



ENGINEERING
COLLEGE OF ENGINEERING
SEOUL NATIONAL UNIVERSITY
서울대학교공과대학

Department of Materials Science and Engineering

Thermodynamics of High and Ultra-high Temperature Ceramics

- Phase diagrams, Chemical reactions,
Computational thermodynamic database -

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- Review of Engineering Thermodynamics
- Computational thermodynamic database
 - Development of CALPHAD thermodynamic database
 - Application to high temperature refractories
 - Application to ultra-high temperature ceramics

REVIEW OF ENGINEERING THERMODYNAMICS

COMPUTATIONAL THERMODYNAMIC DATABASE

Gibbs Energy

$G = H - TS$; G: Gibbs Energy, H: Enthalpy, S: Entropy

1. For pure element or pure compound (Al, O₂, Al₂O₃, etc.)

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_p dT \quad S_T^o = S_{298K}^o + \int_{298K}^T \frac{C_p}{T} dT \quad : C_p = a + bT + cT^2 + dT \ln T + \dots$$

is known (measurable)

Enthalpy for compound at 298 K with reference of pure stable elemental species at 298 K and 1 atm ($H_{0K}^o \neq 0$, unknown)

Standard entropy at 298 K ($S_{0K}^o = 0$)

Standard reference state for H : $\Delta H_{298K}^o = 0$
~~Fe(bcc), Fe(fcc), Fe(l), H₂O(l), H₂O(g), H₂(g), O₂(g), O(g), CaO, FeO, C(s), CO₂, CO, ..~~

* In FactSage compound database, ΔH_{298K}^o , S_{298K}^o , C_p are stored to calculate Gibbs energy of solid, liquid and gas species

Gibbs Energy

2. Chemical reaction between pure compounds (No solution)

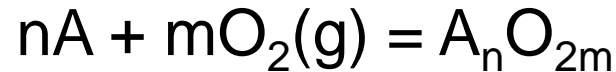


$$\begin{aligned}\Delta G_{rxn}^o &= G_{A_nB_m}^o - (nG_A^o + mG_B^o) \\ &= \Delta H_{rxn}^o - T\Delta S_{rxn}^o\end{aligned}$$

In many thermo books, these ΔH_{rxn}^o , ΔS_{rxn}^o are given. These values are not absolute values, but dependent on each chemical reaction.

→ In the FactSage, absolute Gibbs energy of each species (relative to elemental species) is stored. Then, any reaction Gibbs energy can be automatically calculated from the Gibbs energy of each species.

3. Chemical reaction involving gas



$$\Delta G_{rxn} = G_{A_nO_2}^o - (nG_A^o + mG_{O_2}^o)$$



$$G_i = G_i^o + RT \ln P_i$$

for gas species i

$$= \Delta G_{rxn}^o - mRT \ln P_{O_2}$$

At Equilibrium state $\Delta G_{rxn} = 0$

$$\Delta G_{rxn}^o = -RT \ln\left(\frac{1}{P_{O_2}^m}\right)$$

3. Chemical reaction involving gas (continue)

In general, for $aA + bB(g) = cC + dD(g)$

At Equilibrium

$$\Delta G_{rxn}^o = -RT \ln \left(\frac{P_D^d}{P_B^b} \right)$$

$$\Delta G_{rxn}^o = -RT \ln K_{eq}$$

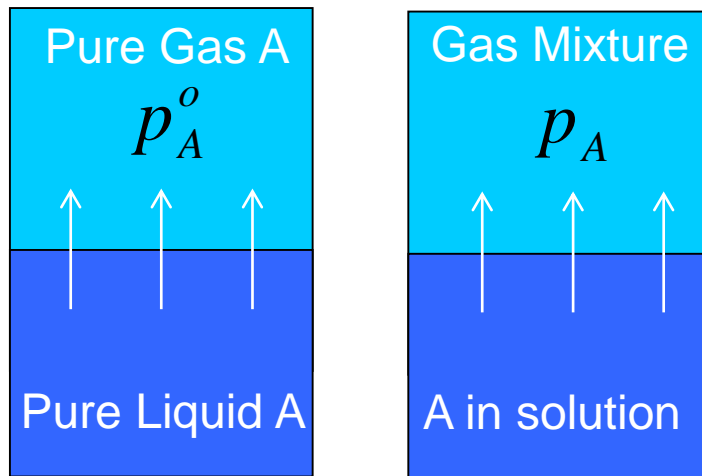
K_{eq} : Equilibrium constant

4. Chemical reaction involving solid or liquid solution

$$G_{i(\text{in soln})} = G_{i(\text{pure})}^{\circ} + RT \ln(a_i) \quad \mathbf{a: \text{ activity}}$$

change of Gibbs energy of i in solution
by interacting with surrounding species

Definition of activity

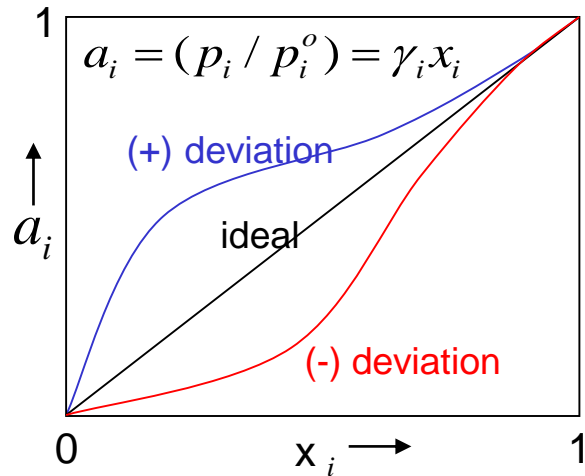


$$a_A = \frac{P_A}{P_A^{\circ}} = \gamma_A x_A$$

\therefore activity is movement of species in solution

4. Chemical reaction involving solid or liquid solution

Definition of activity



(+) deviation: repulsion between i and other species
→ $a_i > x_i$: more active chemical reaction of i

(-) deviation: attraction between i and other species
→ $a_i < x_i$: less active chemical reaction of i

In general, for $aA + bB(g) = cC + dD(g)$

$$\Delta G_{rxn} = \sum G_{products} - \sum G_{reactants}$$

At Equilibrium

$$\Delta G_{rxn}^o = -RT \ln\left(\frac{a_C^c P_D^d}{a_A^a P_B^b}\right)$$

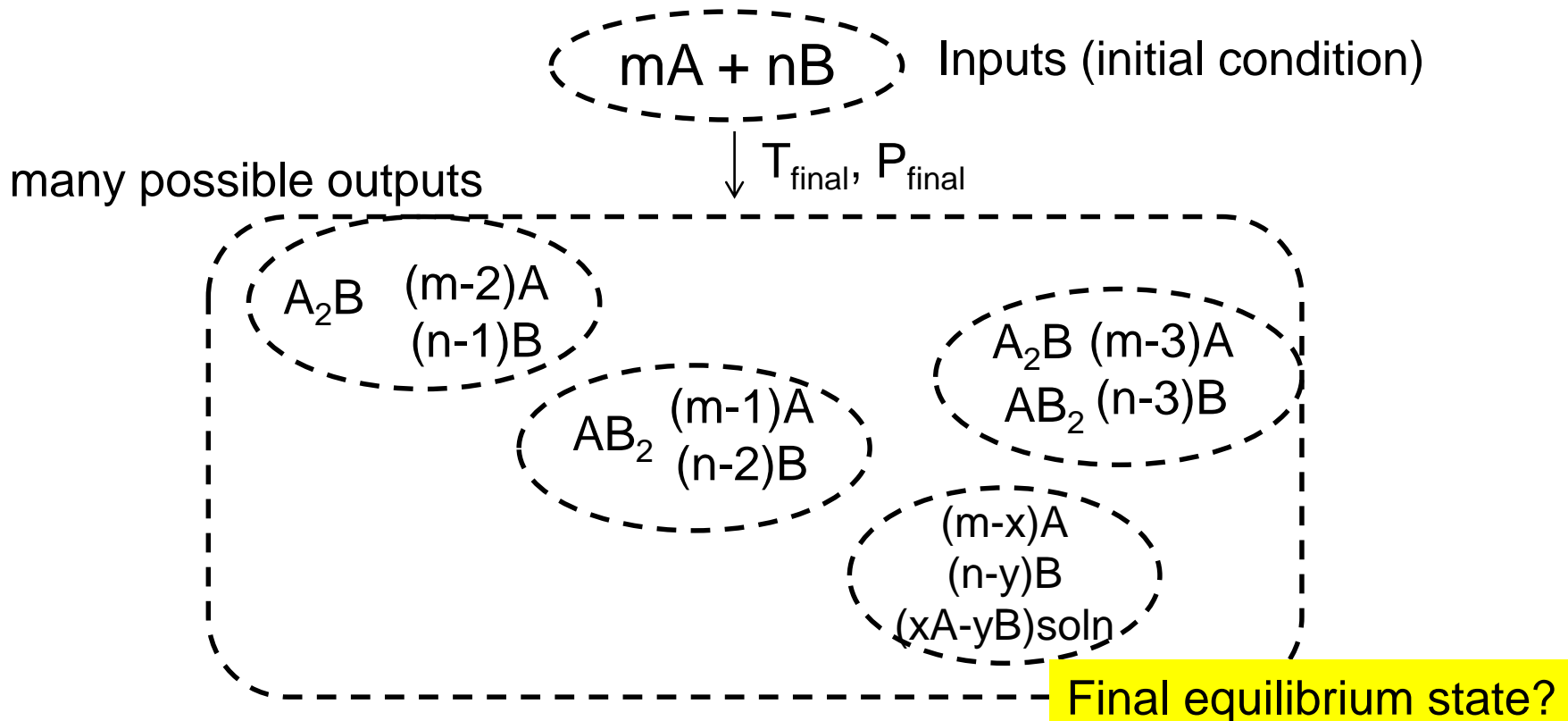
* FactSage solution database contains the model and model parameters to calculate G_i and eventually get a_i

Gibbs Energy

In most of thermodynamic book, we always calculate equilibrium condition

$$\Delta G_{rxn} = 0 \longrightarrow \Delta G_{rxn}^o = -RT \ln K_{eq}$$

But in reality, we want to first know the direction of reaction



Gibbs Energy Minimization

(continue)

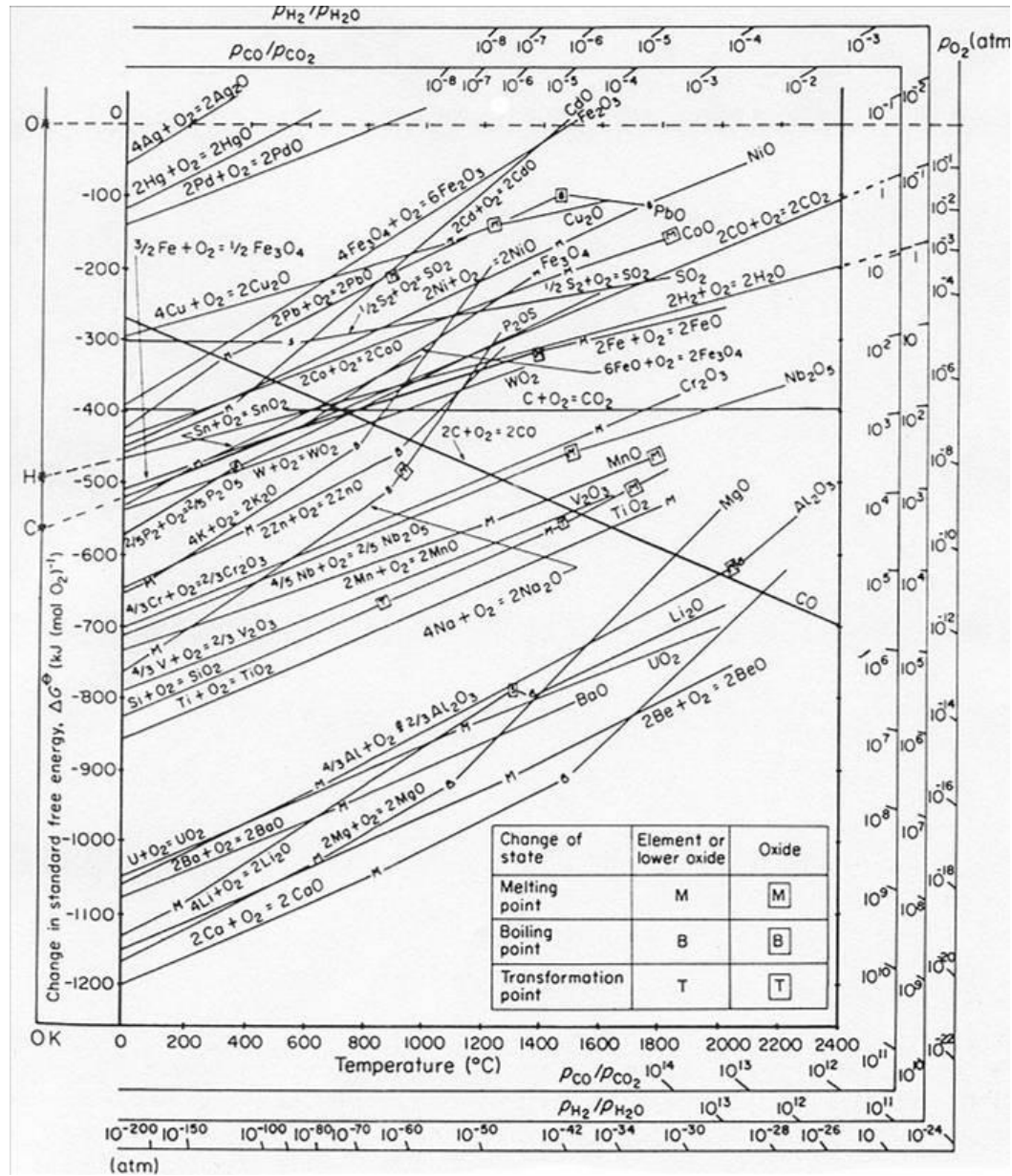
- We have to find out which phase assemblage is the most stable at given T_f and P_f with respect to the mass balance.
- Gibbs energy minimization routine: ChemSage, Solgas-mix, etc.

The most stable phase assemblage has the lowest Gibbs energy.

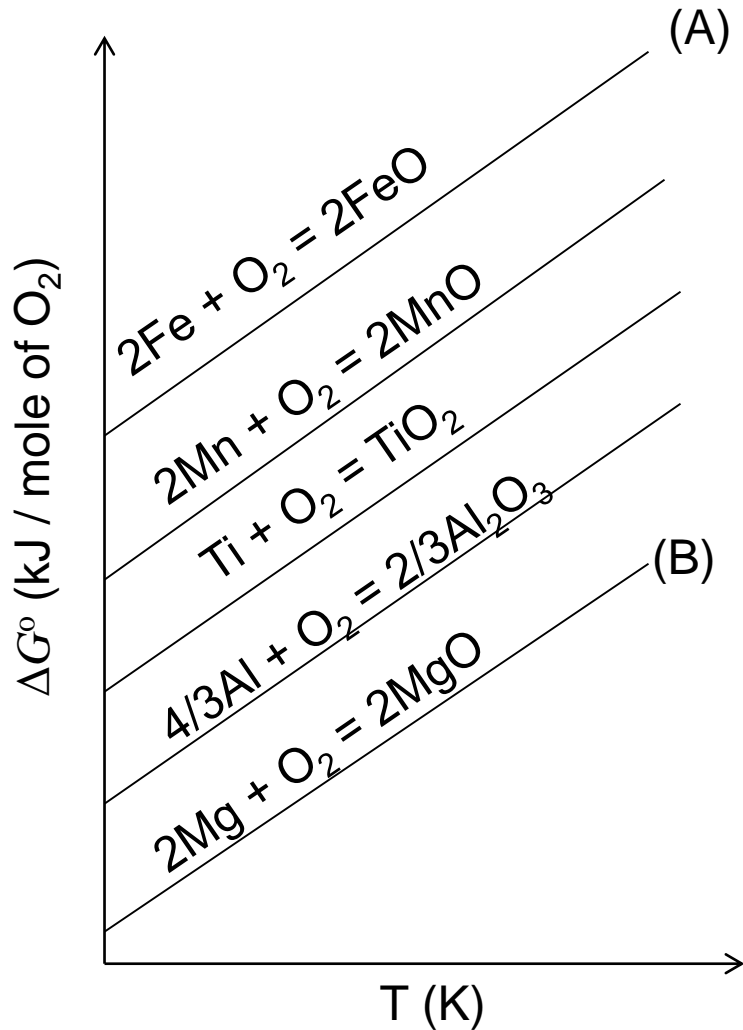
In FactSage

- Put inputs amount
- Select all possible phases (solid compounds, solid solutions, liquid solutions, gases)
- Set T_{final} and P_{final}
- Calculation (Gibbs energy minimization routine)
- Equilibrium phase assemblage

Ellingham Diagram

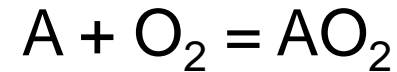


Ellingham Diagram



- Collection of ΔG° for oxidation reaction
 $mA + O_2 = A_m O_2$ (reference: 1 mol of O_2)

- Only consider for pure species.
 (No solutions are considered.)



$$\Delta G = \Delta G^\circ + RT \ln \frac{(a_{AO_2})}{(a_A) (p_{O_2})}, (\Delta G = 0: \text{Equilibrium})$$

$$\Delta G^\circ = RT \ln p_{O_2}$$

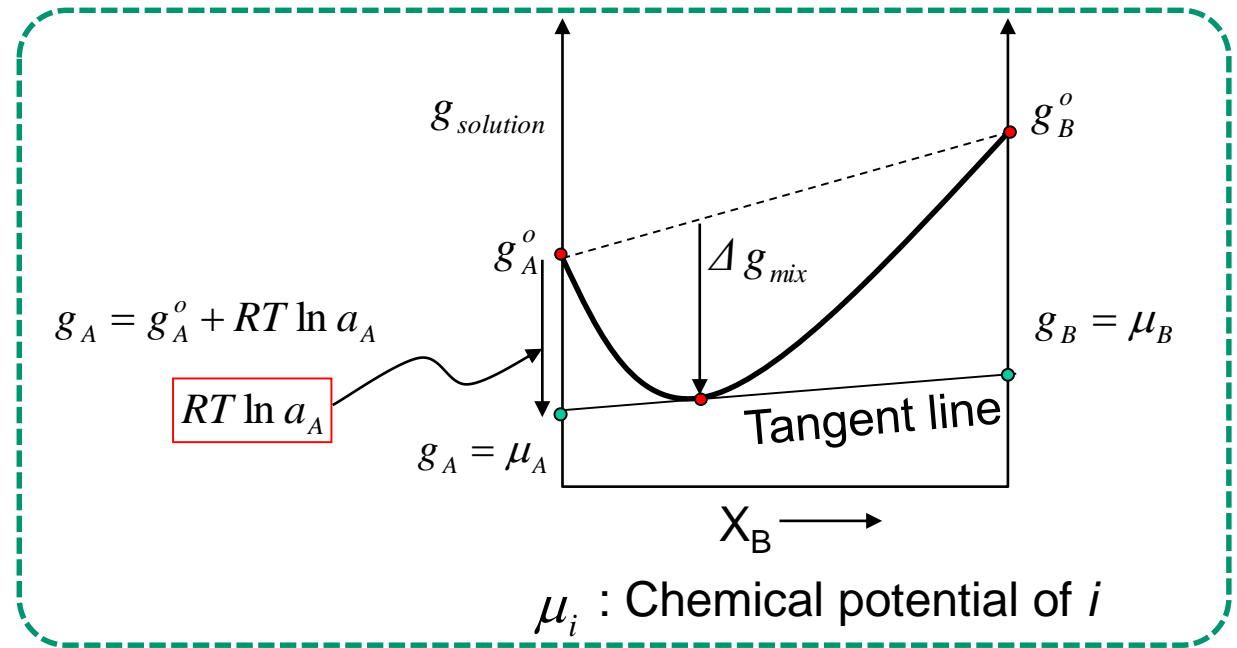
$$\Delta G^\circ = (R \ln p_{O_2}) \times T$$

Solution thermodynamics

A-B solution, (Solid or Liquid solution)

$$G_{\text{solution}} = \sum x_i G_i$$

$$G_i = G_i^o + RT \ln a_i \quad \mathbf{G_i: \text{partial Gibbs energy of } i \text{ in solution}}$$



$$= (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

A-B solution (Solid or Liquid solution)

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

1. Ideal solution: $\gamma_A = 1, \gamma_B = 1$

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B)$$

2. Regular solution: $RT \ln \gamma_A = \Omega_{AB} x_B^2$ Ω : Regular solution parameter

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + \Omega_{AB} x_A x_B$$

A-B solution, (Solid or Liquid solution)

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

3. General solution: $\gamma_A = f(x, T)$

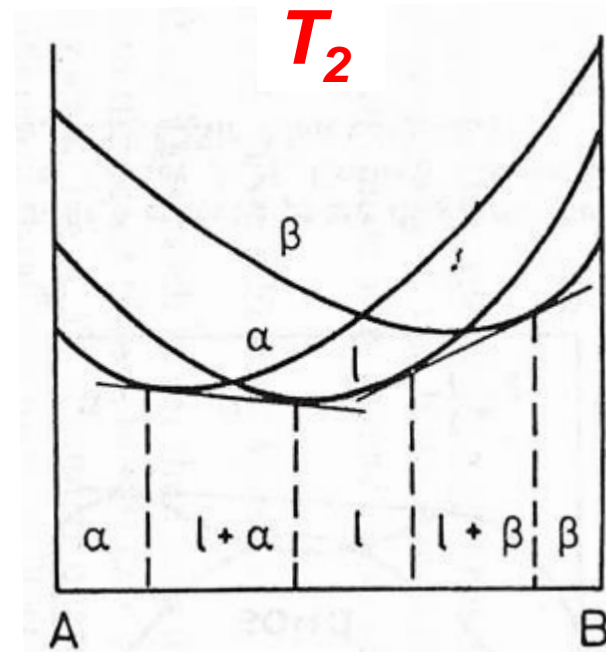
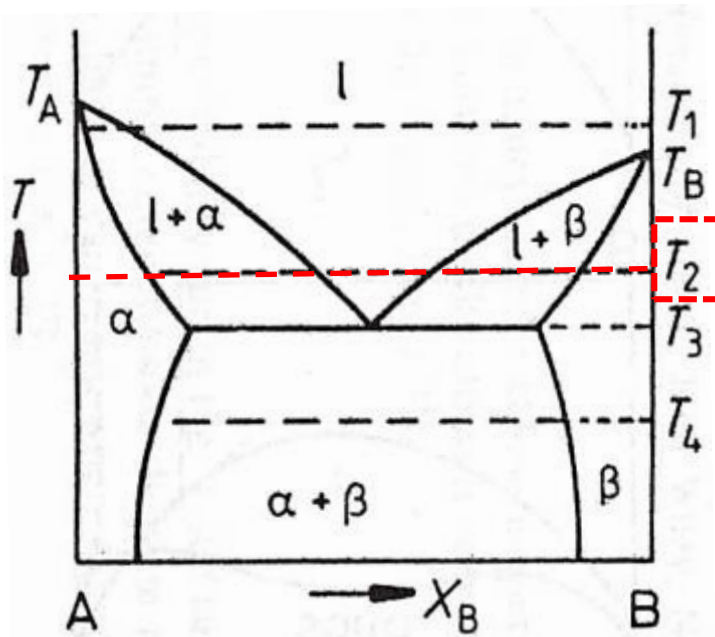
$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}$$

$$G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j$$

* FactSage supports many complex solution models. Solution database (FToxid, FTSalt,) contains optimized model parameters reproducing Gibbs energy of solution.

Gibbs Energy vs. Phase Diagram

→ Phase diagram is the collection of minimum Gibbs energy assemblage of given system with temperature.

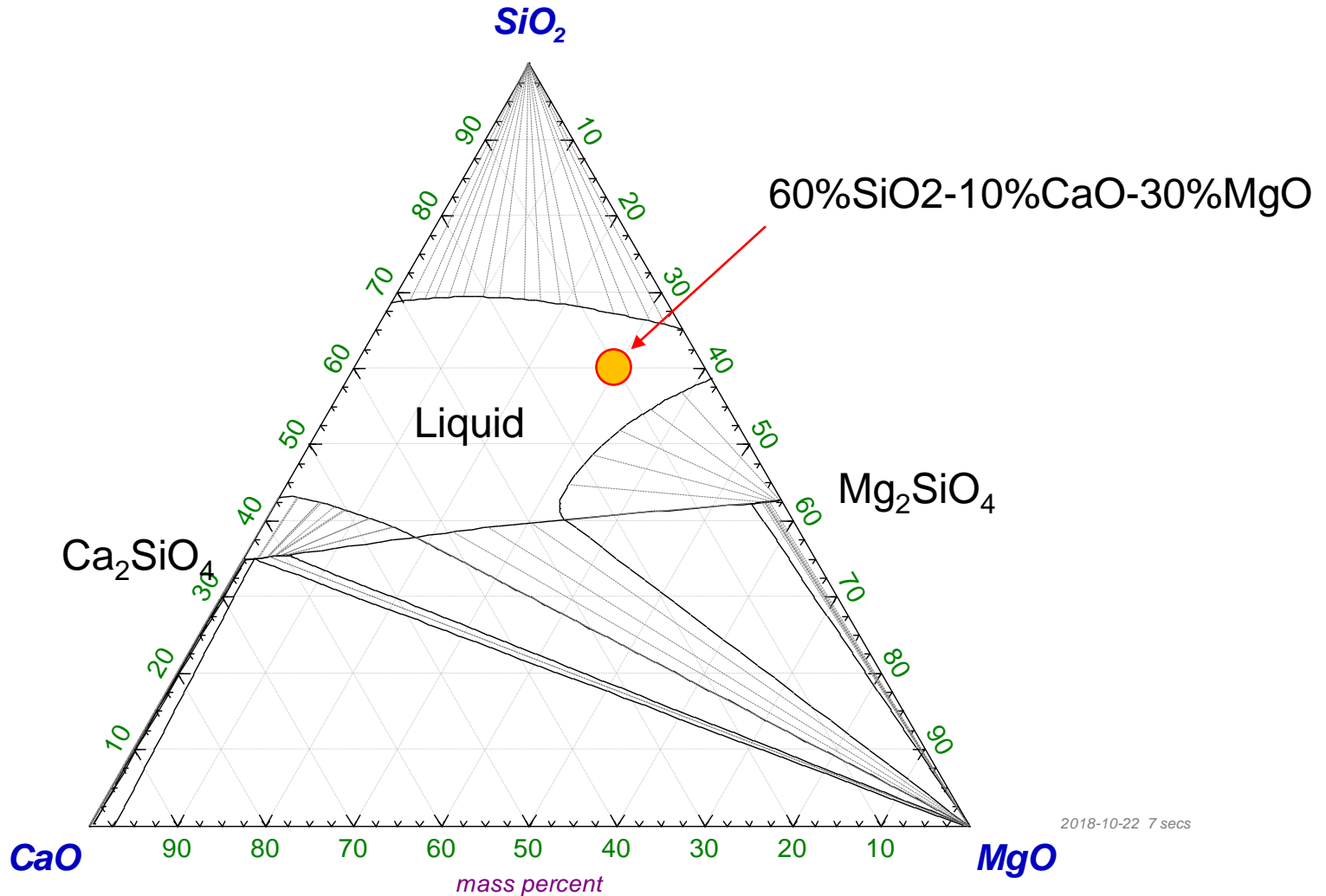


Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2nd Ed. CHAMAN & HALL (1992)

Ternary phase diagram: isothermal phase diagram

CaO - MgO - SiO₂

1600°C, 1 atm

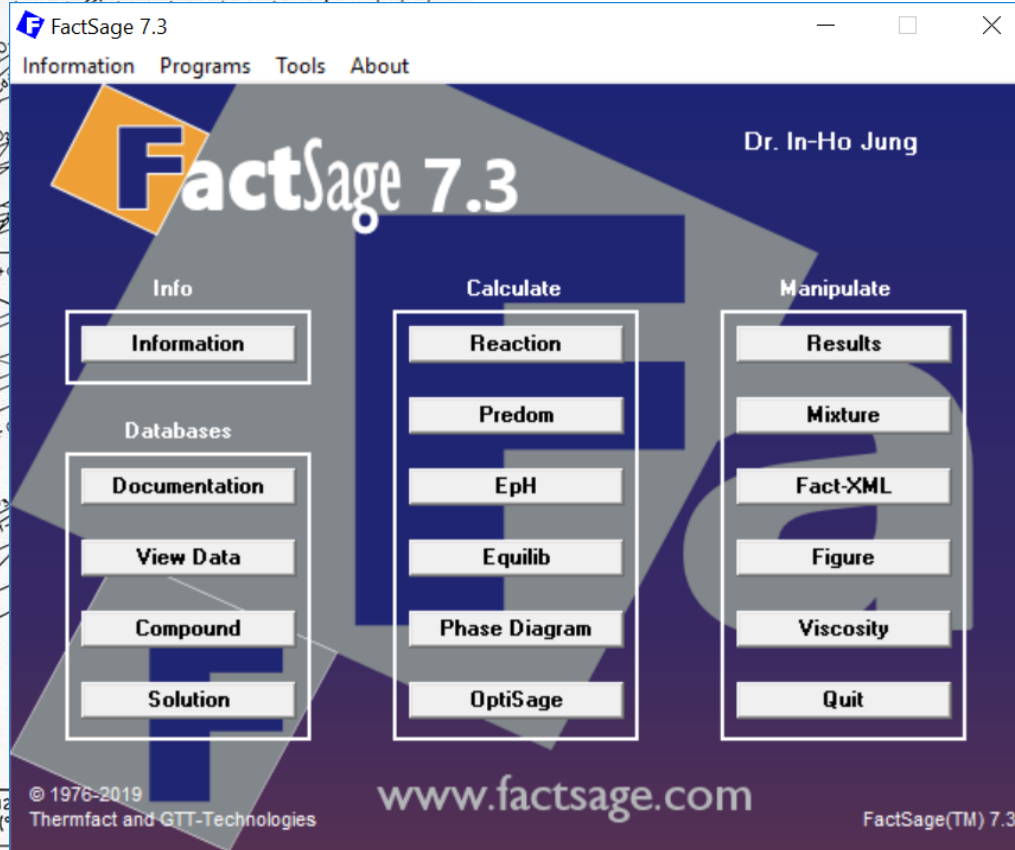
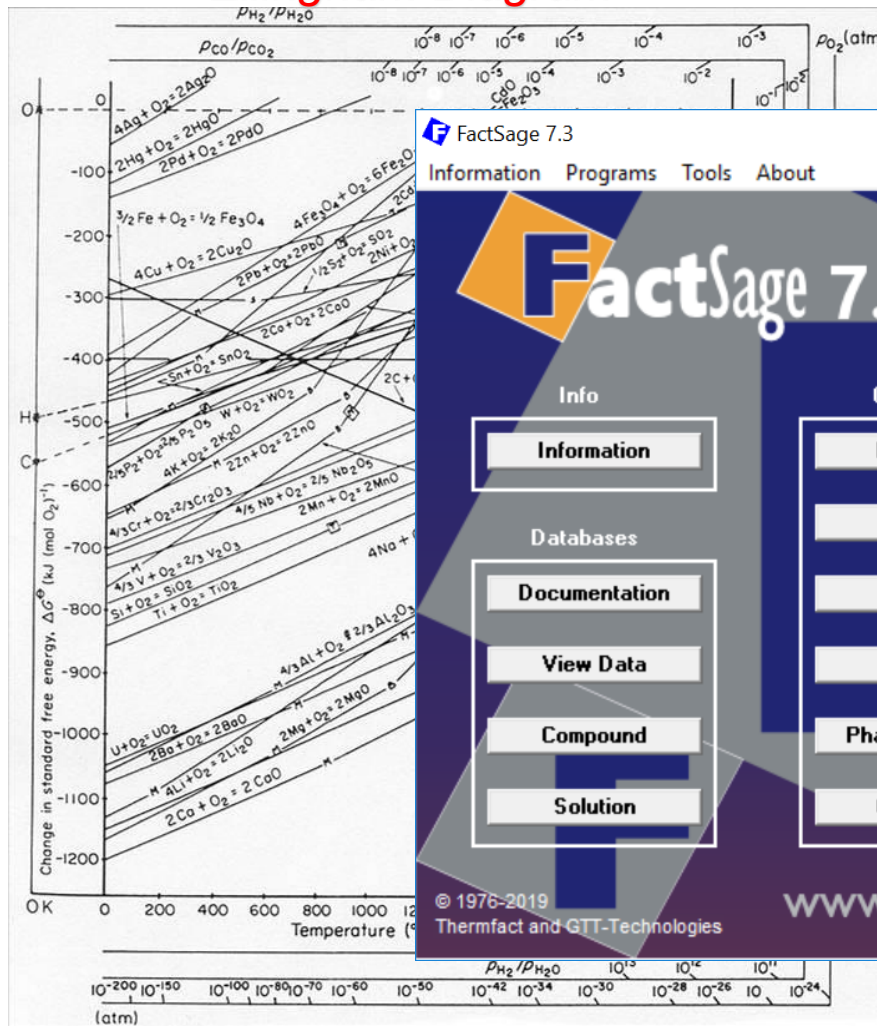


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Advantage of thermodynamic database

Ellingham Diagram

FactSage calculations



FactSage 7.3
 (gram) 40 CaO + 30 SiO₂ + 10 Al₂O₃ + 20

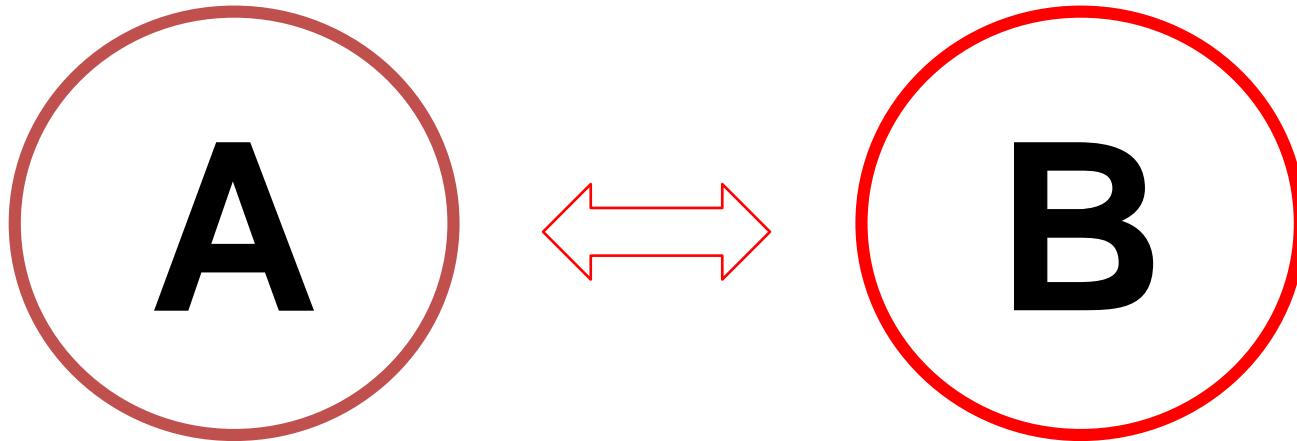
=
 ASlag-liq
 394 mol)
 1 atm, a=1.0000)
 wt.% Al₂O₃
 wt.% SiO₂
 wt.% CaO
 wt.% MgO
 -04 wt.% CrO
 wt.% Cr₂O₃

ASpinel
 221E-02 mol)
 1 atm, a=1.0000)
 wt.% Al₃O₄[1+]
 -07 wt.% Al₁O₄[5-]
 wt.% Mg₁Al₂O₄
 wt.% Al₁Mg₂O₄[1-]
 wt.% Mg₃O₄[2-]
 -06 wt.% Mg₁O₄[6-]
 wt.% Mg₁Cr₂O₄
 -02 wt.% Cr₁Cr₂O₄[1+]
 -03 wt.% Cr₁Mg₂O₄[1-]
 wt.% Al₁Cr₂O₄[1+]

+ 5.7638 gram AMonoxide#1
 (5.7638 gram, 0.13398 mol)
 (1600 C, 1 atm, a=1.0000)
 (0.10016 wt.% CaO
 + 91.310 wt.% MgO
 + 0.18976 wt.% Al₂O₃
 + 8.3998 wt.% Cr₂O₃

- Ellingham diagram : Reaction between pure stoichiome
- FactSage calc.: Multicomponent phase equilibria includ
 - for example, Spinel/Slag/Monoxide

Development of Thermodynamic Database



Gibbs energy between A-B = $f(X, T, P)$
in multicomponent system

→ Thermodynamic Database



CALPHAD

Phase diagram data

- Phase diagram
- S/L/G phase equilibria

Crystal Structural data

Thermodynamic data

- Calorimetric data: Heat capacity, H of mixing, H of melting, etc.
- Vapour pressures
- Chemical Potentials: activity

Pure compound

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298 K}^o + \int_{298 K}^T C_p dT$$

$$S_T^o = S_{298 K}^o + \int_{298 K}^T \frac{C_p}{T} dT$$

$$S_{298 K}^o = \int_{0 K}^{298 K} \frac{C_p}{T} dT$$

- Calorimetry
- emf
- Knudsen cell
- Vapor pressure

Solution

$$G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j$$

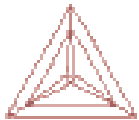
- emf (activity)
- Knudsen cell (activity)
- Vapor pressure (activity)
- Solution calorimetry (enthalpy)
- Phase diagram

Commercial database and software: CALPHAD



F*A*C*T + ChemSage: CRCT, Canada + GTT Tech., Germany
www.crct.polymtl.ca, www.factsage.com

TD: Oxide (slag, inclusion, refractory), Salt, Steel, Light alloy (very good)
Fully Window Interface



Thermo-Calc Software

KTH, Sweden, www.thermocalc.se

TD: Steel, Light Alloy (very good) + poor Oxide
DICTRA (Diffusion Process)
DOS Interface, Window Interface



NPL, UK, www.npl.co.uk/npl/cmmt/mtdata
TD: Oxide, Salt, Steel, Light alloy (good)
Window Interface



SGTE (Europe + Canada + US), www.sgte.org
Organization of Database Development

Overall Goal of FactSage Steelmaking Consortium Project (2009~2020)

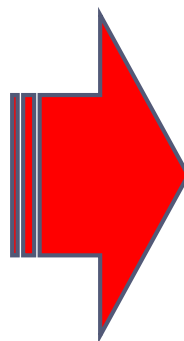


Thermodynamic database

**Slag/Refractory/
Inclusions/Flux/
Steel**

**Slag:
Viscosity,
Molar volume,
Thermal
Conductivity, etc.**

Physical Property database



Kinetic Process Simulation models (EERZ Concept)

- Secondary Refining Units
- Continuous Casting Process

Combining Thermodynamics & Mass transfer based on numerical analysis and plant sampling data

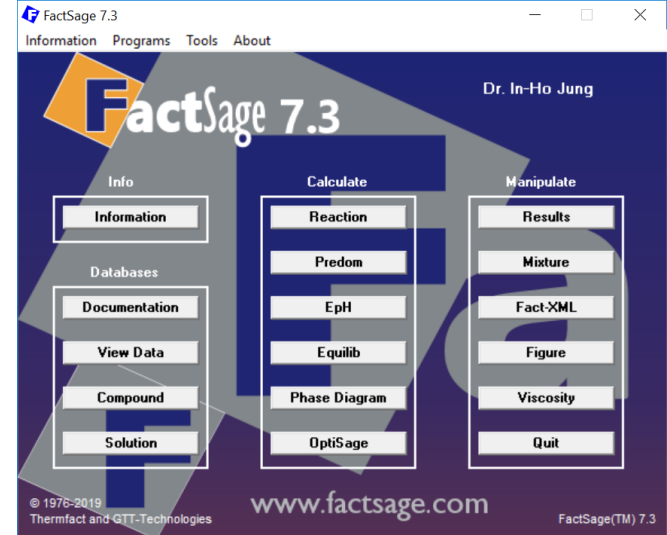
Available Thermodynamic Database – Refractories

Since 1976

Steelmaking, Non-ferrous and Cement industry

MgO-C, Al₂O₃-MgO, MgO-Cr₂O₃, Mullite, Olivine, ZrO₂-based, Al₂O₃-SiC type refractories:

- Reaction with slags, atmosphere, liquid metals
- Refractory mineral phases
 - ✓ Monoxide: MgO-FeO-MnO-CaO
 - ✓ Spinel: (Mg,Mn,Fe,...)[Al,Cr,Fe,..]₂O₄
 - ✓ Olivine: (Mg,Mn,Ca,Fe,...)₂SiO₄
 - ✓ (CaO)_x(Al₂O₃)_y.....
 - ✓ Si-C-N-O..
 - ✓ Cr⁶⁺ : in progress
- Slag phase:
CaO-MgO-Al₂O₃-SiO₂-FeO-Fe₂O₃-MnO-Ti₂O₃-TiO₂-CrO-Cr₂O₃-ZrO₂-P₂O₅...-S-F
- Liquid metallic phase
 - ✓ Fe, Ferro-alloy, Al, Mg, Si, Cu, ...



Glass, Biomass combustion, and Coal combustion industry

- K₂O, Na₂O, Li₂O containing slags: Glass and Biomass application
- V oxide containing slags: Coal combustion – in progress
- Sulphate containing slags: Coal combustion – in progress

Applications of phase diagram: Case Study

MgO solubility in slags

- CaO-MgO-SiO₂ Phase diagram vs. MgO solubility
- BOF slag, LF slag
- Multicomponent slag with CaF₂

Melting temperature of MgO and MgCr₂O₄

- Impurity
- Oxygen partial pressure

Other Slag – Refractory Interactions

- Ladle glaze
- Purging plug – cleaning process

Non-metallic inclusions – Stopper

Nozzle refractory

- Carbothermal reduction process
- Inclusion formation

MgO solubility in slags

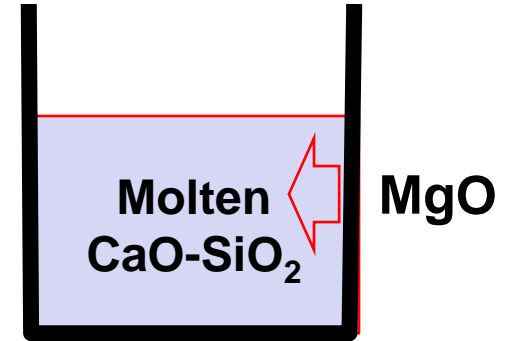
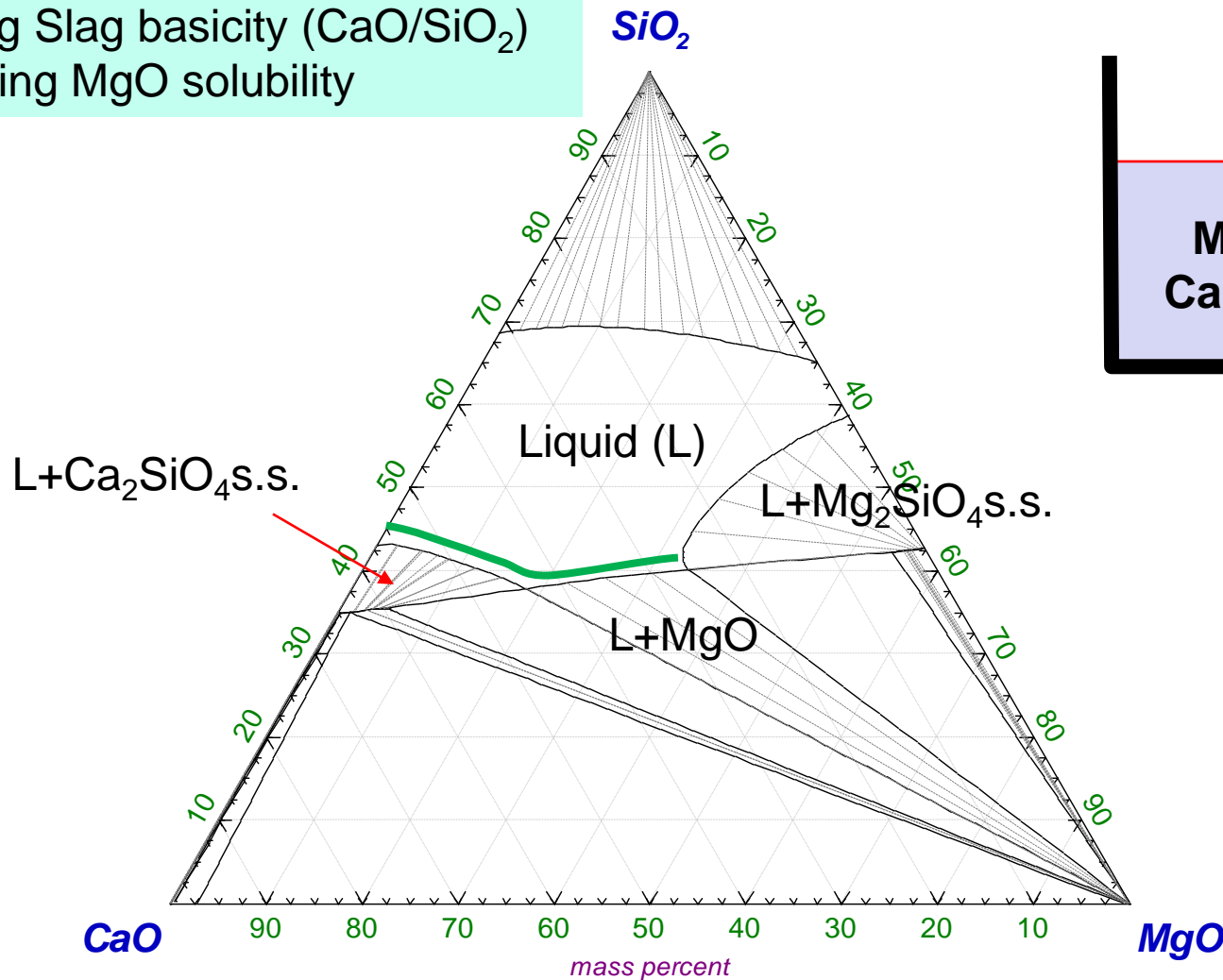
- CaO-MgO-SiO₂ Phase diagram vs. MgO solubility
- BOF slag
- Multicomponent slag with CaF₂
- LF slag

CaO-MgO-SiO₂ phase diagram

CaO - MgO - SiO₂
1600°C, 1 atm

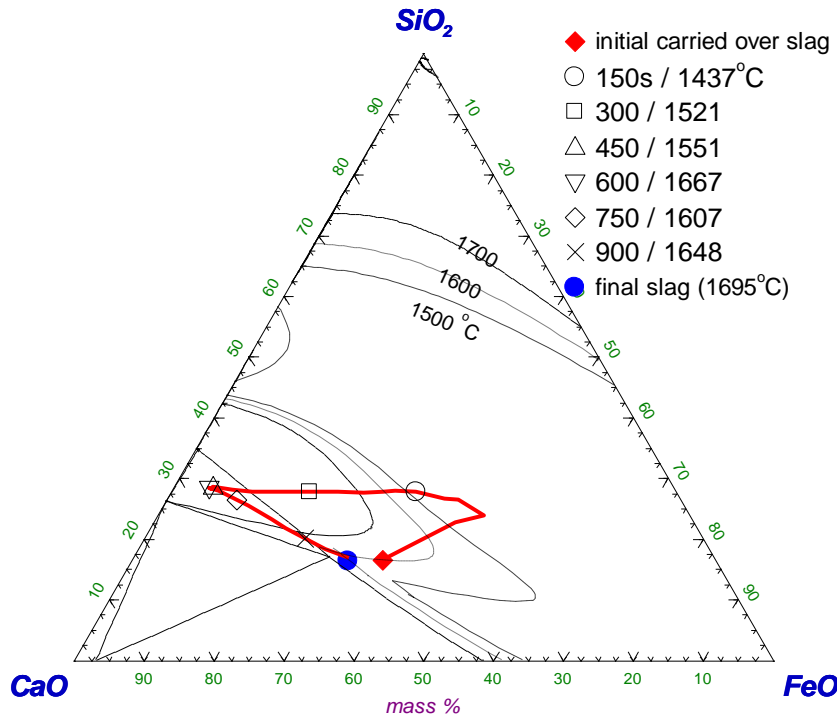


Decreasing Slag basicity (CaO/SiO₂)
→ Increasing MgO solubility



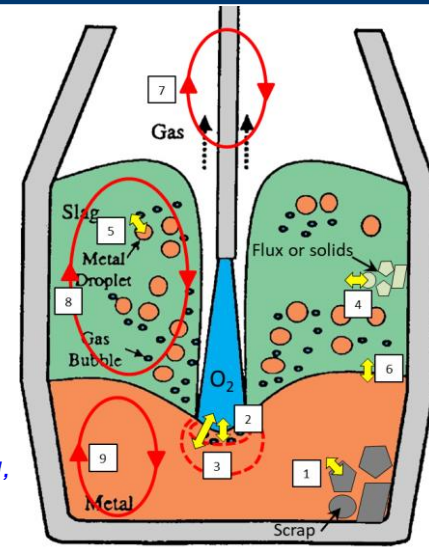
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Refractory: CaO-Fe_tO-SiO₂-5wt%MgO system with Fe saturation



Overall slag chemistry change during BOF process

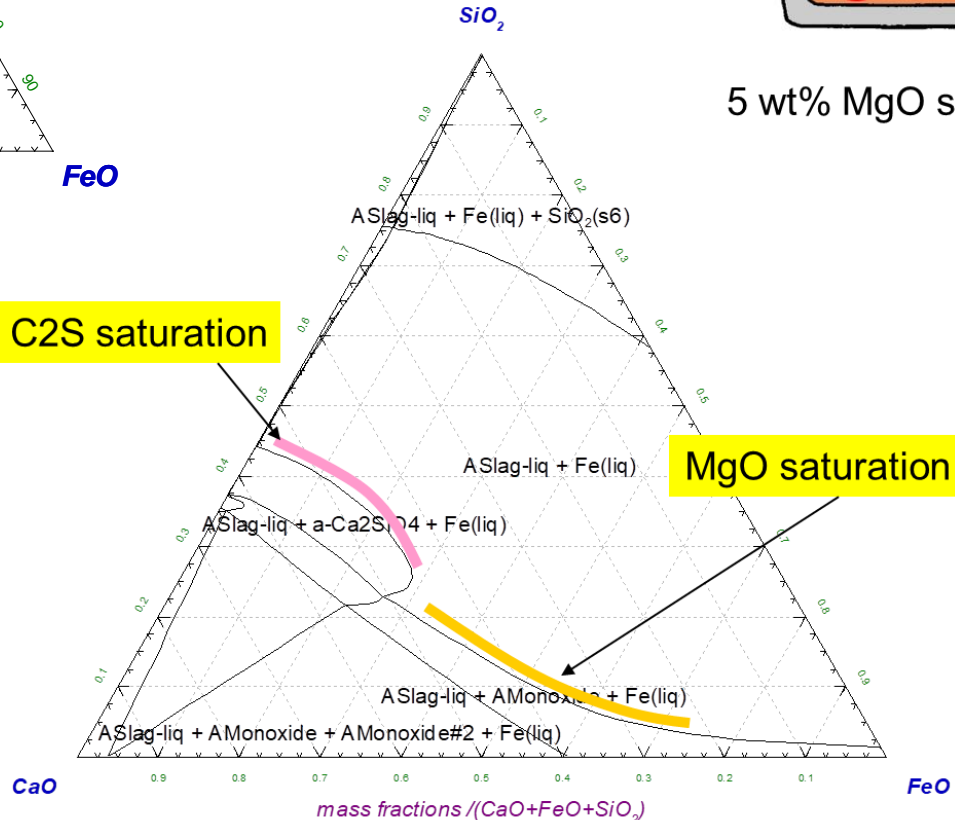
CaO - FeO - SiO₂ - MgO - Fe
 1650°C, MgO/Z (g/g) = 0.05263, Fe/Z (g/g) = 0.001,
 $Z = (\text{CaO} + \text{FeO} + \text{SiO}_2)$



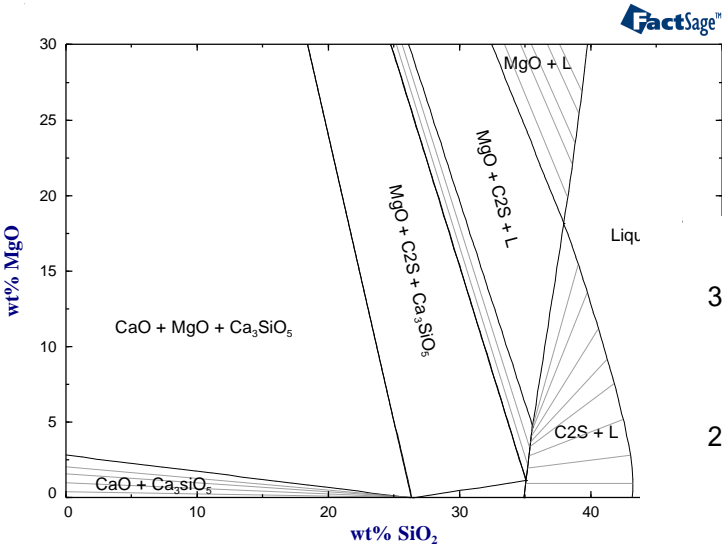
5 wt% MgO section

C2S saturation

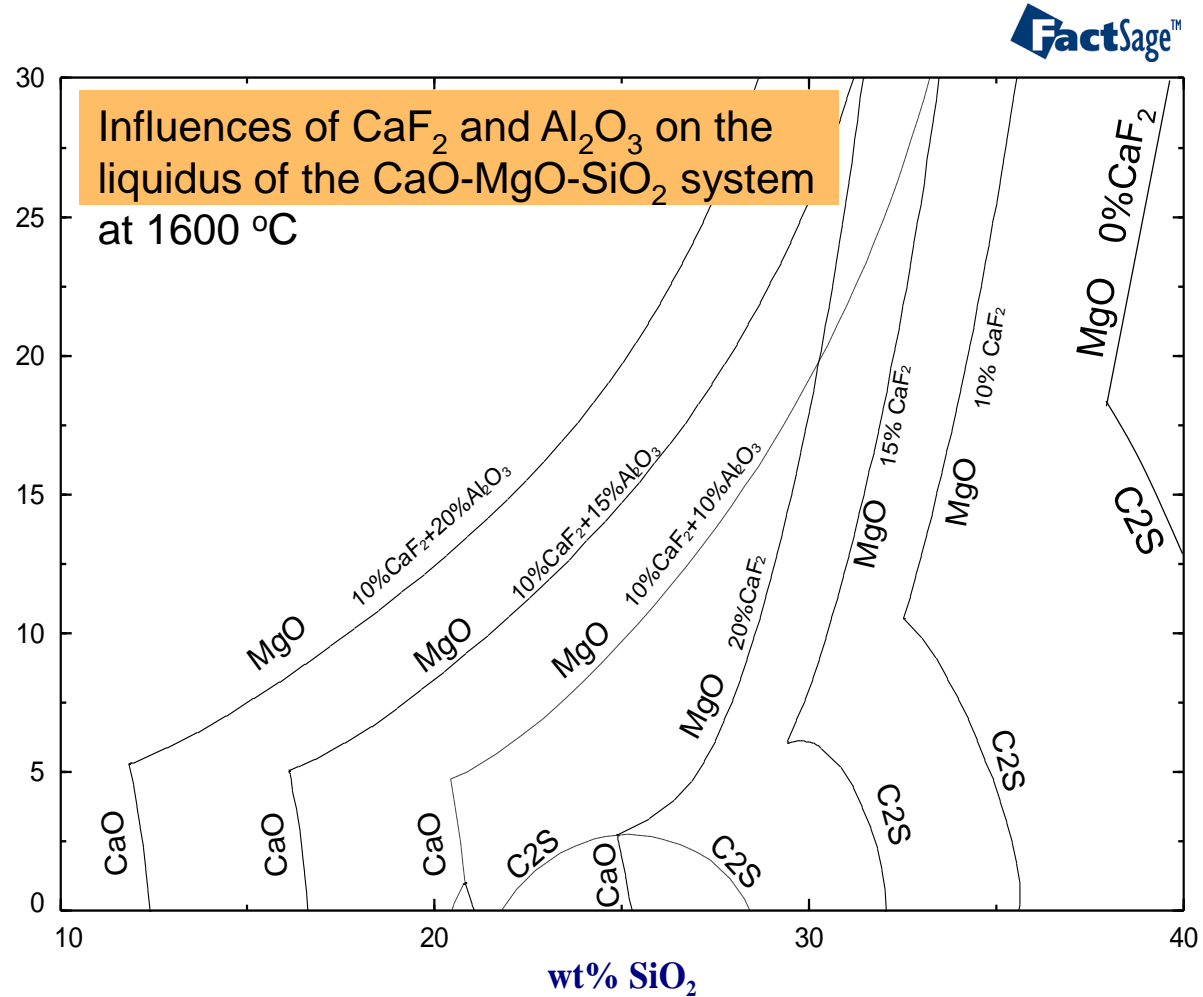
MgO saturation (MgO-FeO)



Refractory reaction with F containing slag/flux

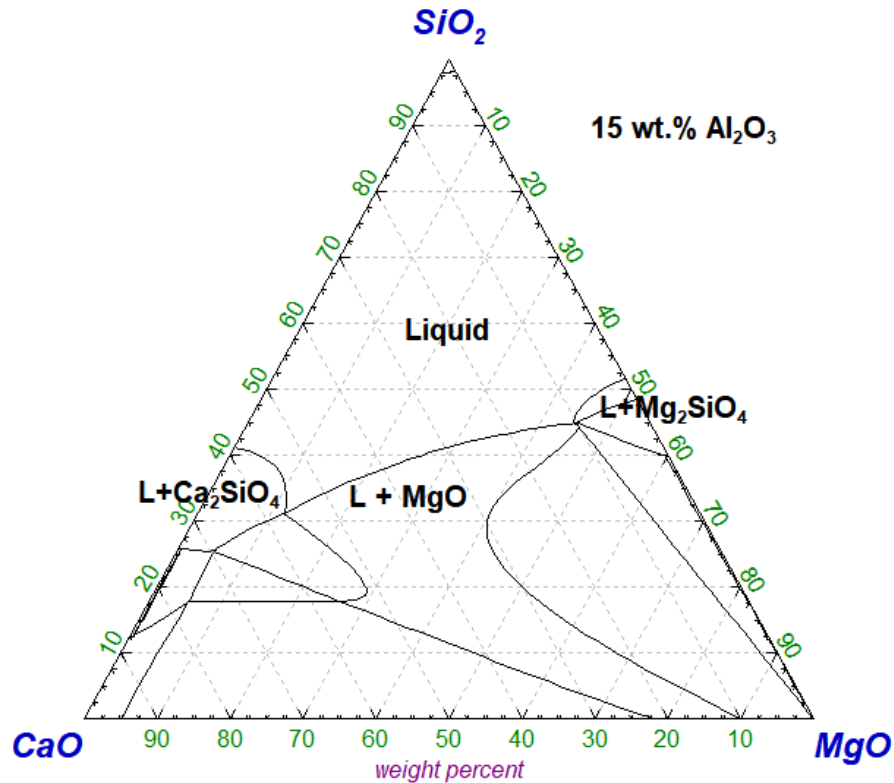


Phase diagram of the CaO-MgO-SiO₂ system at 1600 °C

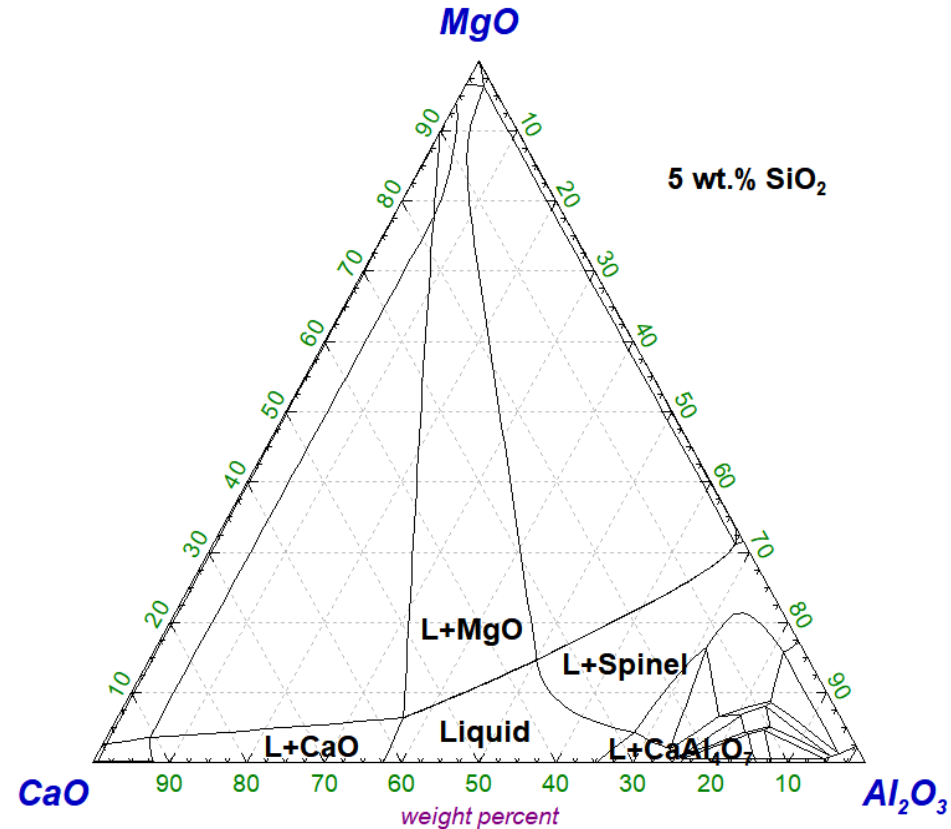


MgO solubility in CaO-SiO₂ and CaO-Al₂O₃ based slags

CaO-SiO₂-15%Al₂O₃ slag with MgO



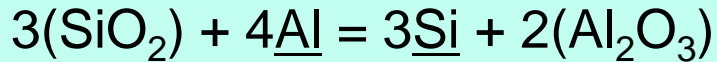
CaO-Al₂O₃-15%SiO₂ slag with MgO



MgO solubility in the CaO-Al₂O₃ based slags is much lower than that in the CaO-SiO₂ based slags

Ladle Furnace (LF) slag

- BOF slag (SiO_2 containing slag)
- Source of SiO_2 in LF slag (earlier stage)
- Al deoxidation: reduction of SiO_2 in slag

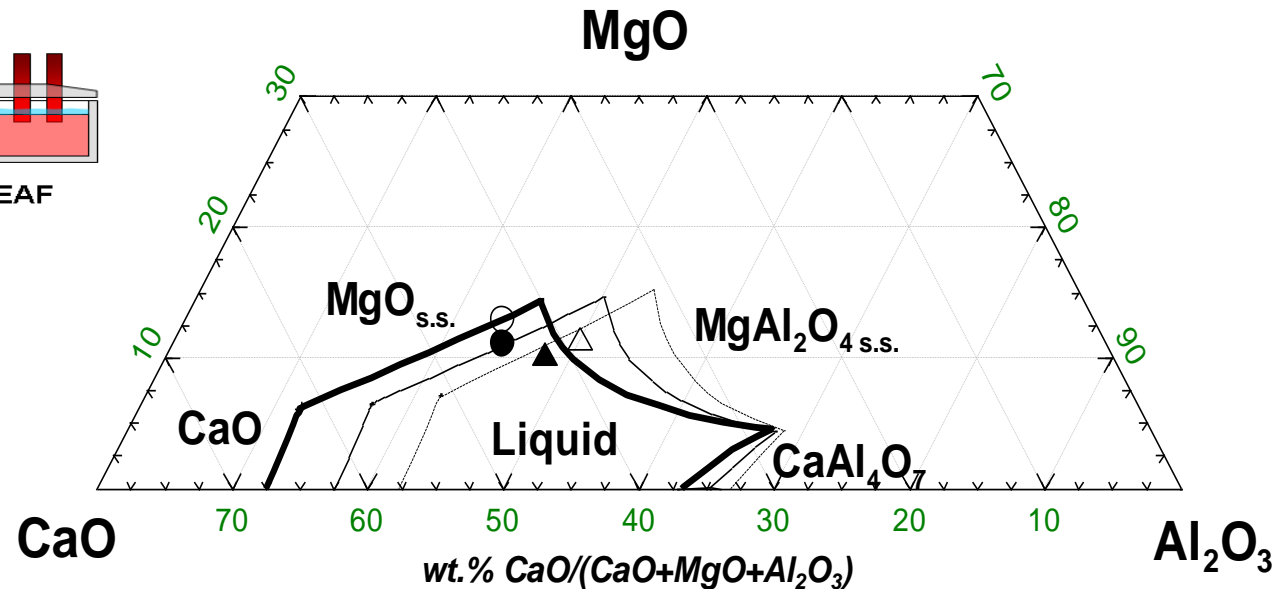
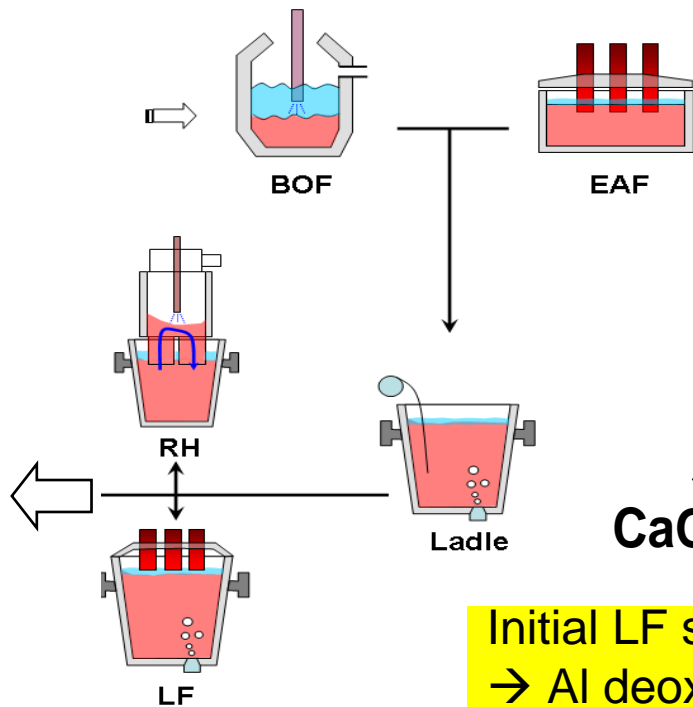


- Can change MgO solubility in LF slag

CaO-MgO- Al_2O_3 -10% SiO_2

CaO-MgO- Al_2O_3 -5% SiO_2

CaO-MgO- Al_2O_3



Initial LF slag: 39.2CaO-39.2 Al_2O_3 -11.6MgO-10 SiO_2 (open circle)
 → Al deoxidation
 → Final LF slag: 38.7CaO-50.1 Al_2O_3 -11.2MgO (open triangle)
 (0.6 wt.% lower than the MgO saturation)

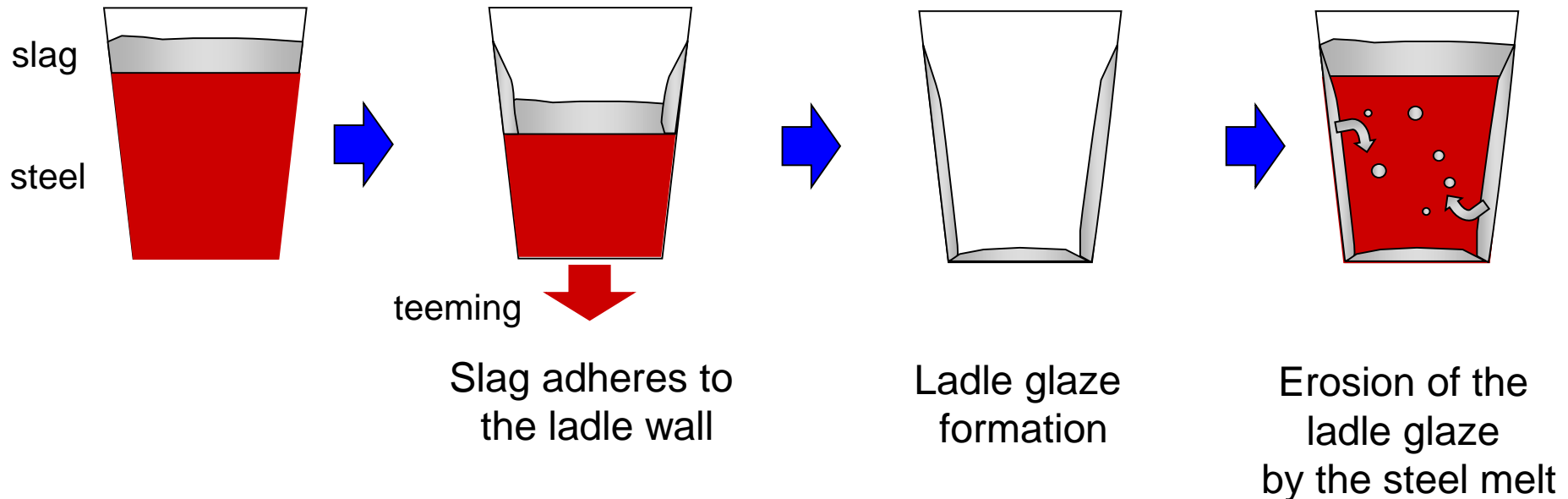
Other Slag – Refractory Interactions

- Ladle glaze
- Purging plug – cleaning process

Ladle Glaze

Ladle Glaze

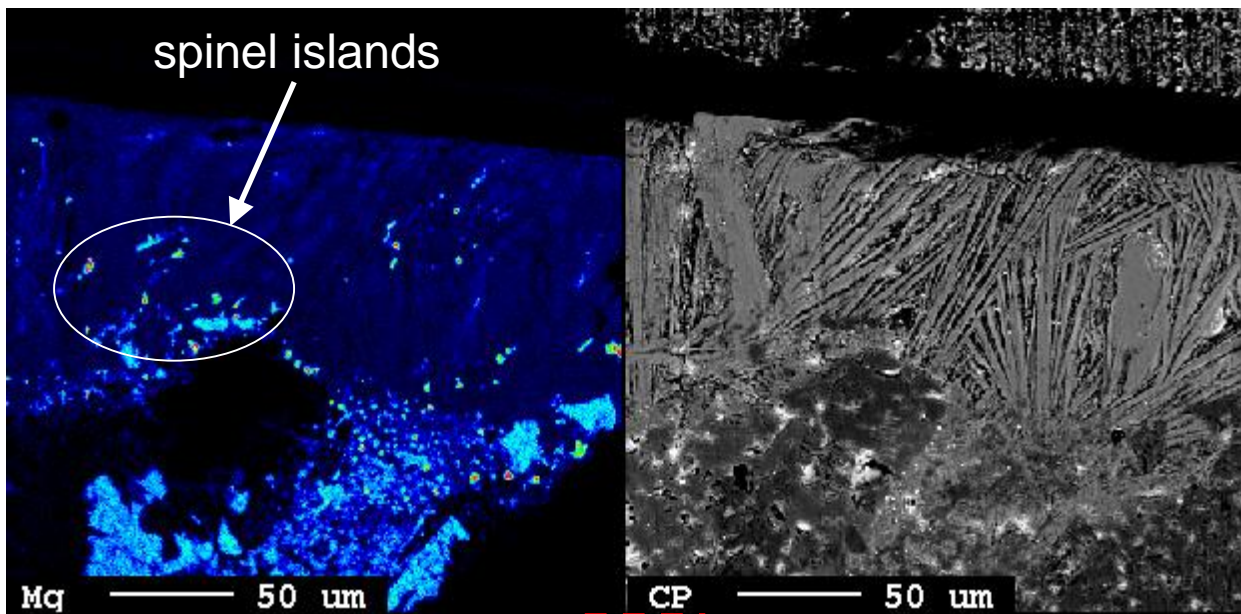
- Reactions with Ladle refractory lining
- Formation of non-metallic Inclusions



Purpose of the present study

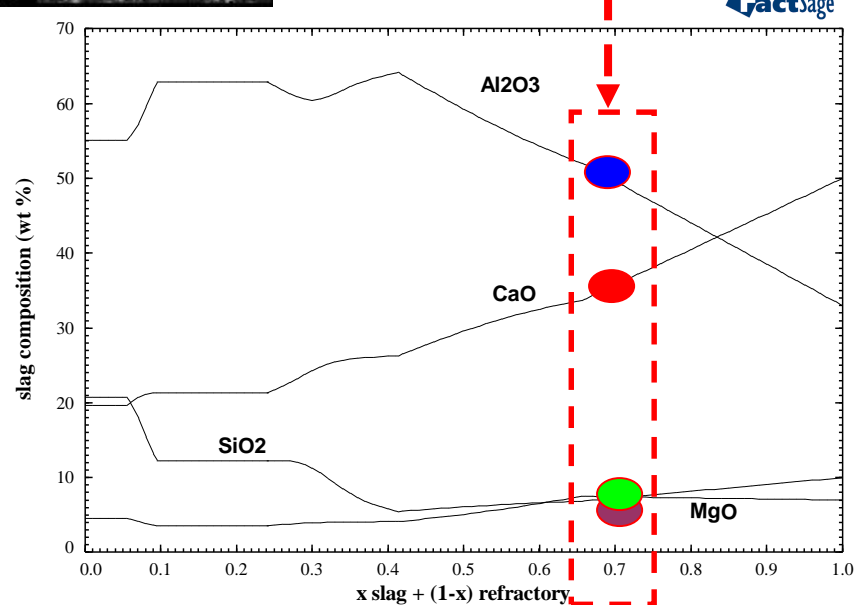
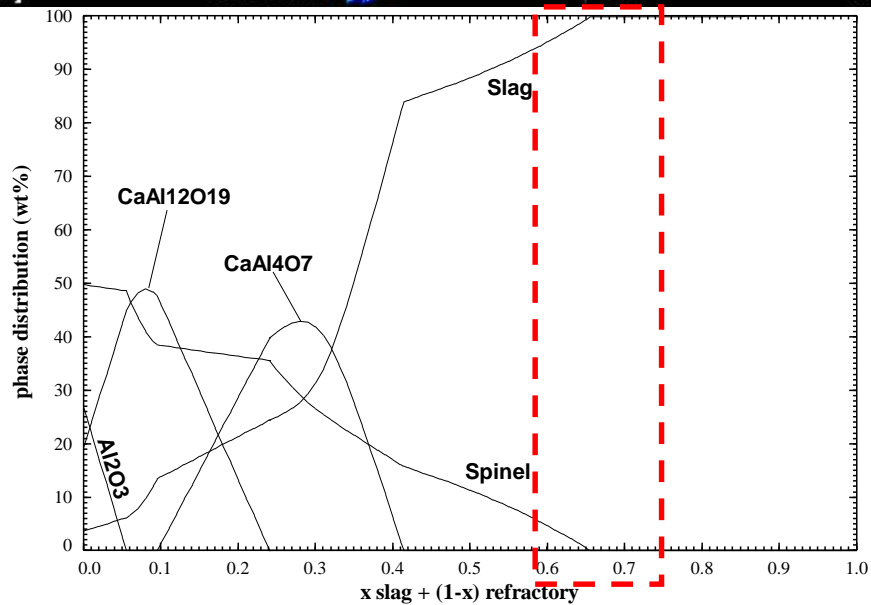
- Glaze formation mechanism / Glazed refractory
- Influence on melt cleanliness (inclusion): Al, Al/Ca

Glaze (Reaction product of slag and refractory)



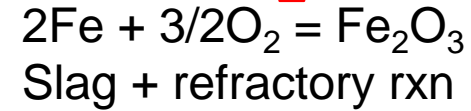
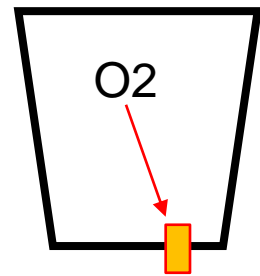
Glaze composition

CaO	SiO ₂	Al ₂ O ₃	MgO
35.8	6.6	51.1	6.5



Corrosion of Ladle purging plug by Fe oxides

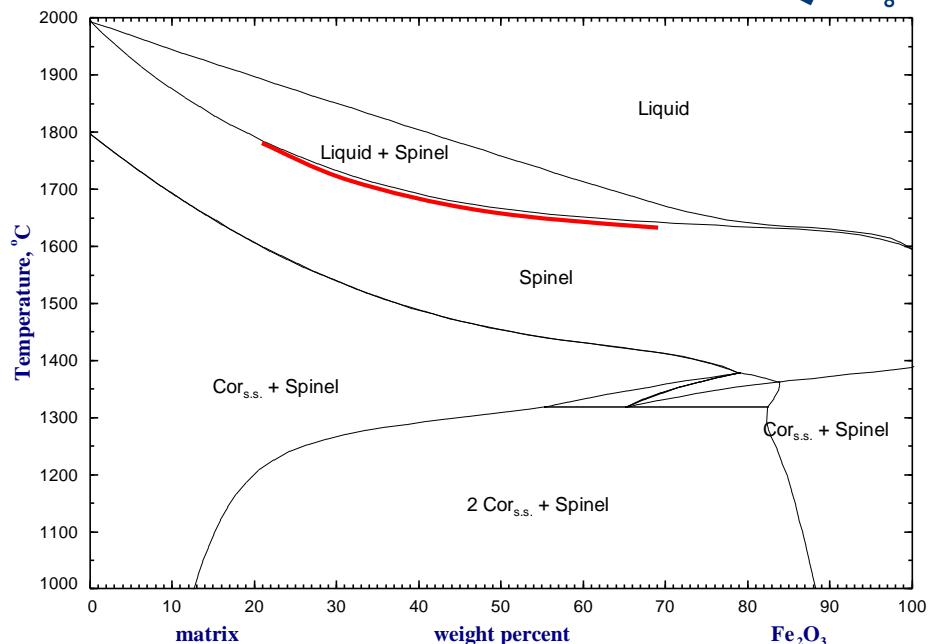
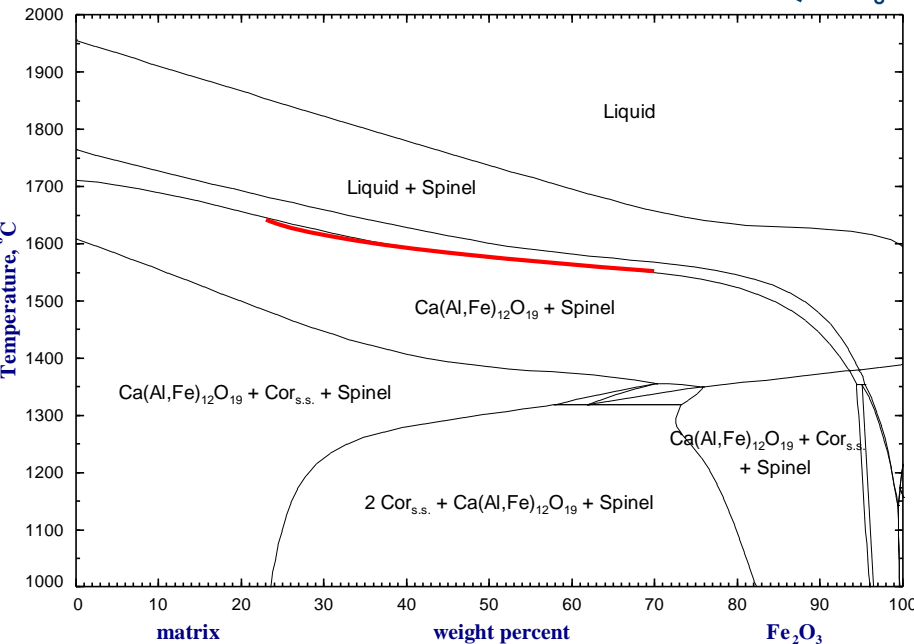
Purging plug: Low- or ultra-low-cement castable (LCC or ULCC) in the Al_2O_3 -MgO-CaO system: Corundum + Spinel



Corrosion during frequent cleaning operations of the clogged purging plug surface by “oxygen lancing”

FactSage

FactSage™



Conventional CaO containing castable:
92.8 Al_2O_3 -5.7MgO-1.5CaO (in wt%)

CaO-free castable:
94.3 Al_2O_3 -5.7MgO (in wt%)

CaO free castable is better against chemical corrosion by high Fe oxide slag

Melting temperature of MgO and MgCr₂O₄

- Impurity
- Oxygen partial pressure

Melting temperature of MgO

Melting temperature of

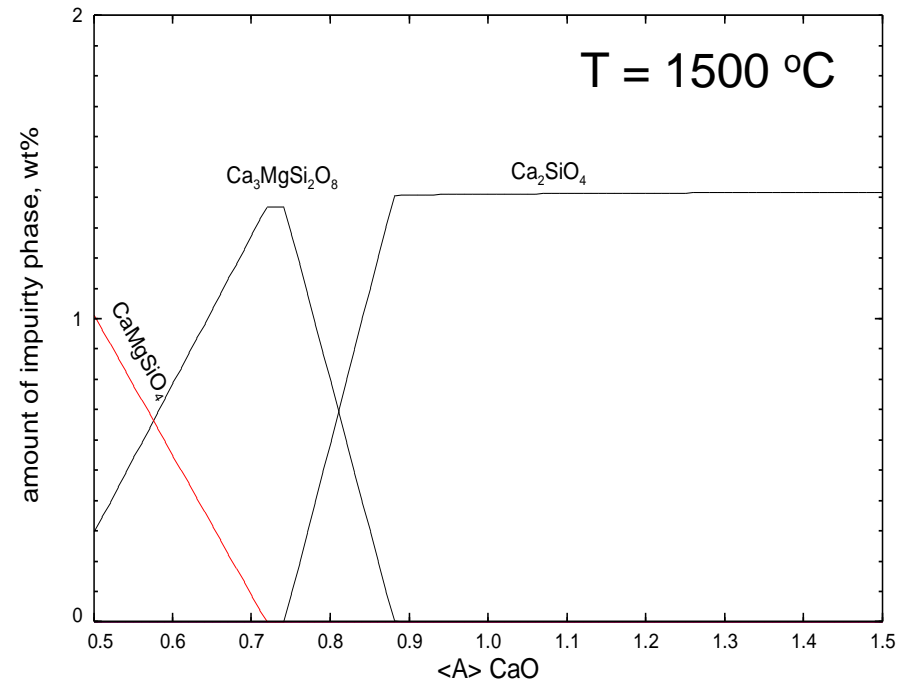
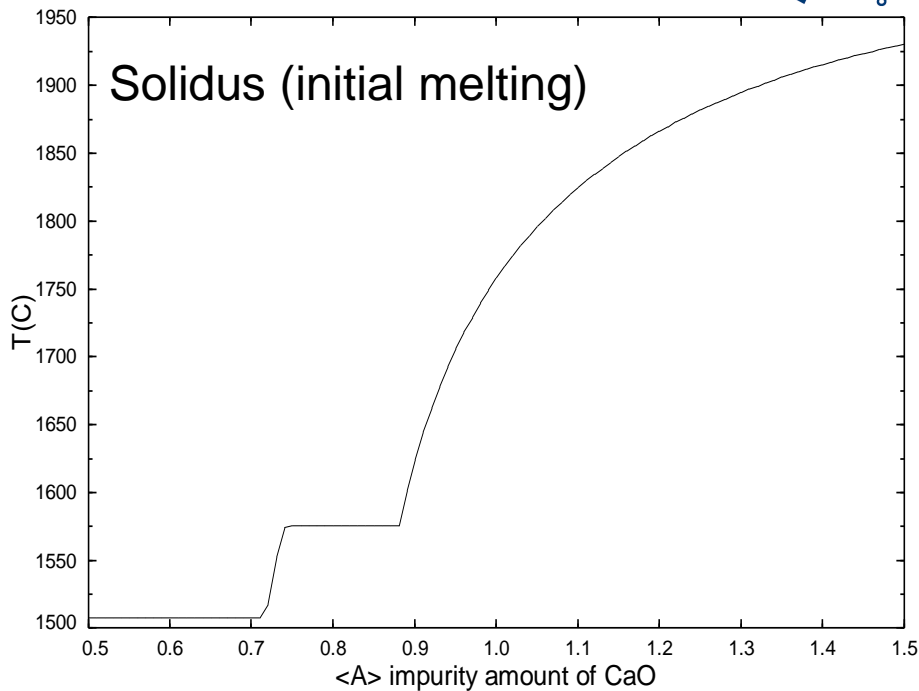
(1) pure MgO = 2825 °C

(2) impure MgO ?

MgO ore – impurity of CaO and SiO₂

<99.5-A> MgO + <A> CaO + 0.5 SiO₂

FactSage™



Melting temperature of MgO

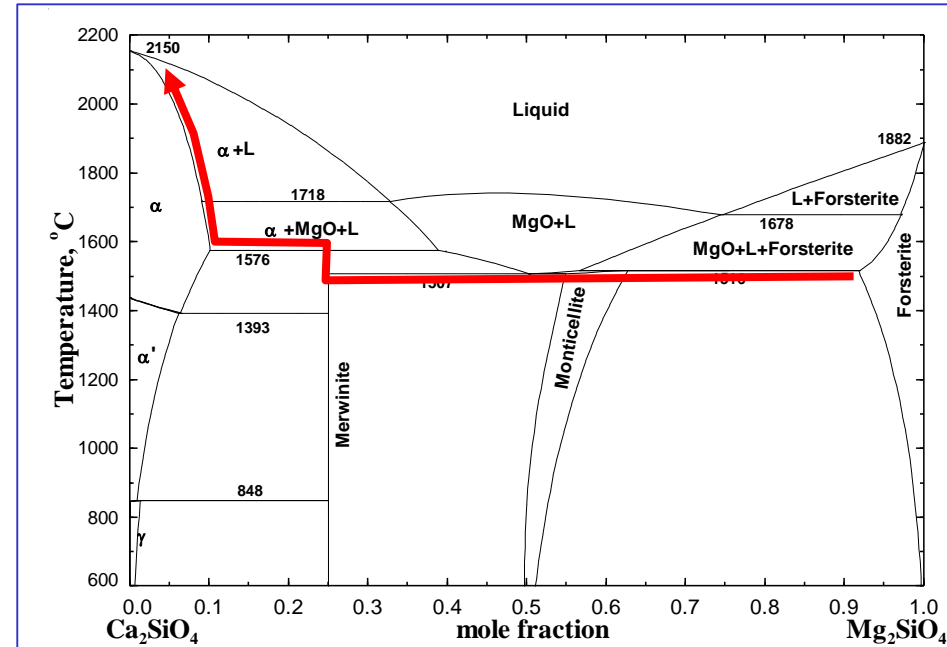
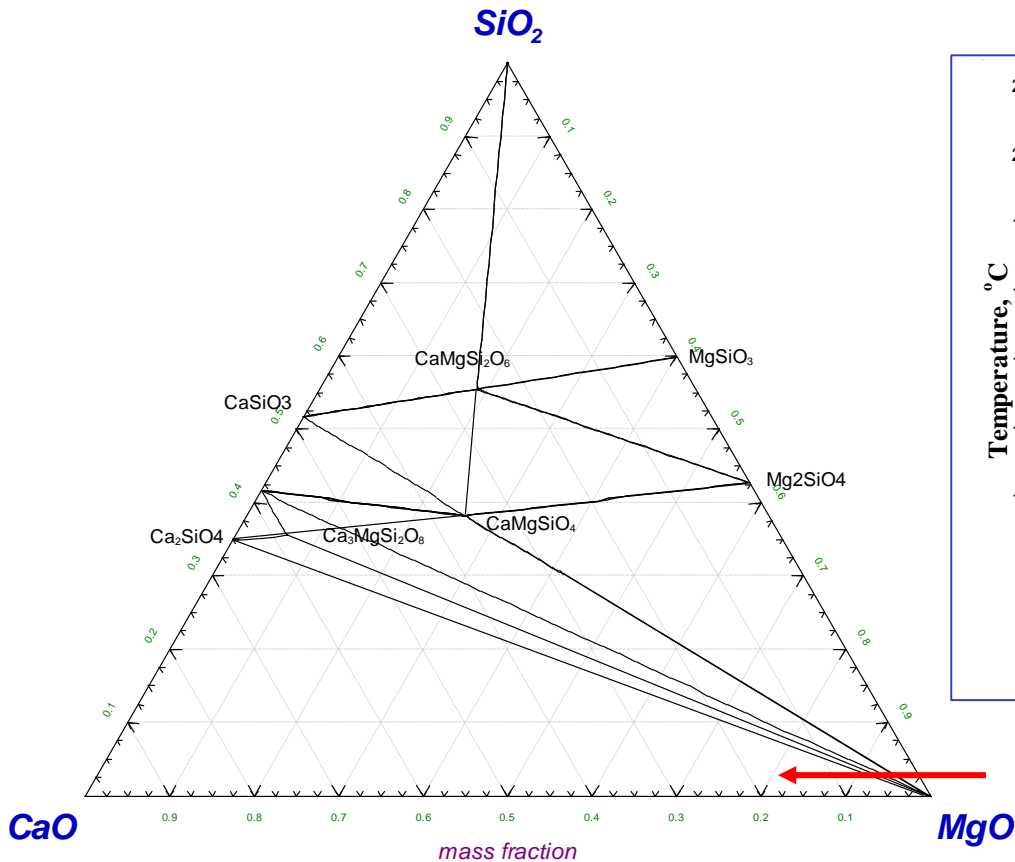
Melting temperature of

(1) pure MgO = 2825 °C

(2) impure MgO ?

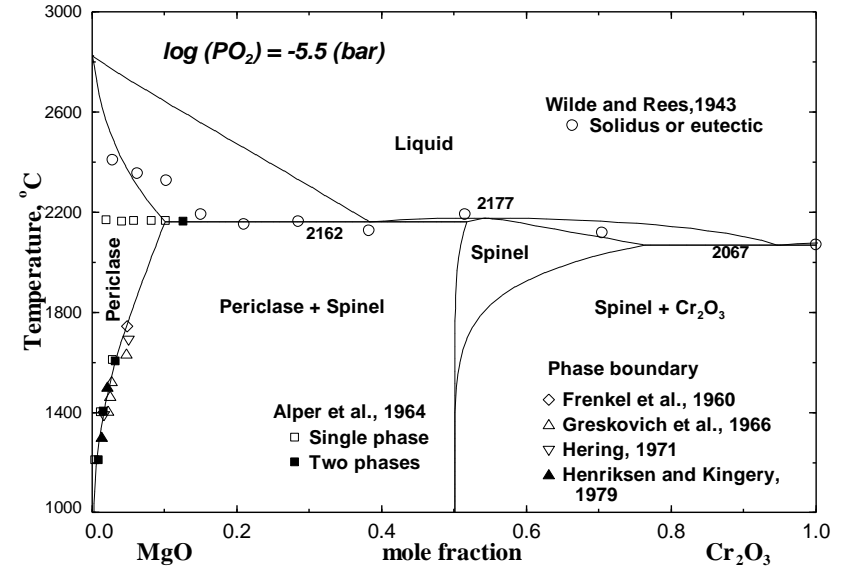
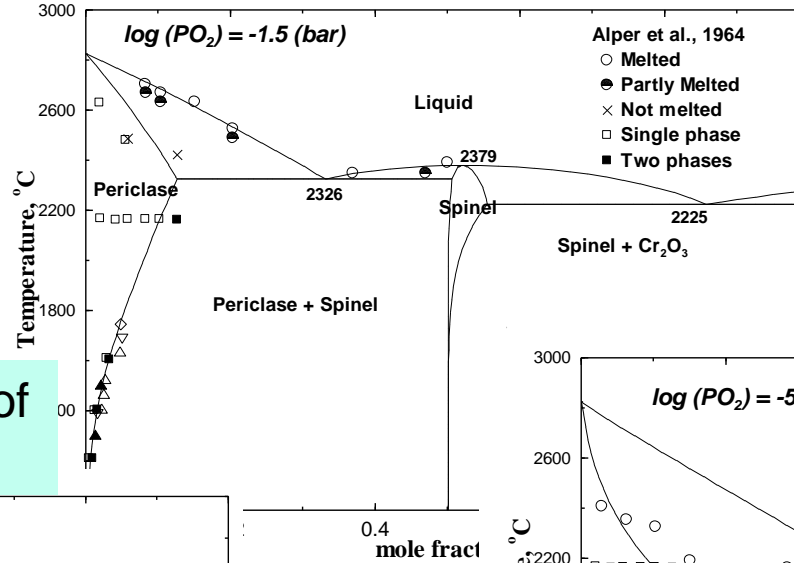
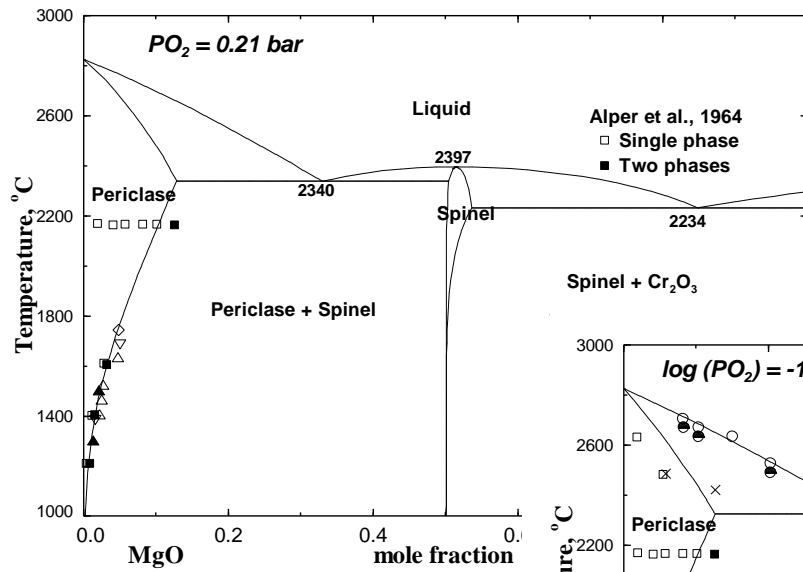
CaO - MgO - SiO₂

25°C, 1 atm

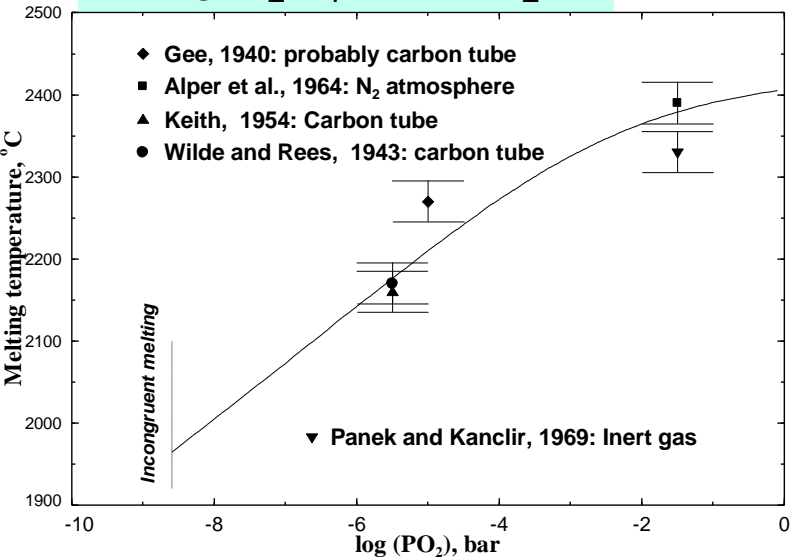


Melting profile with addition of CaO

MgO-Cr₂O₃ phase diagram



Melting temperature of MgCr₂O₄ with PO₂

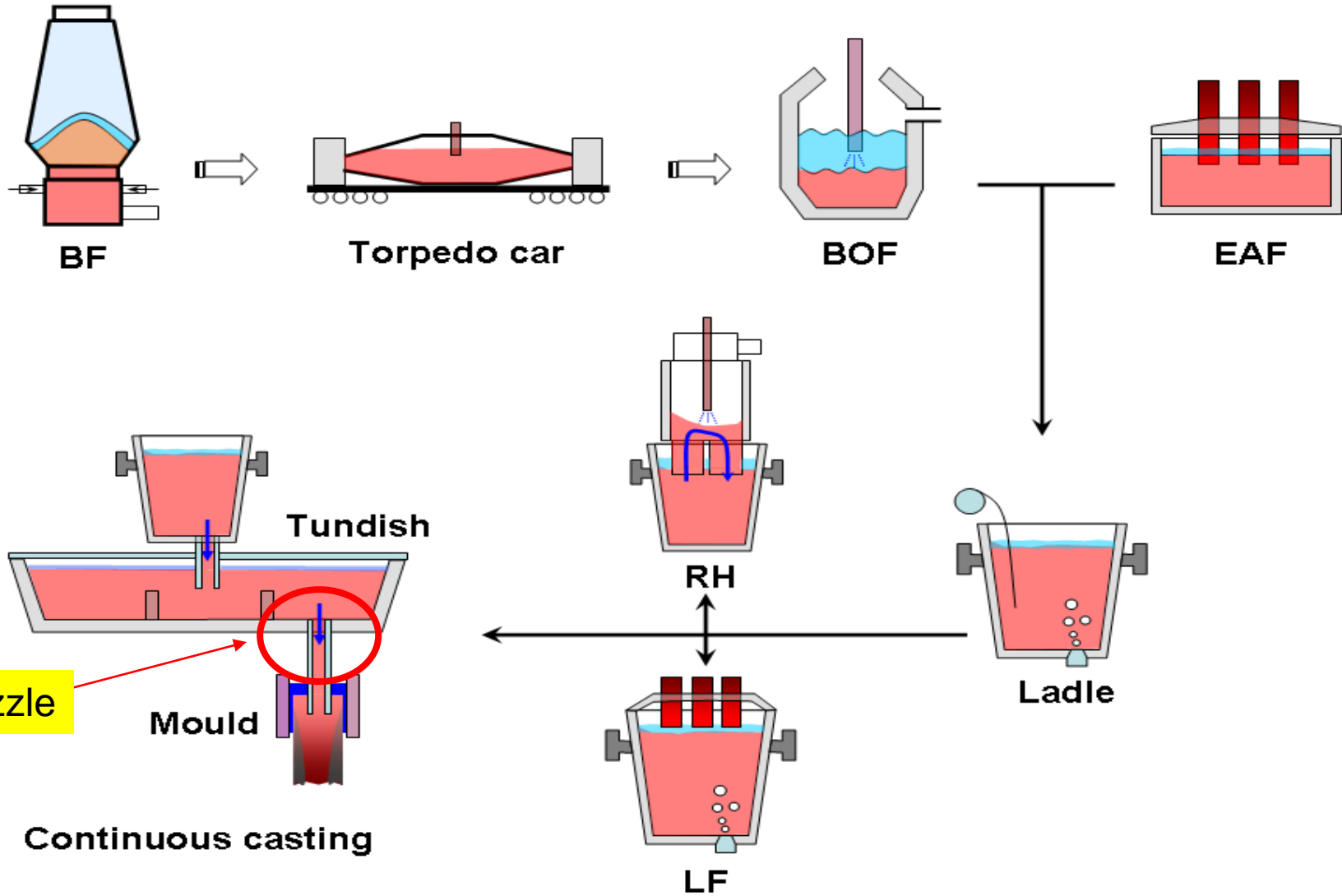


Decreasing
PO₂

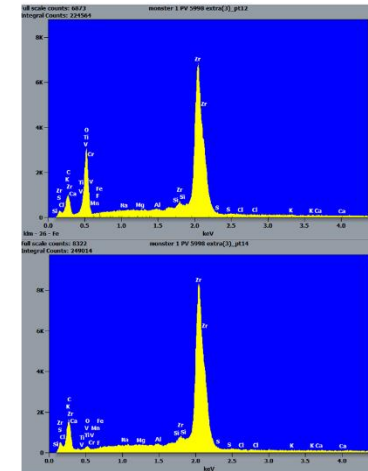
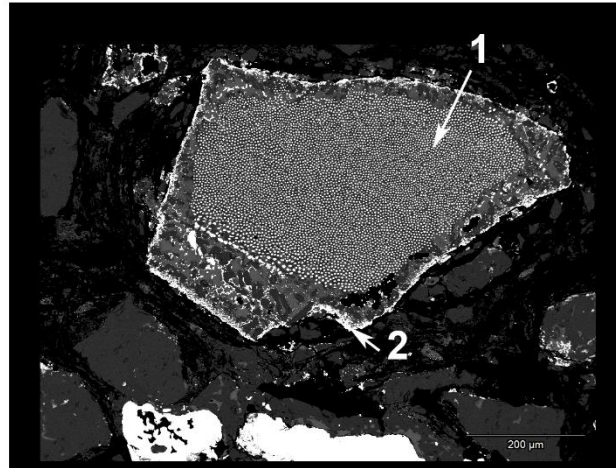
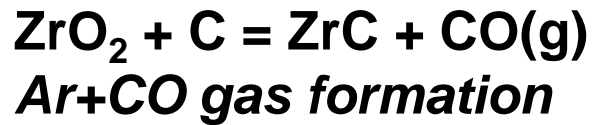
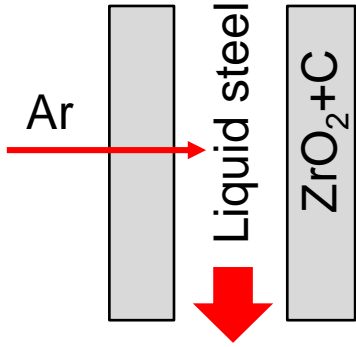
Nozzle refractory

- Carbothermal reduction process
- Inclusion formation

Nozzle clogging

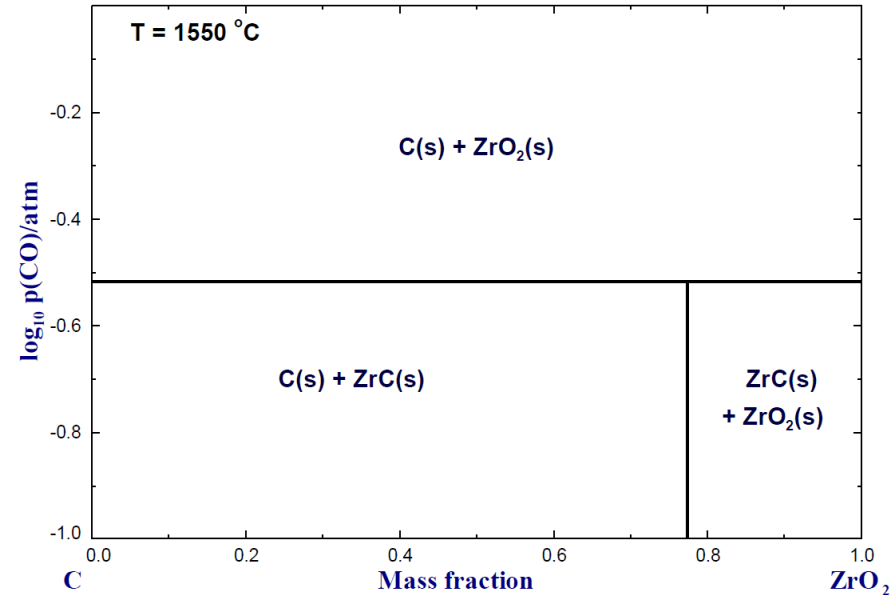
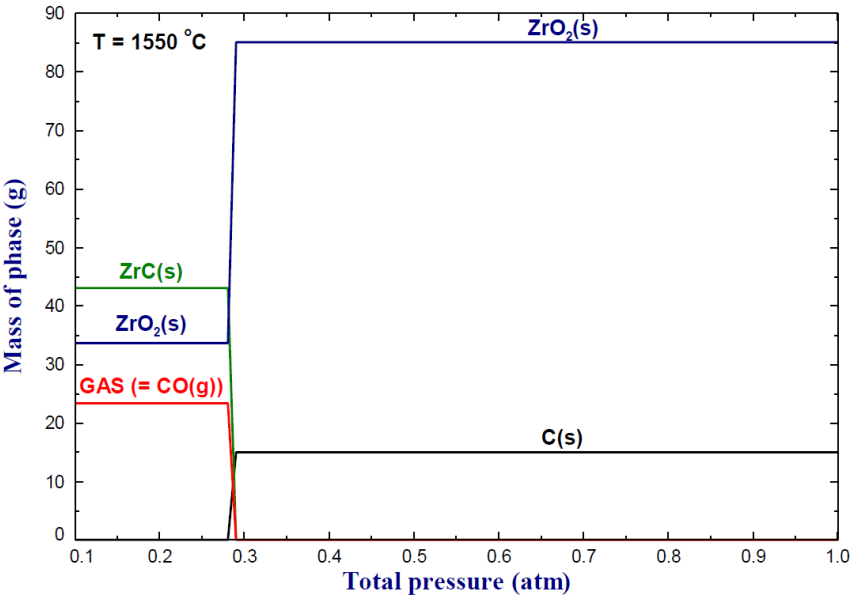


Carbothermic reduction of ZrO_2 to ZrC



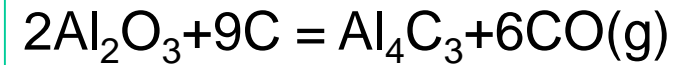
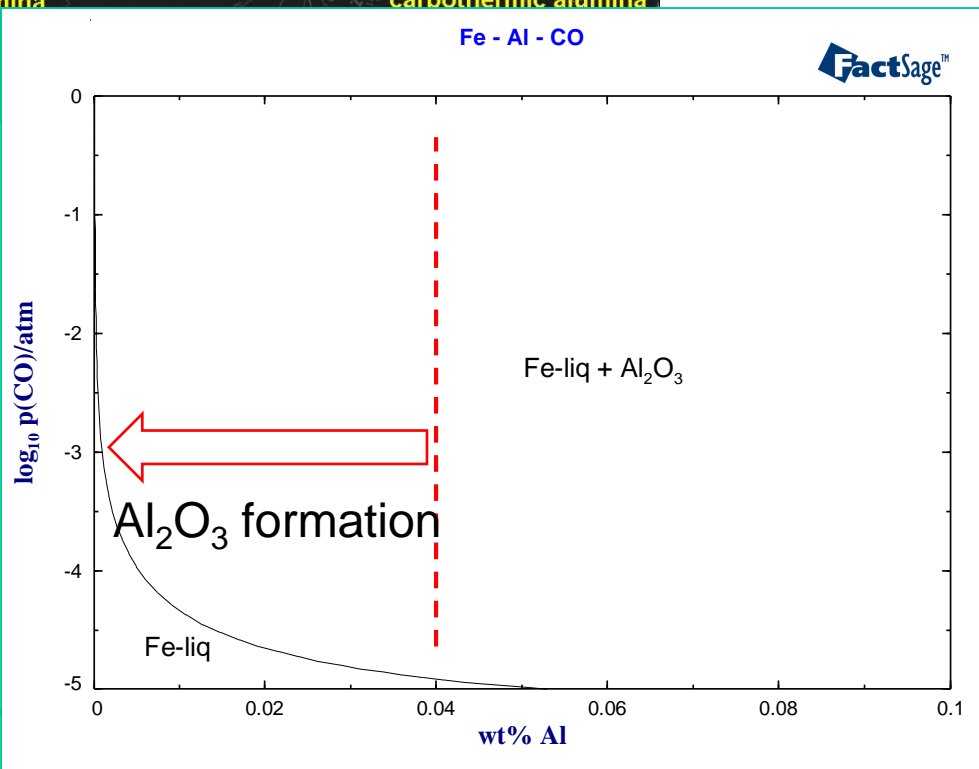
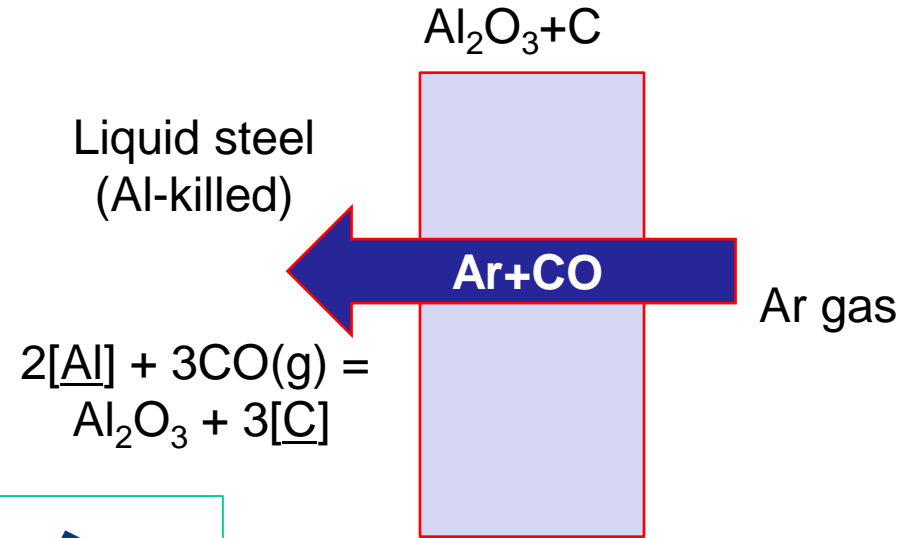
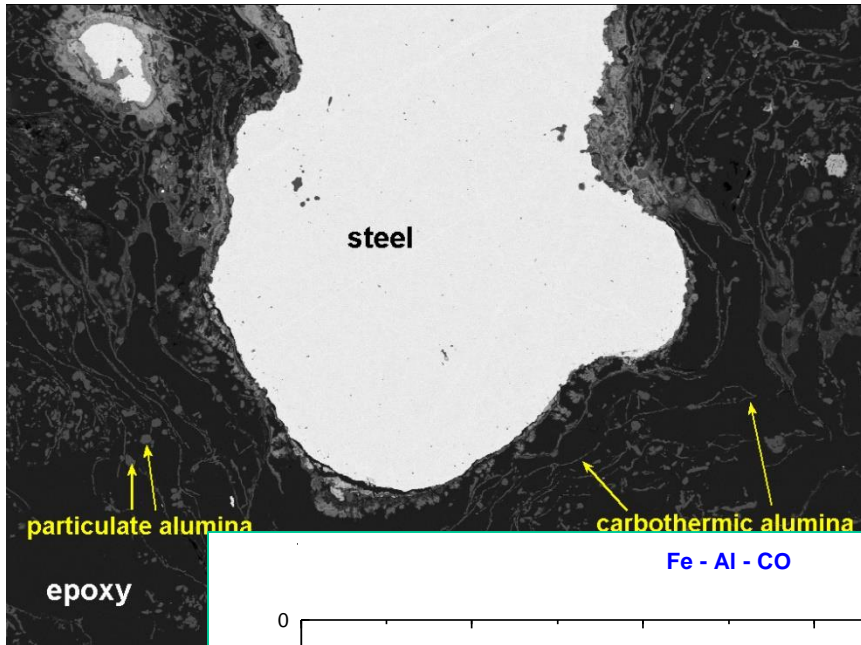
1 ZrO_2

2 ZrC

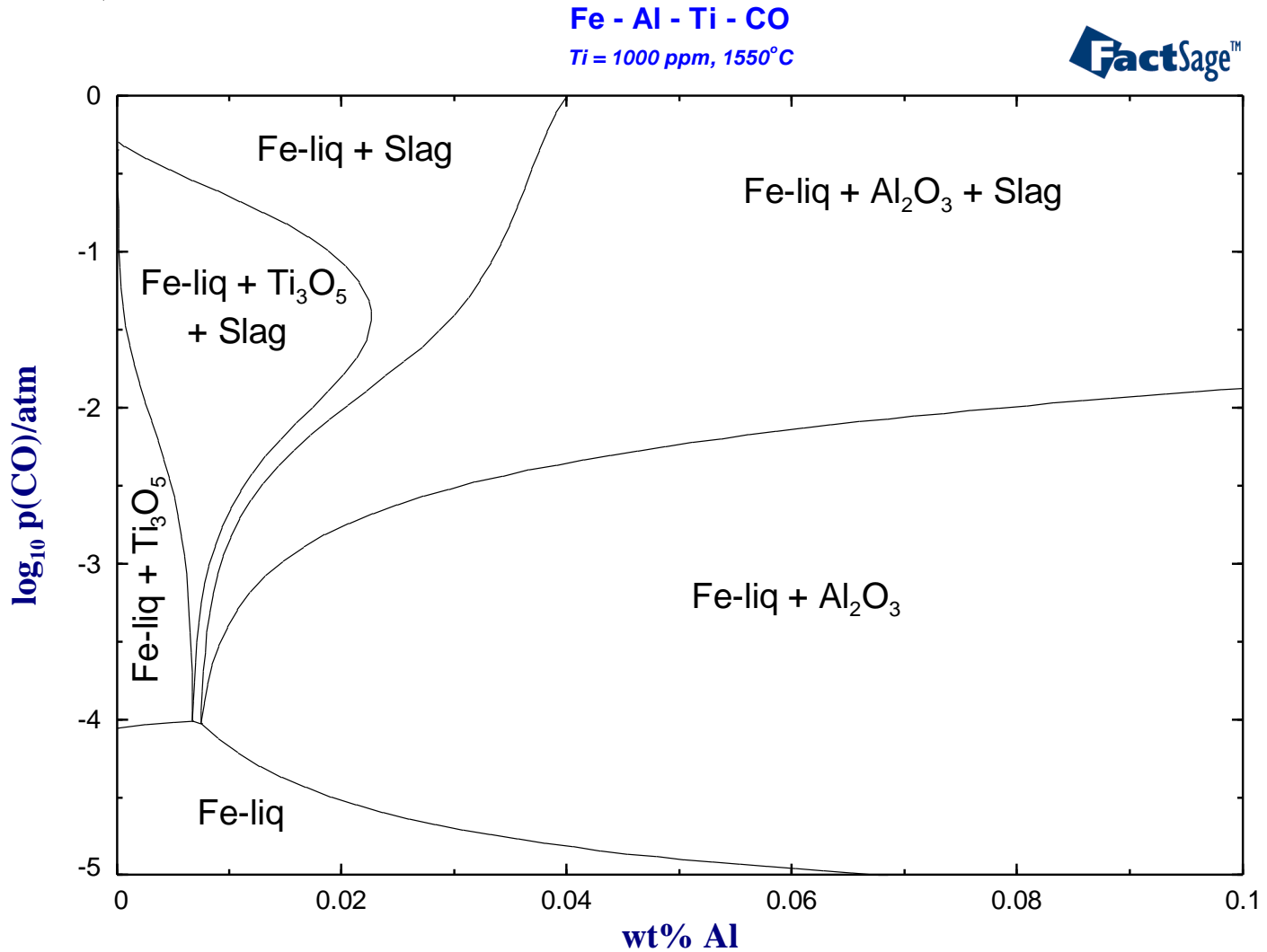


Ar gas injection can effectively reduce CO partial pressure
 → Carbothermal reduction of ZrO_2 to ZrC is possible.

Formation of Al₂O₃ in Nozzle: Al killed steel



Nozzle clogging in Al-Ti killed steel



Reoxidation of steel by CO gas through ceramic nozzle to form slag(Al-Ti-O) and Al₂O₃

Ultra High Temperature Ceramics

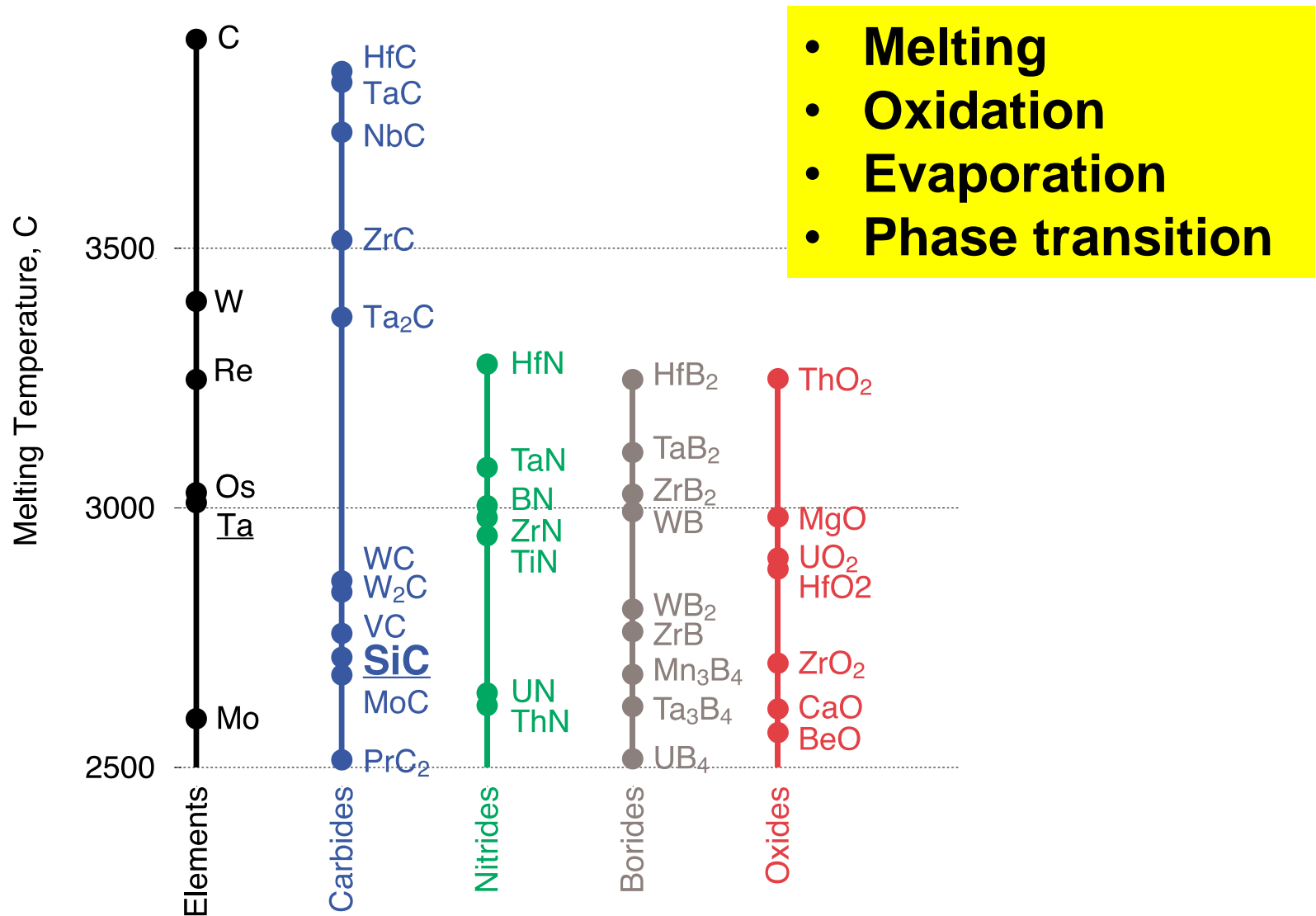
- Ceramic Matrix Composites (CMC)
- TBC coating: ZrO_2 stabilized by CaO , Y_2O_3 , etc.)
- Self-healing materials



LEAP, GE9X Engine



Ultra High Temperature Ceramics



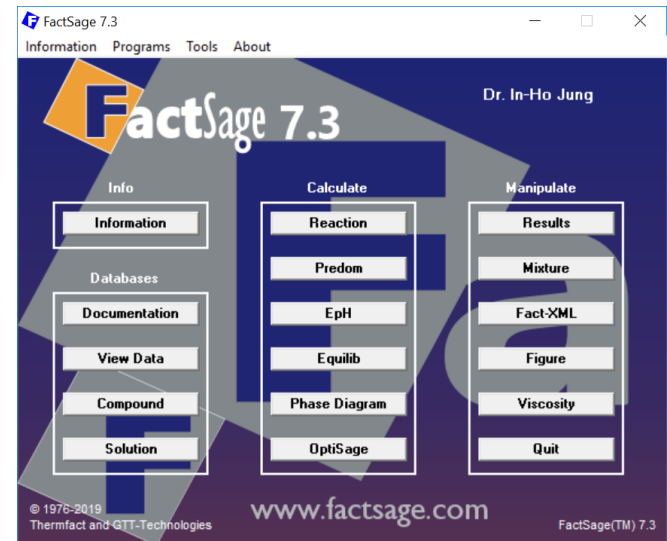
S. V. Ushakov, A. Navrotsky, *J. Am. Ceram. Soc.* 95 (2012) 1463–1482.

Carbides, Nitrides, Borides, Silicides (SpMCBN database)

- All ultra high temperature ceramics
- Oxygen, all other gas species
- Oxides (solid and liquids solutions)

ZrO₂-RE₂O₃ based Oxide

- ZrO₂-CaO, MgO,
- ZrO₂-RE₂O₃ are not available – in progress



Applications of phase diagram: Case Study

Oxidation

- Carbide \rightarrow Oxides
- ZrC, HfC, SiC

Evaporation

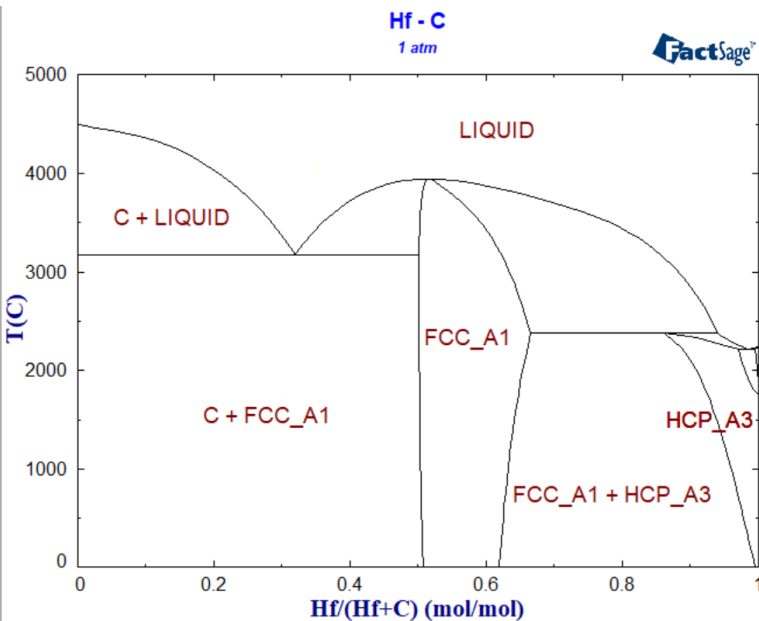
- $\text{SiO}_2 \rightarrow \text{SiO}$ gas

CMC

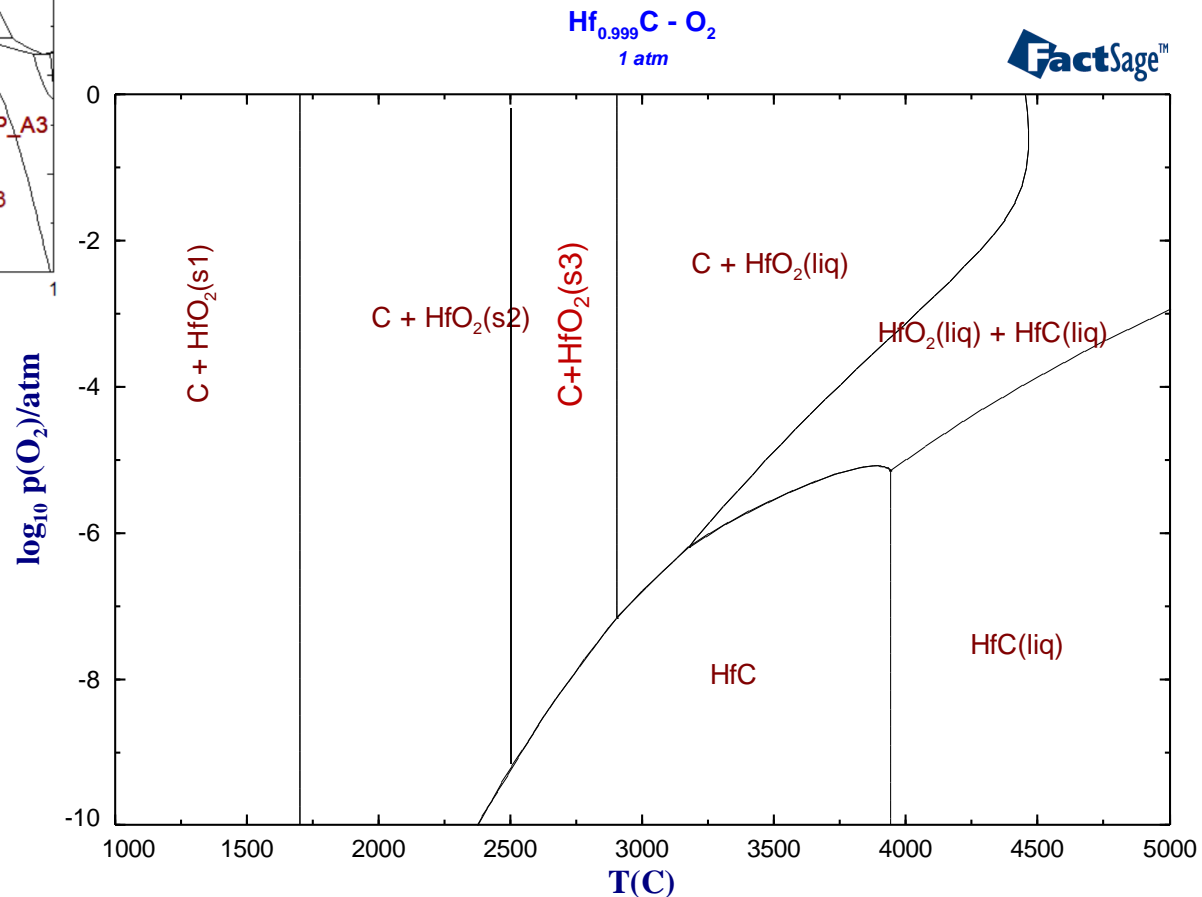
- SiC/SiC_f
- Self healing CMC

ZrO₂-CaO and ZrO₂-RE₂O₃

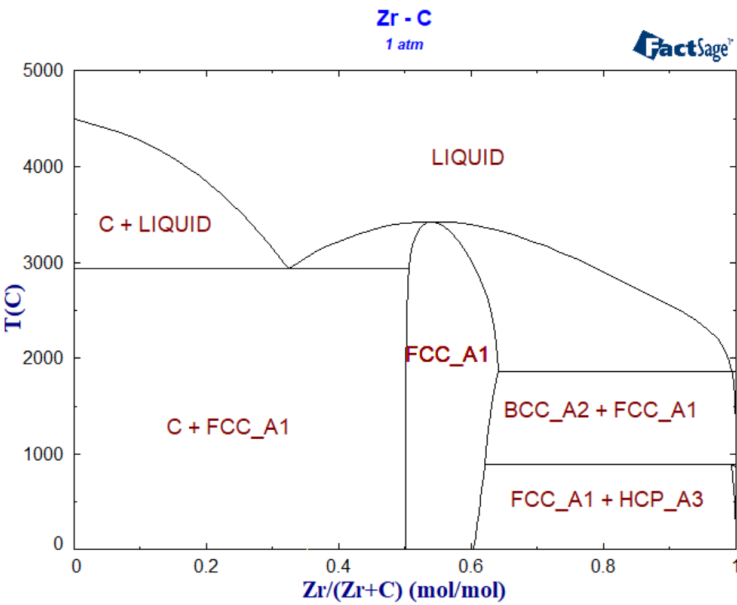
Oxidation: HfC



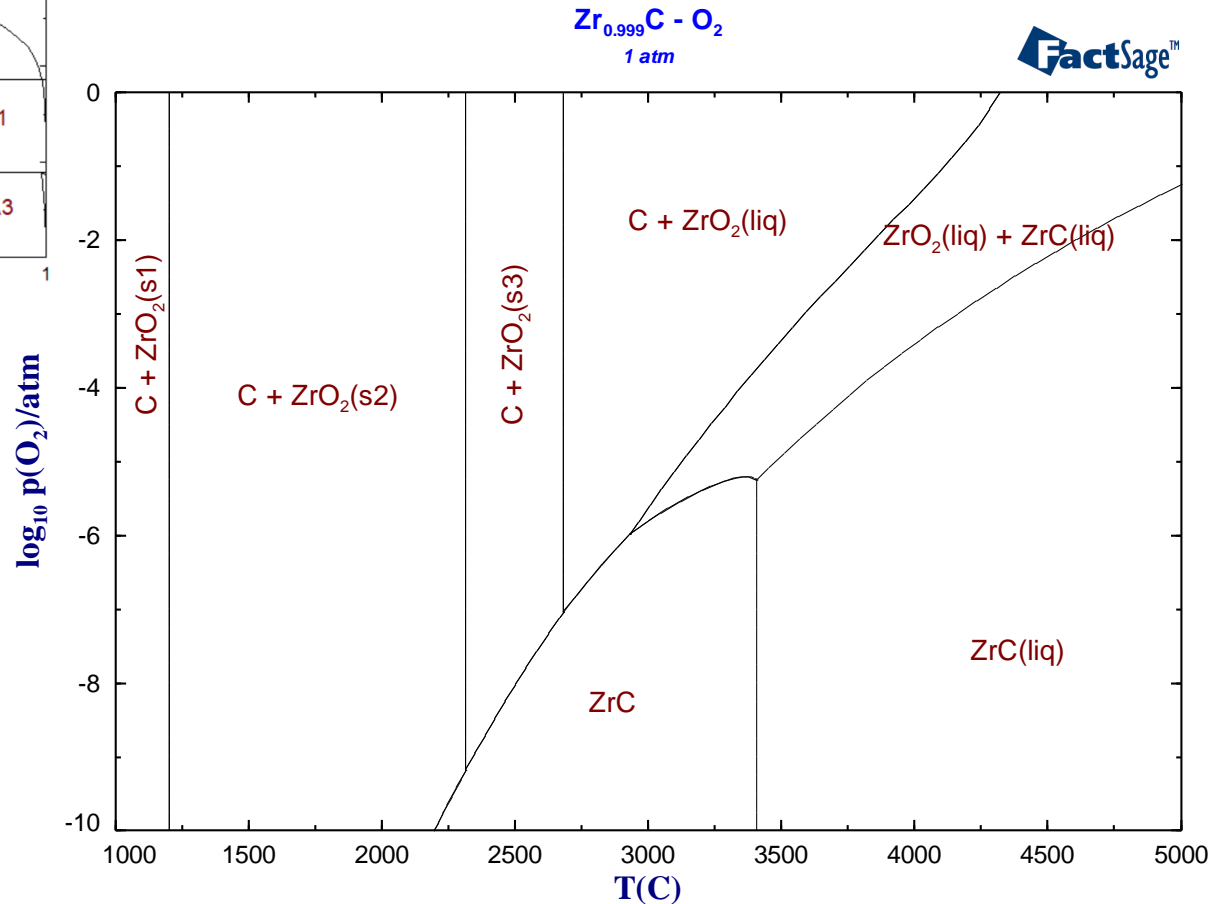
HfO₂
S3: Cubic
S2: Tetragonal
S1: Monoclinic



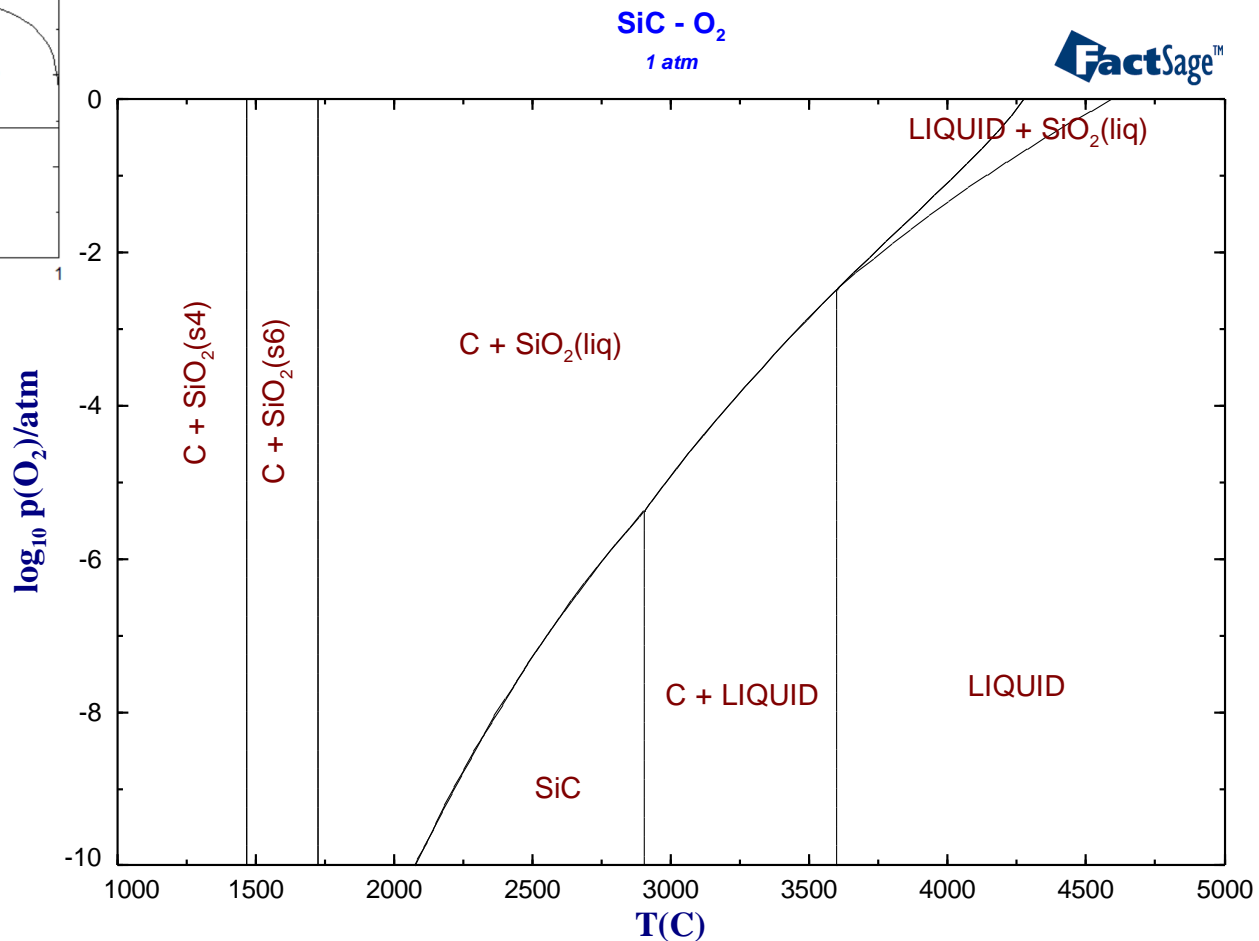
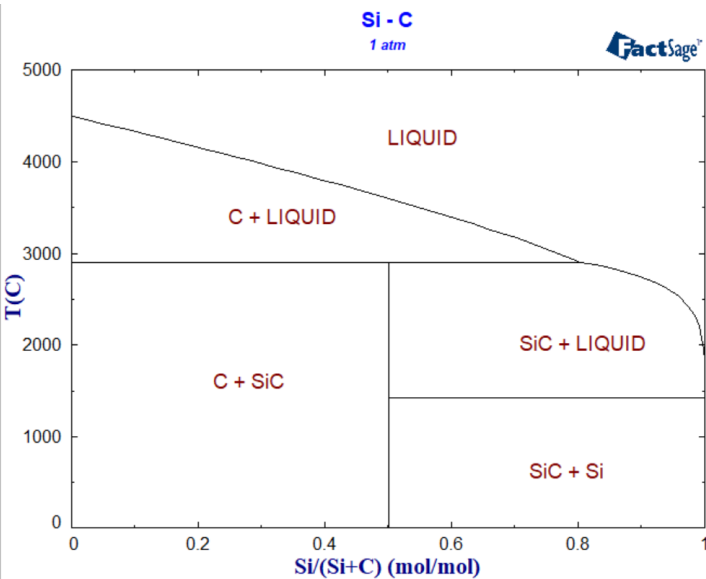
Oxidation: ZrC



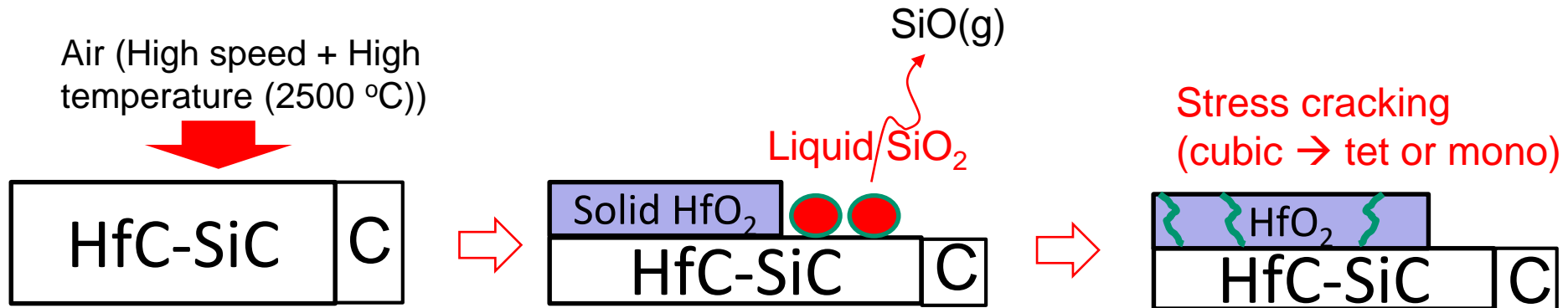
ZrO₂
S3: Cubic
S2: Tetragonal
S1: Monoclinic



Oxidation: SiC



Definition of problem



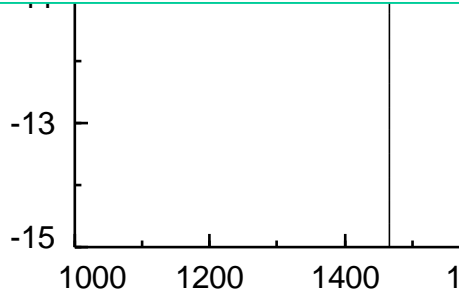
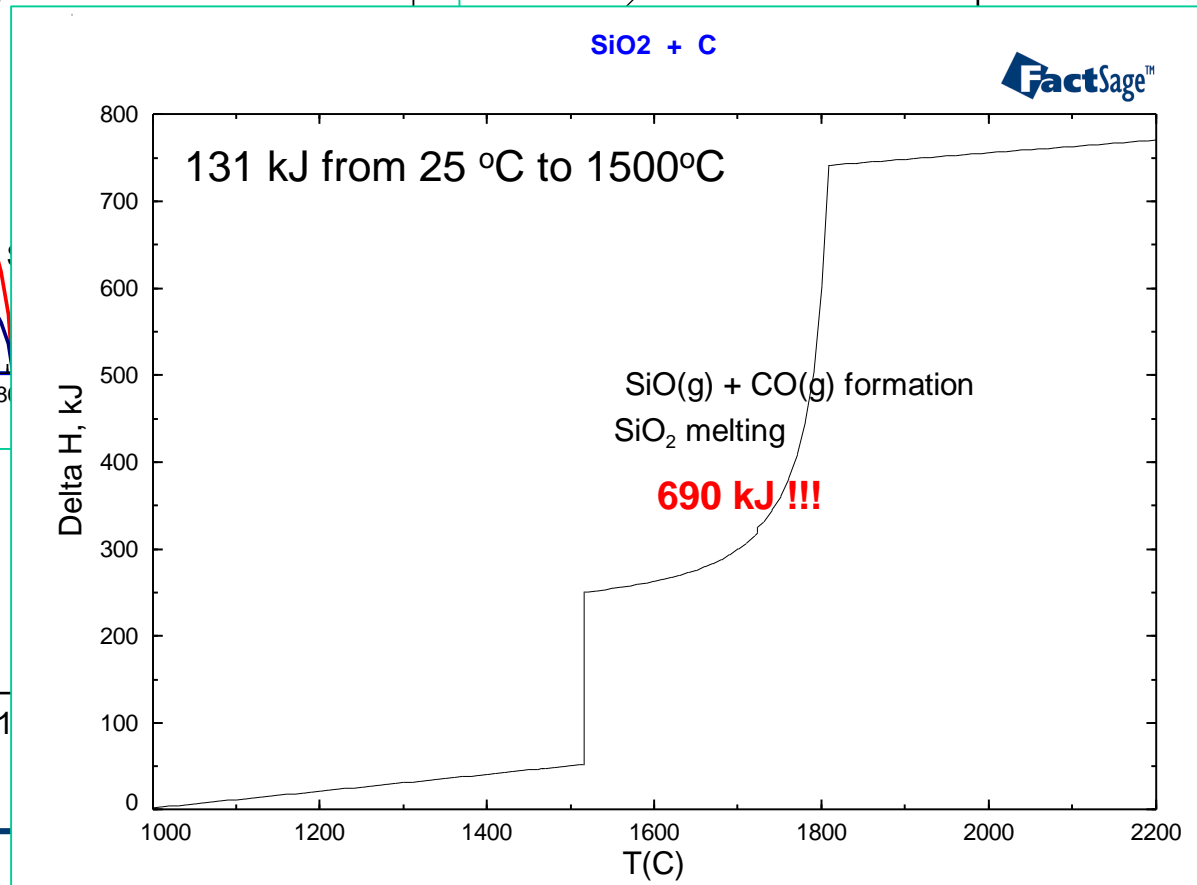
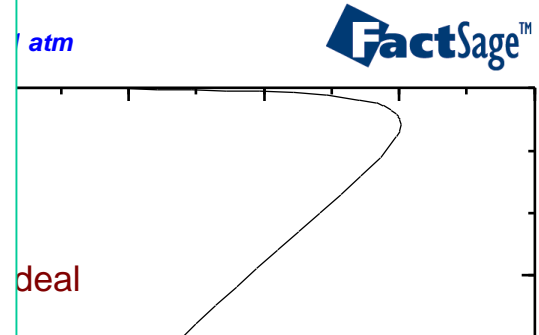
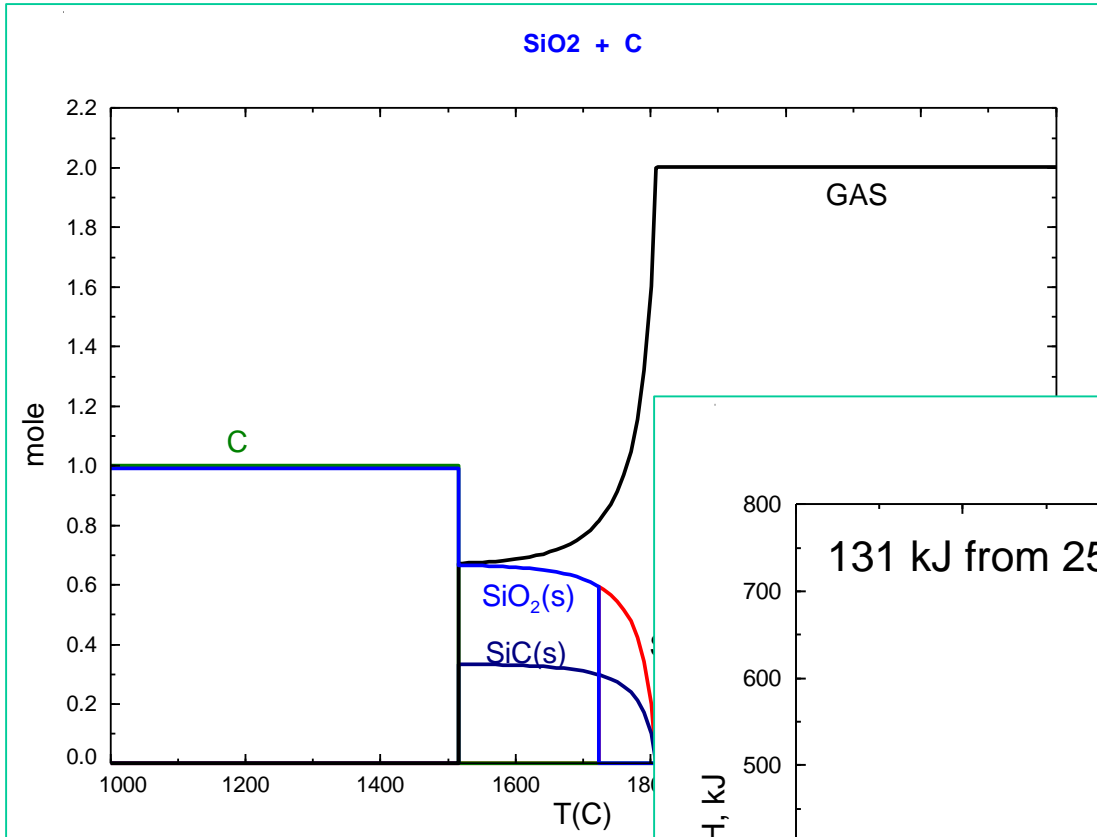
Solution: addition of xO , xC , yO , yC

Selection criteria of cubic HfO₂ stabilizer

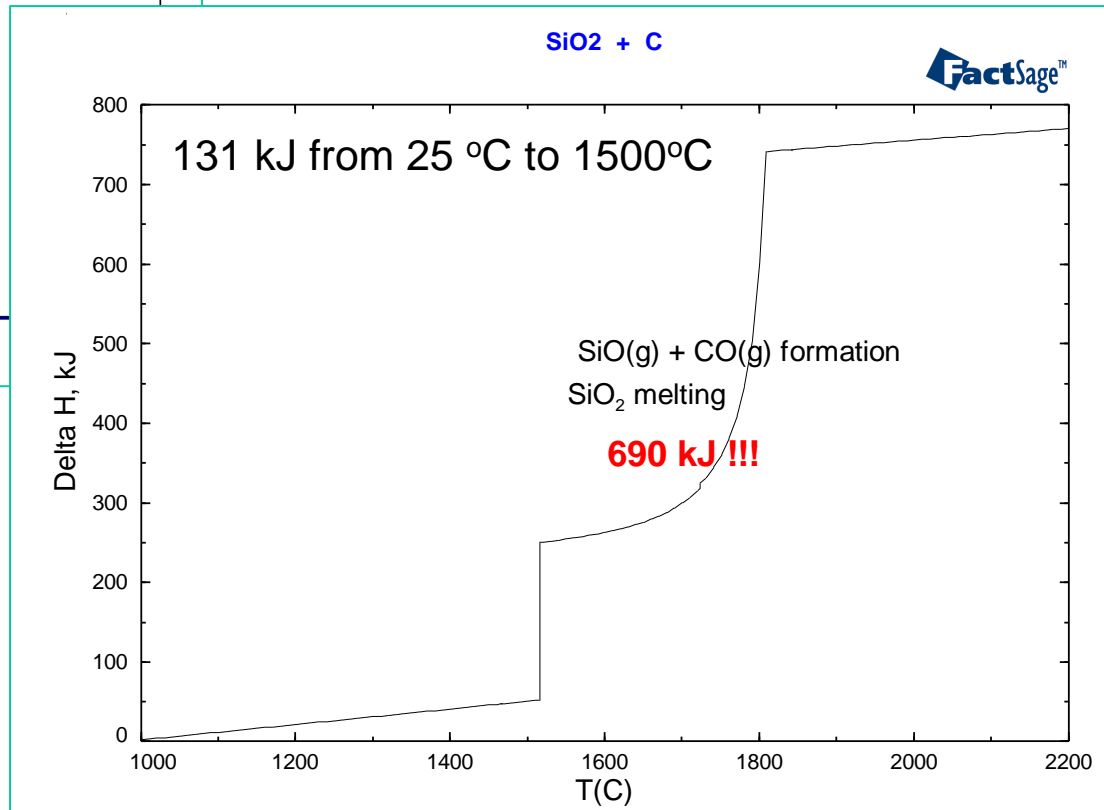
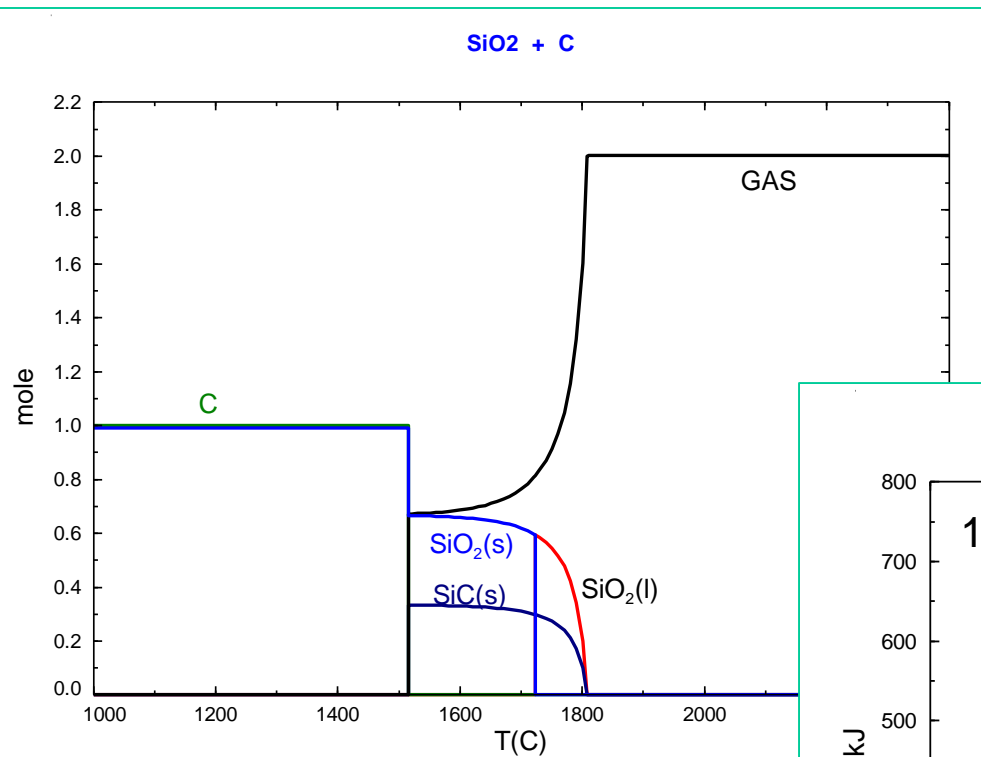
- (i) No melting at 2500 °C
- (ii) No (less) solid solution with HfC below 2000 °C – high thermal conductivity
- (iii) Effective stabilizer with small amount

→ Design the materials based on thermal stability and chemical reactions (phase diagrams)

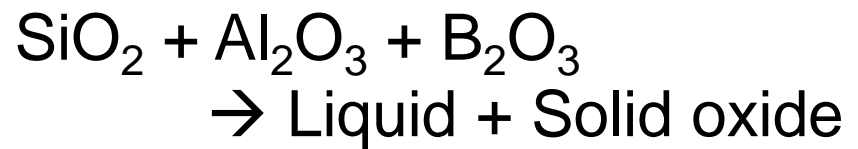
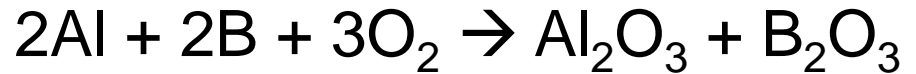
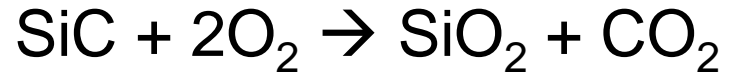
Evaporation: $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g})$



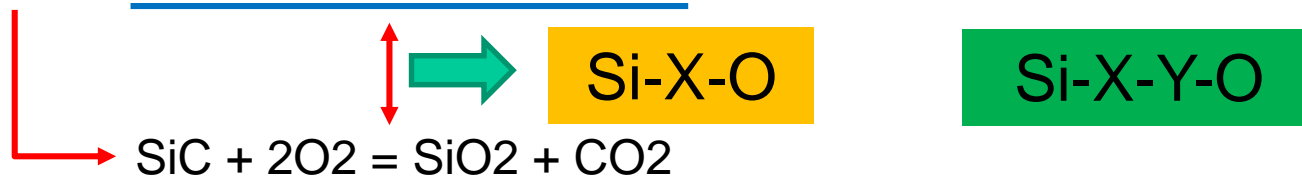
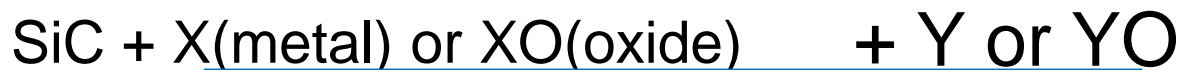
Evaporation: $\text{SiO}_2 + \text{C} \rightarrow \text{SiO}(\text{g}) + \text{CO}(\text{g})$



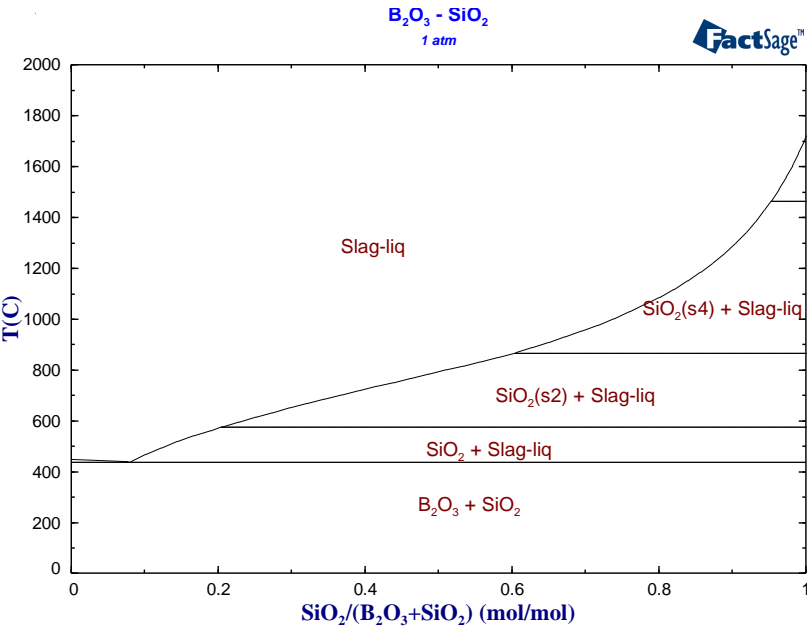
Self healing CMC



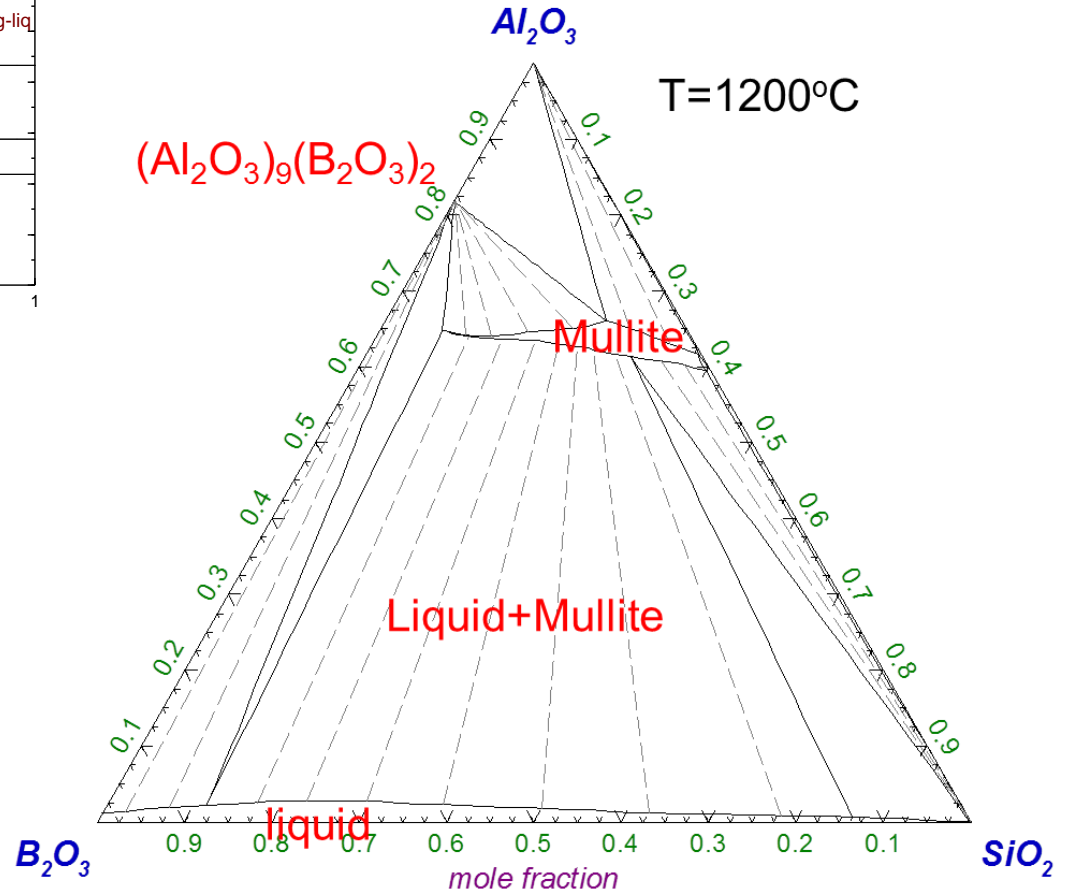
$\text{SiC} + (\text{Al-B})\text{metal} // \text{C}$ (Liquid can fill up the gap)



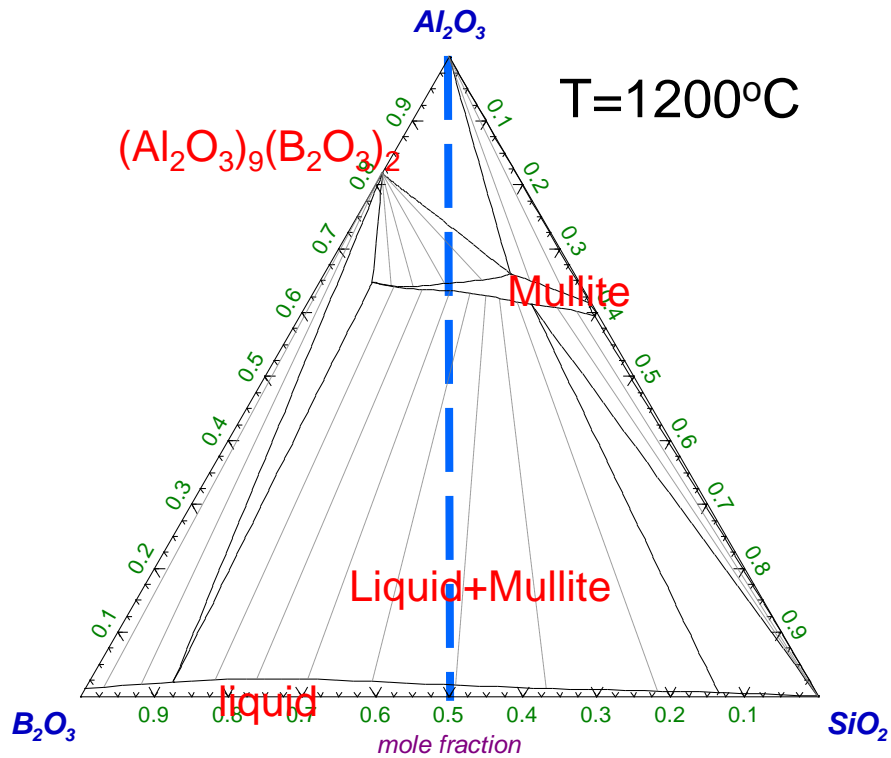
Self healing mechanism: Al_2O_3 - B_2O_3 - SiO_2 system



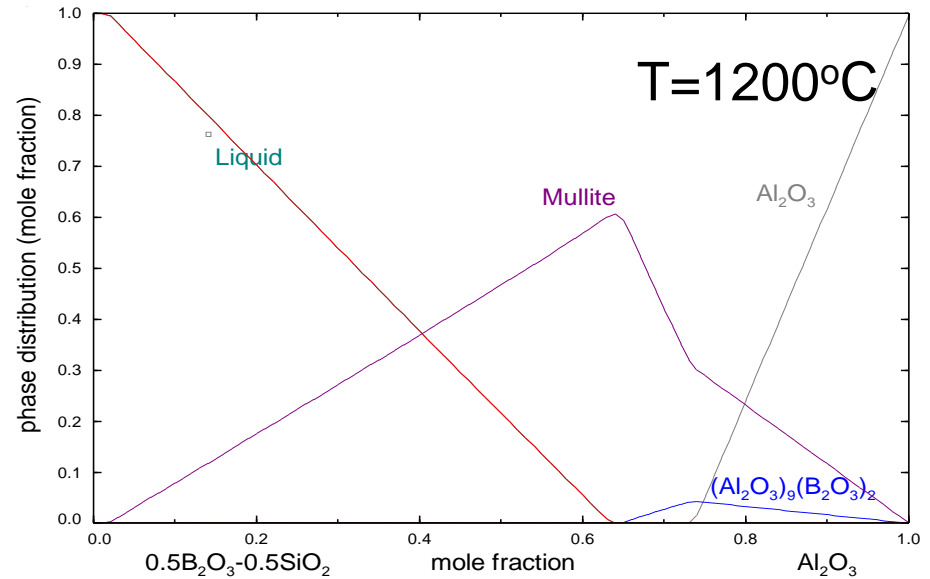
Liquid formation at low temperature



Self healing mechanism: Al_2O_3 - B_2O_3 - SiO_2 system

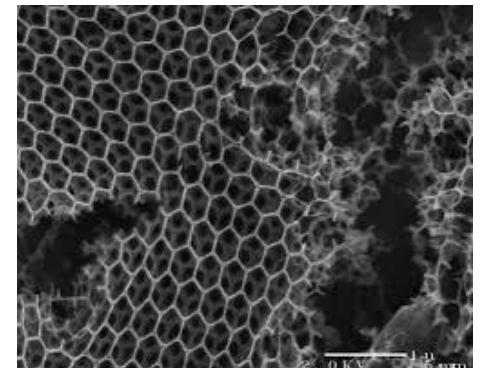


Increasing effective viscosity by forming liquid+solid mixture

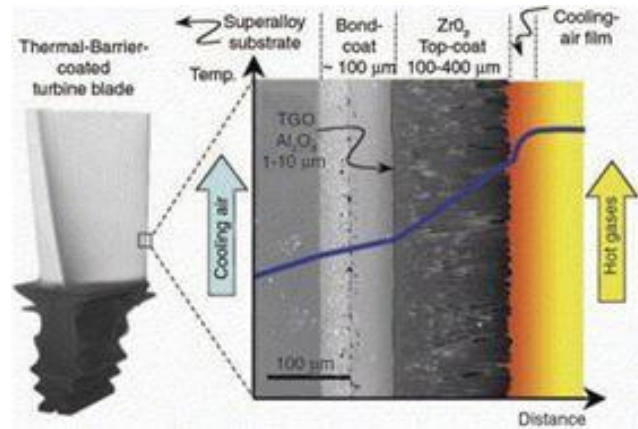


Materials Design and Structure Design

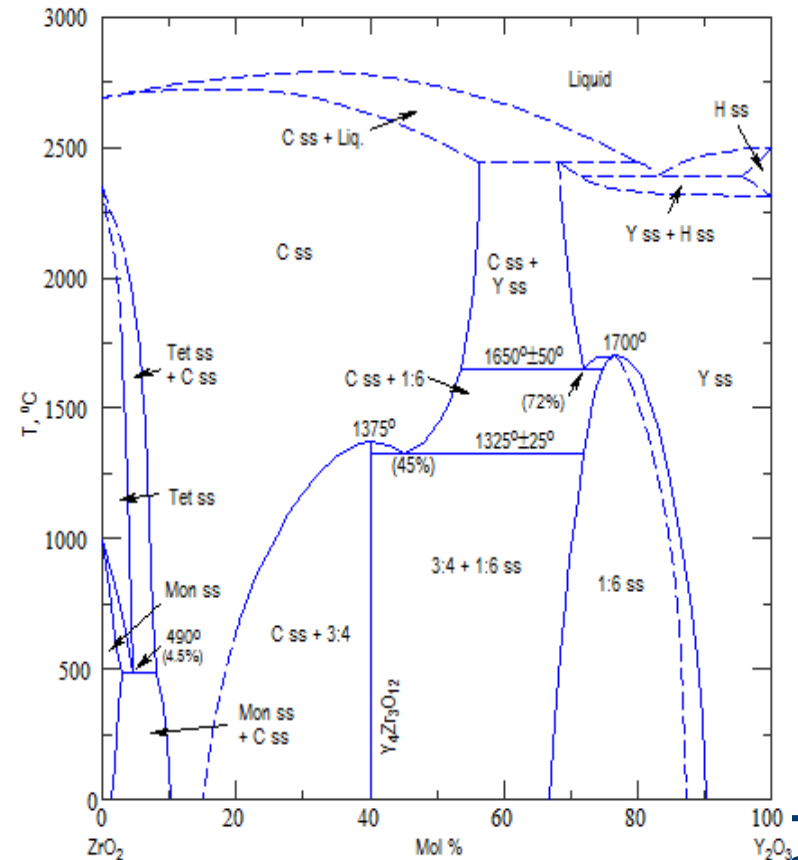
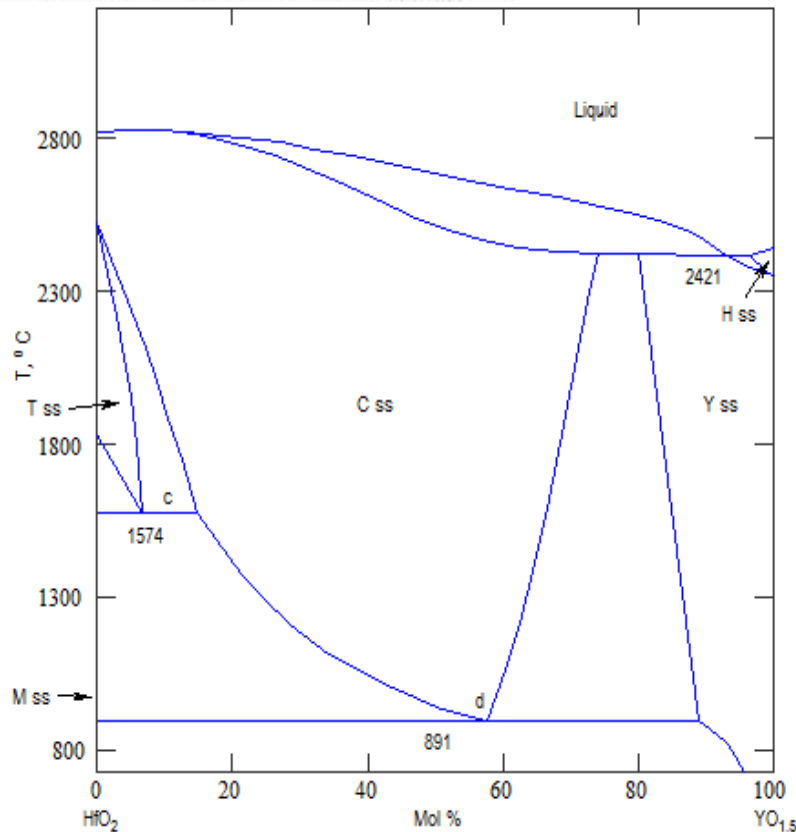
- Si-B-C + Al \rightarrow not good at high temperature because Liquid can be pulled out.
- Si-B-C + porous Al_2O_3 \rightarrow same chemistry but may be Good structure



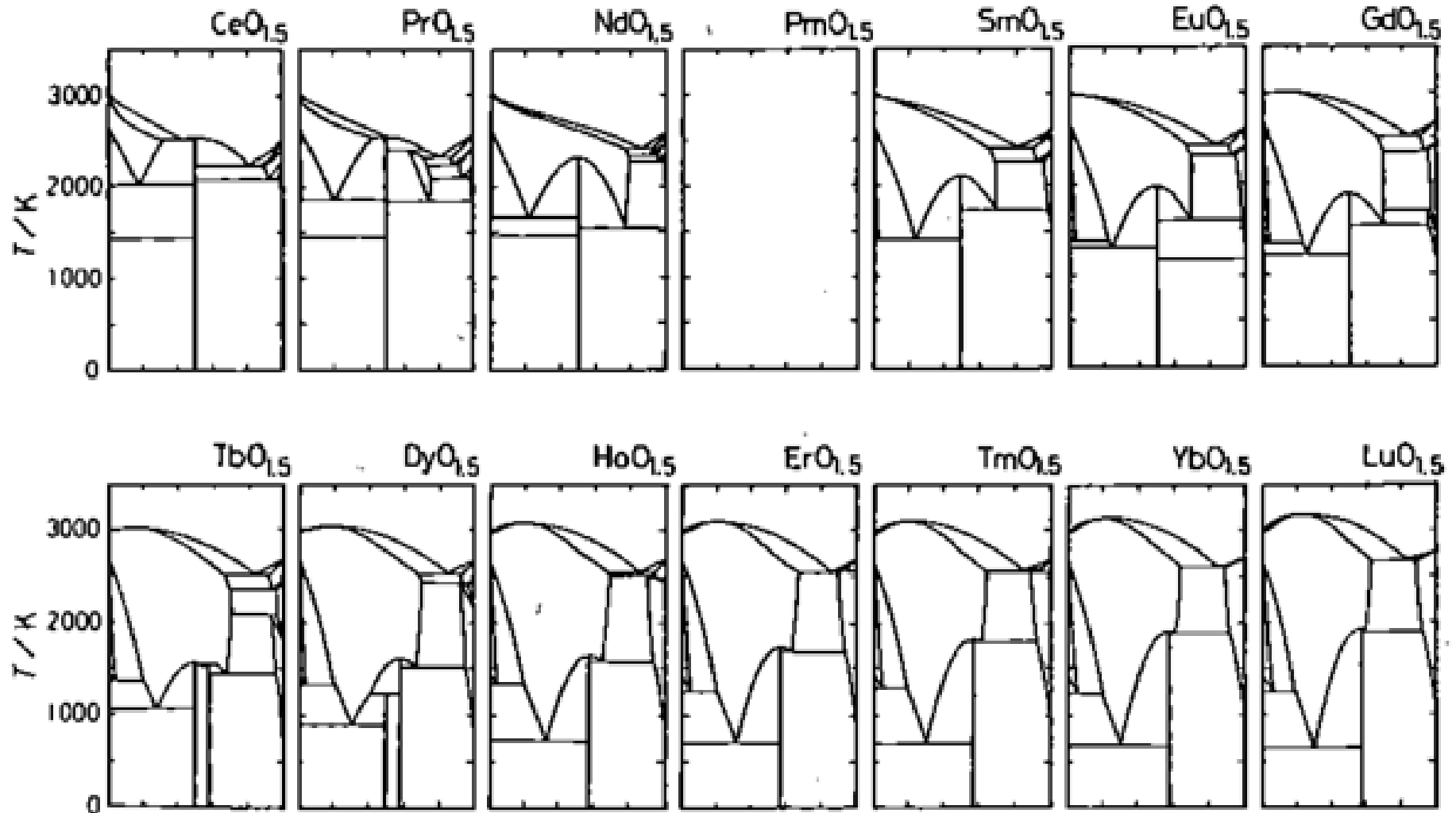
TBC coating: Cubic HfO_2 and ZrO_2 stabilization



Cubic HfO_2 and ZrO_2 stabilization by additives

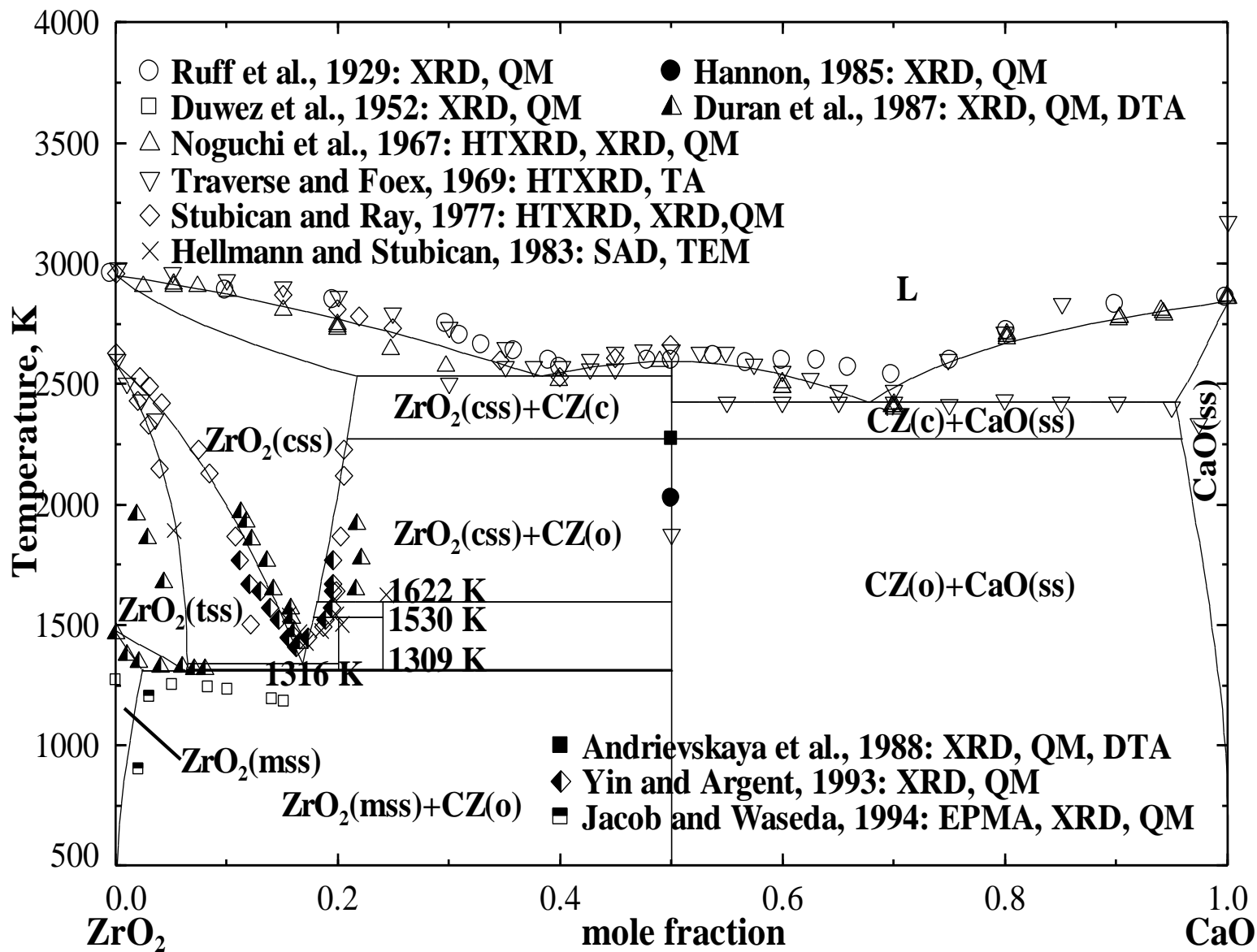


ZrO₂-Re₂O₃ phase diagram (Predicted)



H. Yokokawa, N. Sakai, T. Kawada. (1993), Science and technology of Zirconia V, pp. 59-68.

ZrO₂-CaO



Phase diagram is one of the most fundamental knowledge for the materials design and process optimization

- Continuous support for the experimental phase diagram study and thermodynamic properties measurement are necessary.
- Computational thermodynamic database, such as FactSage, is an useful tool for complex phase diagram and chemical reaction analysis.

Acknowledgement

Steelmaking consortium project (2009~2020) – 2018 Annual meeting, Seoul, Korea



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TATA STEEL

voestalpine

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