



20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

Chemical interaction between uranium dioxide (UO_2), stainless steel (SS) and boron carbide (B_4C)

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Outline

- 1- Context
- 2- Experimental methodology
- 3- Results and comparison with calculations
 - 3.1- Heat treatment
 - 3.2- Gas release
- 4- Conclusions and perspectives



1 ■ Context

Severe accident in Sodium-cooled Fast Reactor

■ Gen IV nuclear reactor

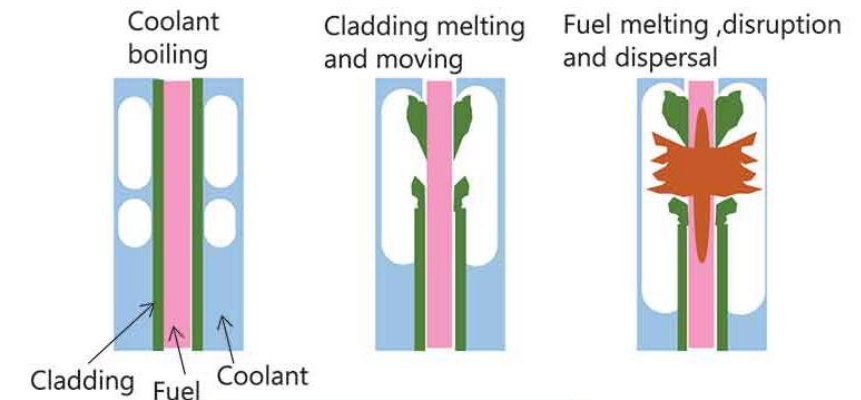
- Sodium-Fast Reactor (SFR) one of the six reactor technologies selected by Generation IV International Forum (GIF)
- SFR: MOX fuel (Mixed Oxide (U,Pu)O₂), stainless steel (SS) cladding, B₄C neutron absorber rods in SS cladding
- Safety studies

■ Severe accident scenarios: ex. Unprotected Loss of Cooling Flow (ULOF)

- At first a reaction may occur between B₄C and the internal surface of SS cladding ⇒ **liquid formation due to eutectic**
- Melt of stainless steel
- Increase of the liquid fraction with temperature
- Contact between the metallic liquid and the fuel

⇒ Understand the mechanism of the material degradation: Fuel-SS-B₄C system

- Beginning with **UO₂-Fe-B₄C** study (heat treatment and gas release)





2 ■ Experimental methodology

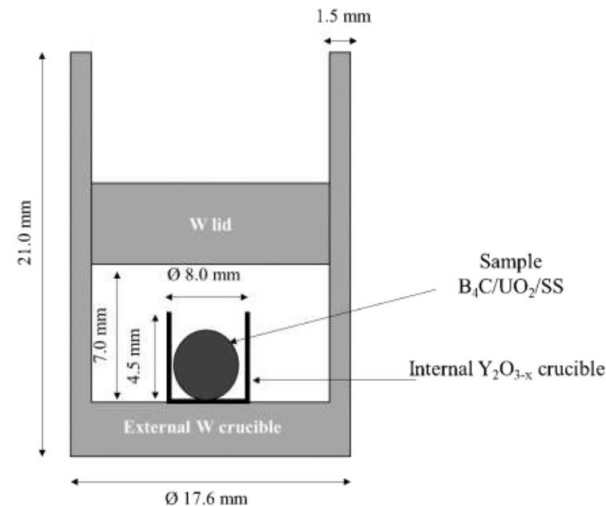
Experimental conditions (1/2)

■ UO_2 -Fe- B_4C samples preparation

- Fe+ B_4C ball synthesised using arc melting and placed on a UO_2 pellet to replicate an accidental scenario
- Y_2O_{3-x} crucible
- Two compositions: Fe/ B_4C $\approx$ 8 and 19. Ratio UO_2 /metal constant

■ Two types of experiments

- Heat treatment: 1 hour @ 1900 °C (1800 °C/h) under secondary vacuum
 - Post-mortem analyses: Scanning Electron Microscope (SEM) + Energy Dispersive Spectroscopy (EDS)



Layout of the crucible assembly used during heat treatment [Garrigue, JNM, 2021]

Experimental conditions (2/2)

Two types of experiments

- Knudsen Effusion Mass Spectrometry (KEMS): gas release study
 - Heating rate of 1000°C/h until 1900 °C
 - Seven species measured in the gas above the UO₂-Fe-B₄C samples

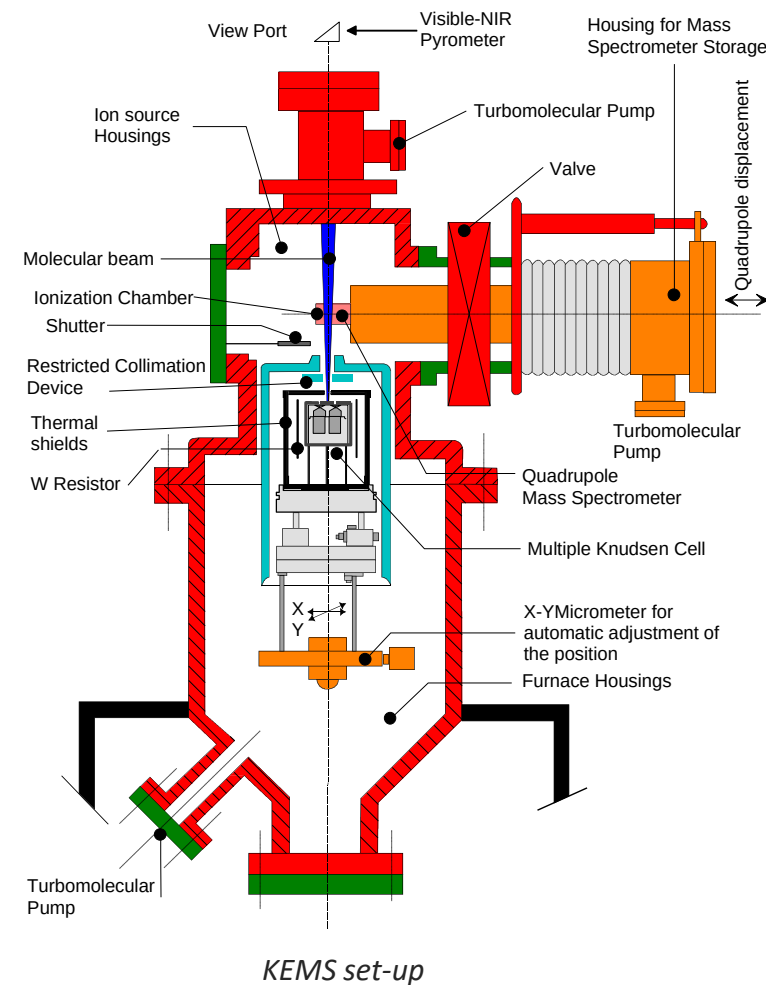
Species measured by KEMS

Species	m/z
BO	27
CO	28
CO ₂	44
Fe	56
U	238
UO	254
UO ₂	270

Vapor pressure measurement

$$P_i = \frac{I_i \times T}{S_i}$$

P_i : vapor pressure of species i
 I_i : ionic intensity of the species i
 T : temperature of the cell
 S_i : sensitivity (Ag calibration)



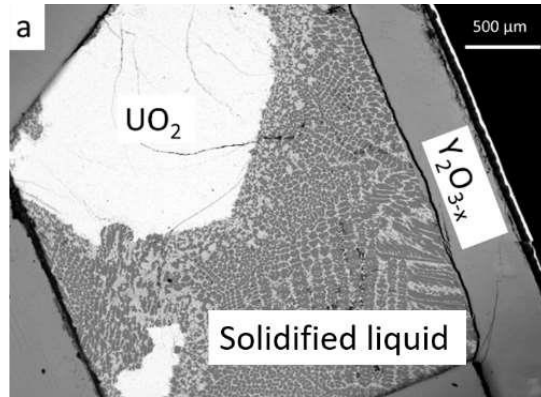


3 ■ Results and comparison with calculations

3.1- Heat treatment (1/3)

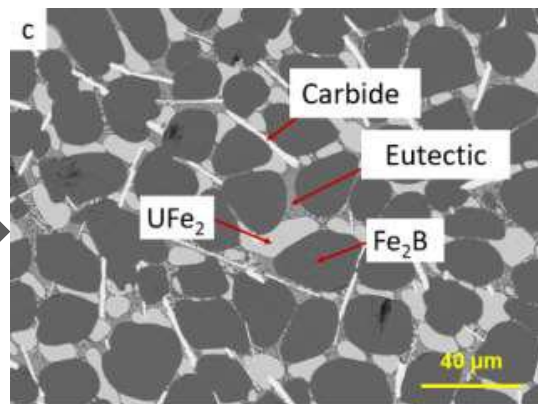
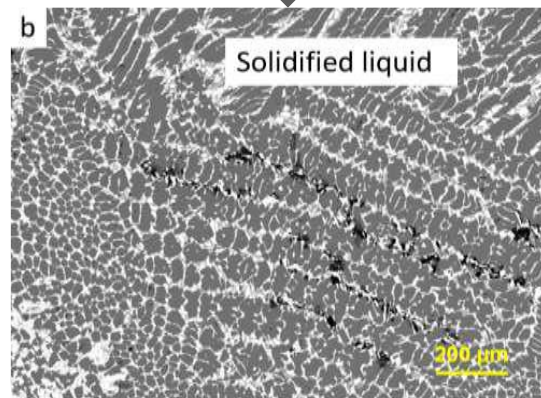
■ Metallographic analyses

$\text{Fe}/\text{B}_4\text{C} \approx 8$

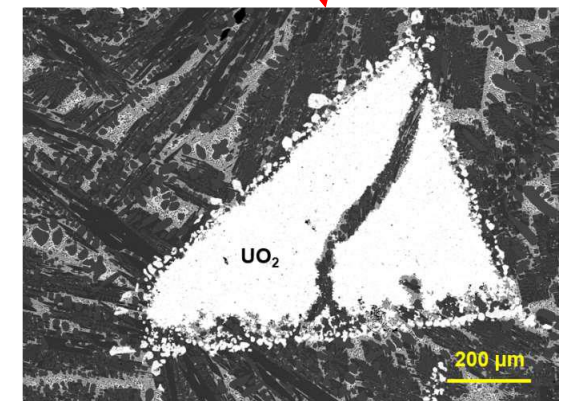
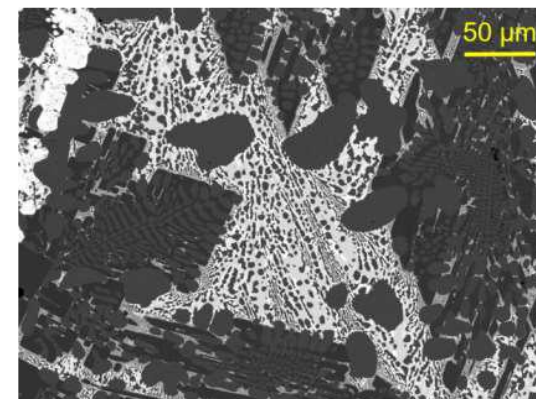
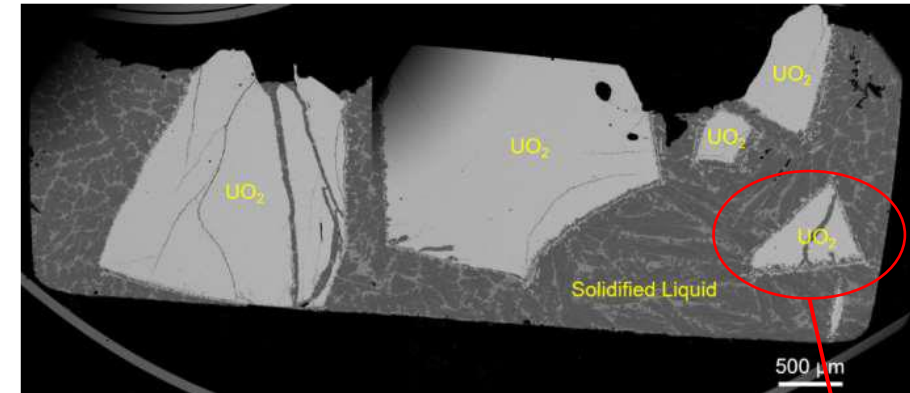


Global composition of the liquid (at. %)

B	C	Fe	O	U
21±8	nd	72±12	2±6	5±1



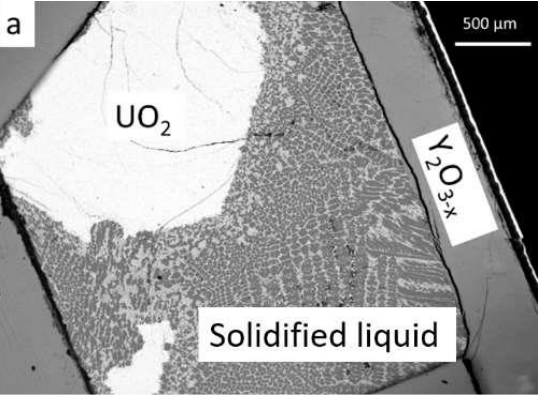
$\text{Fe}/\text{B}_4\text{C} \approx 19$



3.1- Heat treatment (1/3)

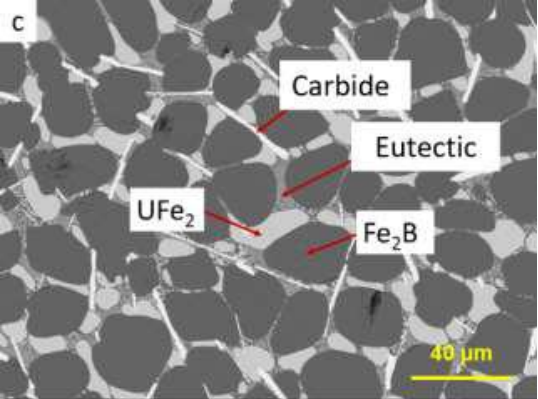
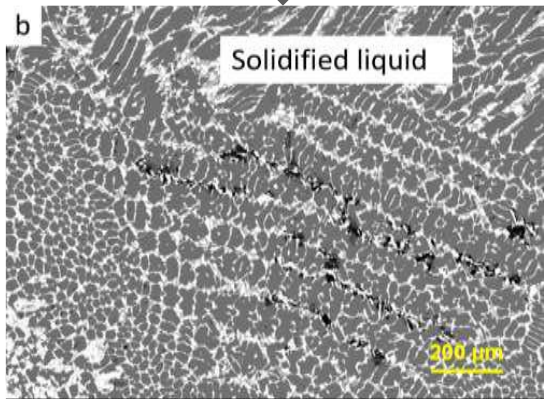
■ Metallographic analyses

Fe/B₄C ≈ 8

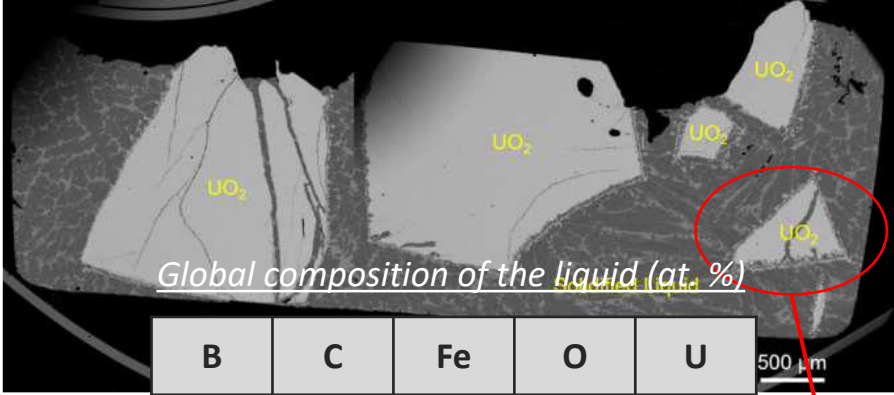


Global composition of the liquid (at. %)

B	C	Fe	O	U
21±8	nd	72±12	2±6	5±1

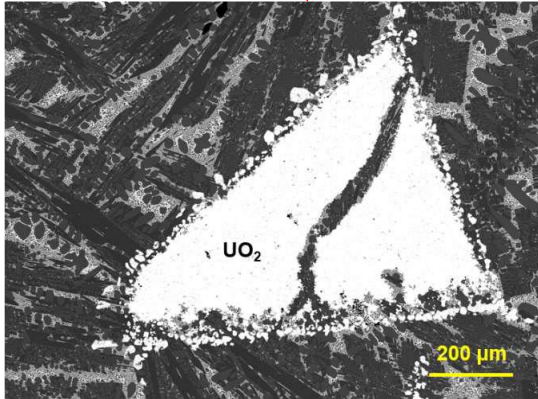
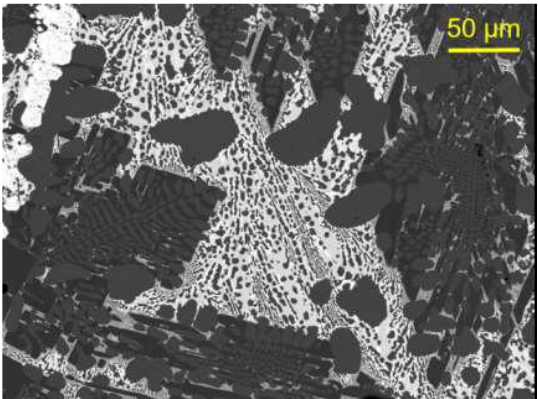


Fe/B₄C ≈ 19



Global composition of the liquid (at. %)

B	C	Fe	O	U
15±10	15±10	65±5	nd	5±1



3.1- Heat treatment (2/3)

■ Thermodynamic calculations at 1900°C with initial composition

	Phase	at% B	at% C	at% Fe	at% O	at% U
Sample B Fe/B ₄ C ≈ 8	(U,Fe)O _{2-x}	-	-	1.7	66.1	32.2
	Liquid	30.9	5.5	62.6	traces	1.0
	Gas (*)	0.04	50.0	0.06	49.9	traces
Sample C Fe/B ₄ C ≈ 19	(U,Fe)O _{2-x}	-	-	2.1	66.0	31.9
	Liquid	17.0	3.8	78.9	traces	0.3

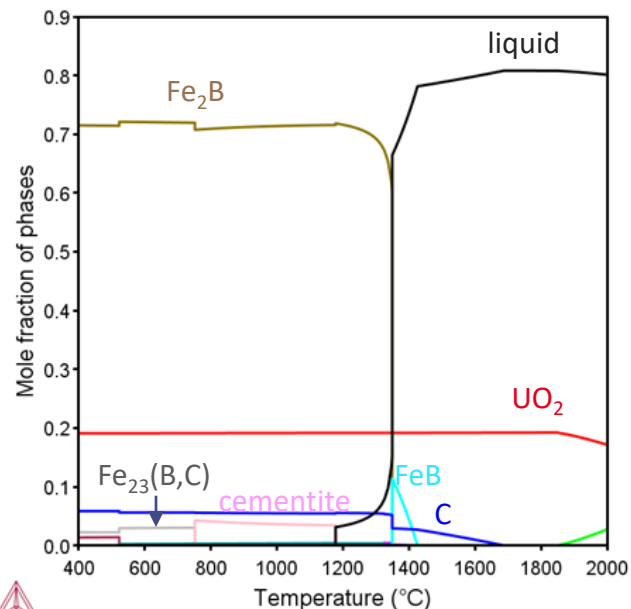
gas phase: 99.9 mol% of CO, 0.09 mol% of Fe and 0.01 mol% of BO+B₂O₂

⇒ Reaction of carbo-reduction

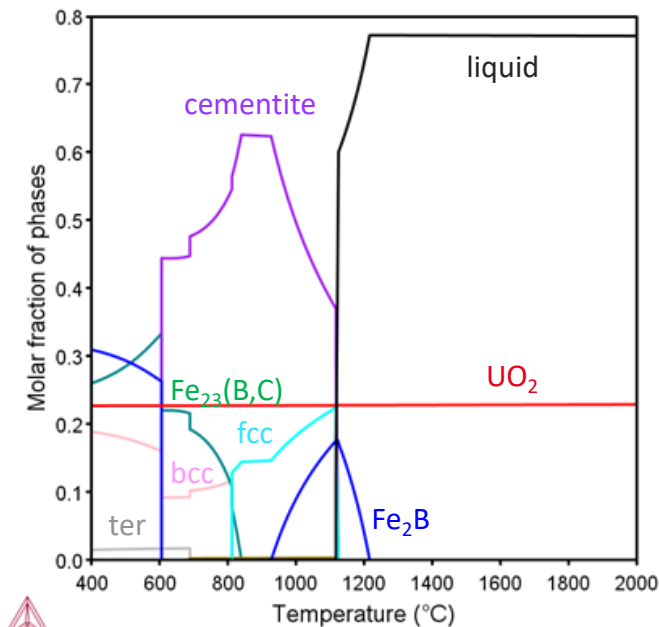
⇒ No carbo-reduction

■ Comparison experiment / thermodynamic calculations

Fe/B₄C ≈ 8

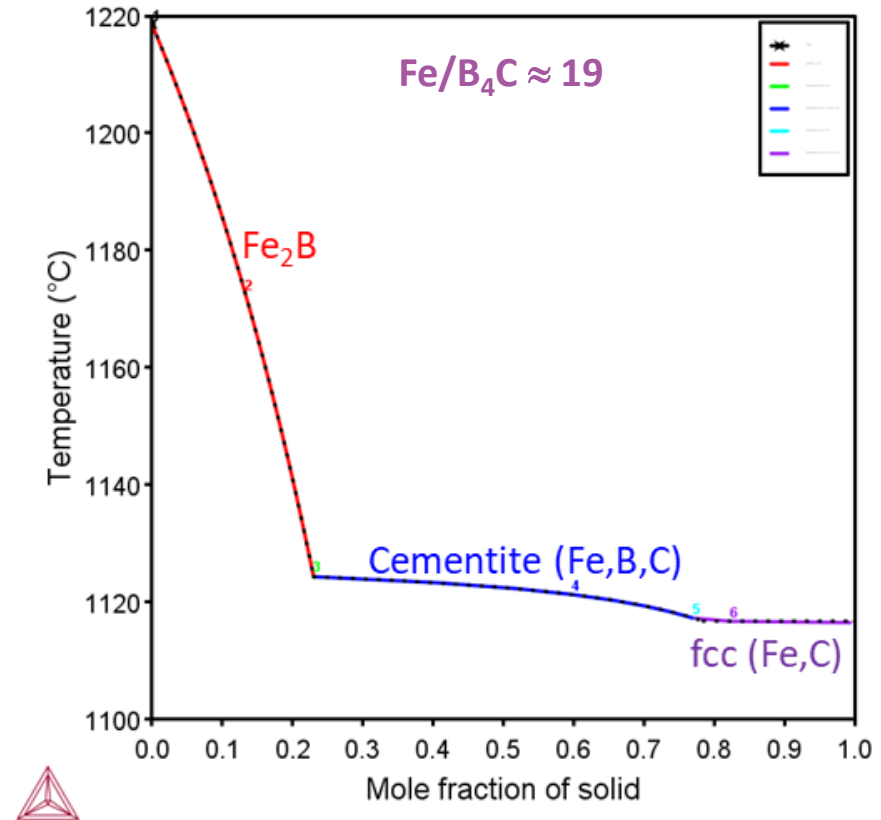
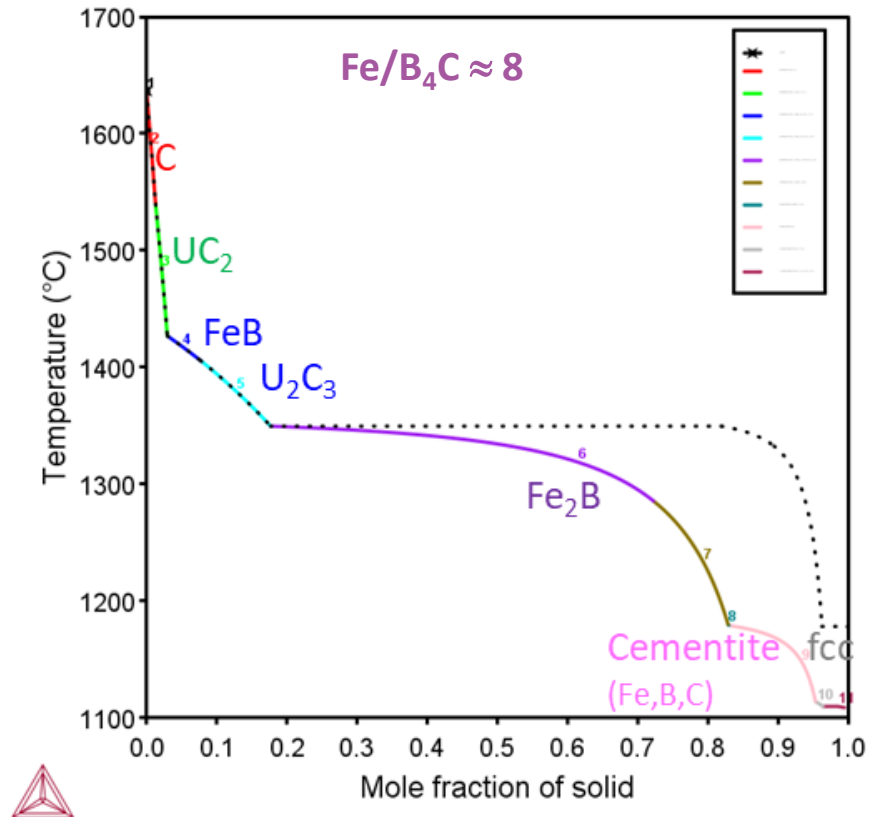


Fe/B₄C ≈ 19



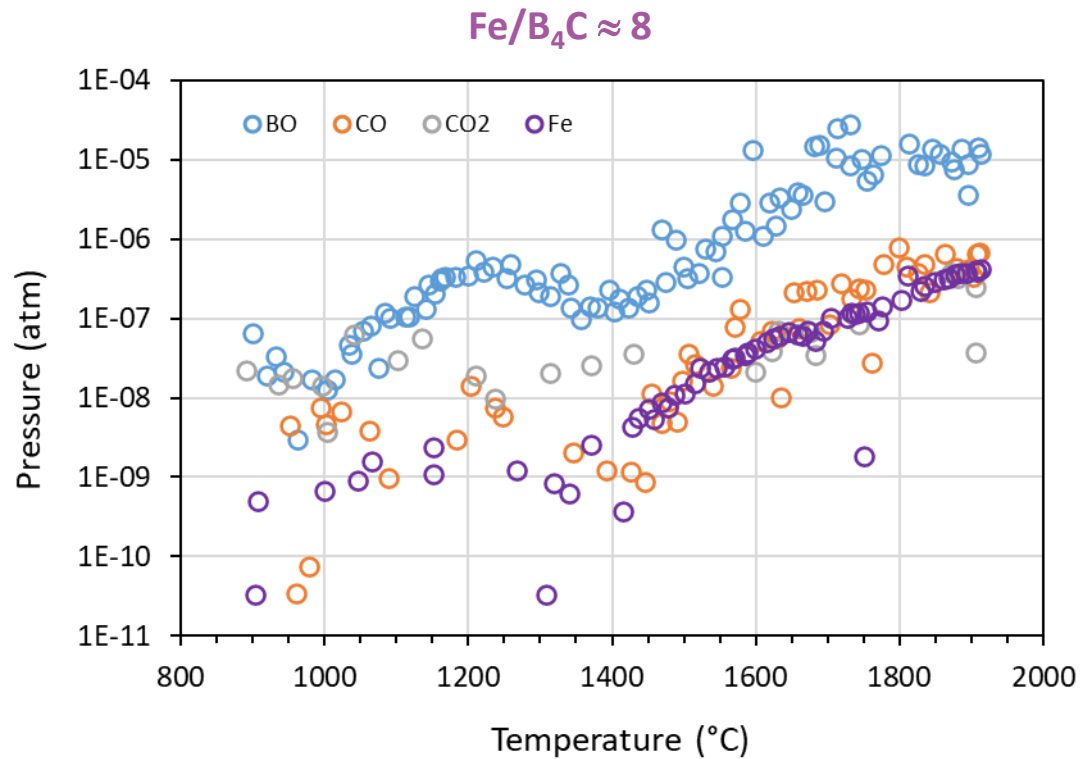
3.1- Heat treatment (3/3)

- Comparison experiment / thermodynamic calculations: solidification pathway with Scheil Gulliver

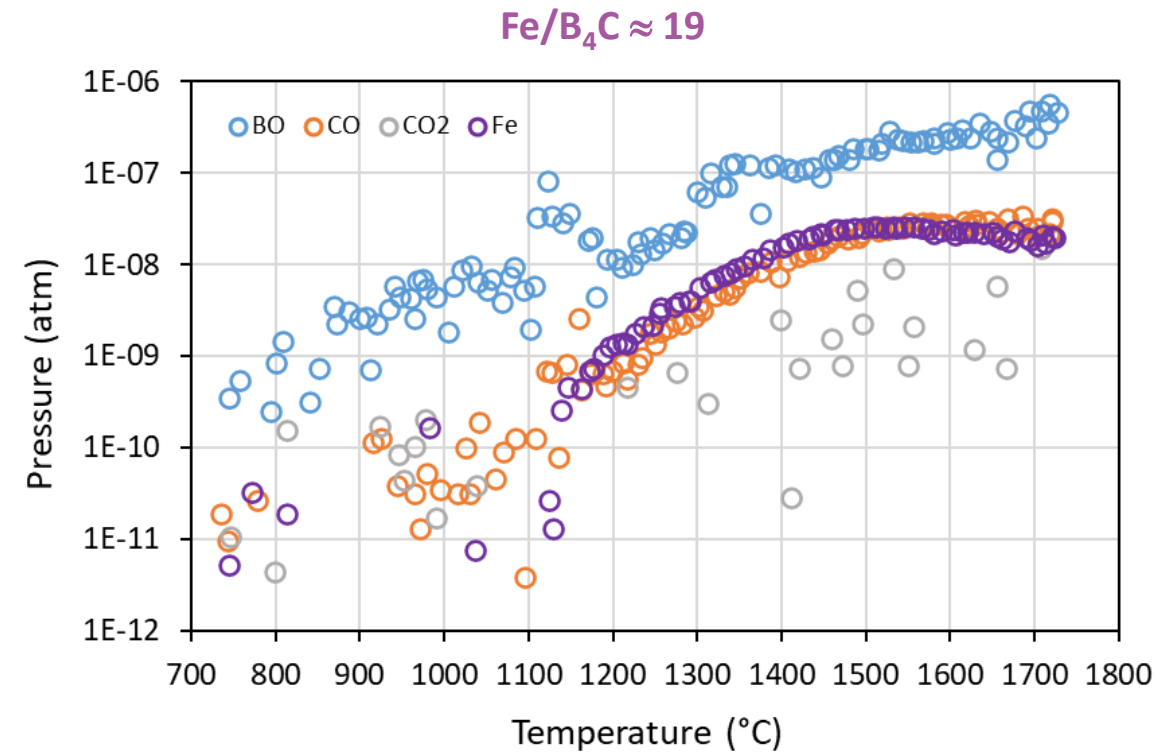


3.2- Gas release (1/3)

■ Results analysed



- Pressure saturation of BO and CO around 1700 °C
- Increase in iron pressure

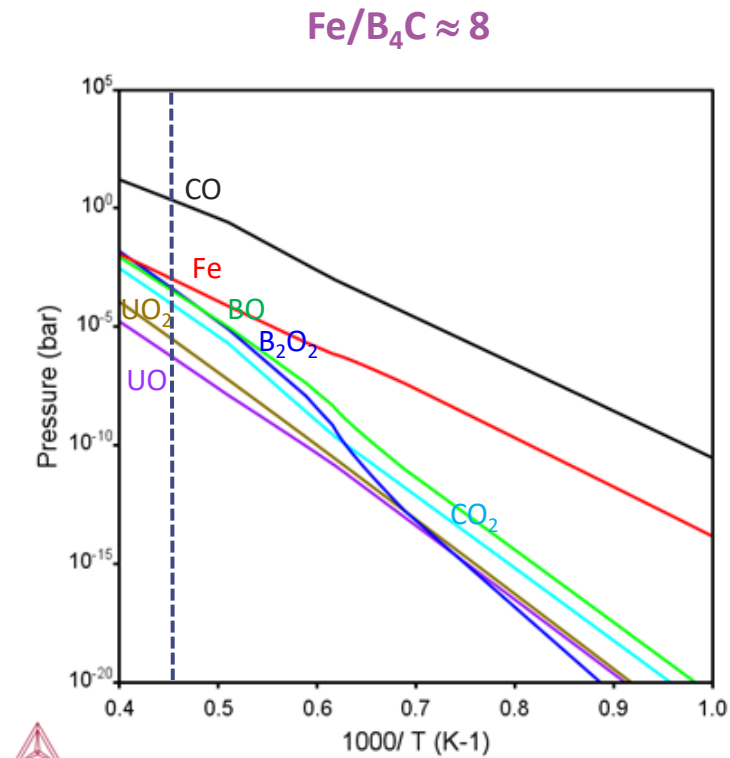


- Pressures saturation around 1500 °C

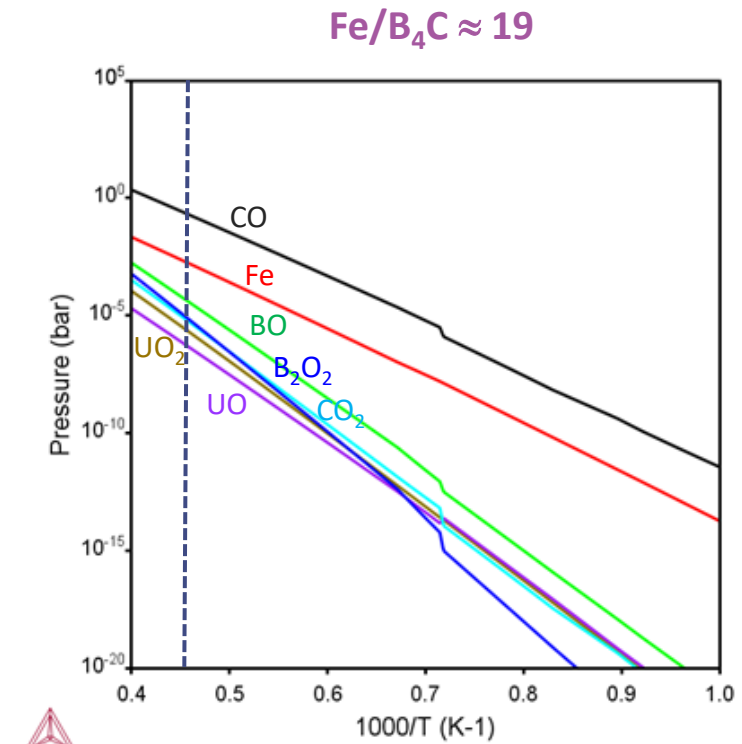
- ⇒ $p(\text{BO}) > p(\text{CO}) \approx p(\text{Fe})$
- ⇒ $p(\text{CO}_2)$ scattered results
- ⇒ Reduction of UO_2 by both C and B ?

3.2- Gas release (2/3)

- Calculation of the partial pressures versus temperature for the initial composition



At $T_{\max}$: $P(\text{CO}) > p(\text{Fe}) \sim p(\text{BO}) \sim p(\text{B}_2\text{O}_2)$



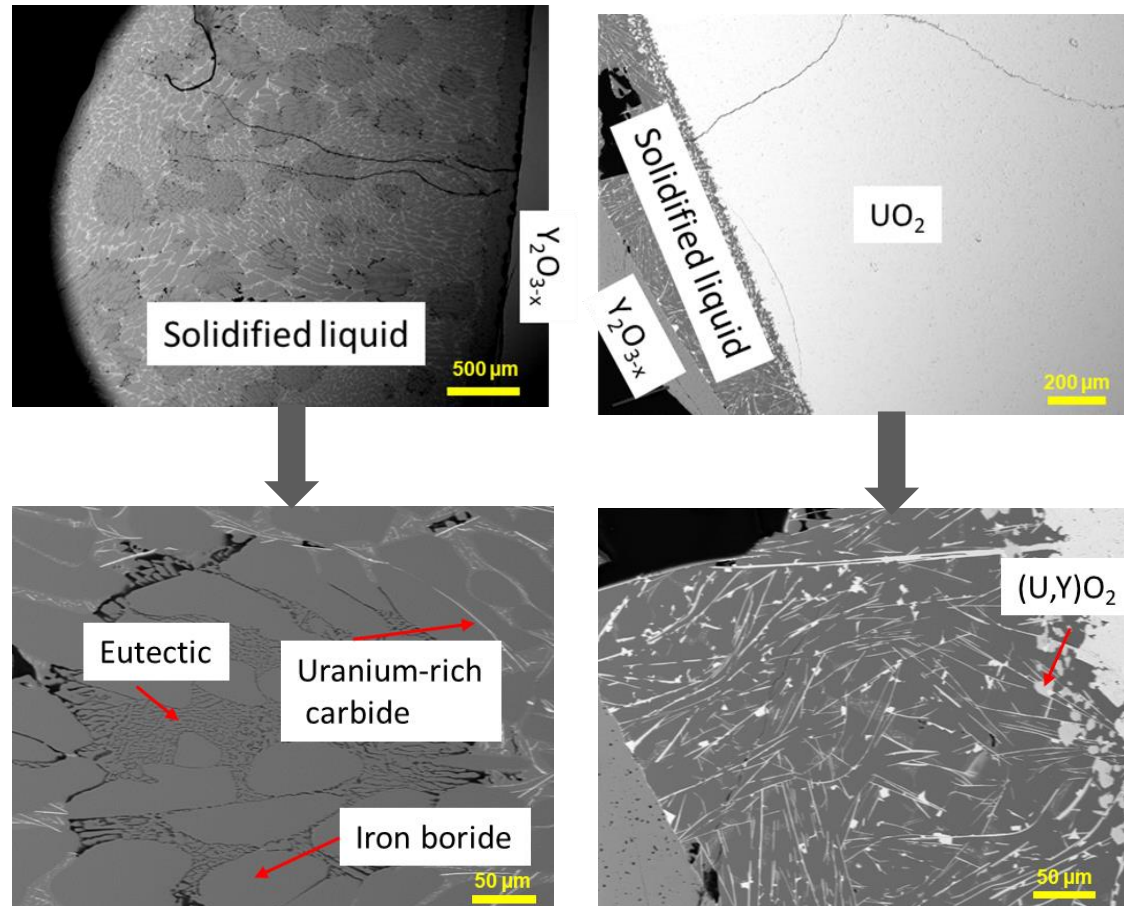
At $T_{\max}$: $P(\text{CO}) > p(\text{Fe}) > p(\text{BO}) > p(\text{B}_2\text{O}_2) \sim p(\text{CO}_2)$

- ⇒ Calculations in disagreement with the KEMS results
- ⇒ Kinetics effect ? Heterogeneity of initial Fe/B₄C sample ?

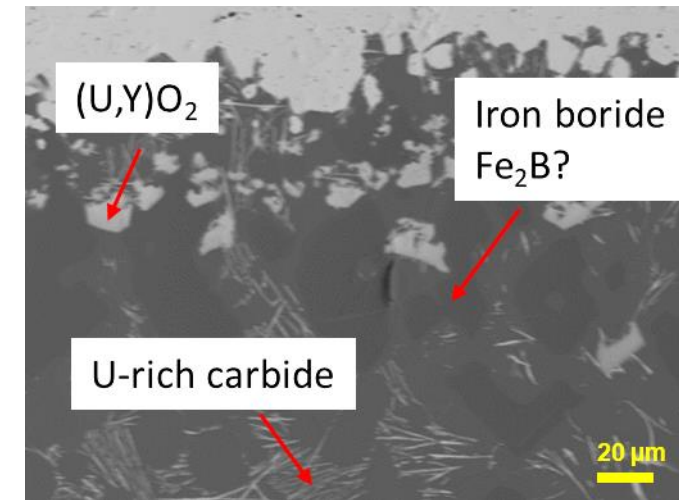
3.2- Gas release (3/3)

■ Metallographic analyses after experiment

$\text{Fe}/\text{B}_4\text{C} \approx 8$



$\text{Fe}/\text{B}_4\text{C} \approx 19$



Results to be confirmed (C pollution)



4 ■ Conclusions and perspectives

Conclusions

■ Heat treatment: effect of B_4C

- Role in the degradation process of UO_2
 - $Fe/B_4C=8$: quasi-complete reduction is observed (C is consumed to reduce UO_2)
 - $Fe/B_4C=19$: significant amount of C in the liquid phase
- Improve the wetting of metallic liquid in UO_2
- Microstructure in quite good agreement with calculations

■ KEMS experiments: gas release

- BO pressure is the highest, CO and Fe pressures are very close
- Little effect of the B_4C content on the results
- Disagreement with the thermodynamic calculations (kinetics ? Heterogeneity of Fe- B_4C sample?)

Perspectives

- Continue the metallographic analyses
- Effect of alloying elements Ni, Cr on the gas release at high temperature
 - KEMS on UO_2 -SS- B_4C samples
- Effect of fission products on the liquid/fuel interaction
 - Heat treatment on SIMFUEL-SS- B_4C
 - SIMFUEL is a simulated fuel with a $(\text{U}, \text{Ce}, \text{Nd}, \text{Zr}, \text{La})\text{O}_{2-x}$ matrix with fission products like Rh, Pd, and Ru.
- Sample characterisation (SEM,EDS)
- Thermodynamic calculations with the TAF-ID



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Thank you for your attention