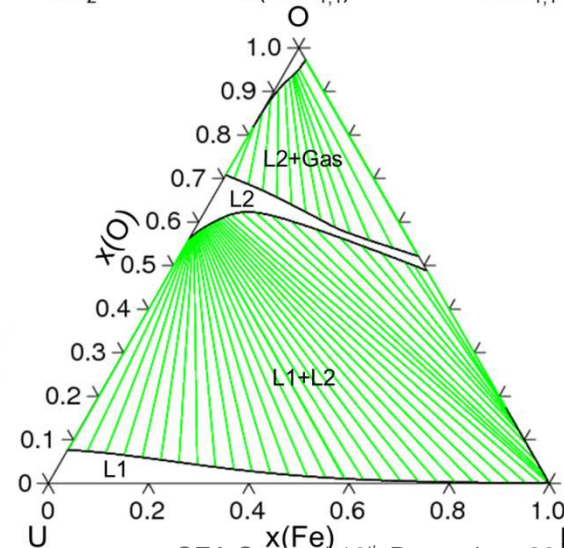
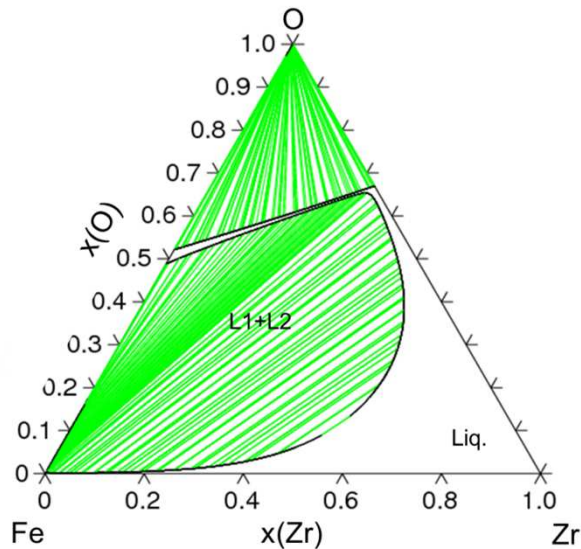
Fe-U-O



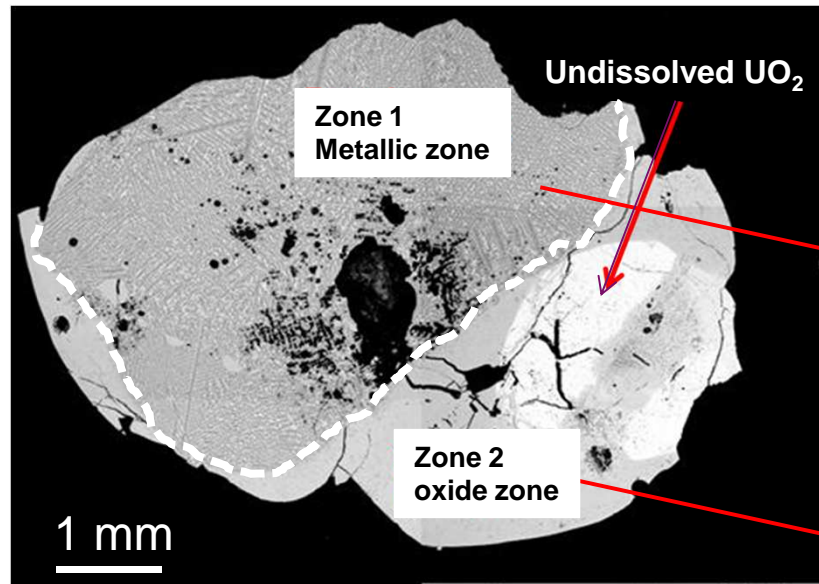
Existence of a MG

Fe-Zr-O, Fe-U-O

NO EXP DATA



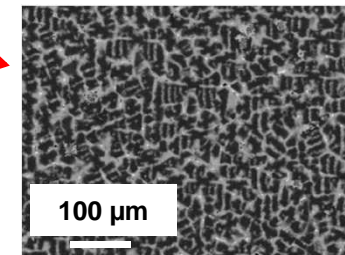
Present TD model of U-Zr-Fe-O system → interpretation of the microstructure



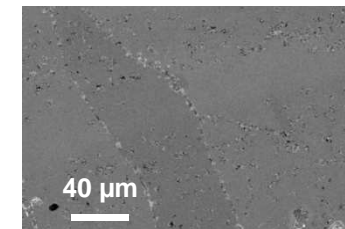
Arc furnace

Component	wt %
UO ₂	52.5
ZrO ₂	6
Zr	18.4
Fe	23.1

Metallic zone



Oxide zone

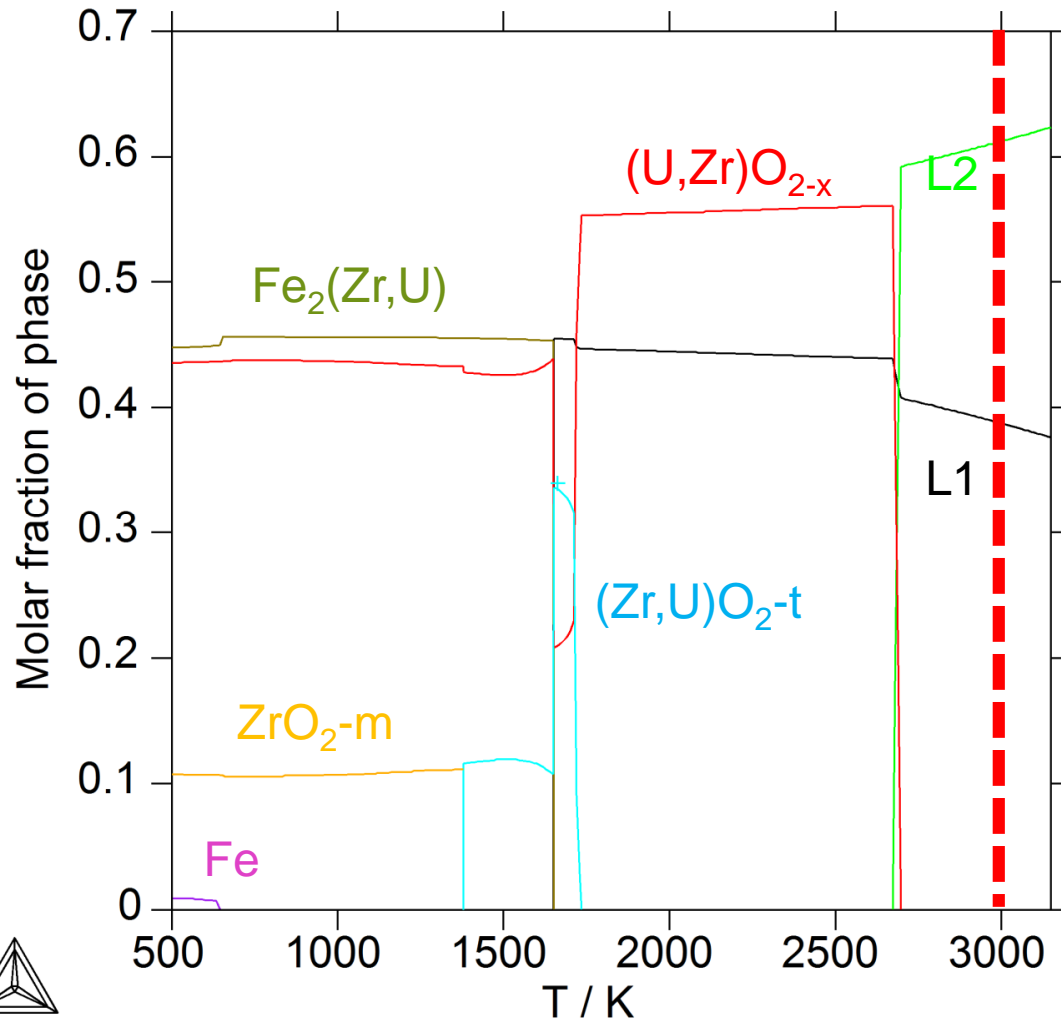


Undissolved UO₂ → T_{arc furnace} < 3120 K

Sharp separation between oxide and metallic region → separated cooling

SEM-EDS/WDS analyses → Distribution of the elements in oxide and metallic liquids

Initial composition $U_{0.145}Zr_{0.185}Fe_{0.308}O_{0.362}$



2 liquids are calculated

Small variation in compositions
+
Sharp separation of the two solidified liquids

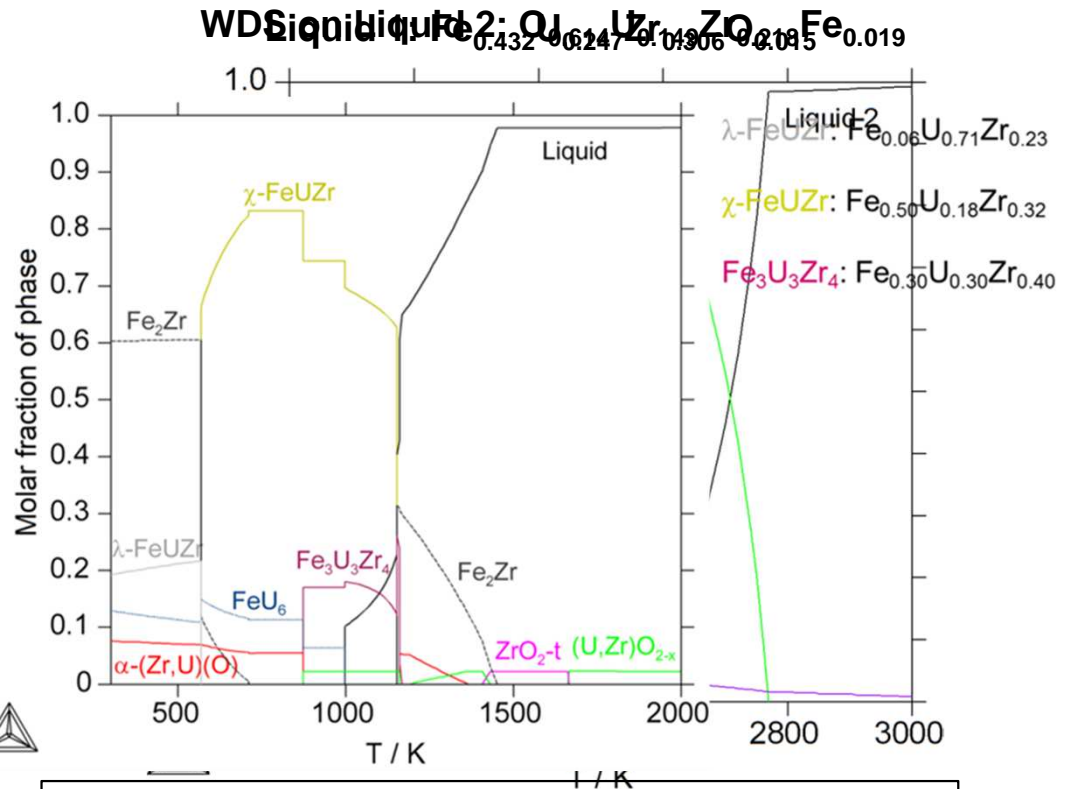
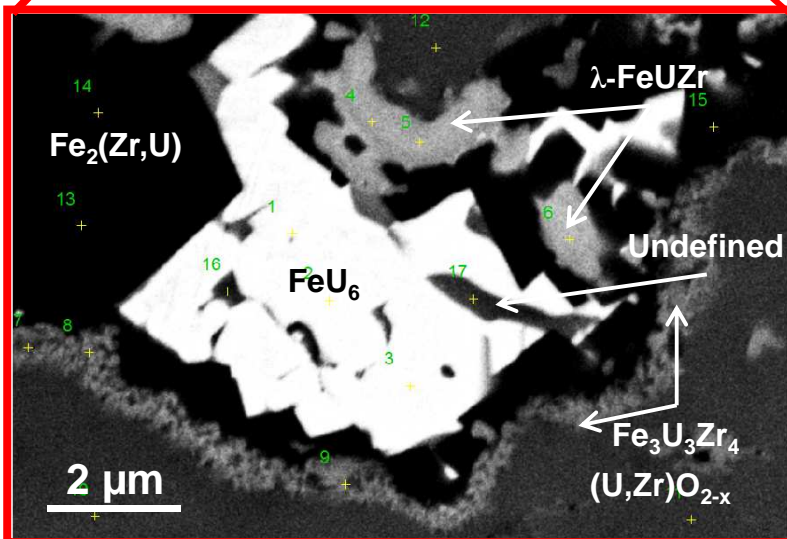
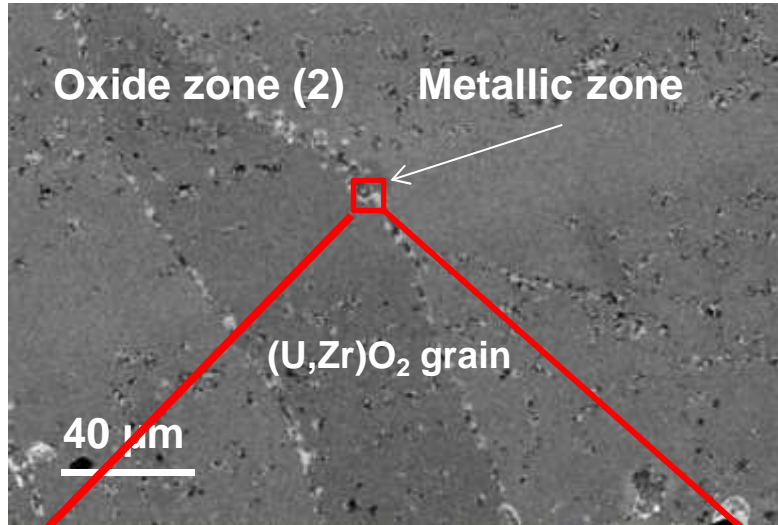
Independent solidification paths using the WDS results on:

Zone 1 (metallic liquid L1)

Zone 2 (oxide liquid L2)



cea den IN-VESSEL CORIUM – OXIDE LIQUID



Qualitative agreement between calculations and experimental observations of (U,Zr)O_{2-x}

U-Zr-O and U-Zr-O-Fe systems

→ Experimental results: U-Zr-O

→ Calculations: U-Zr-O and U-Zr-Fe-O

→ Summary

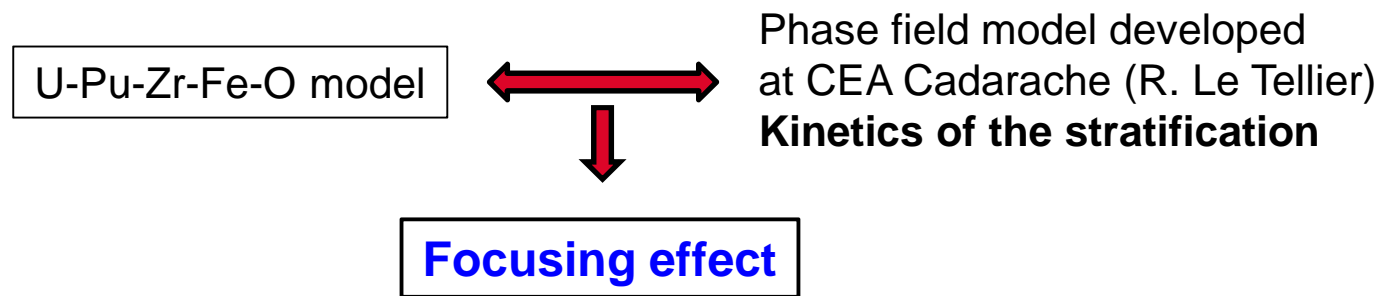
Miscibility gap in the liquid phase of the U-Zr-O system at 2567 K has been observed



Thermodynamic model of the prototypic in-vessel corium U-Pu-Zr-Fe-O



Calculation in accord with experimental results on a U-Zr-Fe-O sample



**Synergic exchange between post-experiment analyses and calculations
Powerful tools for the interpretation of complex microstructure**

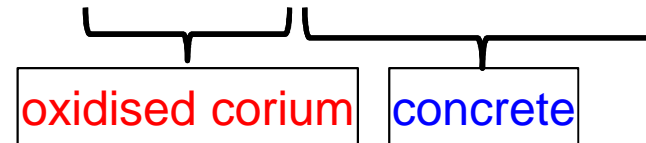
$\text{UO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$ system

→ Experimental results

→ Calculation results: in-vessel corium + TAF-ID database

→ Summary

Simplified system of the ex-vessel corium : $\text{UO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$



CORIUM_1: 80 tons UO_2 + 20 tons ZrO_2 + lime-rich concrete
 CORIUM_2: 80 tons UO_2 + 20 tons ZrO_2 + silica-rich concrete

Composition of the liquid pool after 24h of the MCCI
 Calculation performed using TOLBIAC-ICB (A. Boulin, CEA Cadarache)

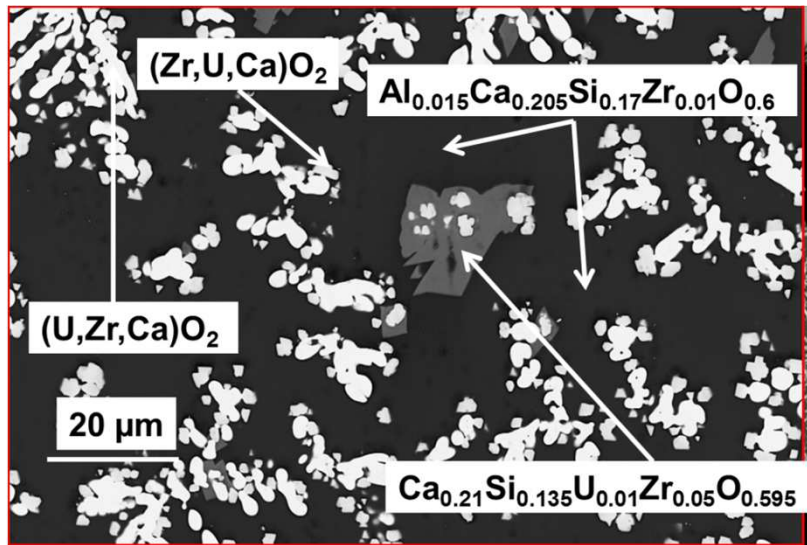
wt%	CORIUM_1	CORIUM_2
Al_2O_3	1,8	2,1
CaO	32,4	11,0
SiO_2	24,6	64,0
UO_2	30,8	15,4
ZrO_2	10,4	7,8

In-situ fabrication starting from Al_2O_3 , CaO, SiO_2 , UO_2 and ZrO_2 powders in W crucible

Joule effect furnace

Heat treatment at 2500 K for 30 minutes

CORIUM_1 (Lime-rich concrete)

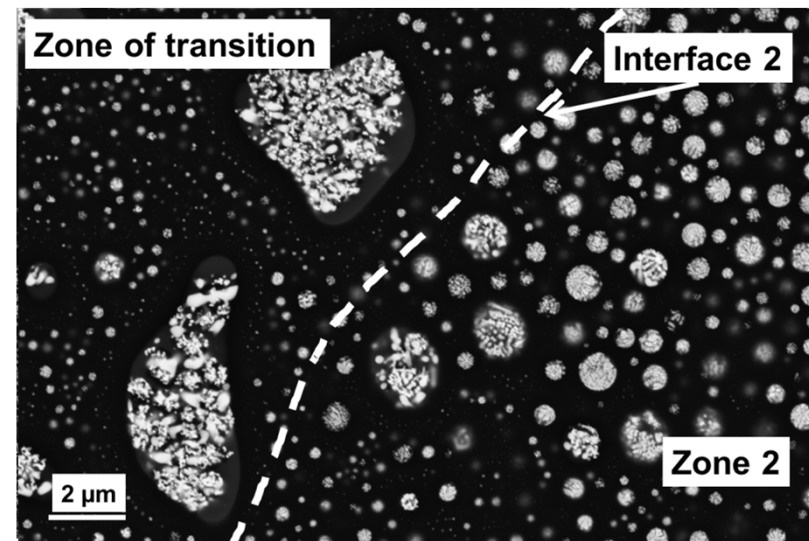


Dendritic structure: $(U,Zr,Ca)O_2$ and $(Zr,U,Ca)O_2$



Single liquid at 2500 K

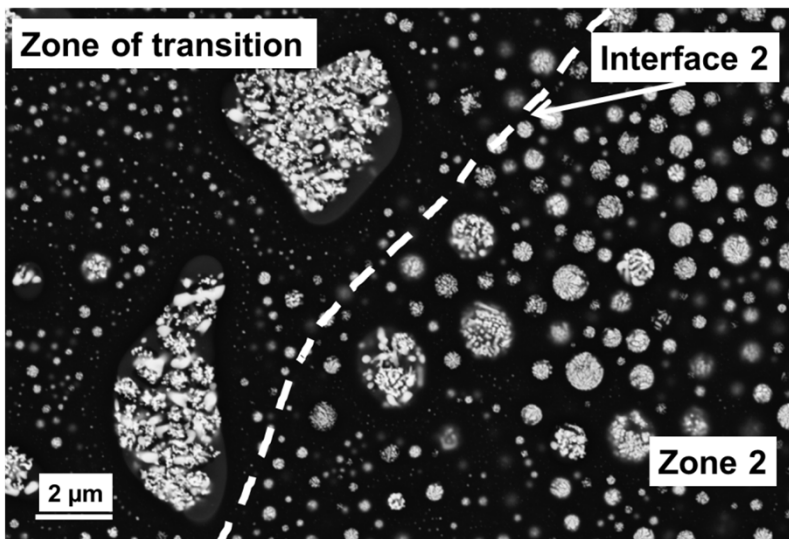
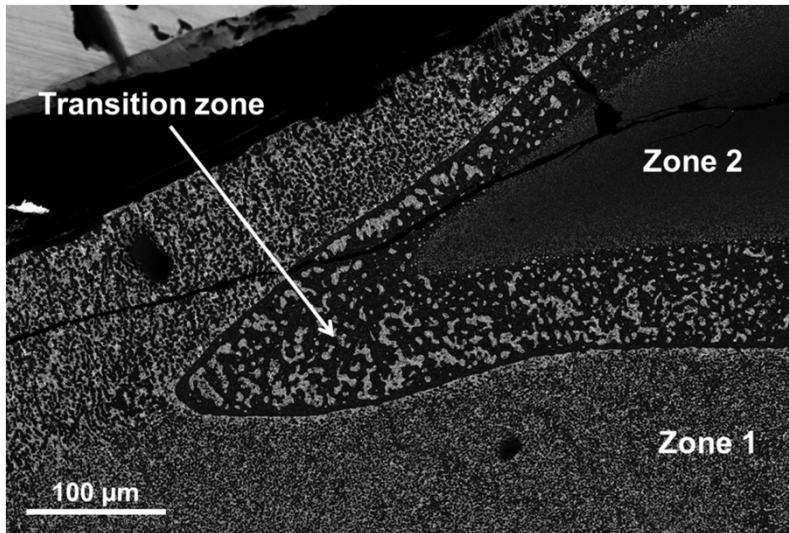
CORIUM_2 (Silica-rich concrete)



SiO_2 based matrix (black matrix) + droplets



Miscibility gap in the liquid phase



SiO₂ based matrix (black matrix) + droplets



Miscibility gap in the liquid phase

Zone 1: enriched in U

Zone 2: U is basically absent



Re-criticality

$\text{UO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$ system

→ Experimental results

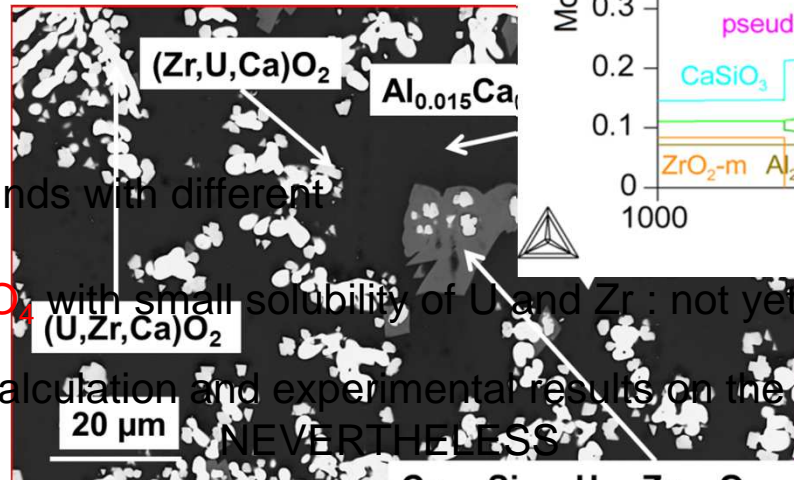
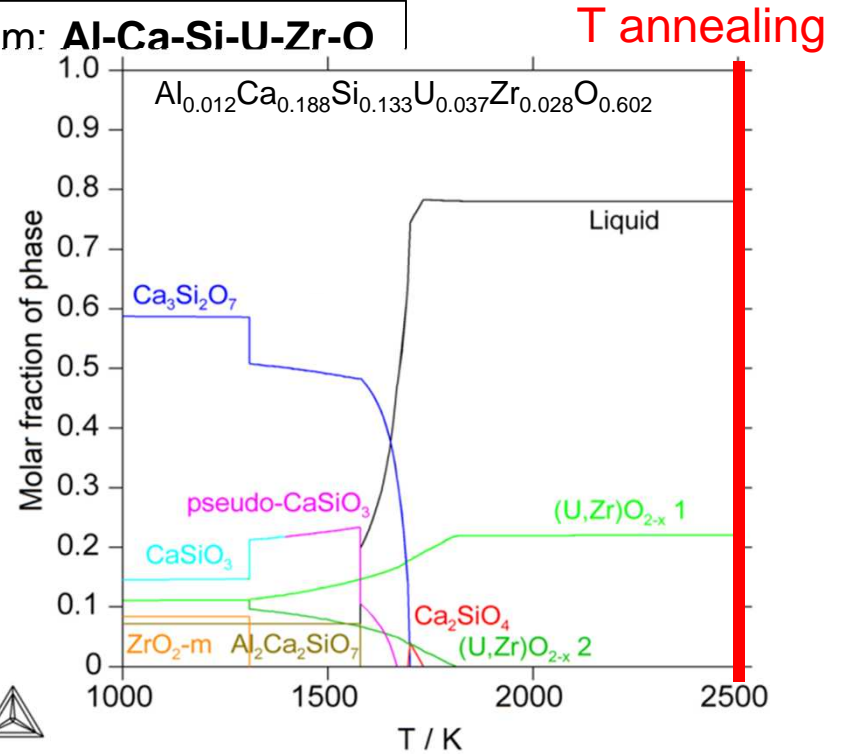
→ Calculation results: in-vessel corium + TAF-ID database

→ Summary

Prototypic ex-vessel corium system: **Al-Ca-Si-U-Zr-O**

In-vessel corium: this work + TAI

Approach to interpret the ex-vessel corium



Two (U,Zr,Ca)O₂ compounds with different compositions: OK

Minor grey phase: Ca₂SiO₄ with small solubility of U and Zr : not yet modelled

Disagreement between calculation and experimental results on the liquidus temperature

		at % Al	at % Ca	at % Si	at % U	at % Zr	at % O
Liquid	Exp.	1.5±1.0	20.5±2.0	17.0±2.0	/	1.0±1.0	60.0±2.0
	Calc.	1.5	22.5	17.0	/	/	58.9

$\text{UO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$ system

→ Experimental results

→ Calculation results: in-vessel corium + TAF-ID database

→ Summary

Experiments performed under controlled conditions + accurate temperature monitoring

Corium / Calcia-rich concrete: single liquid phase

Corium / Silica-rich concrete: miscibility gap in the liquid state

→ U-enriched liquid

→ non-containing U liquid



Re-criticality issue

In-vessel corium TD model + TAF-ID database



Supplementary tool for experiments interpretation
Coupling with severe accident codes

Improve the model for the liquidus temperature prediction
Improve the model of the Ca_2SiO_4 → solubility of U and Zr
Introduce the model for the USiO_4 (Tchernobylite)

Advanced Temperature and Thermodynamics Investigation by a Laser Heating Approach



Development of a versatile experimental setup

ATTILHA

Aerodynamic levitation
Containerless measurements



Experimental data at high temperature ($T > 2300$ K) on complex systems



Phase diagram data (liquidus, solidus, eutectics)
Thermo-radiative properties (emissivity)
Thermo-physical data (surface tension, density)

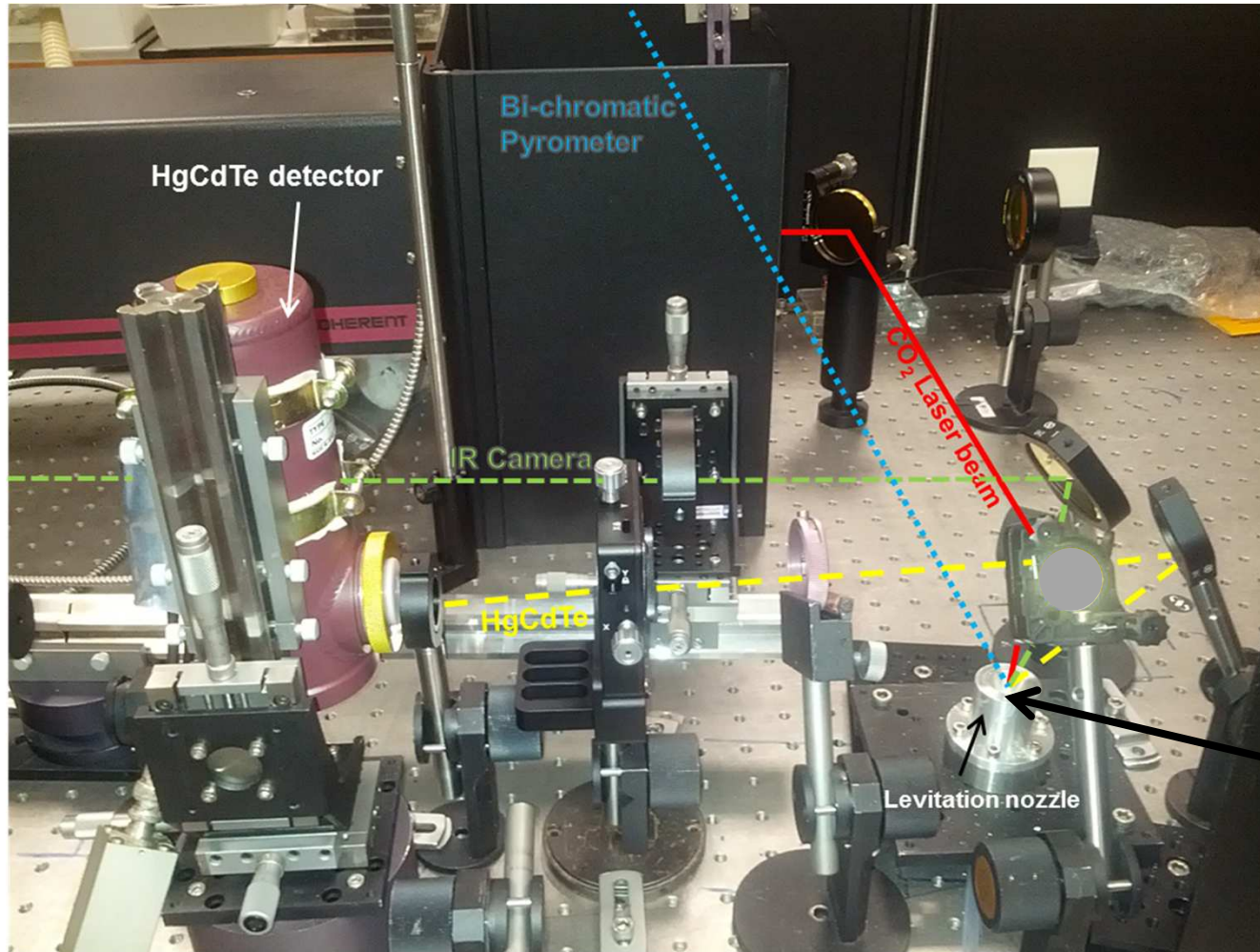
ATTILHA setup

→ Description of the apparatus

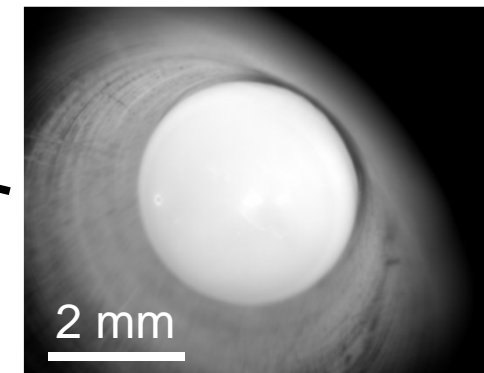
→ Results

→ Summary and perspectives

ATTILHA SETUP



Levitating Al₂O₃ droplet
in the Al-nozzle



→ Optimisation of the instrumentation position on the optical table



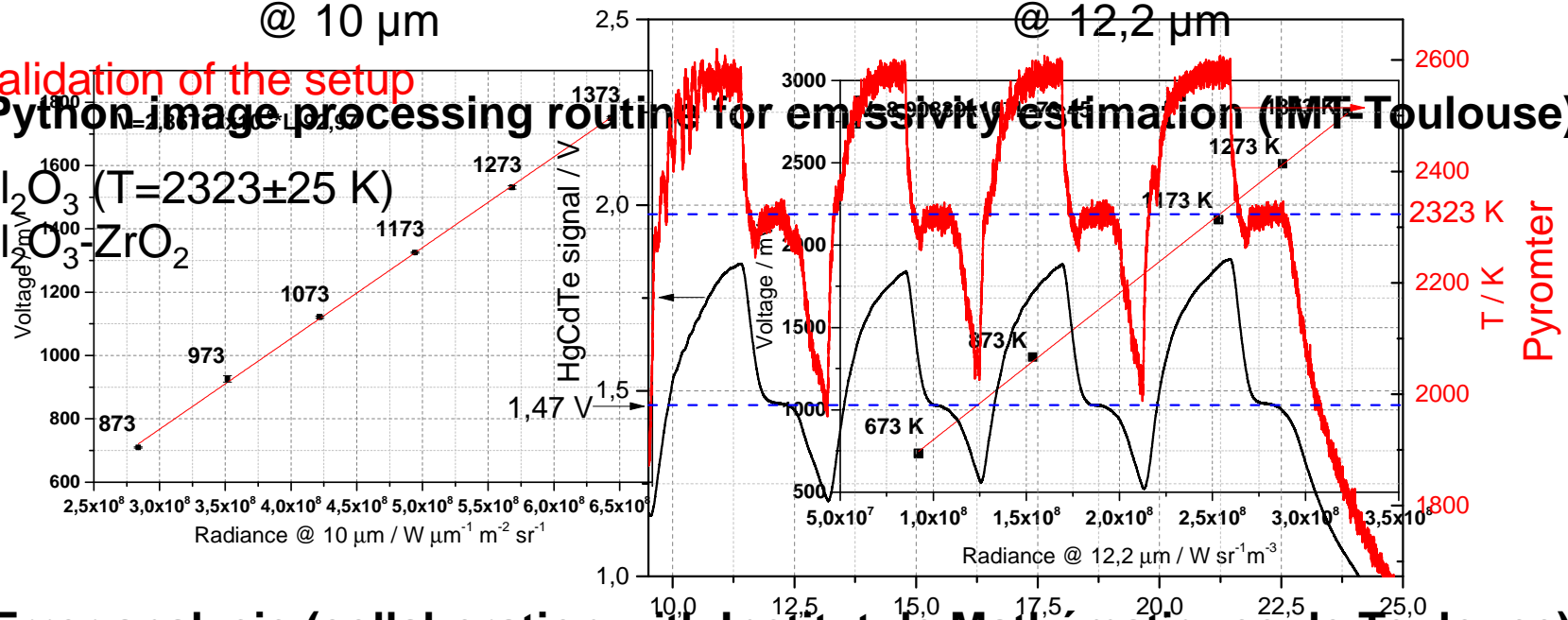
→ Verification of the measurement capabilities against a qualified black-body
 Christiansen point Al₂O₃:410 nm, ZrO₂:12.7 μm
 @ 10 μm @ 12,2 μm

→ Validation of the setup

→ Python image processing routine for emissivity estimation (IMT-Toulouse)

→ Al₂O₃ (T=2323±25 K)

→ Al₂O₃-ZrO₂



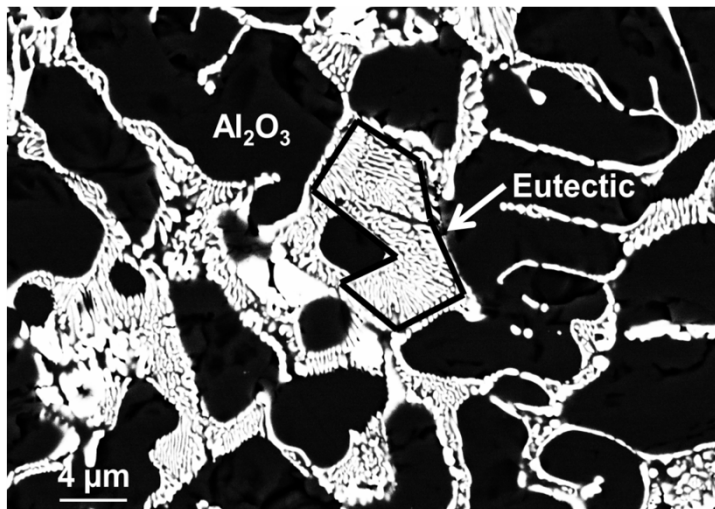
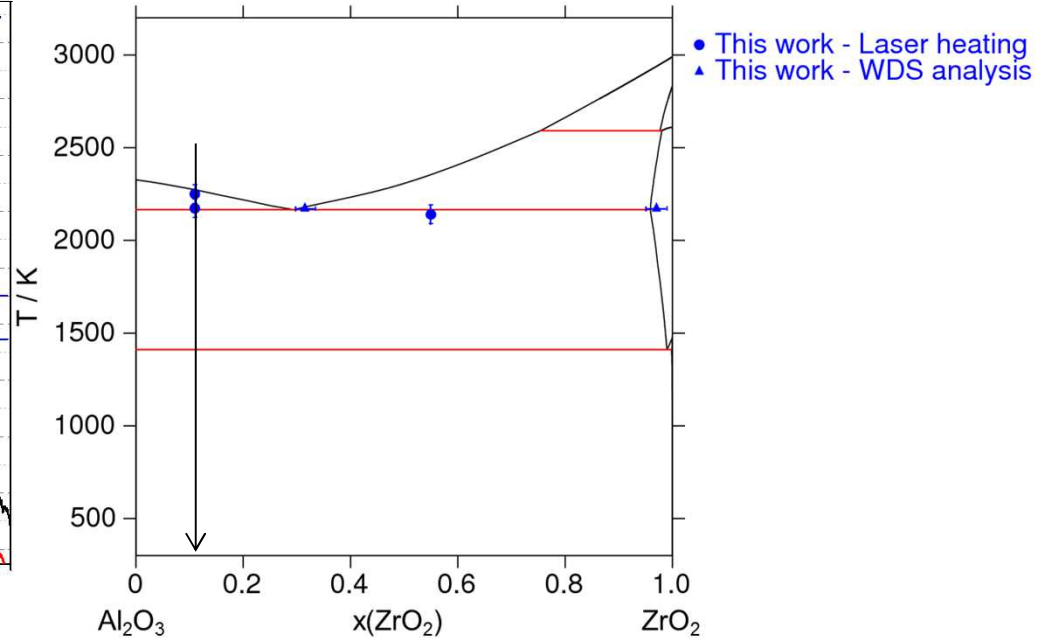
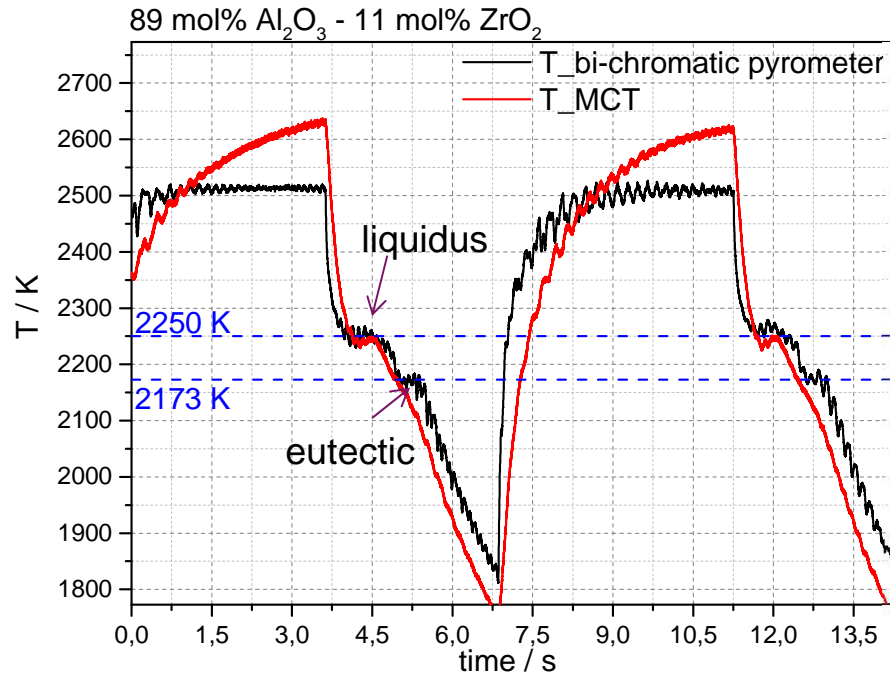
→ Error analysis (collaboration with Institut de Mathématiques de Toulouse)

ATTILHA setup

→ Description of the apparatus

→ Results: $\text{Al}_2\text{O}_3\text{-ZrO}_2$

→ Summary and perspectives



$T_{\text{liquidus}} + T_{\text{eutectic}} \rightarrow$ good agreement with literature

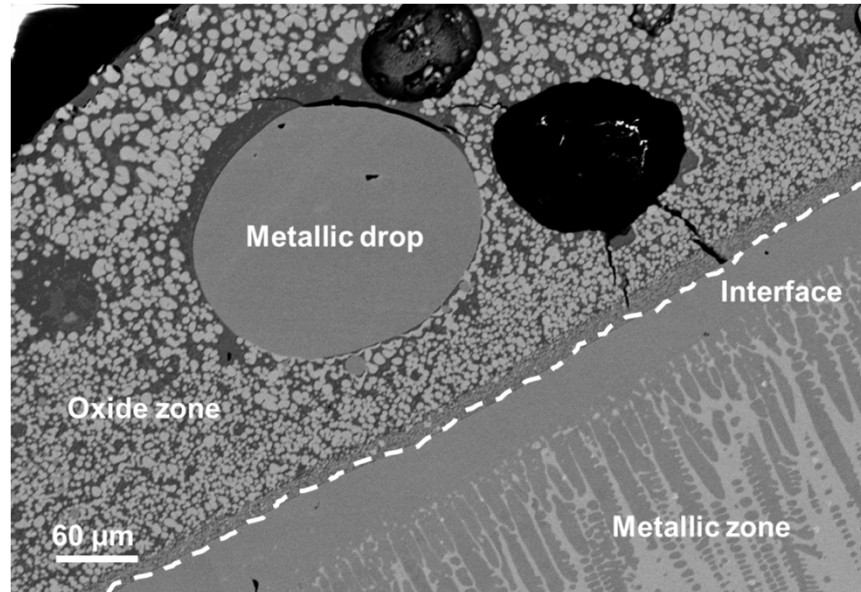
Eutectic composition \rightarrow good agreement with literature

ATTILHA setup

→ Description of the apparatus

→ Results: MG in the Fe-Zr-O system

→ Summary and perspectives



New result

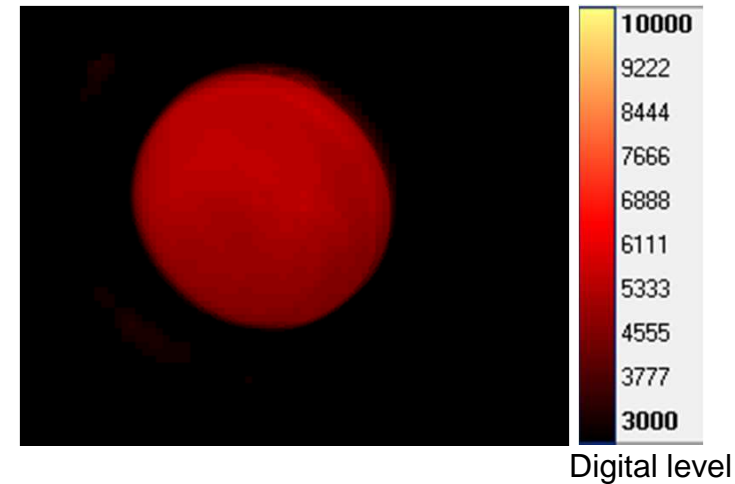
Starting composition: $\text{Fe}_{0.85}\text{Zr}_{0.15}$

↓ Levitation gas: He

Composition moved into the ternary Fe-Zr-O system

tie-line: $\text{Fe}_{0.97}\text{O}_{0.03} - \text{Fe}_{0.05}\text{Zr}_{0.32}\text{O}_{0.63}$

Infrared camera footage



Acquisition 200 Hz
Video player 12.5 Hz

Observation of dynamic phenomena:

→ **Formation of 2 liquids in-situ**

Estimation of the emissivity ratio between the two liquids

→ $\epsilon_{\text{oxide}} \sim 2\epsilon_{\text{metal}}$

ATTILHA setup

→ Description of the apparatus

→ Results: MG in the Fe-Zr-O system

→ Summary and perspectives

ATTILHA → Versatile experimental setup

Investigation of the thermochemical and thermo-physical properties of corium

Validation of the technique on Al_2O_3 and $\text{Al}_2\text{O}_3\text{-ZrO}_2$

Preliminary results on the extension of the miscibility gap in the liquid state of the Fe-Zr-O system

Future developments

→ Nuclearisation of the setup → investigation of prototypic U-containing coria
Ultra rapid camera (5 kHz) → viscosity and density measurement



ATTILHA

- Aerodynamic levitation
- Containerless
- Flexibility in wavelengths choice

High temperature dynamic phenomena
- Formation of MG (Fe-Zr-O)

Thermochemistry of corium (T_{liquidus} , T_{solidus})

- Validation on Al_2O_3 and $\text{Al}_2\text{O}_3\text{-ZrO}_2$
- Python code for image processing → emissivity estimation
- Miscibility gap in the Fe-Zr-O system

Experiments

Pu-containing systems

T_{liquidus} and T_{solidus}
measurement on in-vessel
and ex-vessel mixtures

Modelling

Validation of the current
database

Liquidus for in-vessel and
ex-vessel mixtures

Vaporisation of Pu-
containing species

U and Zr solubilities in the
 Ca_2SiO_4 model

Coupling with severe
accident codes and phase
field codes

ATTILHA

Nuclearization of the setup

Prototypic coria samples

Ultra rapid visible camera
to obtain thermal-physical
properties (surface tension,
viscosity) of coria

Acknowledgments

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R. Belin (LCC)

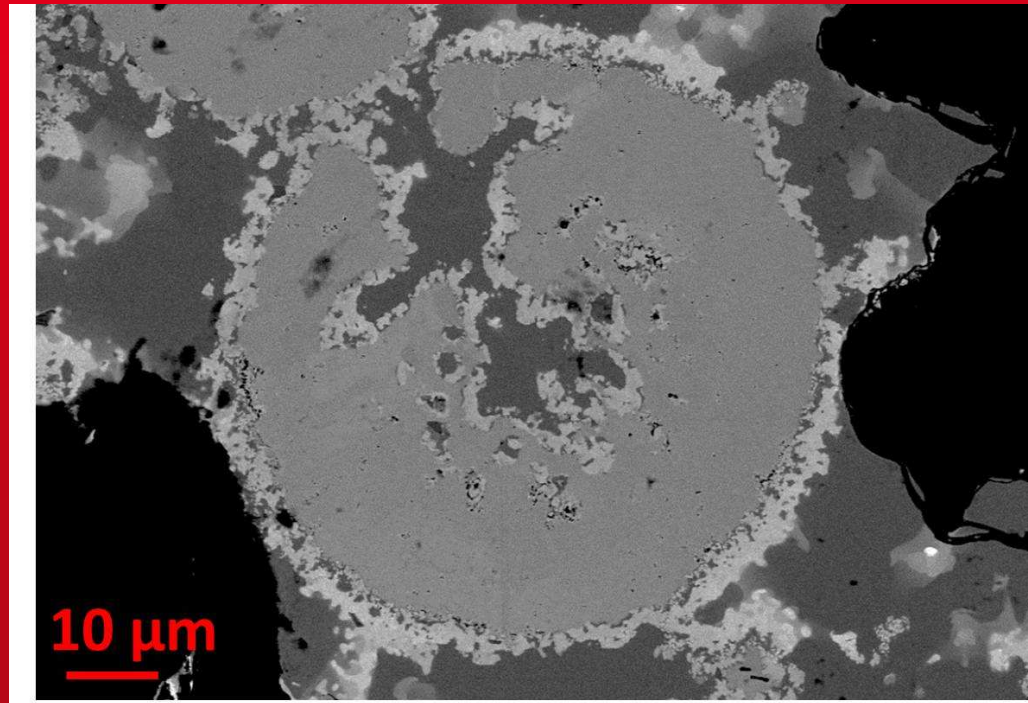
M. Tabarant (LISL)

D. Manara, A. Smith, P.E. Raison (JRC-ITU)

F. Gamboa, L. Risser (IMT Toulouse)

**Eric Lizon A Lugrin, Thierry Alpettaz
and the LM2T team**

THANK YOU FOR YOUR ATTENTION



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