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Experimental investigation and thermodynamic modeling of the C-Me-O systems (where Me = Hf, Zr)

F. Réjasse¹, O. Rapaud¹, G. Trolliard¹, A. Maître¹

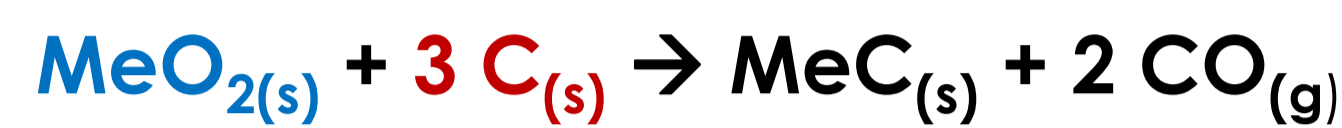
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Introduction

- Zirconium and hafnium carbide (ZrC_x and HfC_x) are considered as Ultra High Temperature Ceramics (UHTC) which can be easily oxidized under flowing dioxygen.
- Oxygen atoms can substitute carbon atoms in the crystalline lattice of carbides involving the formation of oxycarbide phases ZrC_xO_y and HfC_xO_y .
- The thermodynamic modeling of the C-Me-O ternary phase diagrams requires thermodynamic and diagrammatic data especially to determine the solubility of the oxygen into the carbide sublattice.

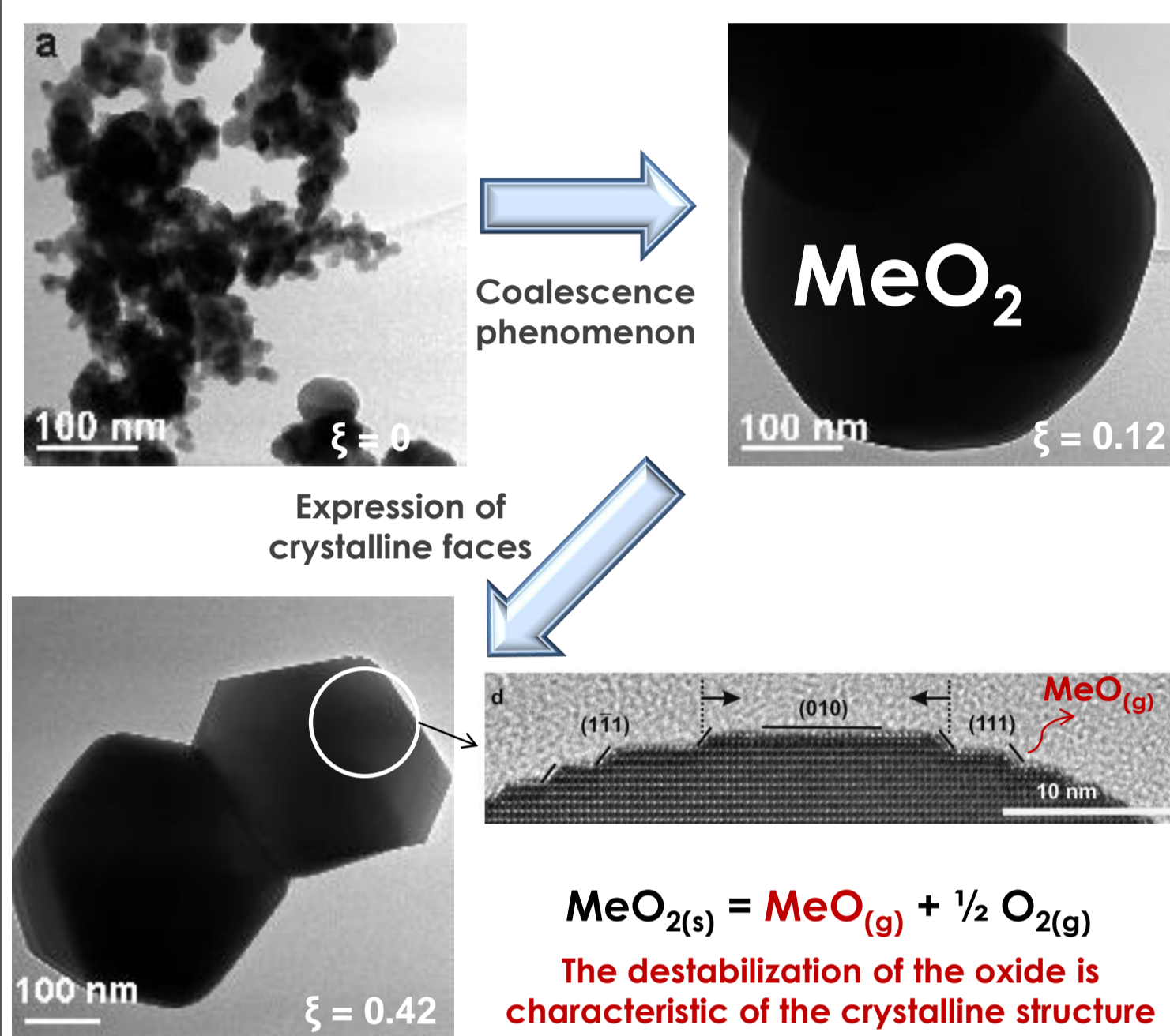
Experimental

Reaction mechanisms involved during the carbothermal reduction of ZrO_2 and HfO_2 ^{a, b}

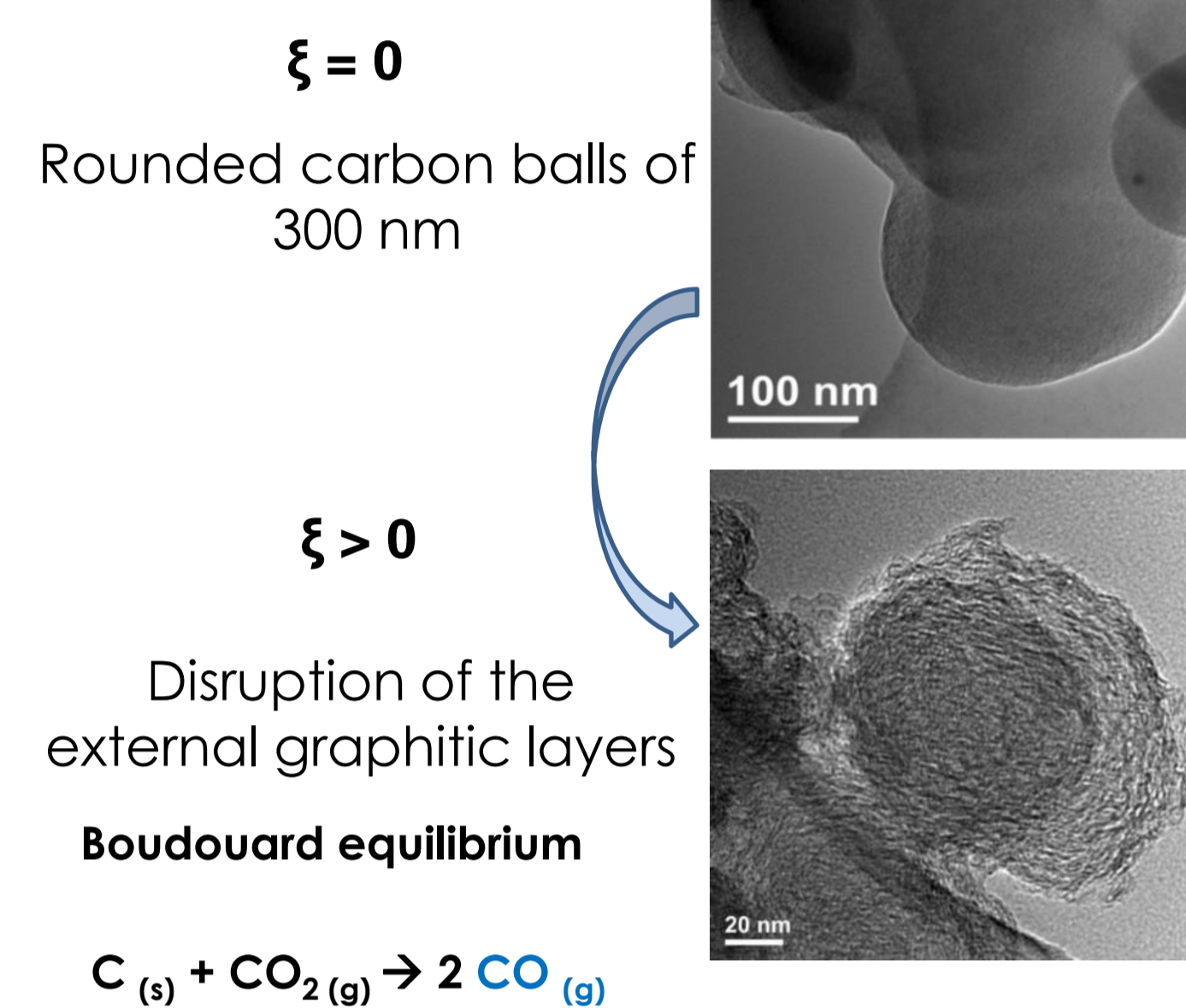


Structural approach by **XRD** and **TEM** → understanding of the reaction mechanisms involved for **different advancements ξ** .

Destabilization of ZrO_2 and HfO_2



Destabilization of C

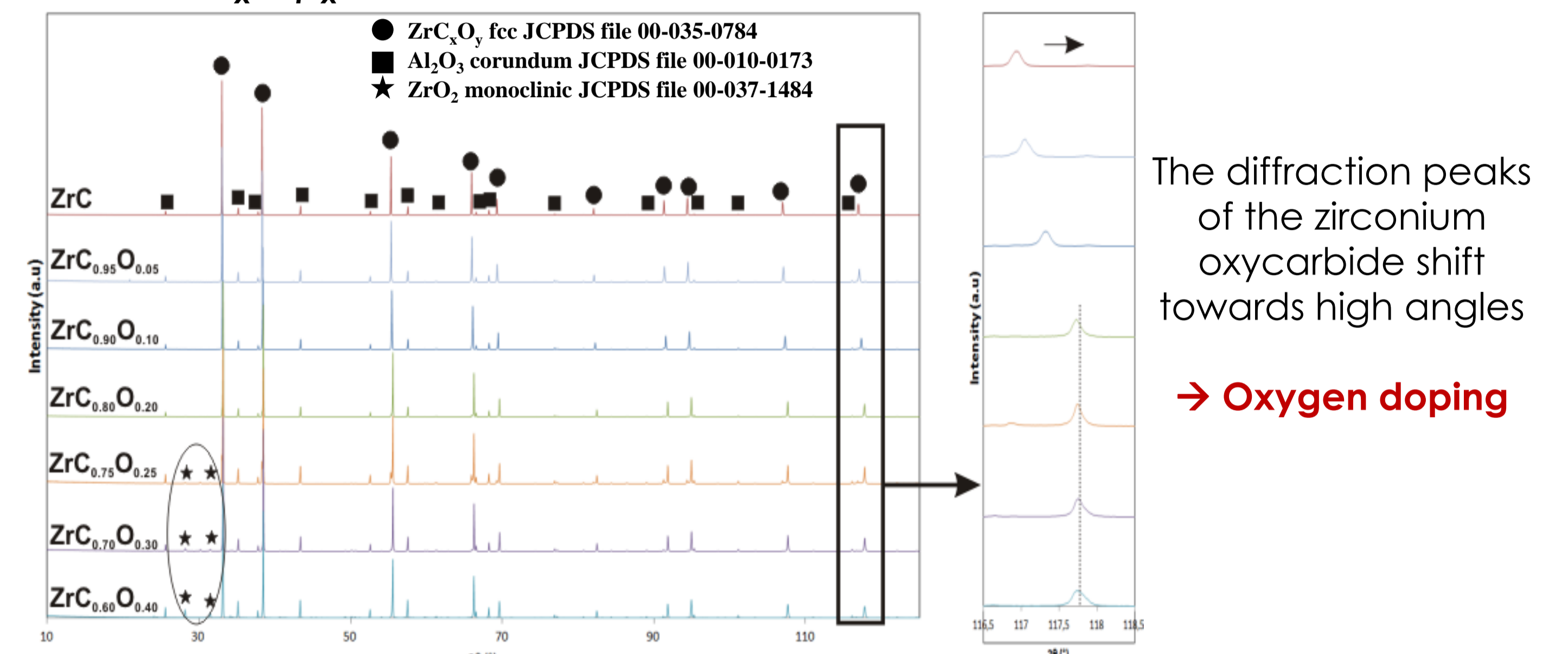


Experimental determination of solid solution boundaries by carbothermal reduction



- The amount of initial reactants is adjusted to produce several oxycarbide stoichiometries.
- Heat treatment in a graphite furnace under flowing argon at **1650°C, 1750°C and 1850°C** during 8 hours ($\xi = 1$).

→ For ZrC_xO_{1-x}

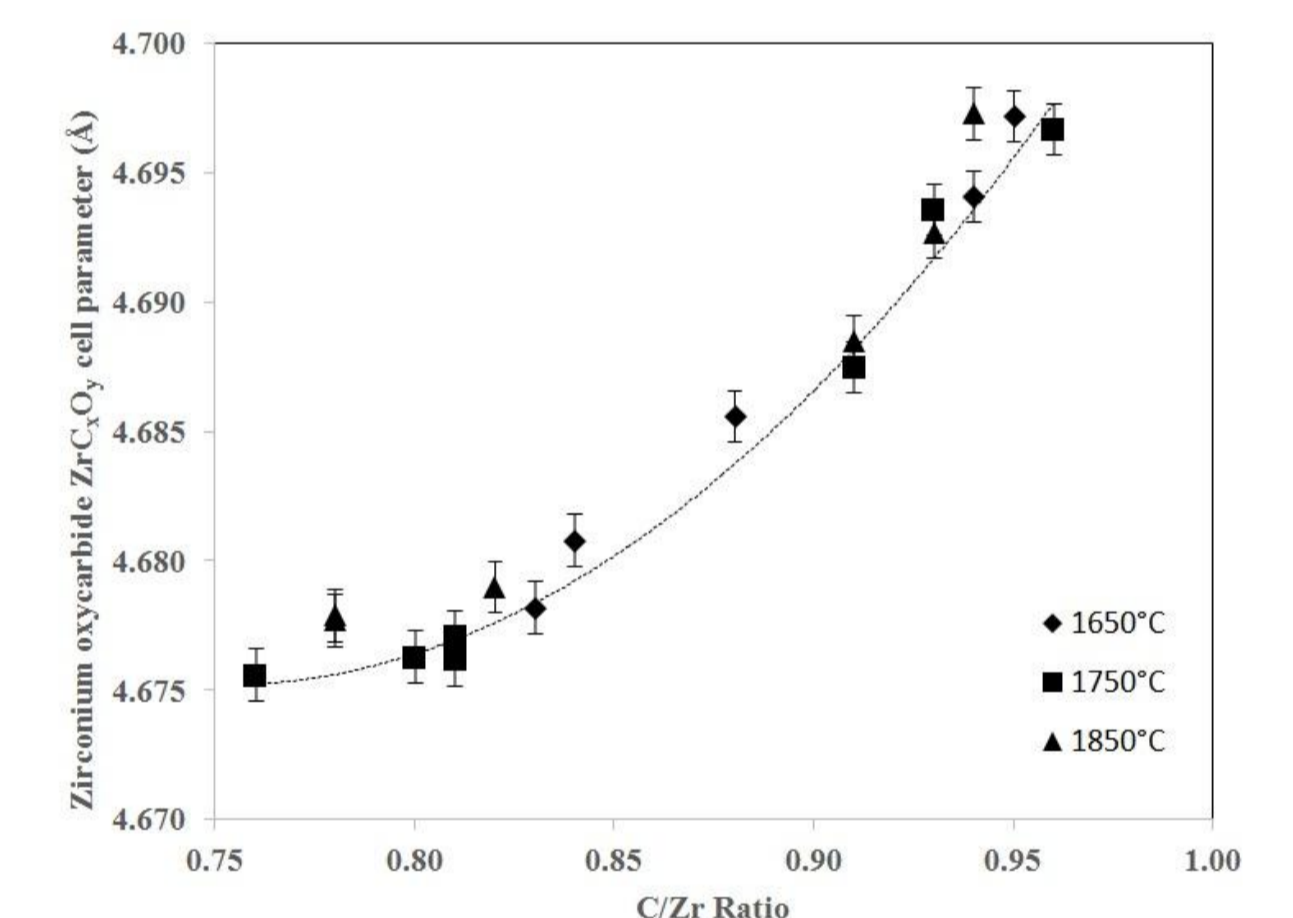


Stoichiometries in C and O of each sample computed by elemental analysis :

Temperatures	Low boundary	High boundary
1650°C	$ZrC_{0.83}O_{0.17}$	$ZrC_{0.94}O_{0.03}$
1750°C	$ZrC_{0.80}O_{0.20}$	$ZrC_{0.96}O_{0.04}$
1850°C	$ZrC_{0.78}O_{0.22}$	$ZrC_{0.94}O_{0.03}$

- Increase of the maximum solubility of O with the increase of the temperature**
- No modification of the maximum solubility of C with the temperature**

An **abacus** can be created correlating the lattice parameter and the stoichiometry of ZrC_xO_{1-x}

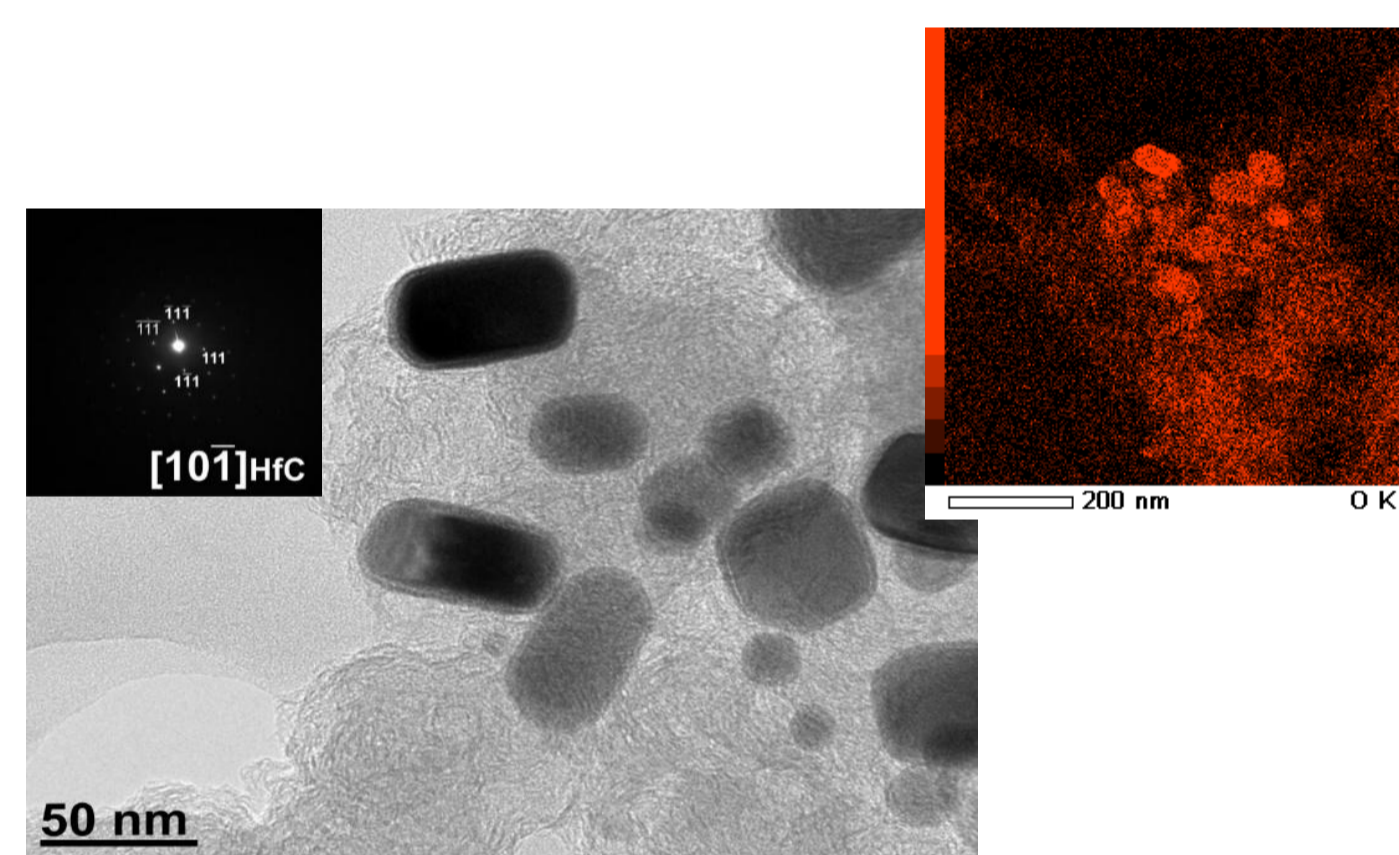
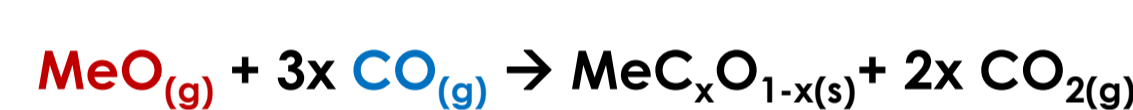


→ For HfC_xO_{1-x}

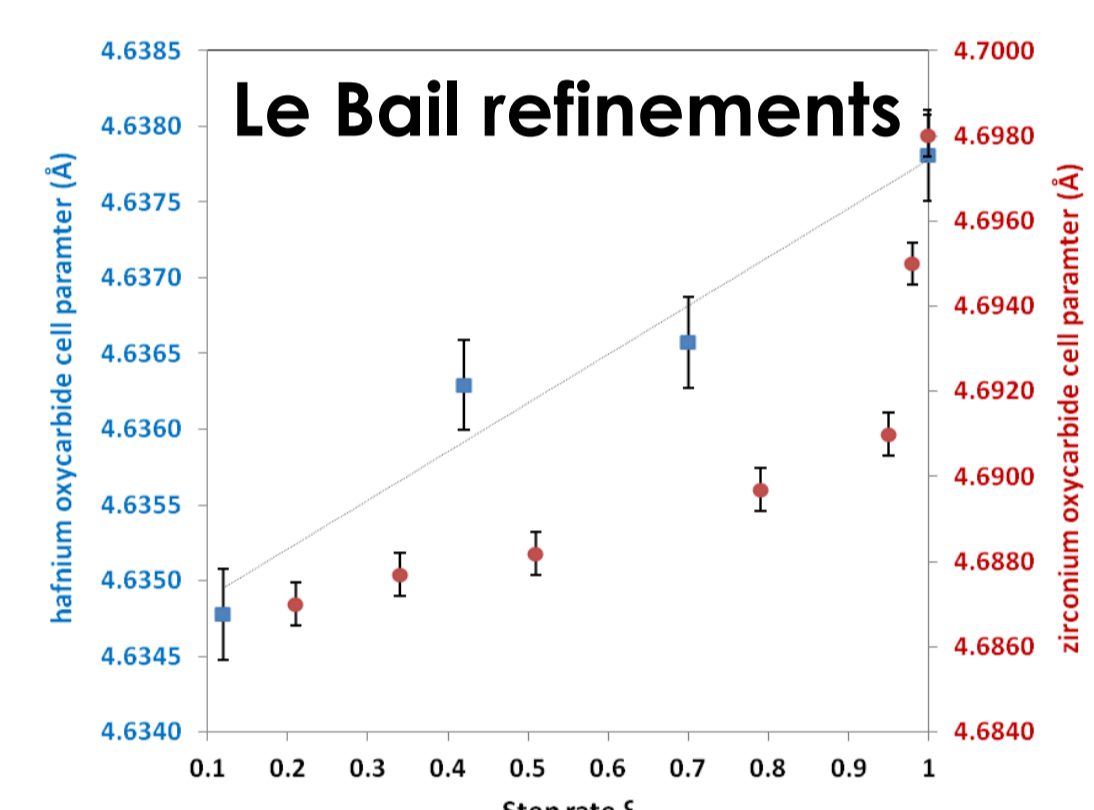
- Between 1650°C and 1750 °C : no evolution of the solubility of O
- At the same temperature, the stability domain of HfC_xO_{1-x} solid solution is narrower than ZrC_xO_y**

Nucleation of the MeC_xO_{1-x} phase

Co-condensation reaction of $MeO_{(g)}$ and $CO_{(g)}$ within carbon-rich areas



Evolution of the MeC_xO_{1-x} phase

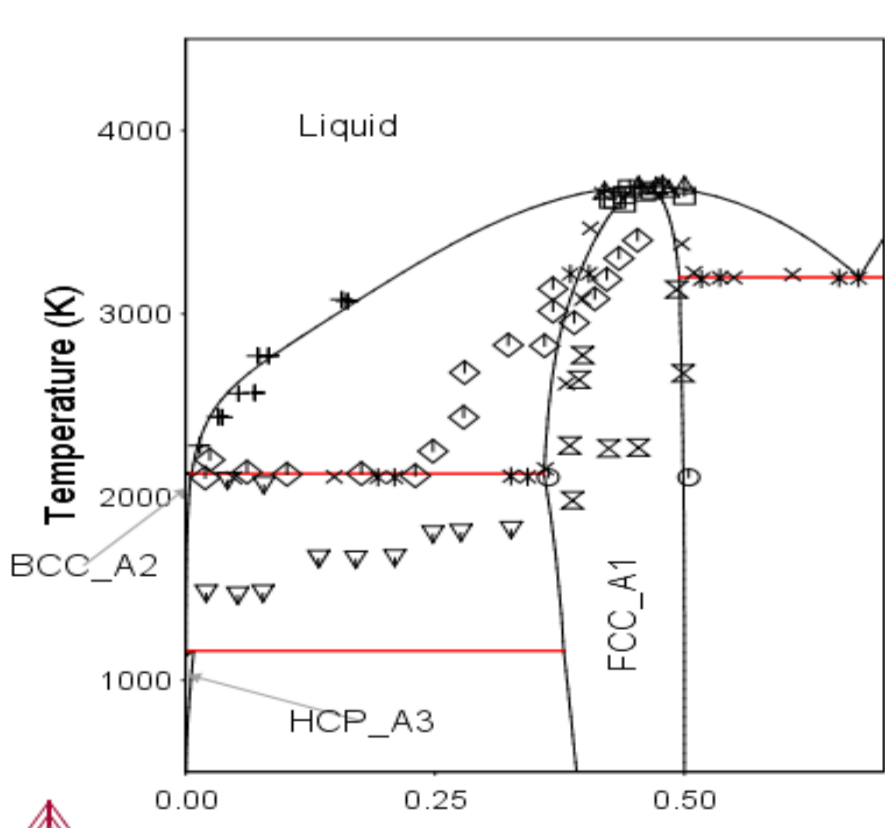


The increase of the carbon amount in the crystalline structure implies the increase of the MeC_xO_{1-x} lattice parameter.

Purely reconstructive reaction → Impossible to obtain nanosized carbides by this synthesis way

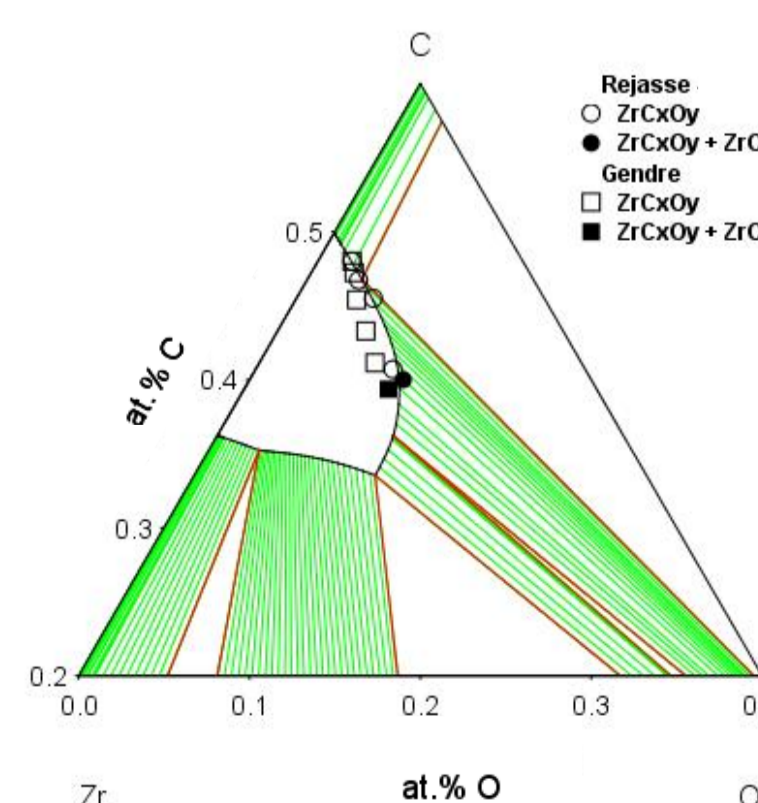
Thermodynamic Modeling

Binary diagram Zr-C ^c

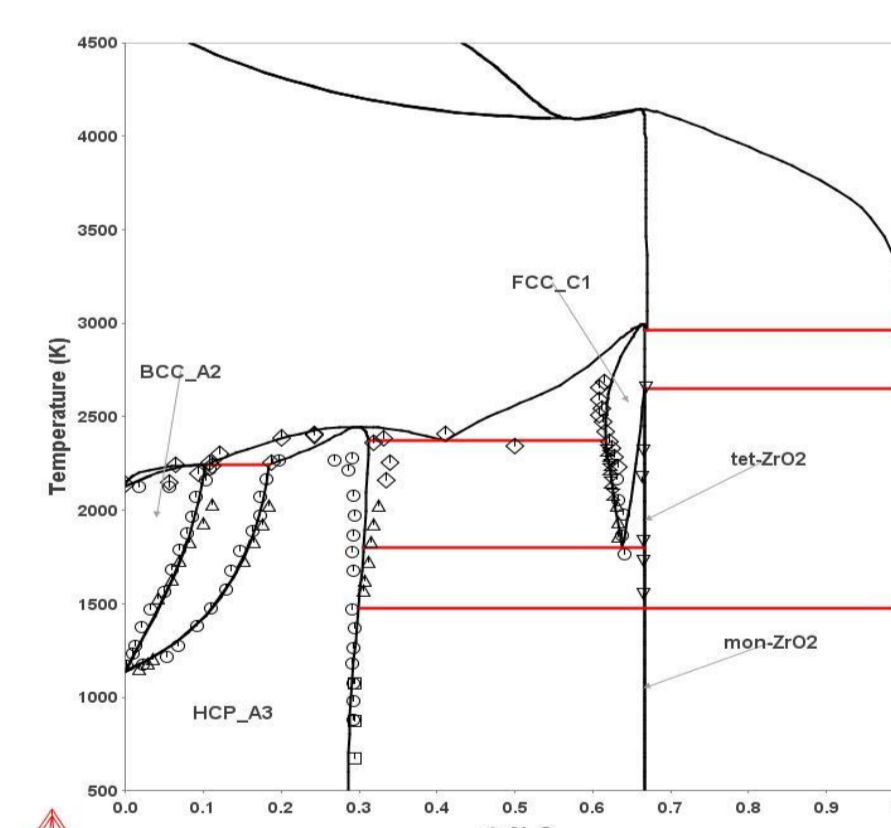


- FCC_A1 : $(Zr)_1(C,Va)_1 / L^0, L^1$
- C Graphite
- BCC_A2 : $(Zr)_1(C,Va)_3 / L^0$
- HCP_A3 : $(Zr)_1(C,Va)_{0.5} / L^0$
- Liquid : $(Zr,C)_1 / L^0, L^1, L^2$

Extrapolation in the ternary system and result of optimisation



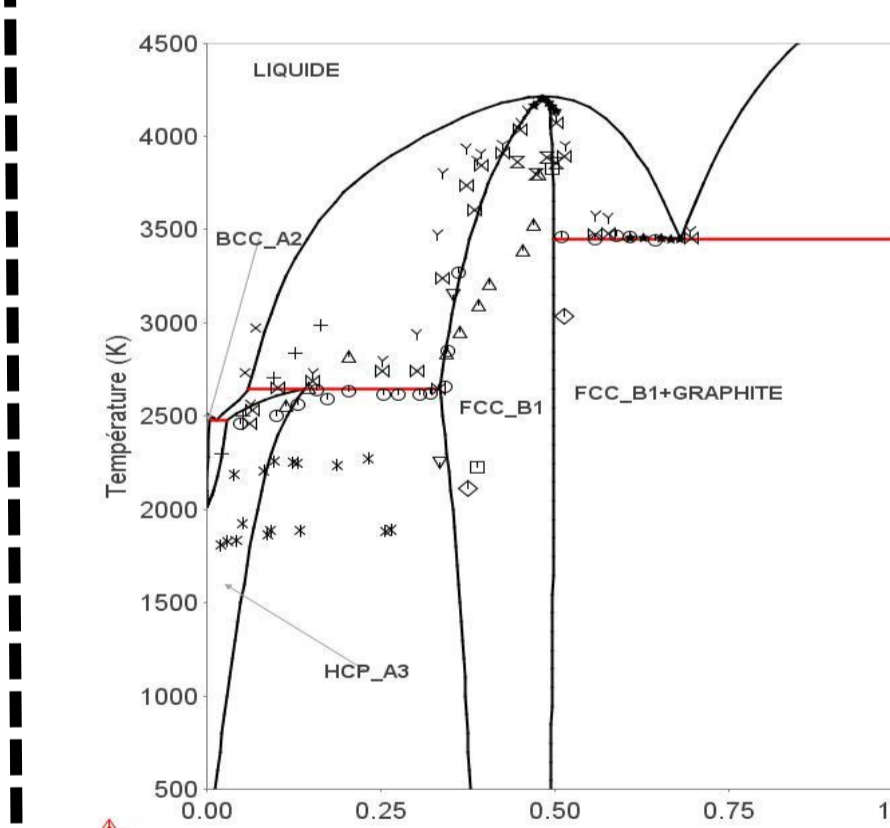
Binary diagram Zr-O ^d



- FCC_C1 : $(Zr)_1(O,Va)_2(O,Va)_1 / L^0, L^1, L^2$
- BCC_A2 : $(Zr)_1(O,Va)_3 / L^0$
- HCP_A3 : $(Zr)_1(O,Va)_{0.5} / L^0$
- Liquid : $(O,ZrO_2, Zr)_1 / L^0, L^1, L^2$

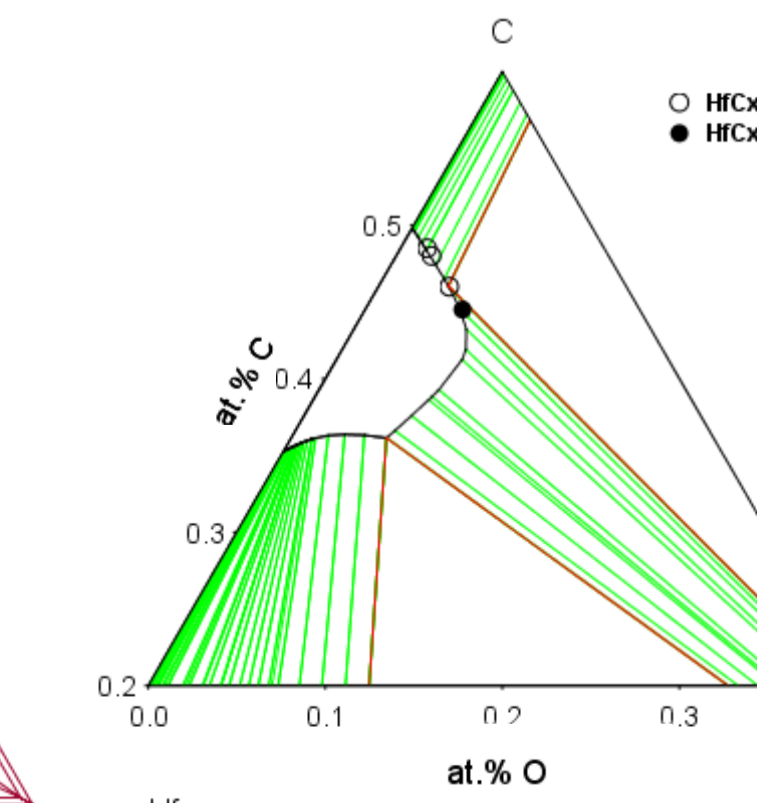
At 1750°C

Binary diagram Hf-C ^e



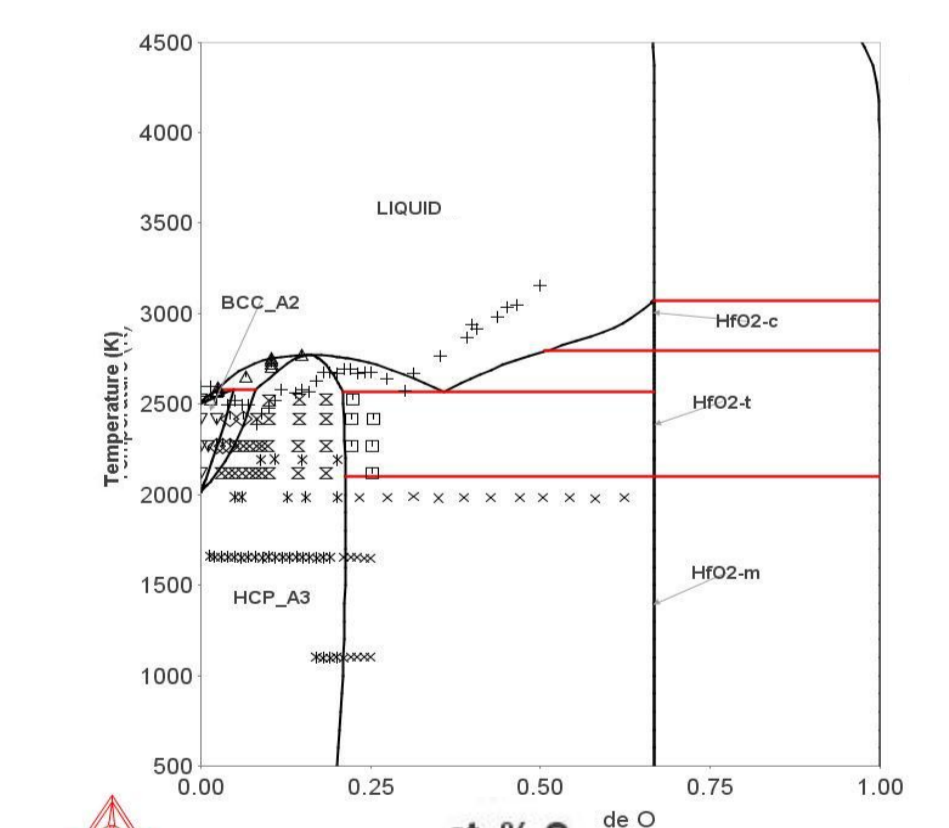
- FCC_B1 : $(Hf)_1(C,Va)_1 / L^0, L^1$
- C Graphite
- BCC_A2 : $(Hf)_1(C,Va)_3 / L^0$
- HCP_A3 : $(Hf)_1(C,Va)_{0.5} / L^0, L^1, L^2$
- Liquid : $(Hf,C)_1 / L^0, L^1, L^2, L^3$

Extrapolation in the ternary system and result of optimisation



At 1750°C

Binary diagram Hf-O ^f



- BCC_A2 : $(Hf)_1(O,Va)_3 / L^0$
- HCP_A3 : $(Hf)_1(O,Va)_{0.5} / L^0, L^1$
- Liquid : Ionic / L^0, L^1, L^2

Summary

- The carbothermal reaction is a **purely reconstructive reaction** which operates through solid-gas equilibriums.
- This reaction allowed to determine the stability domains of MeC_xO_y solid solutions. On the Zr-C-O system, the extent of the domain increases with the temperature. At the same temperature, the domain of HfC_xO_y is narrower than ZrC_xO_y .
- These **experimental data** were used to assess the **two ternary phase diagrams** and to describe the evolution of the solid solutions with the temperature