Mixing of Uranium Dioxide an Hafnium at high temperature. Potential application to mitigate criticallity risks in fast reactors

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DE LA RECHERCHE À L'INDUSTRIE

MIXING OF URANIUM DIOXIDE AND HAFNIUM AT HIGH TEMPERATURE. POTENTIAL APPLICATION TO MITIGATE CRITICALITY RISKS IN FAST REACTORS

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OUTLINE

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CONTEXT

- One of the main safety issues in the severe accident phases of a Sodium Fast Reactor is to guarantee non criticality of the molten fissile fuel.
- In this respect, absorbing materials can be added before corium spreads on the core catcher.
- They could be added to the molten fuel near the reactor core or on the core catcher, as sacrificial materials.
  - Prevent criticallity
  - Mixes well with fissile melt
- Hafnium is a candidate absorbing material.
- HfO_2 has previously been studied at CEA as an oxidic sacrificial material
  - K. Plevacova, C. Journeau, P. Piluso, J. Poirier, Eutectic crystalization in the UO_2-Al_2O_3-HfO_2 ceramic phase diagram, Ceramics International, 40 (2014) 2565-2573.

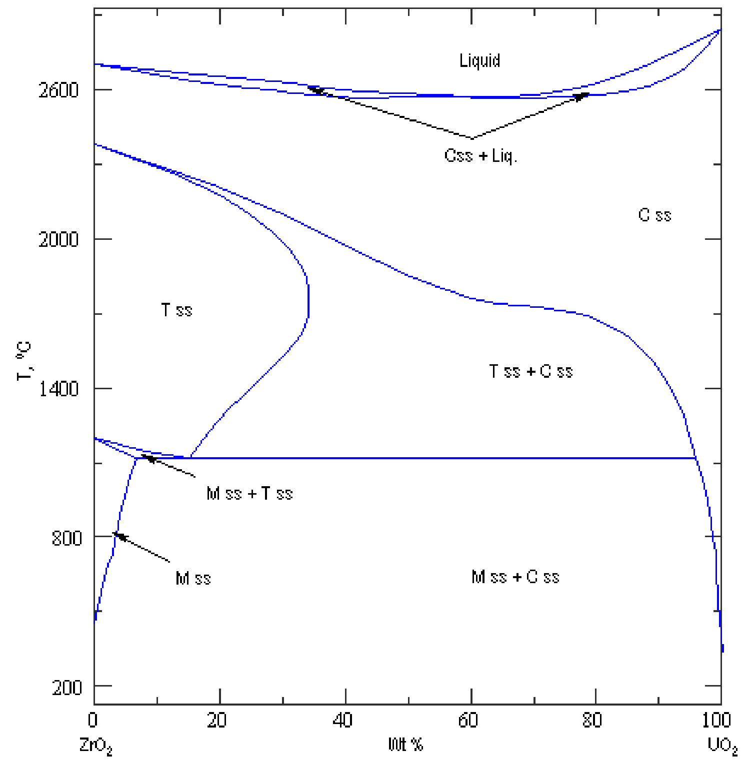
UO_2 – HFO_2 BINARY PHASE DIAGRAM

- Not well established to date
- Hafnium being very close of Zirconium
  - Assumption of (mole-wise) similarity with UO_2 – ZrO_2 phase diagram*

➔ « Azeotropic point » estimated at 46 wt% UO_2 – 54 wt% HfO_2

➔ Liquidus around 2600°C

➔ Formation of a $(U_{1-x}Hf_x)O_2$ solid solution

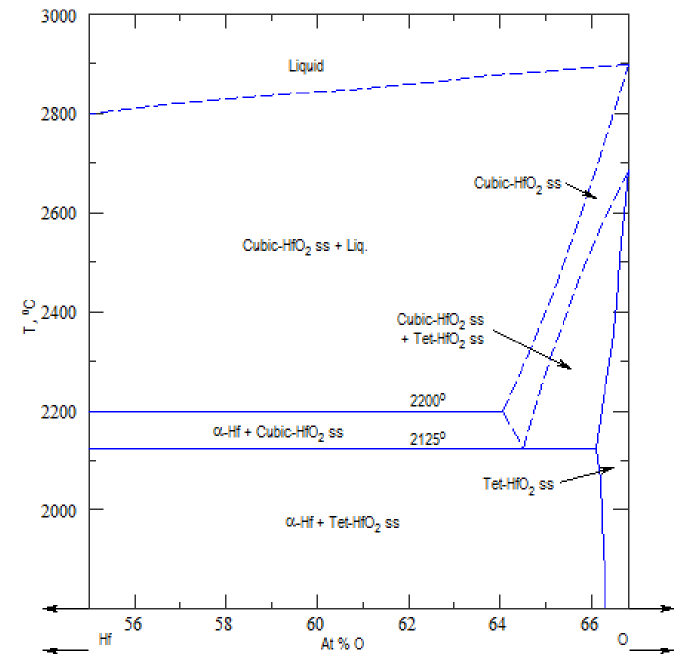


** M. Yashima et al., Thermodynamic assessment of the zirconia – urania system, J. Am. Ceram. Soc. 79 [2] 521-524 (1996)*

METALLIC HAFNIUM WITH OXIGEN AND URANIUM

Analogy with metallic zirconium

- Total miscibility between liquid Zr and ZrO_2
  - No miscibility gap between an oxidic and a metallic liquid
  - Experimentally verified
    Ruh & Patel, JACS 56, 606-7 (1973)



- In the U, Hf, O ternary
  - Miscibility gap expected
  - Expected oxido-reduction
    - $Hf + UO_2 \rightarrow HfO_2 + U$
    - Metallic uranium in metallic phase (with molten steel)
    - Oxidized hafnium with oxidic phase Molten $(U,Hf)O_{2-x}$
  - 2 advantages:
    - Mixing absorber and fissile melt
    - Extracts fissile from oxidic phase and mixes it with steel (diluant)
  - Risk:
    - If metallic uranium does not mix with steel….

CORSICCA 3 EXPERIMENT

EXPERIMENTS IN VITI FACILITY

Studied mixture (≈ 40 g) placed in a protected graphite or tungsten crucible

Inductive heating until **2600°C**

Adjustable atmosphere

(2 bars, under argon ≈ 5 L/min)

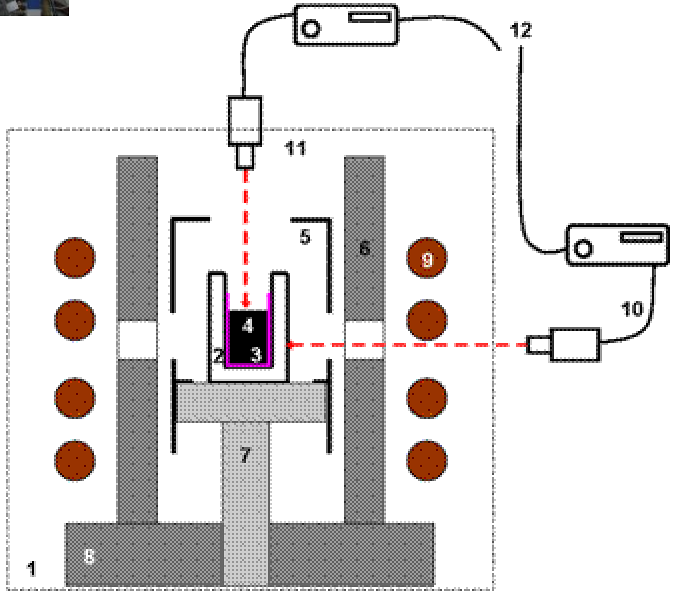
Measurements during the experiments:

Melting temperature
→2 pyrometers
Quantity of formed gas
→ measure of pressure and gas flows

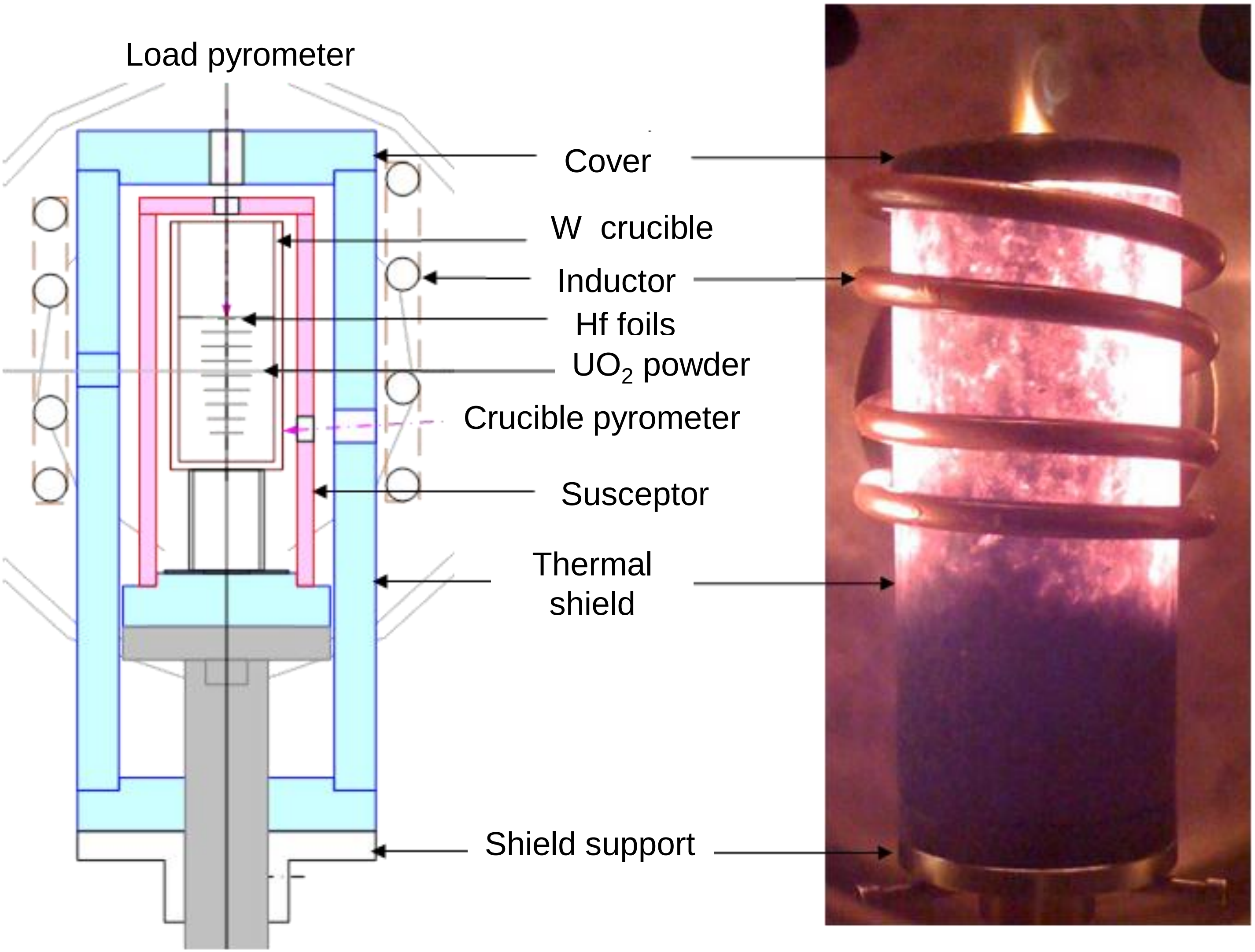
Post-mortem sample analysis: identification of different formed products

General view of VITI facility

Induction furnace



(1) VITI tank, (2) Crucible, (3) Protective coating, (4) Mixture, (5)Graphite susceptor, (6)Thermal shield, (7) Support for crucible, (8) Support for thermal shield, (9) Inductance coil, (10) Pyrometer, mesure of Tmixture, (11) Pyrometer, mesure of Tcrucible, (12) Data acquisition



Load pyrometer
Cover
W crucible
Inductor
Hf foils
UO_2 powder
Crucible pyrometer
Susceptor
Thermal shield
Shield support

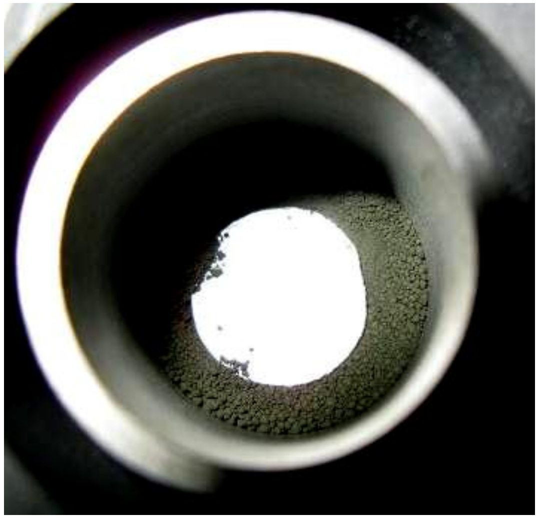
90% UO_2 - 10wt% Hf LOAD

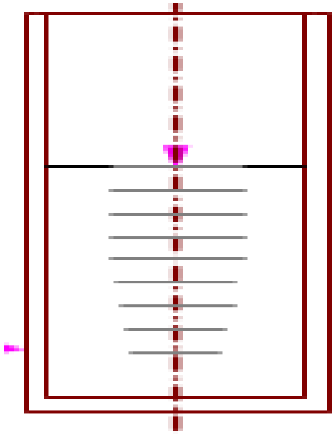
- Tungsten crucible chosen to prevent Hf-C and U-C reactions
  - Height 58 mm
  - Diameter 23 mm

- Load:
  - Depleted UO_2 powder
  - Hafnium
    - Powders are pyrophoric : discarded
    - Wire : practical difficulties
    - 0.25 mm thick foils

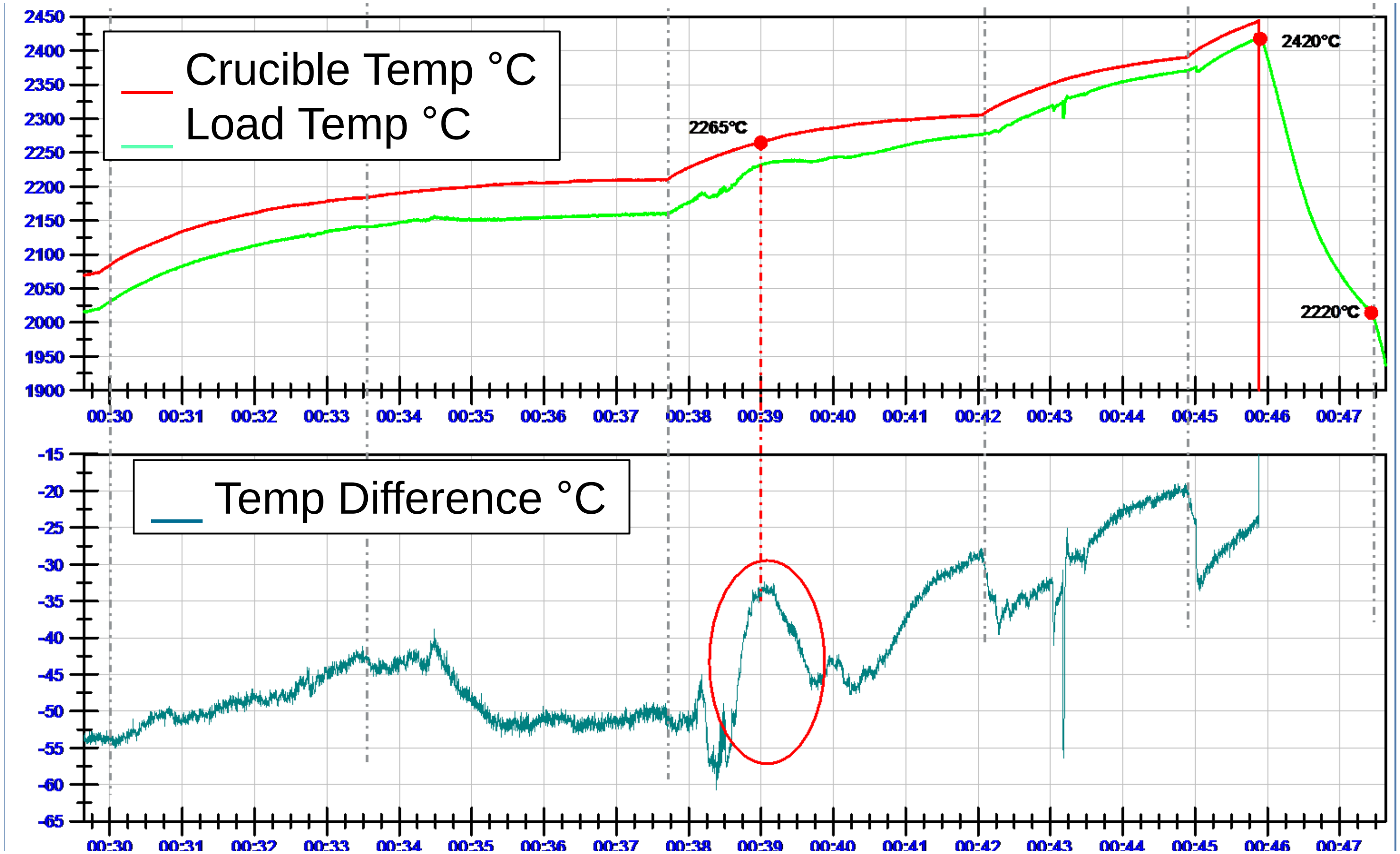
    Positioned far from W walls to present Hf-W interactions.

    5 12-mm disks + chips
  - Total mass = 38.3 g (3.84 g Hf)



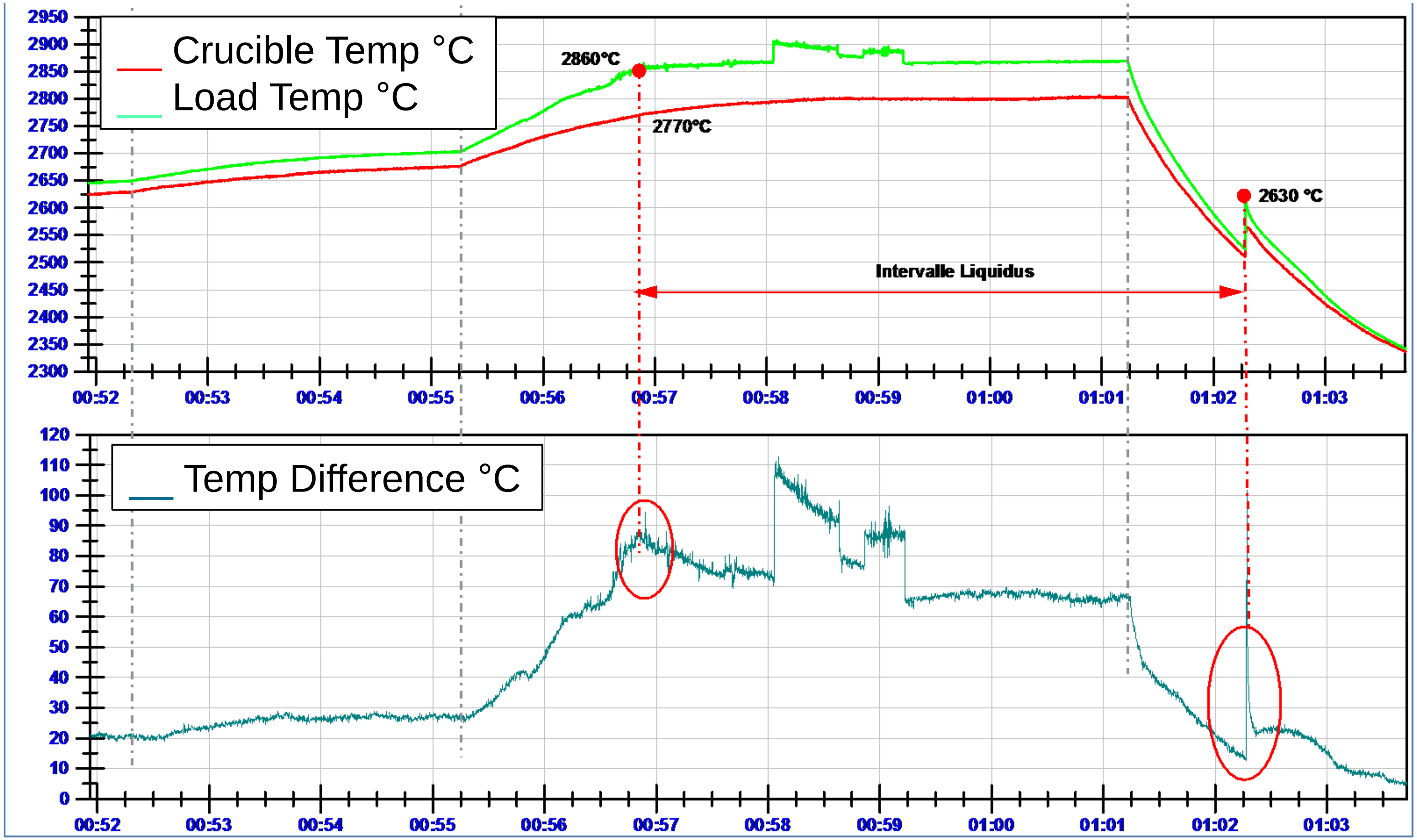


1ST HEAT-UP (Hf MELTING)



- Hf melting around 2265 ± 30°C [Literature: 2230°C]
- Test halted at 2420°C
  - Load has been sintered

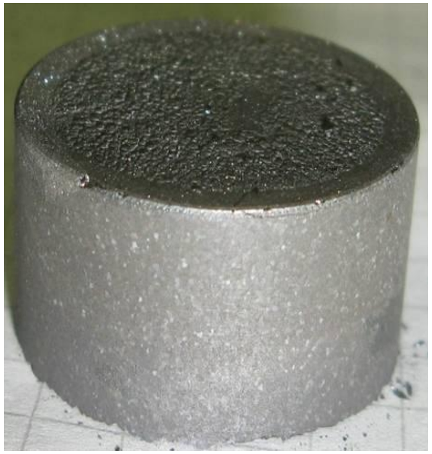
2ND HEAT UP



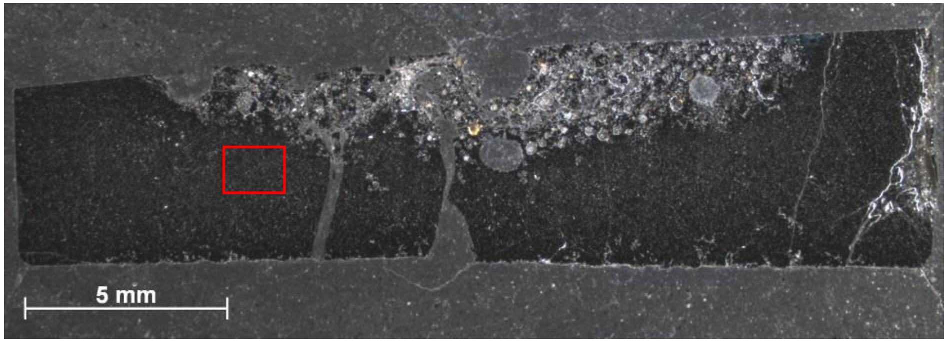
- Melting (of $UO_{2\pm x}$) at 2770-2800°C
- Cooling
  - Undercooling
  - Solidification of (U,Hf,O) mixture at 2630°C

POST TEST EXAMINATION

- Melted aspect
- Not sticking to crucible
- Density 9.9



- Cut view (macrograph)
  - Major phase (gray)
  - Orange/purple minor phase



MATERIAL ANALYSES

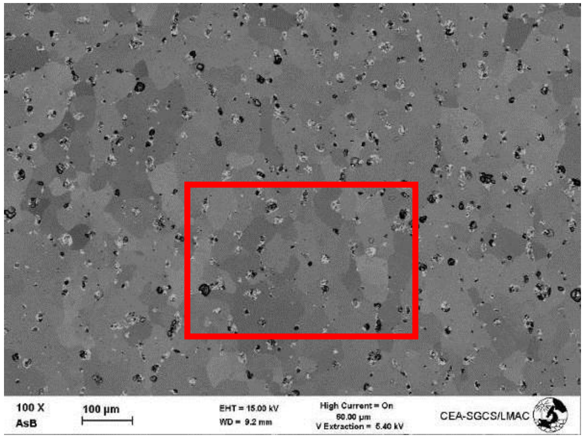
SEM/EDX

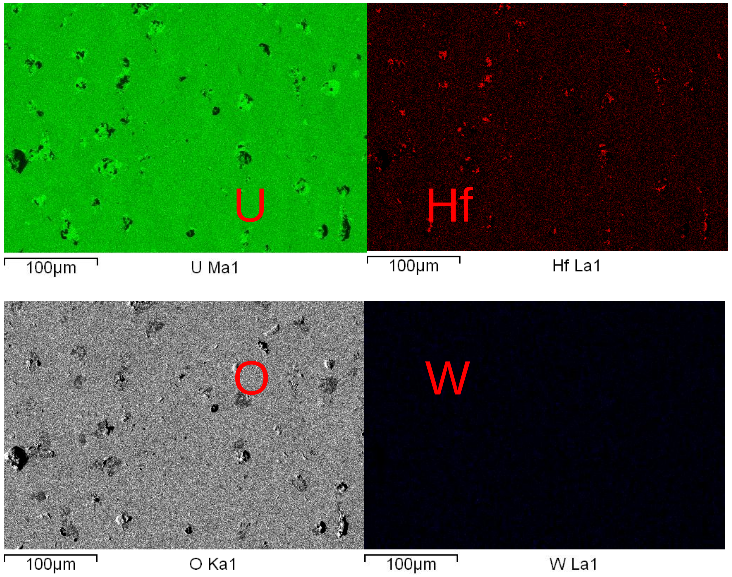
- Major phase UO_2 with some dissolved Hf
- Minor phase HfO_2 with dissolved U
  - Red dots on Hf map
- Minor phase : metallic U
  - Light green phase in U map

- No pollution of sample by W

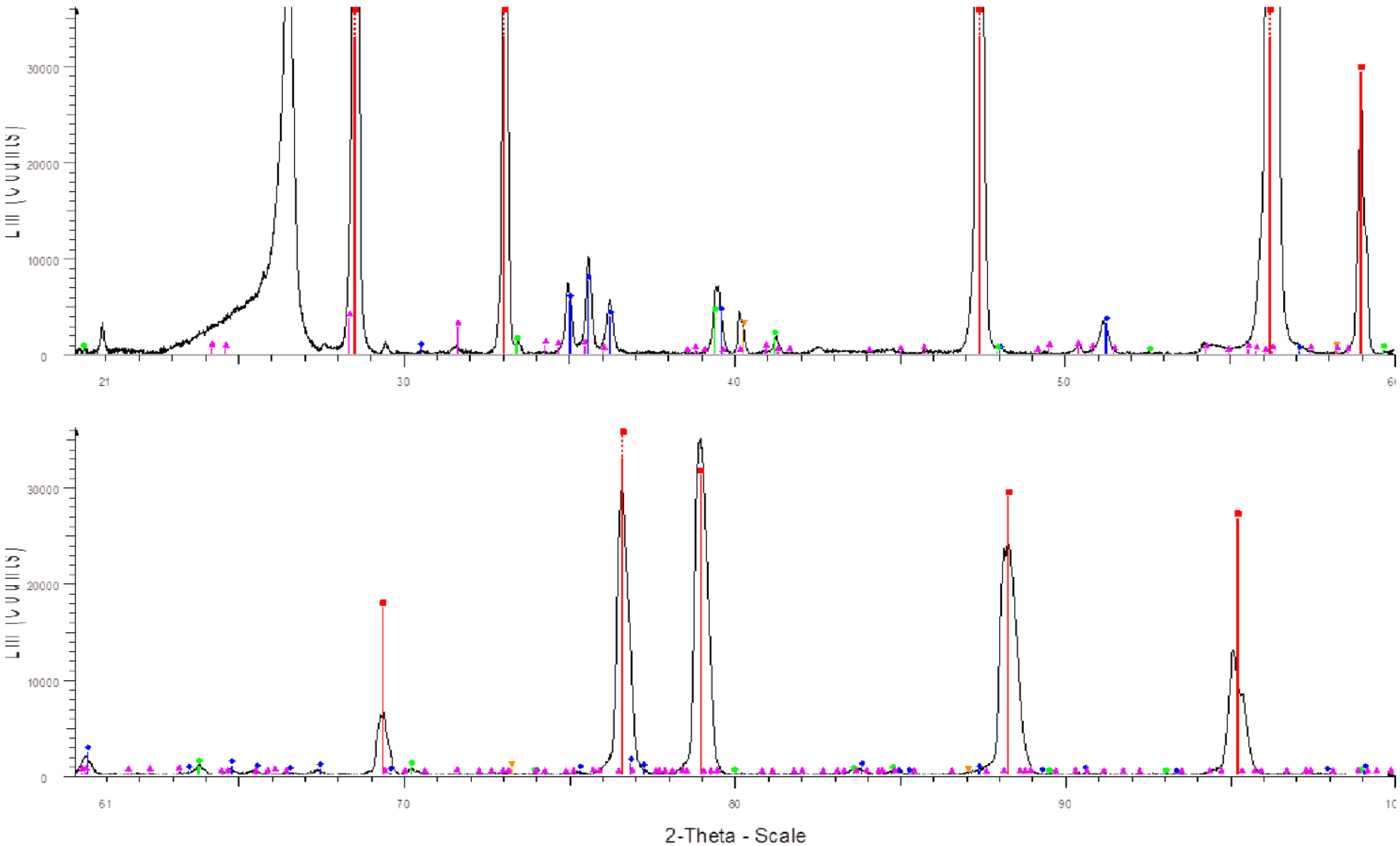
	U	O	Hf	W
Core	73.2%	15.8%	10.9%	0%
Near walls	73.3%	16.1%	10.5%	0%
Bulk Bottom	73.0%	15.7%	10.3%	0,9%
Porous bottom	**72.1%**	**16.1%**	**9.4%**	**2.4%**

- EDX shows good homogeneity of melt
- Except small W pollution at bottom (HfW_2, W)
  - Discarded in further intepretation





XRD

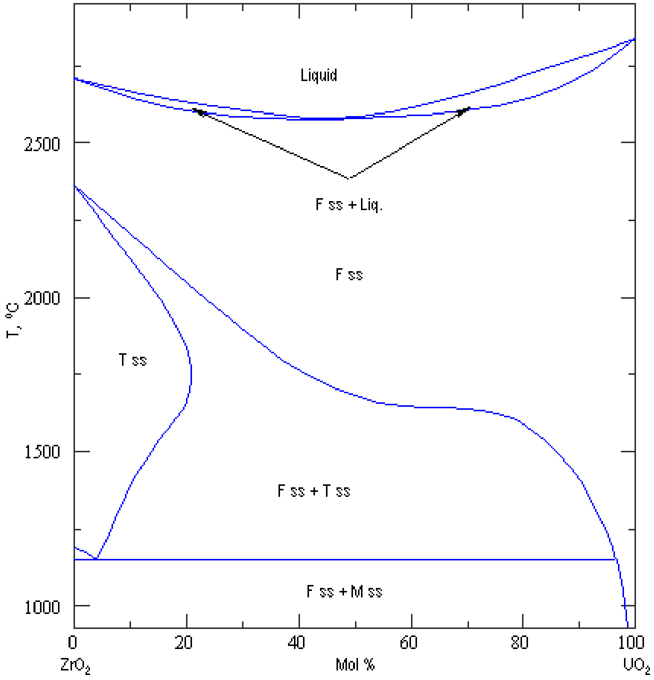


- 20°-100° scanning, steps of 0.01°; 6s/step
- Major phase $UO_{2.11}$
  - Overstoechometry estimated without taking into account effect of dissolved Hf.
- Metallic U and HfO_2 observed
- *HfW_2 and W observed in bottom sample.*

INTERPRETATION AND CONCLUSION

INTERPRETATION

- $(U,Hf)O_2$ phase close to a $(U,Hf)O_2$ solid is similar to what is observed in solidified $(U,Zr)O_2$ corium samples (from LWR studies)
  - Demixtion from $(U,Hf)O_2$ [resp. $(U,Zr)O_2$] melt into UO_2rich FCC and HfO_2 [resp. ZrO_2] rich Tetragonal phase.
- Consistent with y Hf + $UO_2 \rightarrow$ (1-z)$(U,Hf)O_2$ + z U oxido-reduction reaction



CONCLUSIONS (U,HF,O)

- Experimental confirmation that, with UO_2, Hf behaves as Zr
  - Elevated temperature (> 2600°C)
  - Formation of (U,Hf)O2 liquid phase and metallic uranium
    - Demixtion between two liquid phases
    - Demixtion (micro scale) of ceramic in U-rich crystals and Hf-rich crystal

- Hf and HfO2 are interesting candidates if neutron absorbers are needed

- Other studied solution: Eutectic mixture 50 wt% HfO_2 50% Al_2O_3
  - Lower liquidus: ~1730°C
    - Favorable for mixing and spreading
    - Reduce the risk of steel boiling in core catcher
  - Lower density
    - Metallic phase below the oxide

- Alternate option: use of geometry to prevent recriticallity (under study)
  - Sacrificial material has only thermal role
    - Less expensive material: ZrO_2

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