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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FactSage™

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Content

- 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, O_2, Al_2O_3, etc.)

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

$$H_T^o = \Delta H_{298\,K}^o + \int_{298\,K}^{T} C_p dT \qquad S_T^o = S_{298\,K}^o + \int_{298\,K}^{T} \frac{C_p}{T} dT$$

: $C_p = a + bT + cT^{-2} + dT\ln T + \cdot\cdot\cdot$ 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)~~, ~~H_2O(l)~~, ~~H_2O(g)~~, H_2(g), O_2(g), ~~O(g)~~, ~~CaO~~, ~~FeO~~, C(s), ~~CO_2~~, ~~CO~~,.

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

Gibbs Energy

2. Chemical reaction between pure compounds (No solution)

$$nA + mB = A_nB_m$$

$$\Delta G^o_{rxn} = G^o_{A_nB_m} - (nG^o_A + mG^o_B)$$

$$= \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

In many thermo books, these ΔH^o_{rxn} , ΔS^o_{rxn} 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.

Gibbs Energy

3. Chemical reaction involving gas

$$nA + mO_2(g) = A_nO_{2m}$$

$$\Delta G_{rxn} = G^o_{A_nO_2} - (nG^o_A + mG_{O_2})$$

$$\Big\downarrow$$

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

for gas species i

$$= \Delta G^o_{rxn} - mRT\ln P_{O_2}$$

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

$$\Delta G^o_{rxn} = -RT\ln(\frac{1}{P_{O_2}{}^m})$$

Gibbs Energy

3. Chemical reaction involving gas (continue)

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

At Equilibrium

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

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

K_{eq}: Equilibrium constant

Gibbs Energy

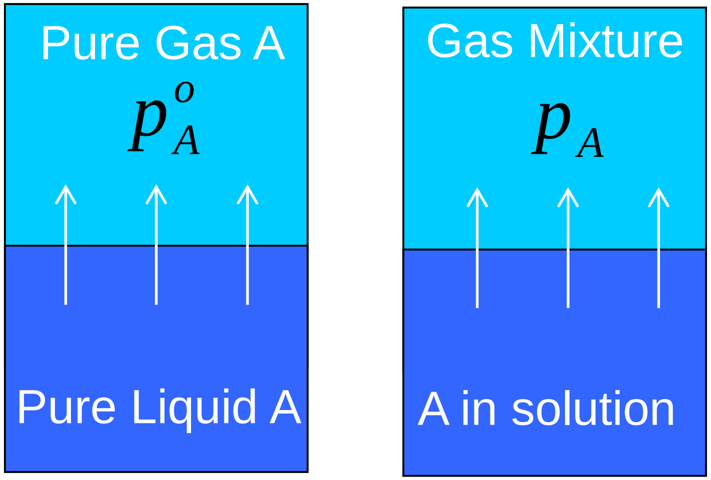
4. Chemical reaction involving solid or liquid solution

$$G_{i(in\,soln)} = G^{o}_{i(pure)} + RT\ln(a_i)$$

a: activity

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

Definition of activity



Pure Gas A

p^{o}_{A}

Pure Liquid A

Gas Mixture

p_A

A in solution

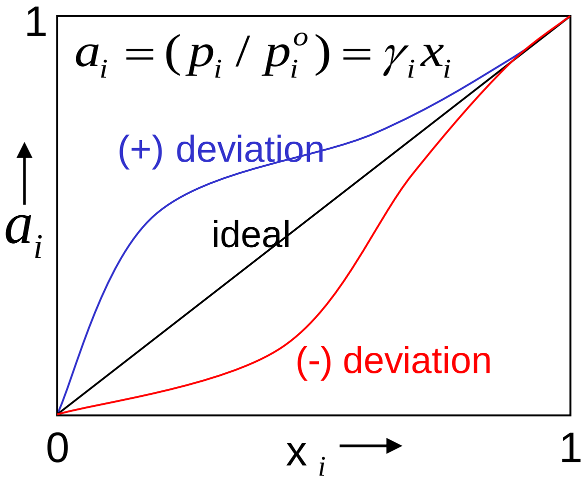
$$a_A = \frac{P_A}{P^{o}_{A}} = \gamma_A x_A$$

∴ activity is movement of species in solution

Gibbs Energy

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

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

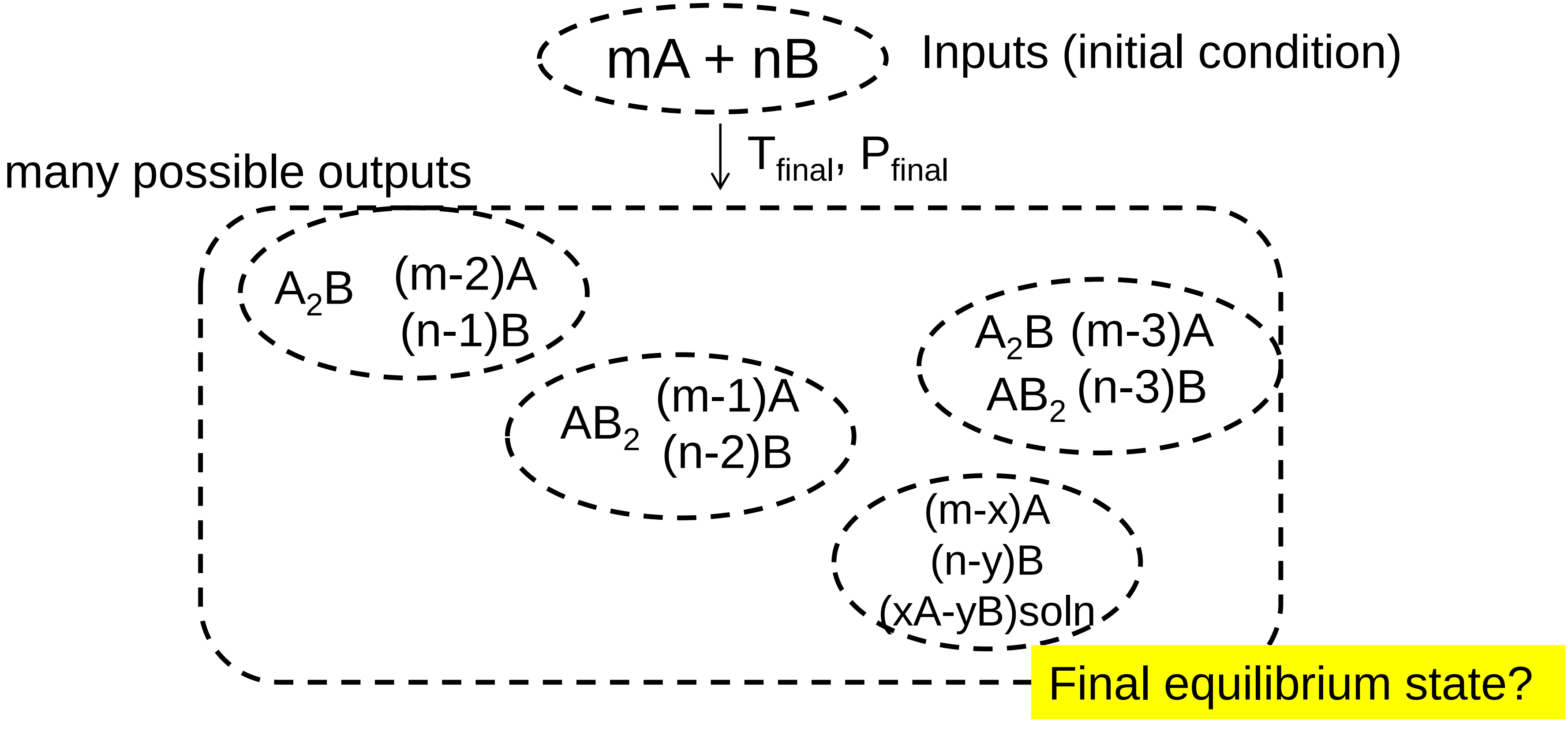
* FactSage solution database contains the model and model parameters to calculate G_i and eventually get a_i

Gibbs Energy

In most of thermodynamic book, we always calculate equilibrium condition

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

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



mA + nB

Inputs (initial condition)

T_{final}, P_{final}

many possible outputs

A_2B (m-2)A (n-1)B

AB_2 (m-1)A (n-2)B

A_2B (m-3)A AB_2 (n-3)B

(m-x)A (n-y)B (xA-yB)soln

Final equilibrium state?

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

i) Put inputs amount

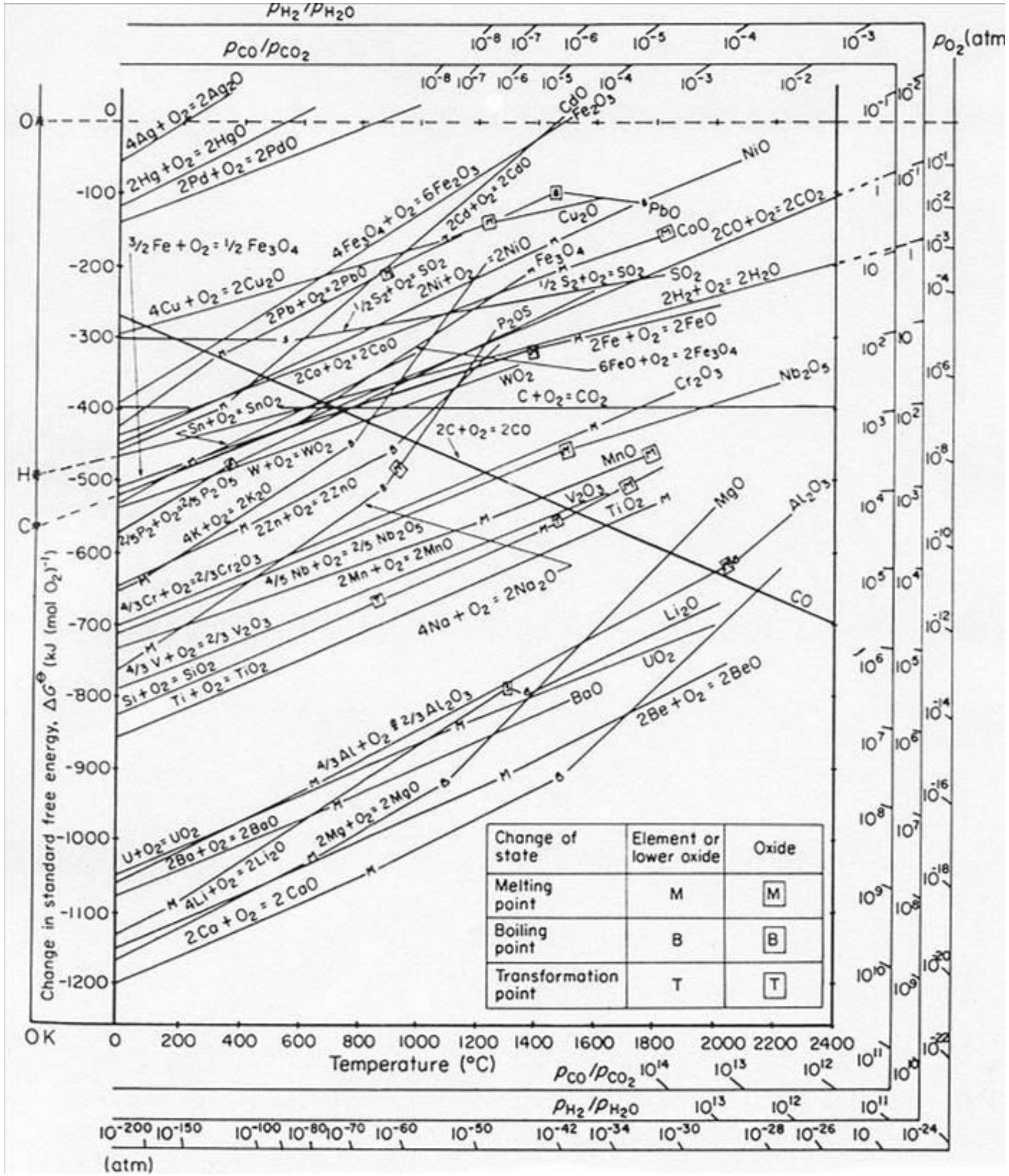
ii) Select all possible phases (solid compounds, solid solutions, liquid solutions, gases)

iii) Set T_{final} and P_{final}

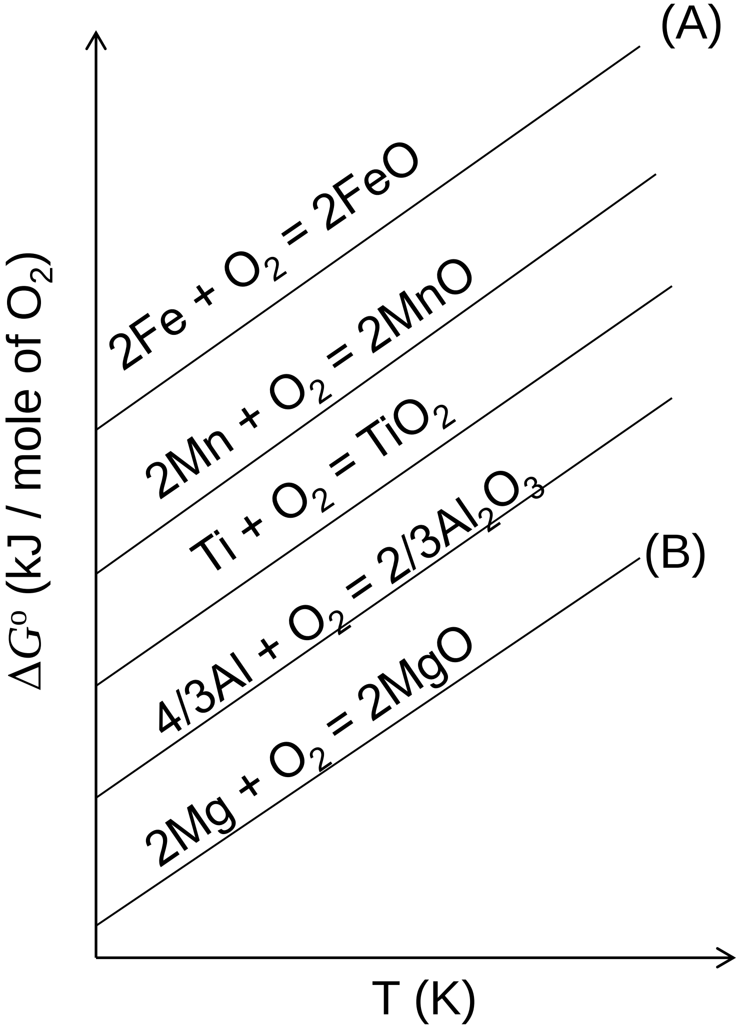
iv) Calculation (Gibbs energy minimization routine)

v) Equilibrium phase assemblage

Ellingham Diagram



Ellingham Diagram



- Collection of ΔG^o for oxidation reaction

$mA + O_2 = A_mO_2$ (reference: 1 mol of O_2)

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

$$A + O_2 = AO_2$$

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

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

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

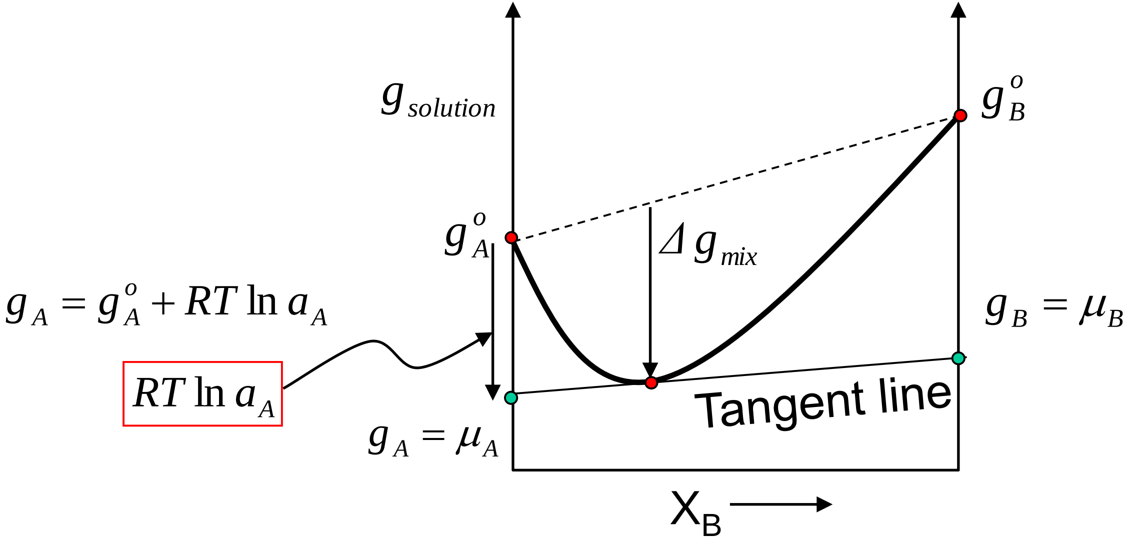
Solution thermodynamics

A-B solution, (Solid or Liquid solution)

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

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

G$_i$: partial Gibbs energy of *i* in solution



μ_i : Chemical potential of *i*

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

Solution thermodynamics

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

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

Solution thermodynamics

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: $\gamma_A = f(x, T)$

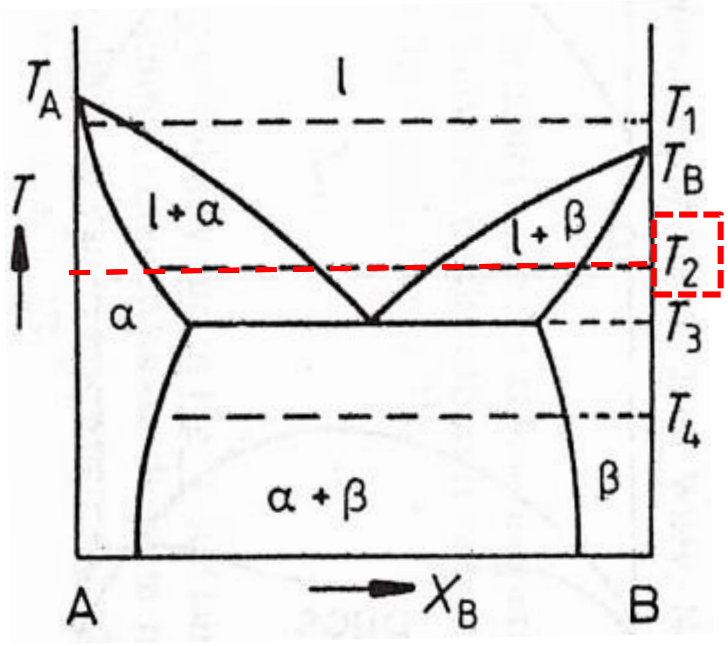
$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}$$

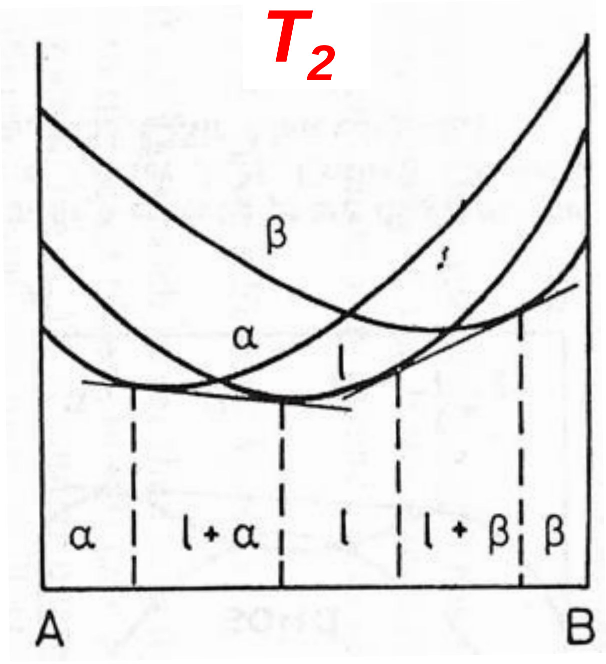
$$G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j$$

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

Gibbs Energy vs. Phase Diagram

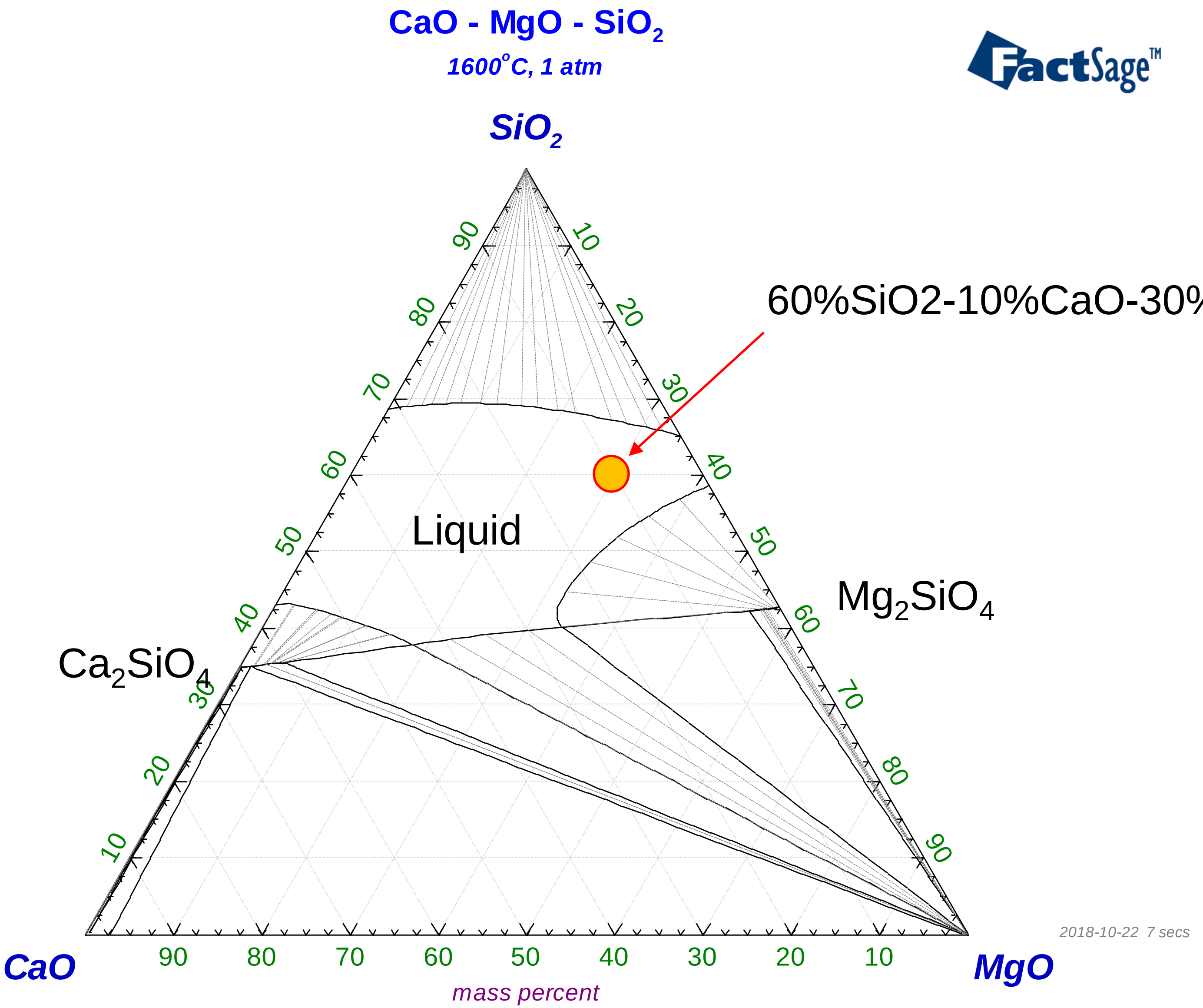
→ Phase diagram is the collection of minimum Gibbs energy assemblage of given system with temperature.





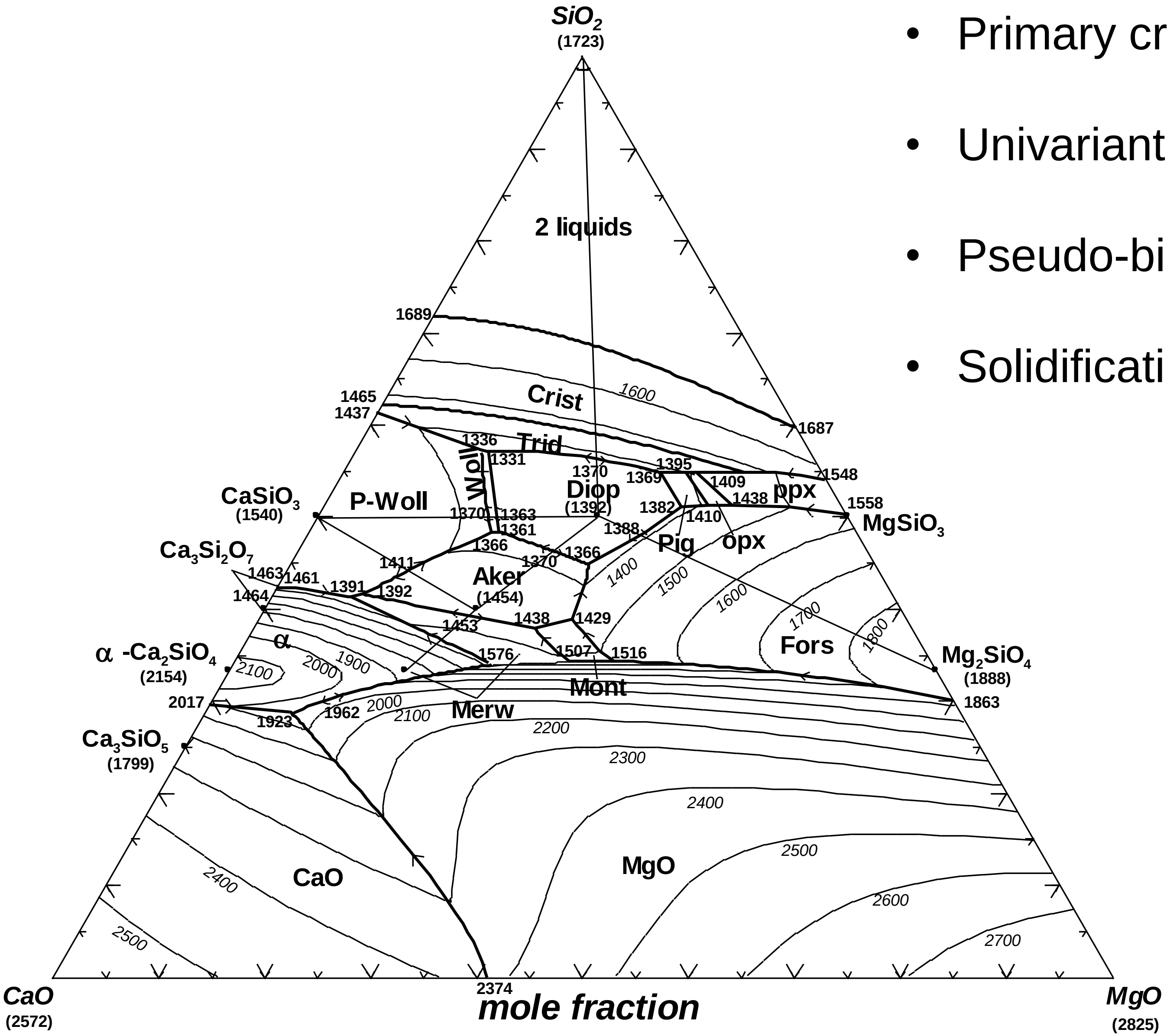
Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2nd Ed. CHAMAN & HALL (1992)

Ternary phase diagram: isothermal phase diagram



60%SiO2-10%CaO-30%MgO

Ternary phase diagram: Liquidus projection

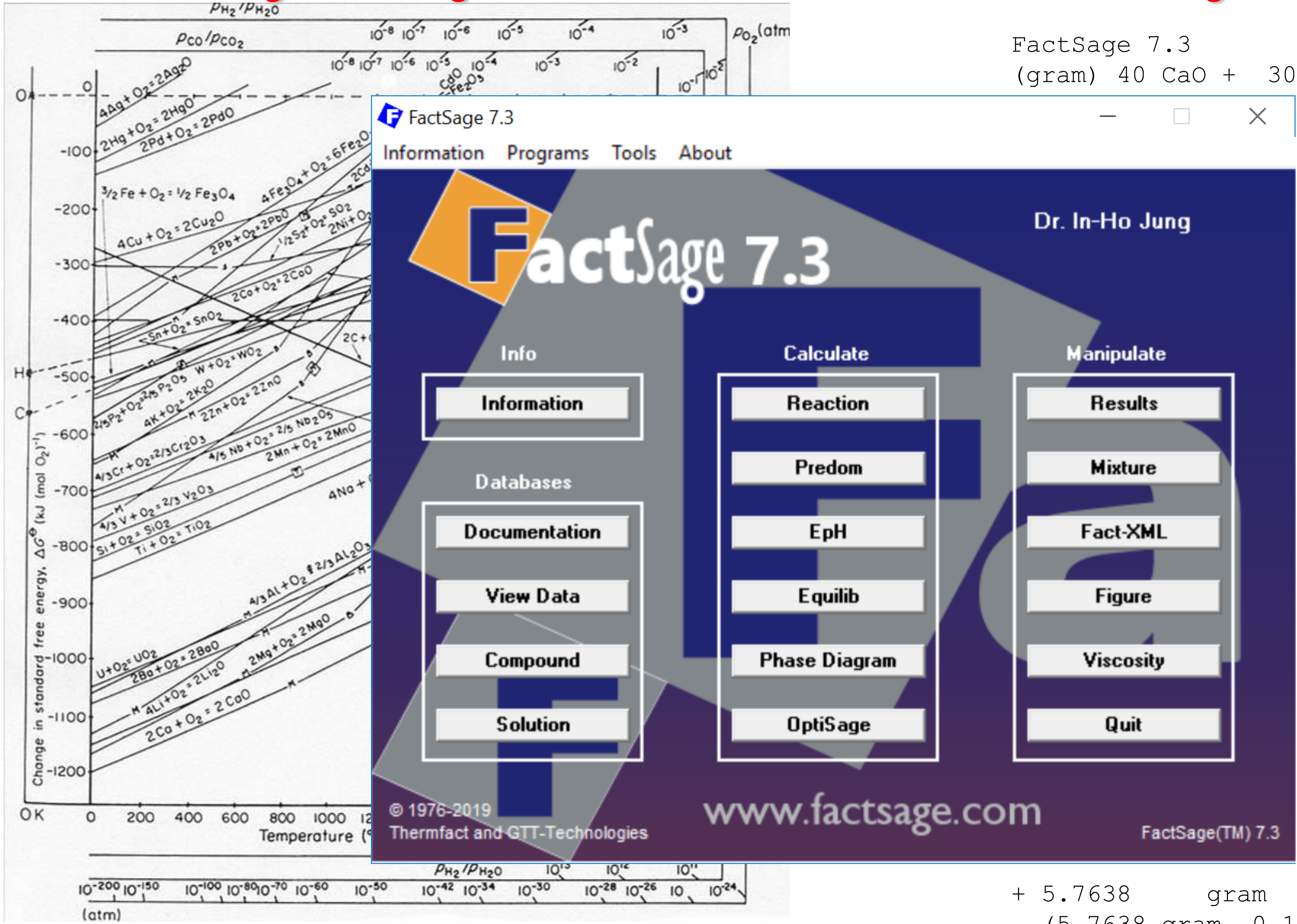


- Primary crystalline phase
- Univariant line
- Pseudo-binary phase diagram
- Solidification pass

Advantage of thermodynamic database

Ellingham Diagram

FactSage calculations

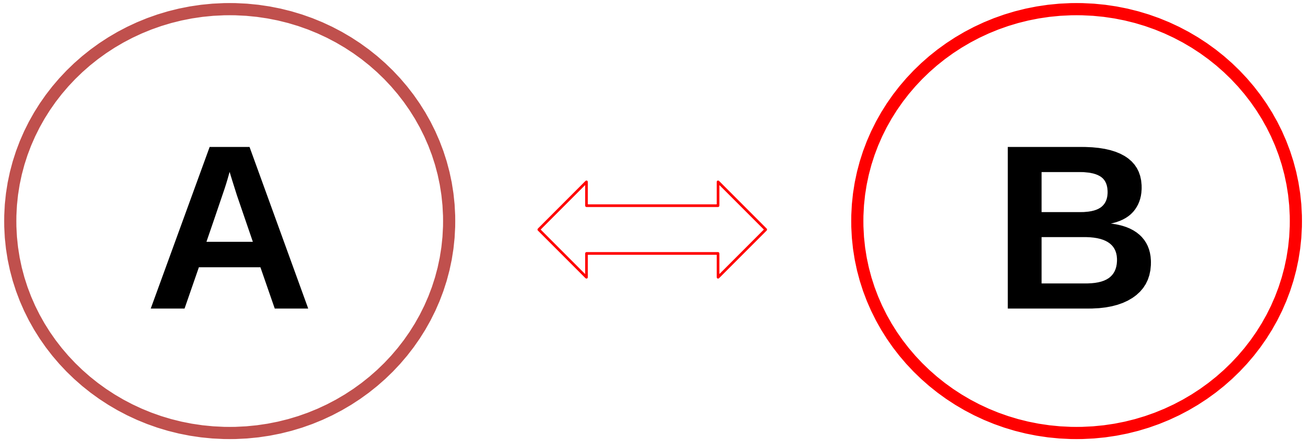


```
FactSage 7.3
(gram) 40 CaO +  30 SiO2 +  10 Al2O3 +  20
                                          =

                                         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**

Thermodynamic Database

Pure compound

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

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

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

- ➢ 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

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
Orginazation of Database Development

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

HYUNDAI STEEL
TATA STEEL
voestalpine
NUCOR
posco
RHI MAGNESITA
NIPPON STEEL & SUMITOMO METAL
JFE
DOOSAN
Doosan Heavy Industries & Construction
SeAH Besteel
RioTinto
SCHOTT
glass made of ideas

Thermodynamic database

Slag/Refractory/ Inclusions/Flux/ Steel

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

Physical Property database

Kinetic Process Simulation models (EERZ Concept)

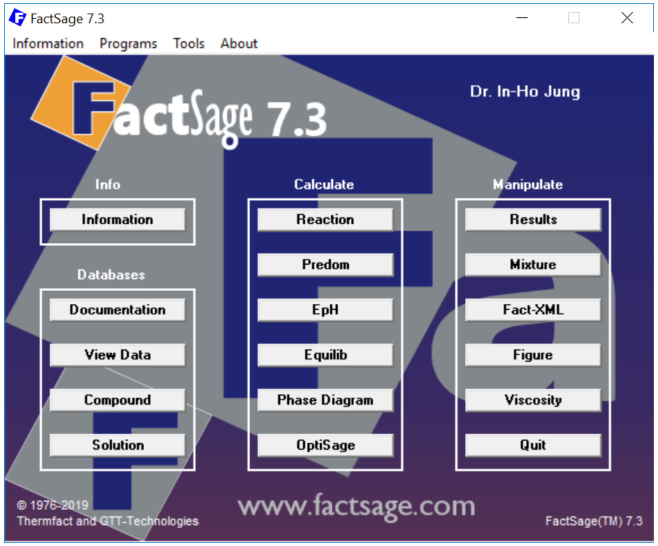
- **Secondary Refining Units**
- **Continuous Casting Process**

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

Available Thermodynamic Database – Refractories

Steelmaking, Non-ferrous and Cement industry

Since 1976



MgO-C, Al_2O_3-MgO, MgO-Cr_2O_3, Mullite, Olivine, ZrO_2-based, Al_2O_3-SiC type refractories:

- Reaction with slags, atmosphere, liquid metals
- Refractory mineral phases
  - ✓ Monoxide: MgO-FeO-MnO-CaO ….
  - ✓ Spinel: $(Mg,Mn,Fe,..)[Al,Cr,Fe,..]_2O_4$
  - ✓ Olivine: $(Mg,Mn,Ca,Fe,..)_2SiO_4$
  - ✓ $(CaO)_x(Al_2O_3)_y$…..
  - ✓ Si-C-N-O..
  - ✓ Cr^{6+} : in progress
- Slag phase:
  CaO-MgO-Al_2O_3-SiO_2-FeO-Fe_2O_3-MnO-Ti_2O_3-TiO_2-CrO-Cr_2O_3-ZrO_2-P_2O_5…-S-F
- Liquid metallic phase
  - ✓ Fe, Ferro-alloy, Al, Mg, Si, Cu, …

Glass, Biomass combustion, and Coal combustion industry

- K_2O, Na_2O, Li_2O 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

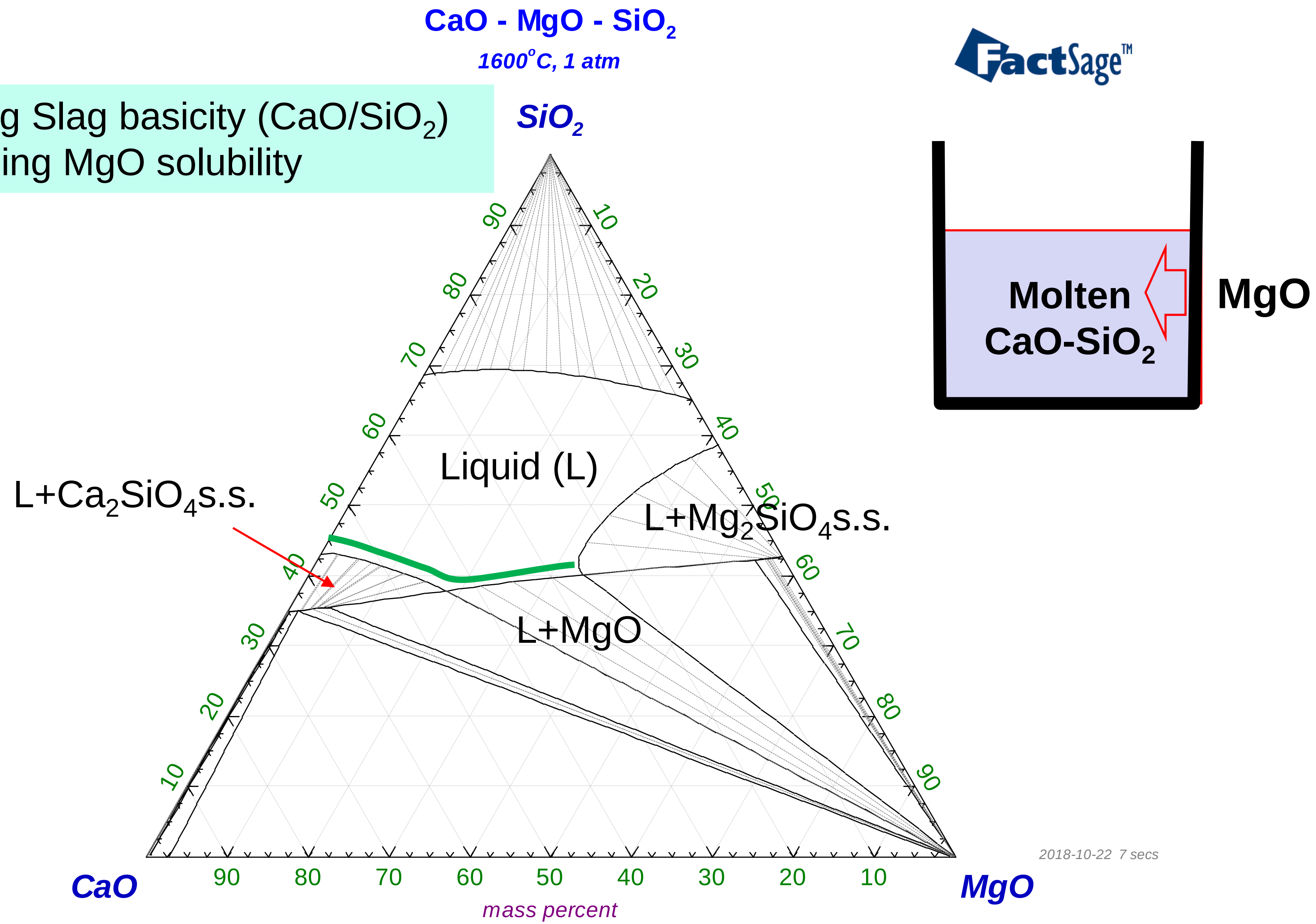
- Carbothermal reduction process
- Inclusion formation

MgO solubility in slags

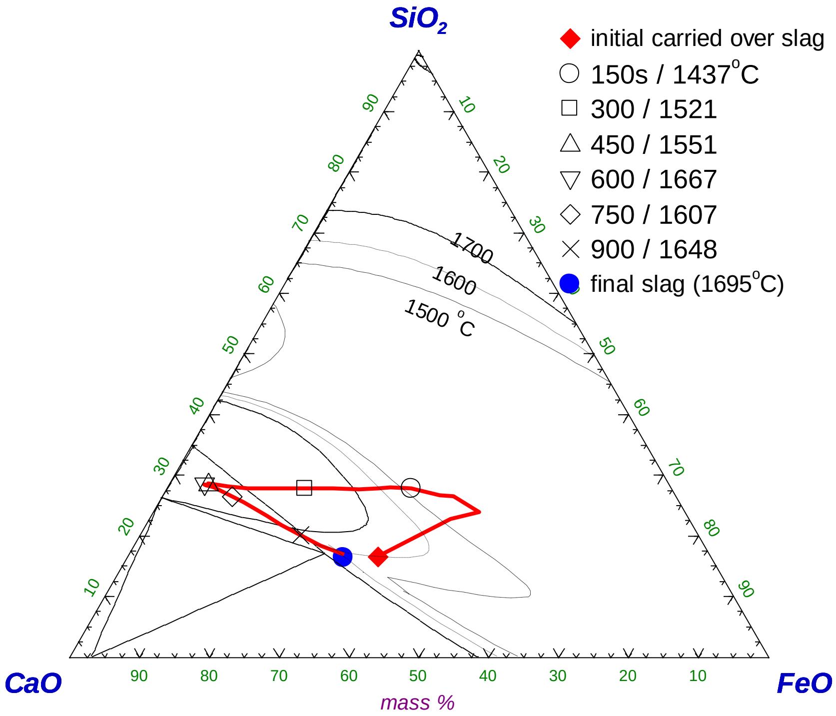
- CaO-MgO-SiO2 Phase diagram vs. MgO solubility
- BOF slag
- Multicomponent slag with CaF2
- LF slag

CaO-MgO-SiO$_2$ phase diagram

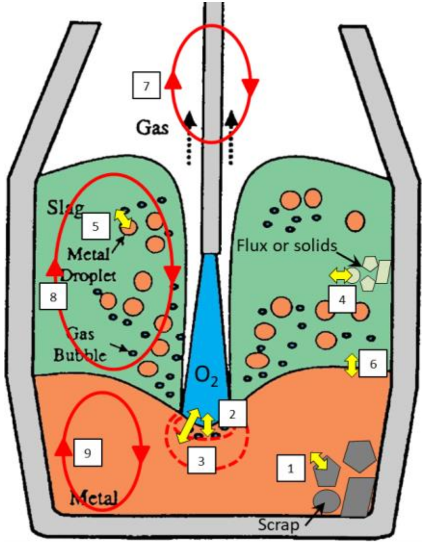
Decreasing Slag basicity (CaO/SiO$_2$)
→ Increasing MgO solubility



Refractory: CaO-Fe_tO-SiO_2-5wt%MgO system with Fe saturation



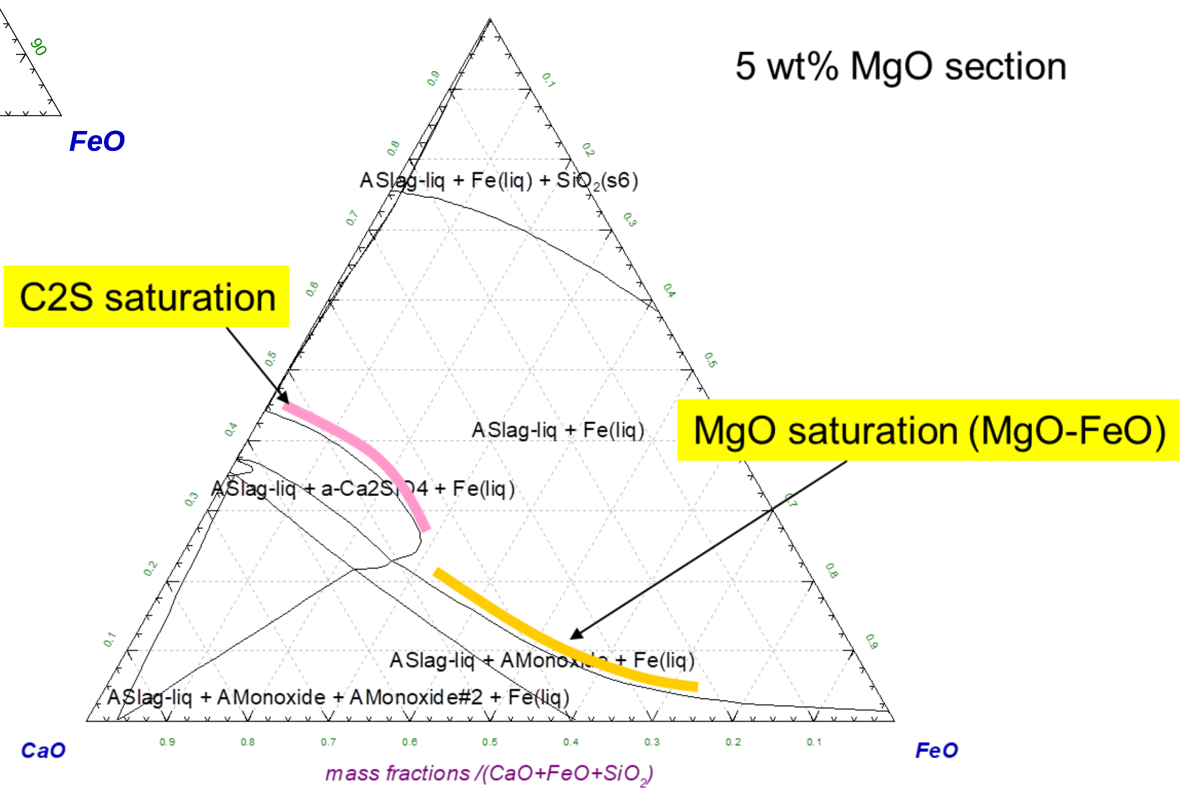
Overall slag chemistry change during BOF process



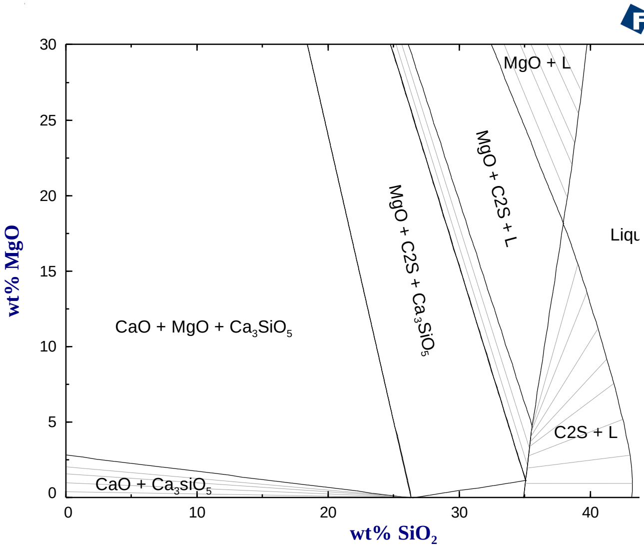
CaO - FeO - SiO_2 - MgO - Fe

1650°C, MgO/Z (g/g) = 0.05263, Fe/Z (g/g) = 0.001, Z=(CaO+FeO+SiO_2)

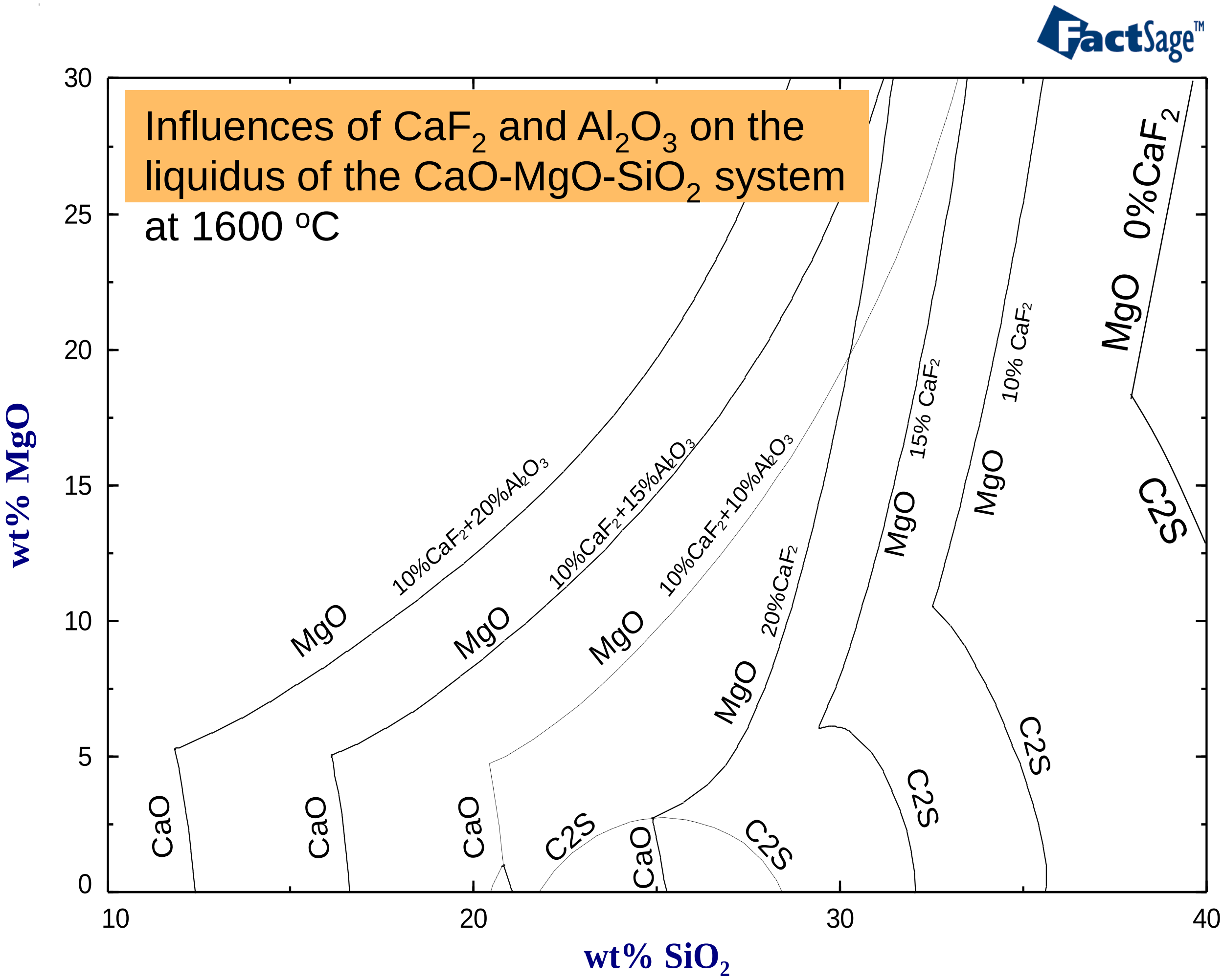
5 wt% MgO section



Refractory reaction with F containing slag/flux



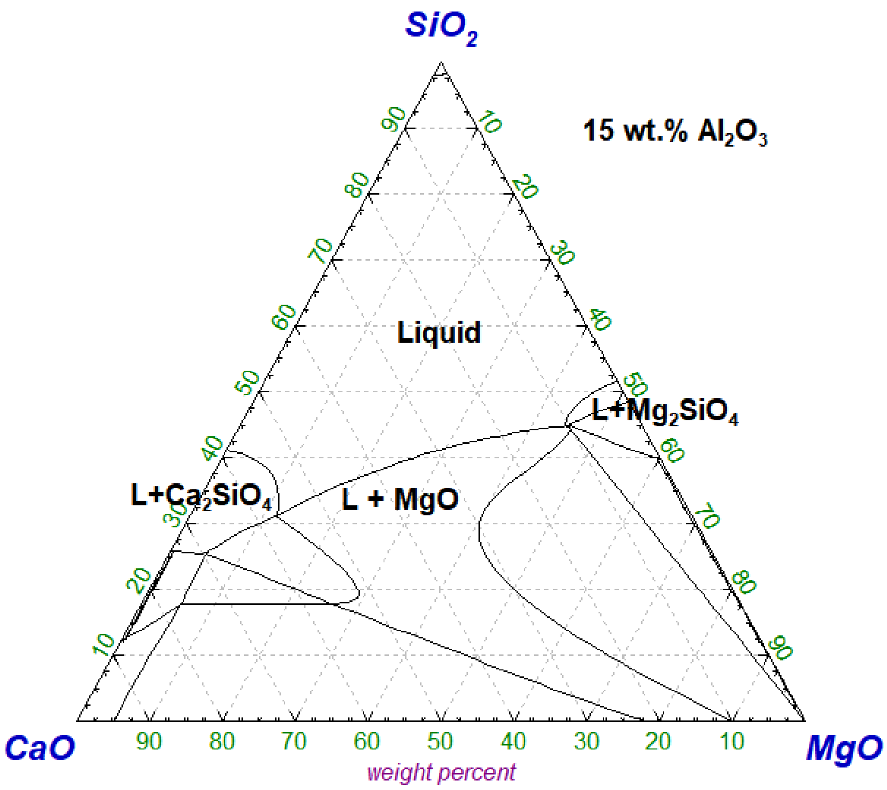
Phase diagram of the CaO-MgC
system at 1600 °C



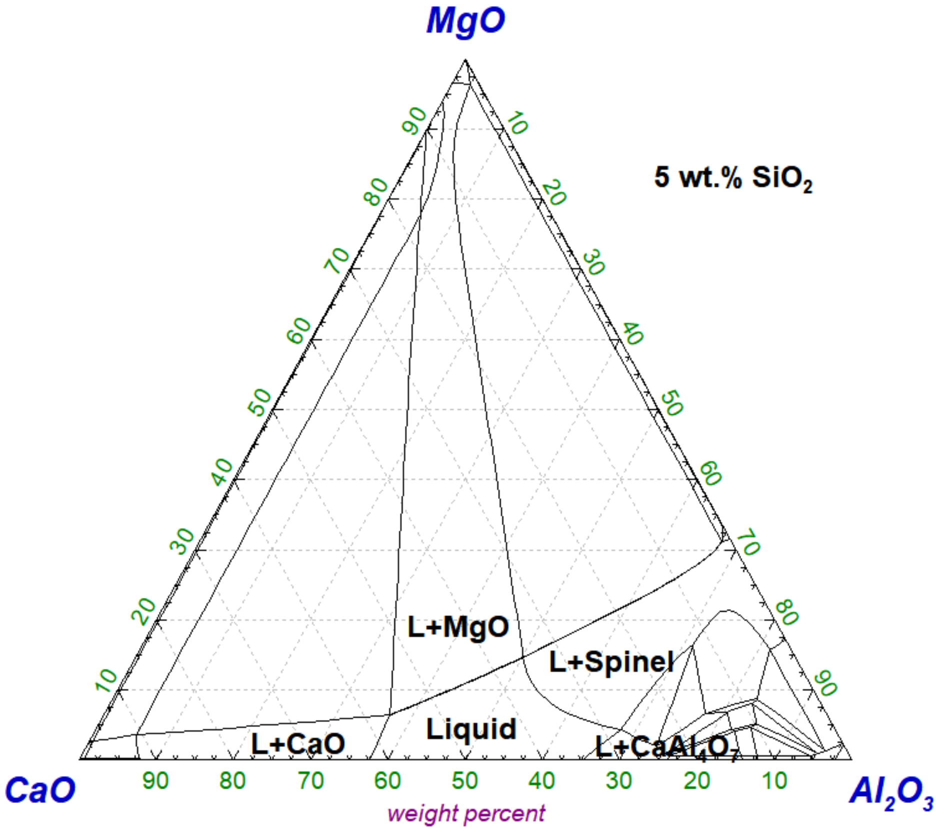
Influences of CaF_2 and Al_2O_3 on the liquidus of the CaO-MgO-SiO_2 system at 1600 °C

MgO solubility in CaO-SiO_2 and CaO-Al_2O_3 based slags

CaO-SiO_2-15%Al_2O_3 slag with MgO



CaO-Al_2O_3-15%SiO_2 slag with MgO



MgO solubility in the CaO-Al_2O_3 based slags is much lower than that in the CaO-SiO_2 based slags

Ladle Furnace (LF) slag

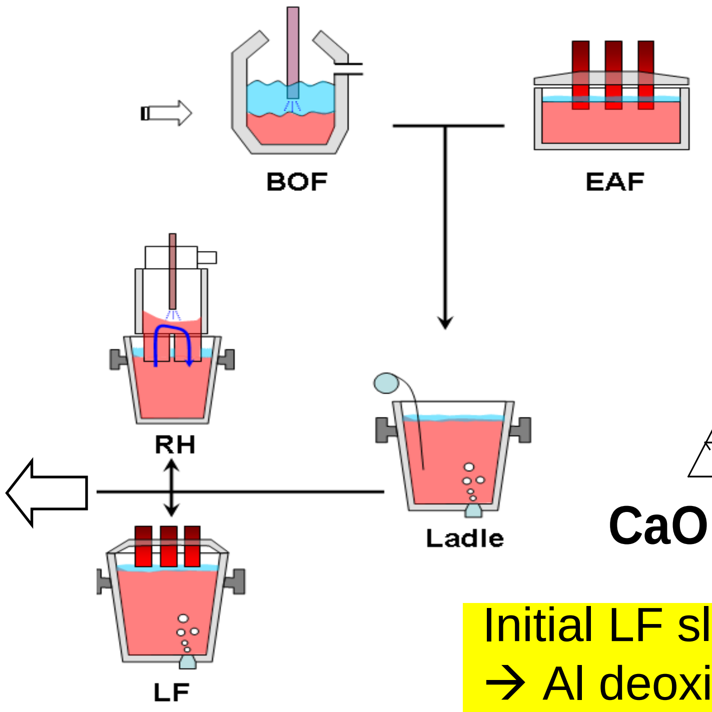
BOF slag (SiO_2 containing slag)

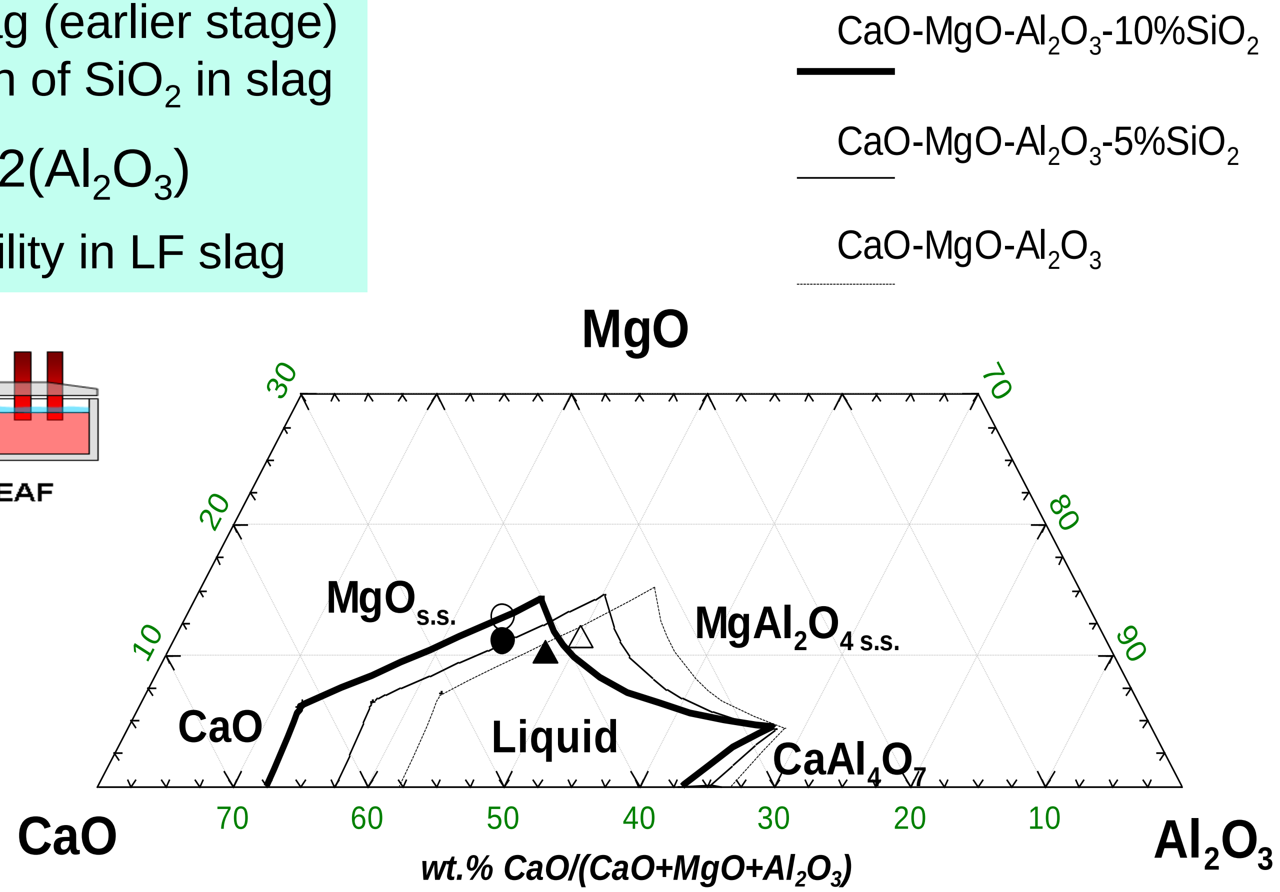
→ Source of SiO_2 in LF slag (earlier stage)

→ Al deoxidation: reduction of SiO_2 in slag

$$3(SiO_2) + 4\underline{Al} = 3\underline{Si} + 2(Al_2O_3)$$

→ Can change MgO solubility in LF slag





Initial LF slag: 39.2CaO-39.2Al_2O_3-11.6MgO-10SiO_2 (open circle)

→ Al deoxidation

→ Final LF slag: 38.7CaO-50.1Al_2O_3-11.2MgO (open triangle)

(0.6 wt.% lower than the MgO saturation)

Contents

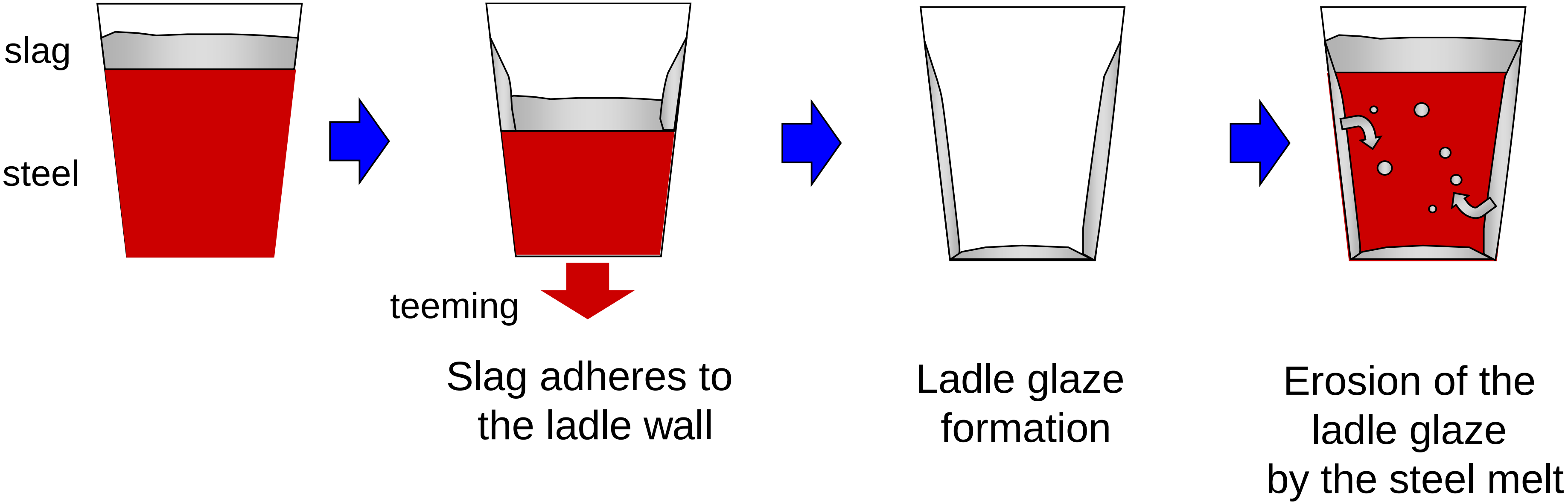
Other Slag – Refractory Interactions

- Ladle glaze
- Purging plug – cleaning process

Ladle Glaze

Ladle Glaze

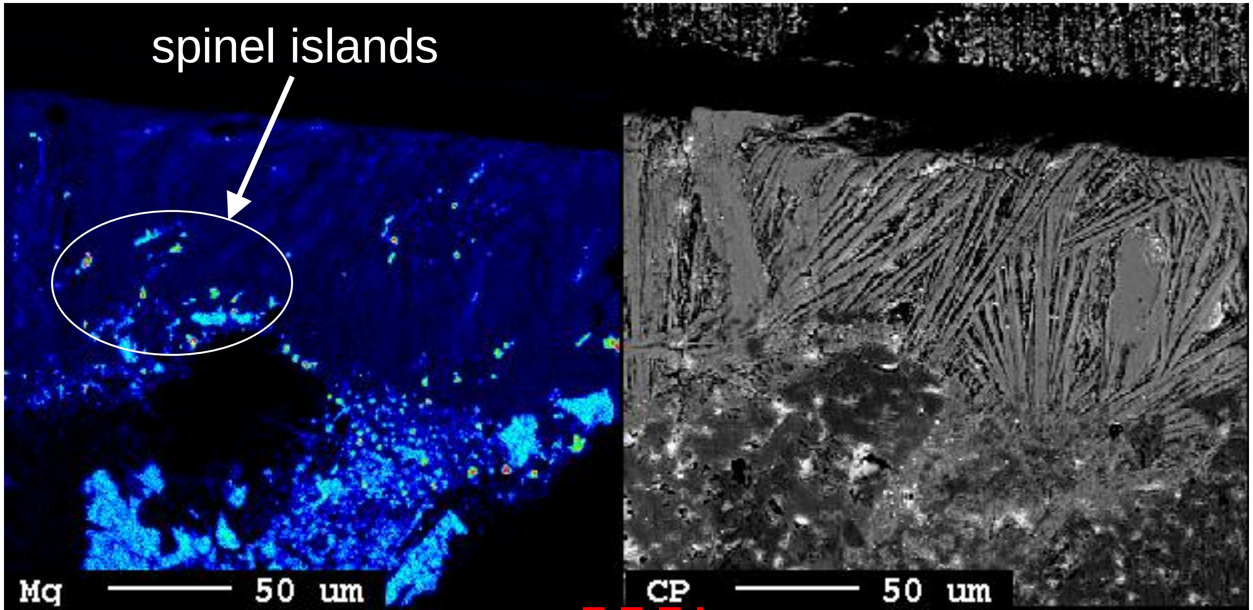
- Reactions with Ladle refractory lining
- Formation of non-metallic Inclusions



Purpose of the present study

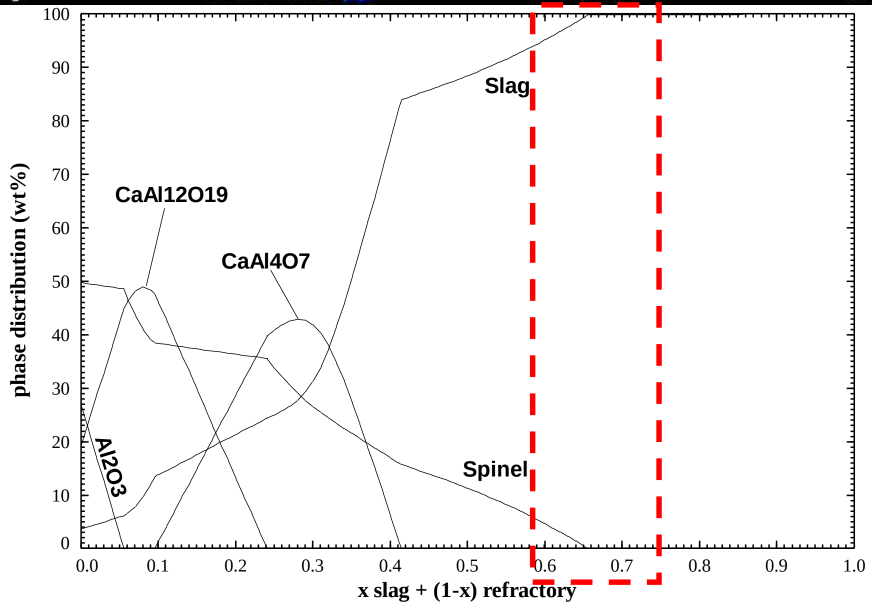
- Glaze formation mechanism / Glazed refractory
- Influence on melt cleanliness (inclusion): Al, Al/Ca

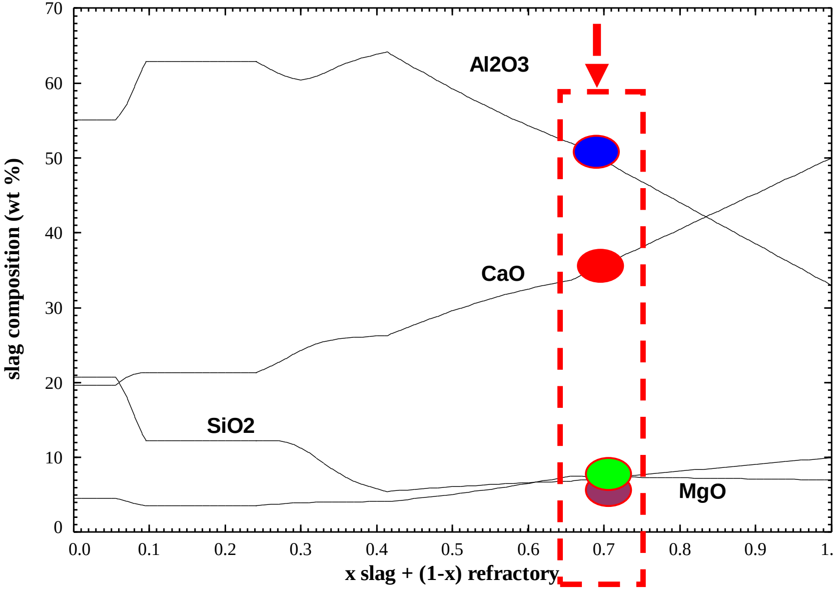
Glaze (Reaction product of slag and refractory)



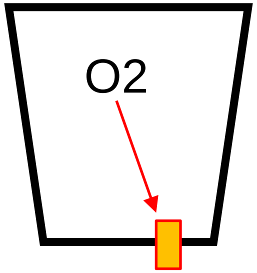
Glaze composition

CaO	SiO2	Al2O3	MgO
35.8	6.6	51.1	6.5





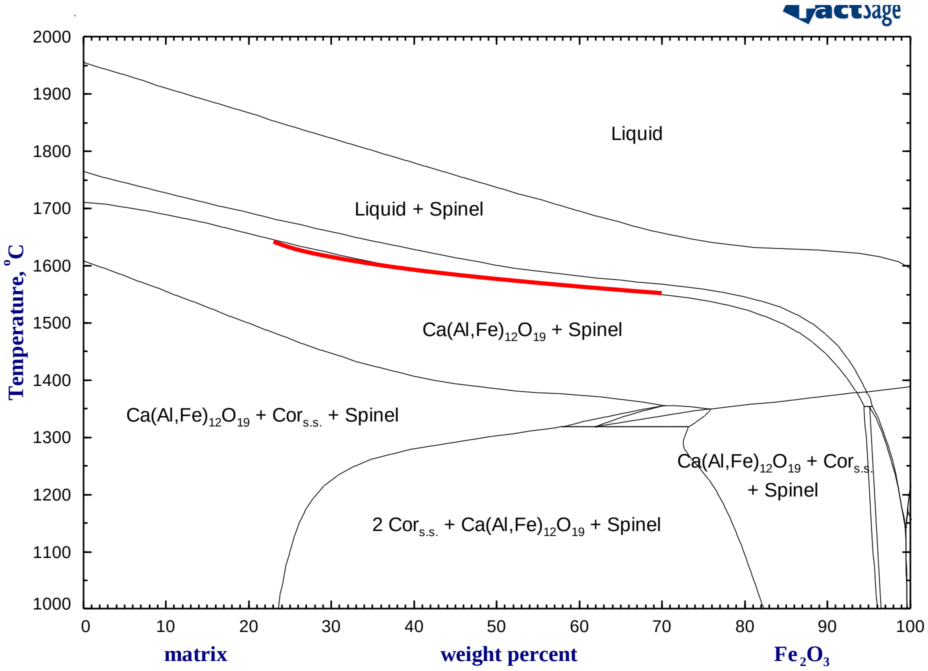
Corrosion of Ladle purging plug by Fe oxides

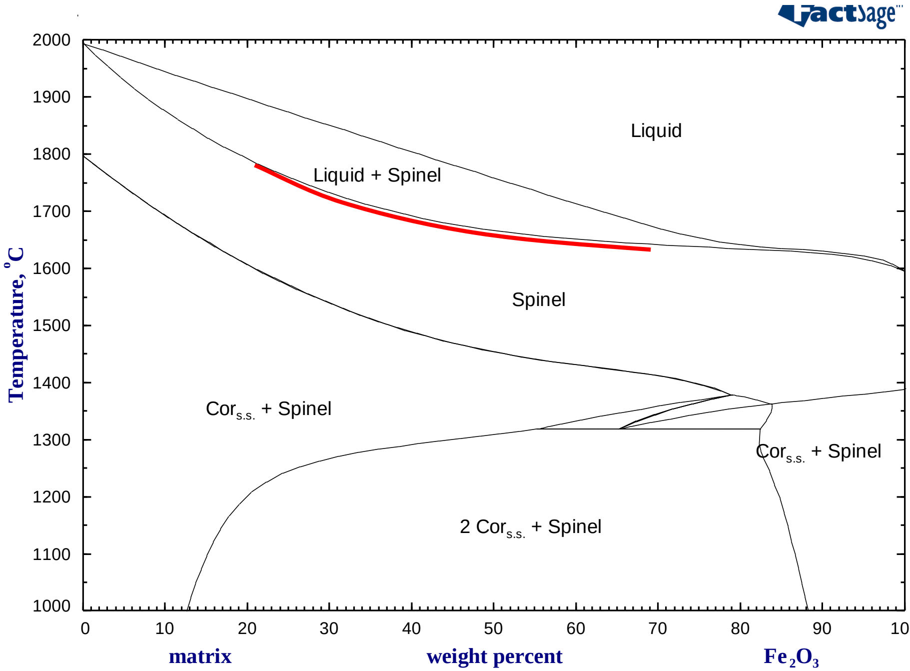


Purging plug: Low- or ultra-low-cement castable (LCC or ULCC) in the Al_2O_3-MgO-CaO system: Corundum + Spinel

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

$2Fe + 3/2O_2 = Fe_2O_3$
Slag + refractory rxn





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

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

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

Melting temperature of MgO and $MgCr_2O_4$

- Impurity
- Oxygen partial pressure

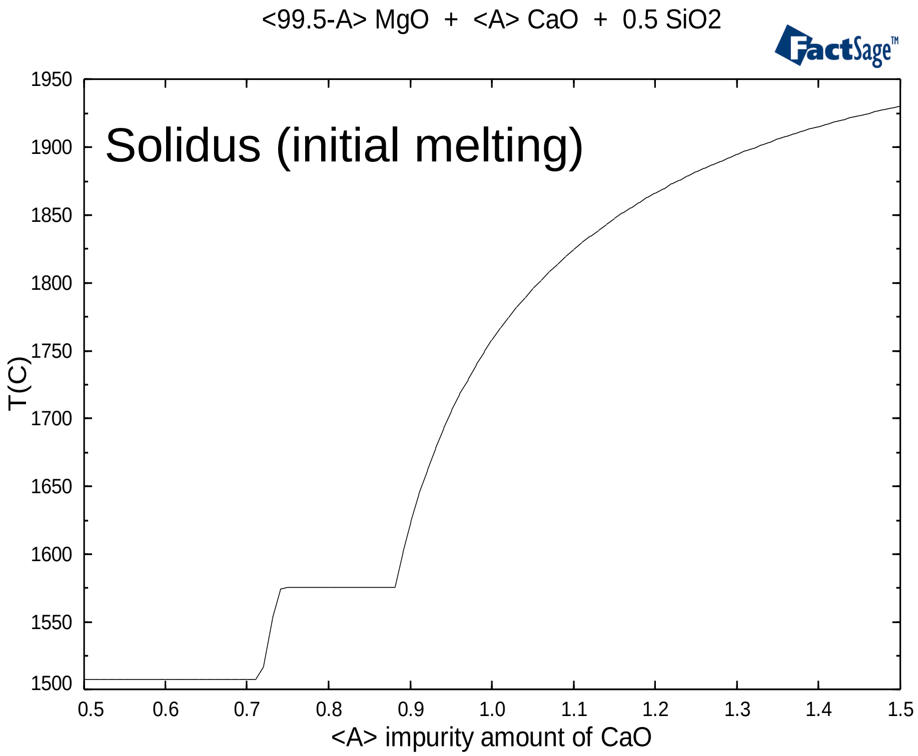
Melting temperature of MgO

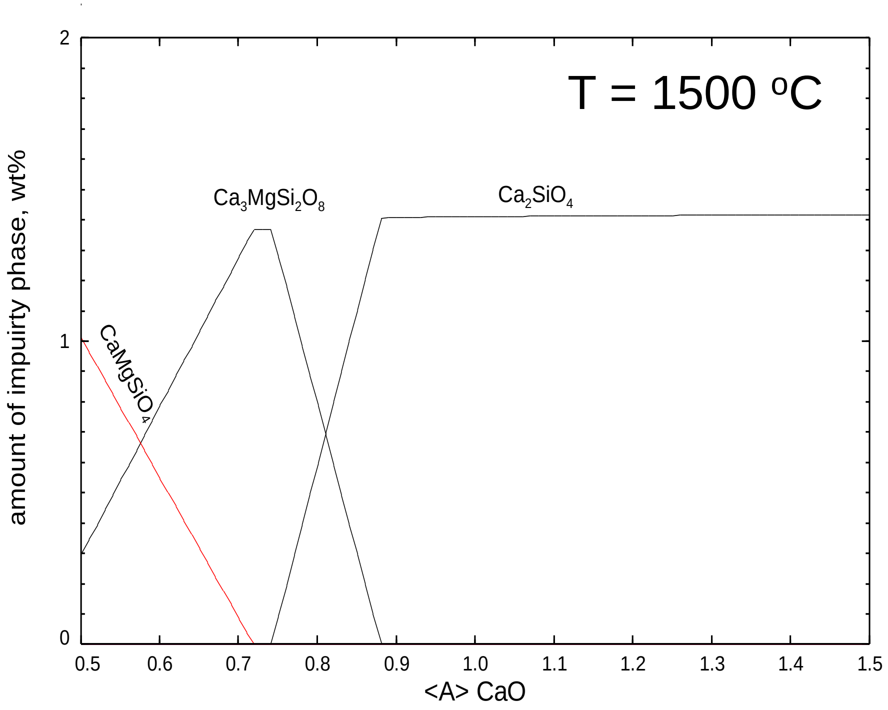
Melting temperature of

(1) pure MgO = 2825 ^{o}C

(2) impure MgO ?

MgO ore – impurity of CaO and SiO_2





Melting temperature of MgO

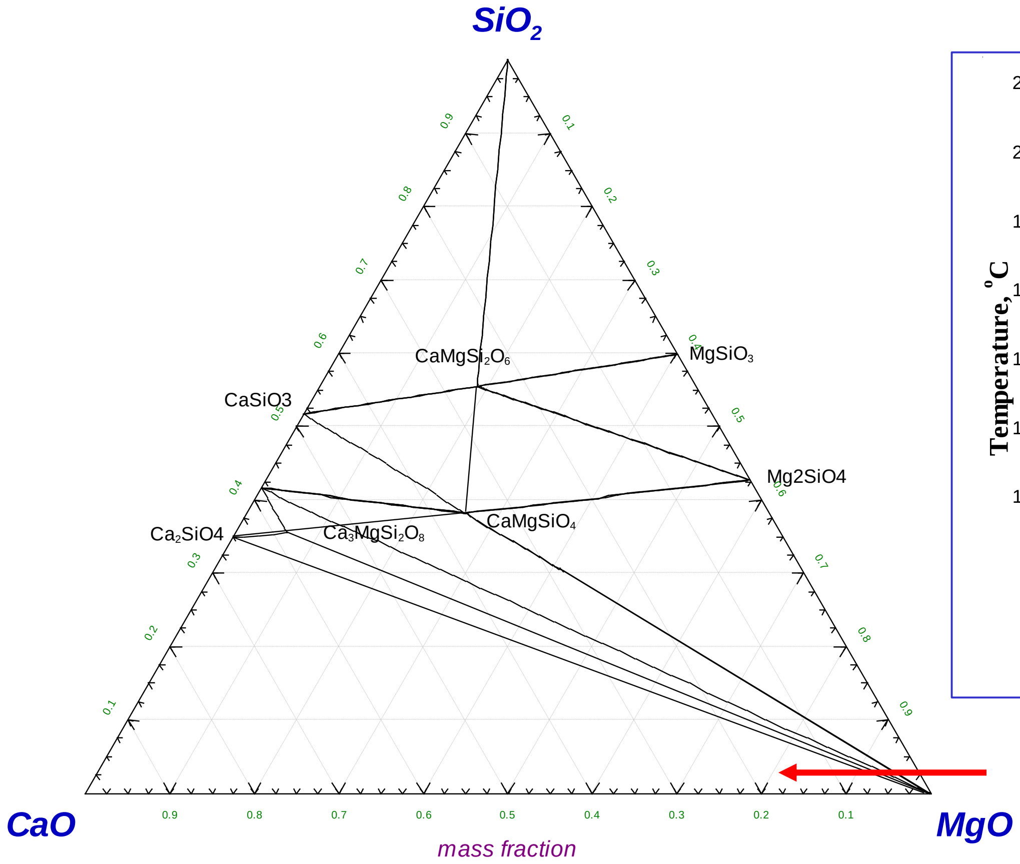
Melting temperature of

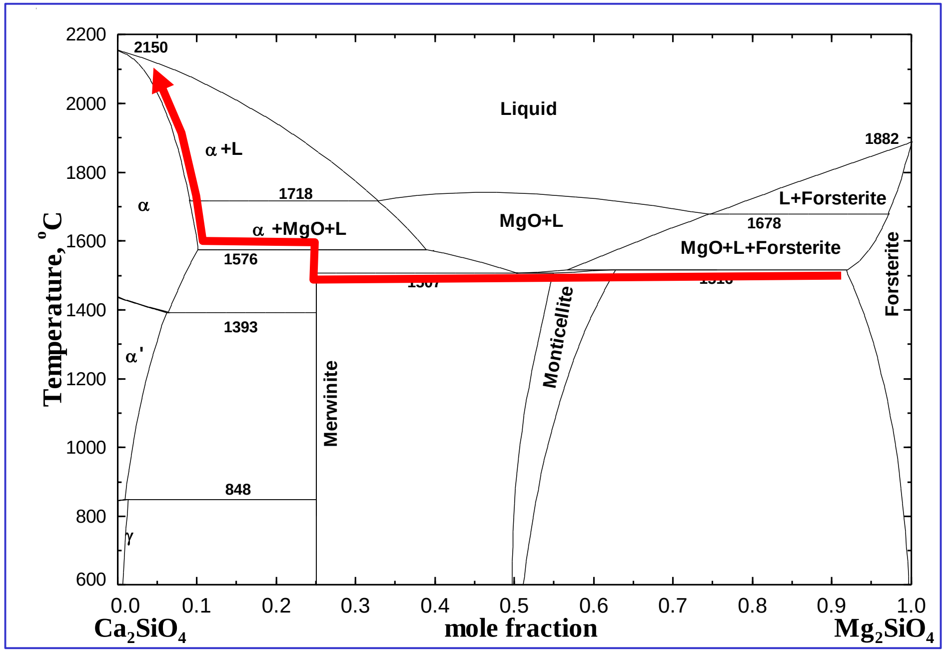
(1) pure MgO = 2825 °C

(2) impure MgO ?

CaO - MgO - SiO$_2$

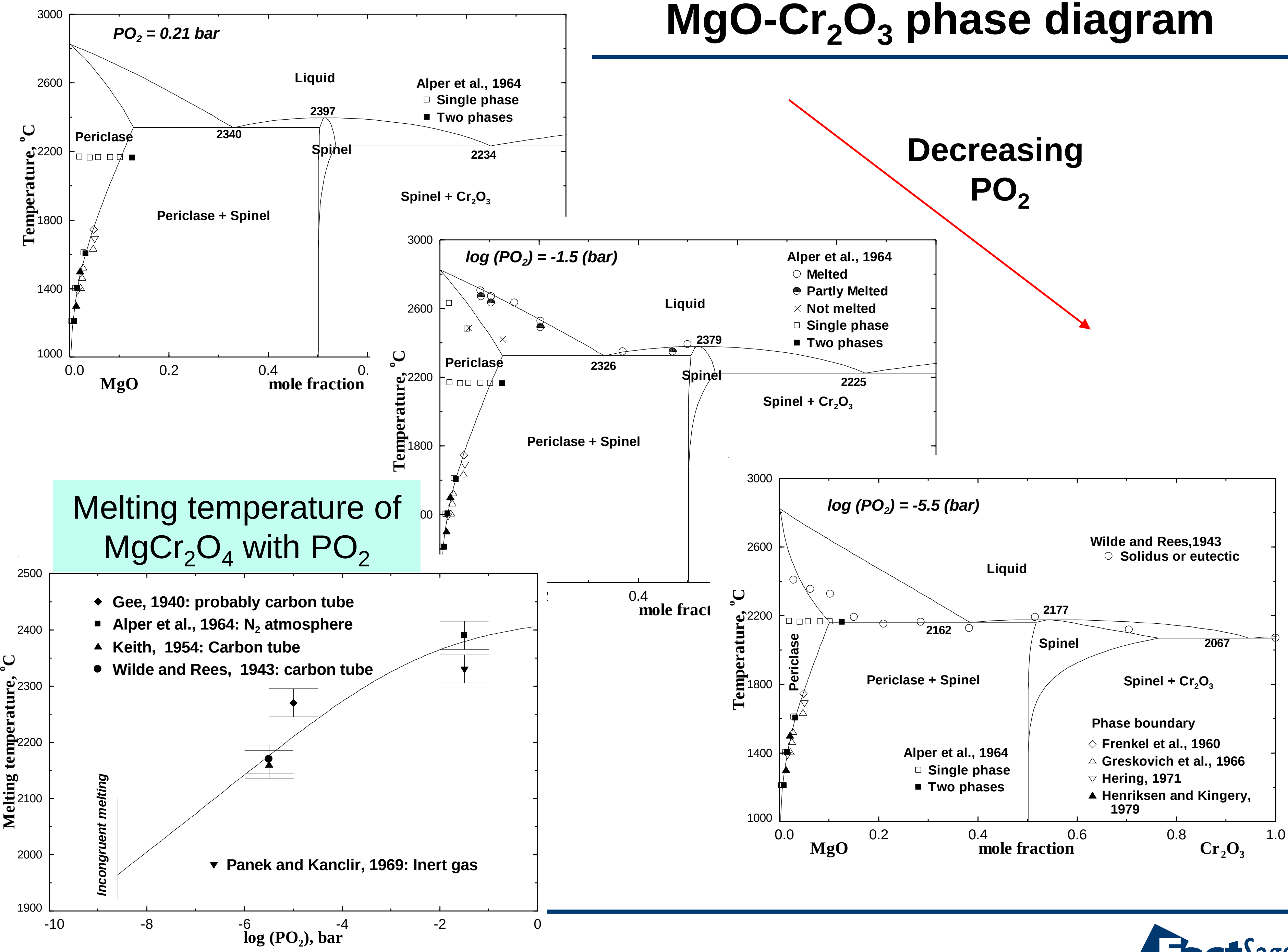
25°C, 1 atm





Melting profile with addition of CaO

MgO-Cr_2O_3 phase diagram



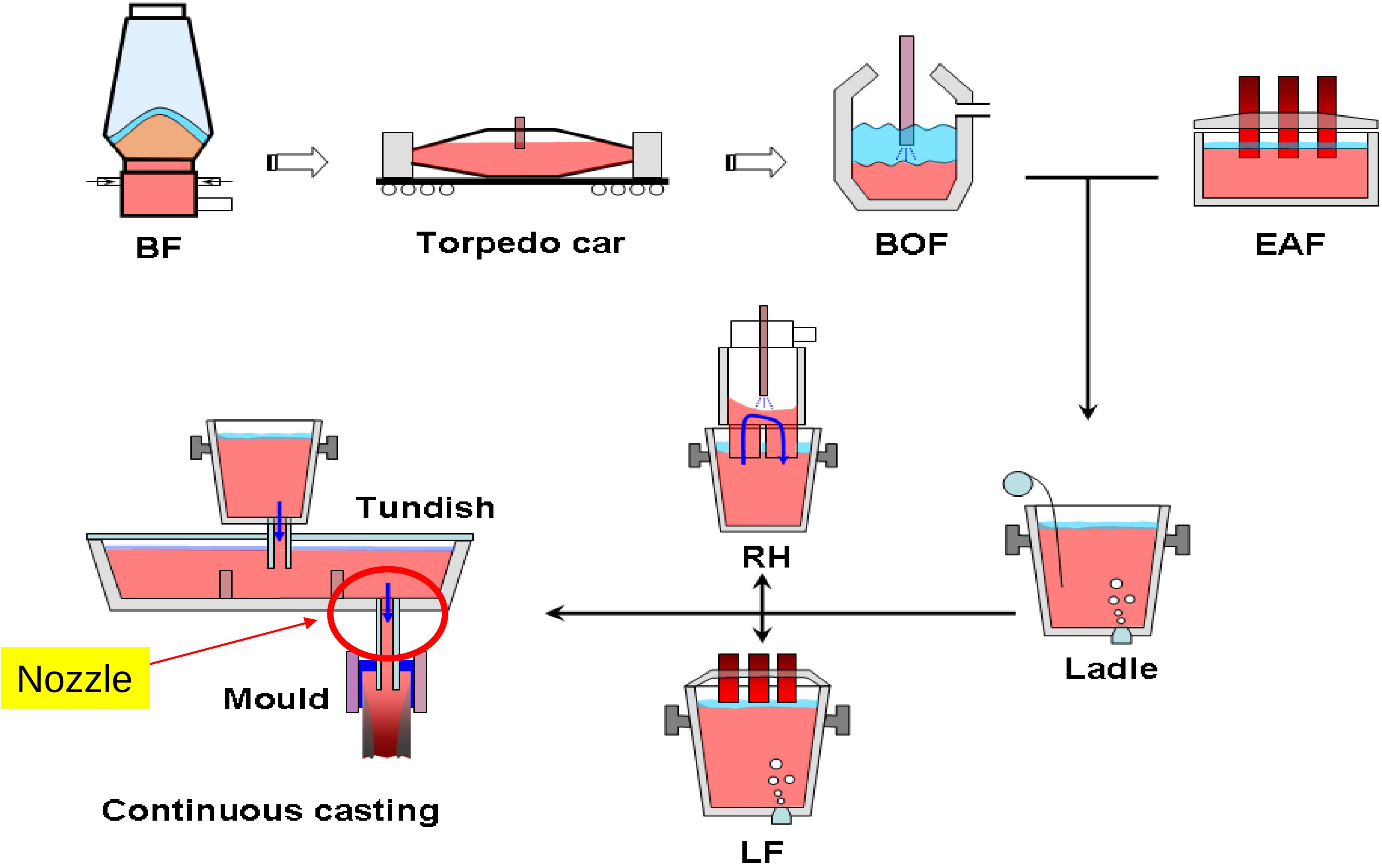
Decreasing PO_2

Melting temperature of $MgCr_2O_4$ with PO_2

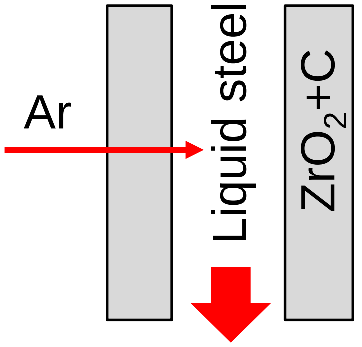
Nozzle refractory

- Carbothermal reduction process
- Inclusion formation

Nozzle clogging

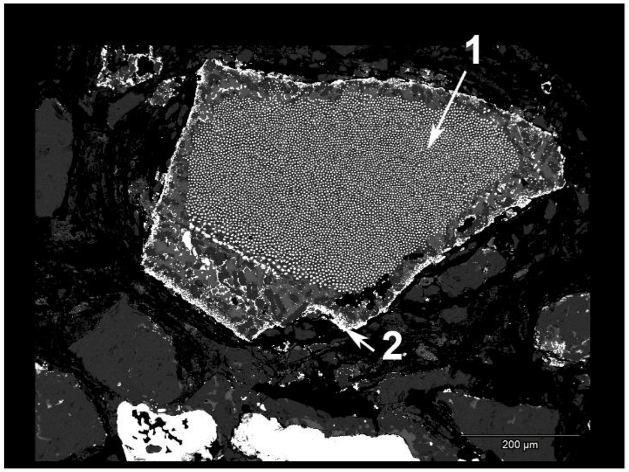


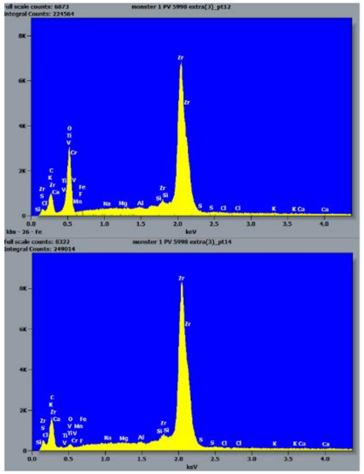
Carbothermic reduction of ZrO_2 to ZrC



$ZrO_2 + C = ZrC + CO(g)$

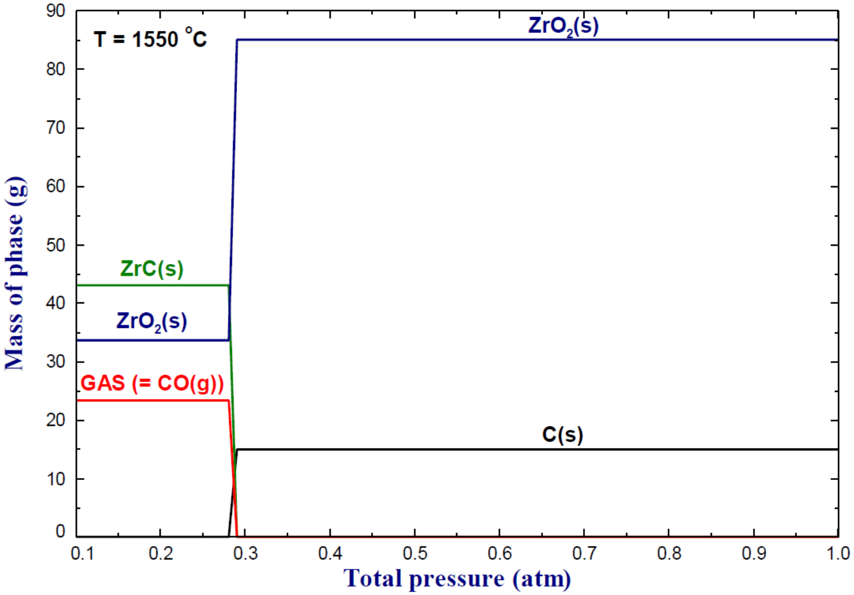
Ar+CO gas formation

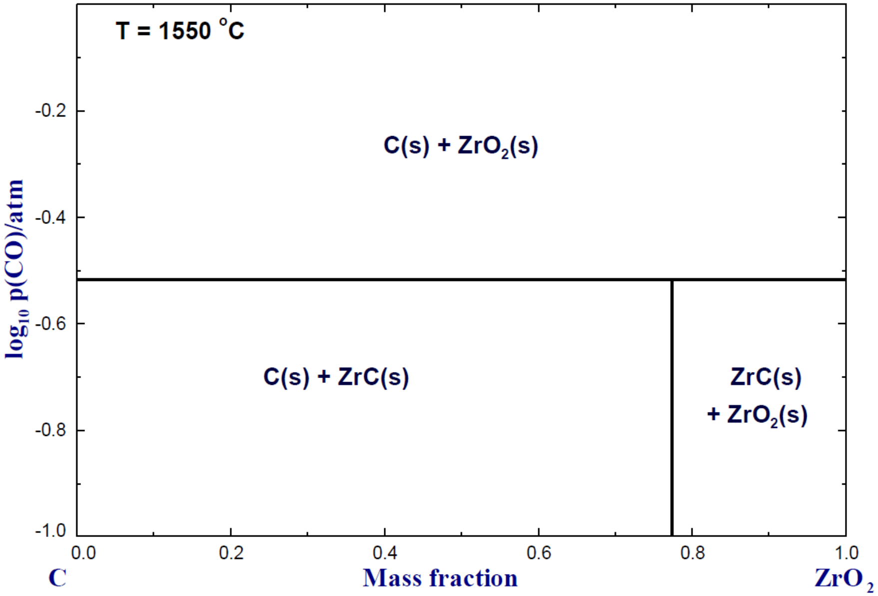




1 ZrO2

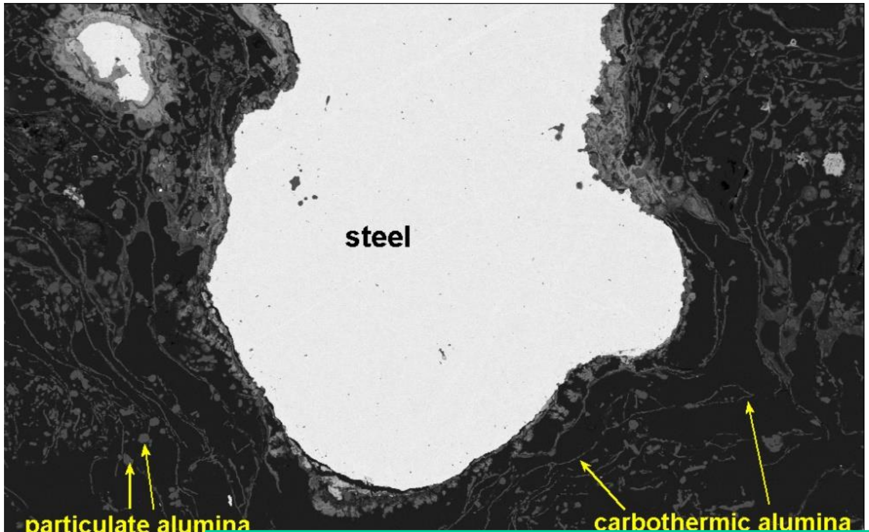
2 ZrC

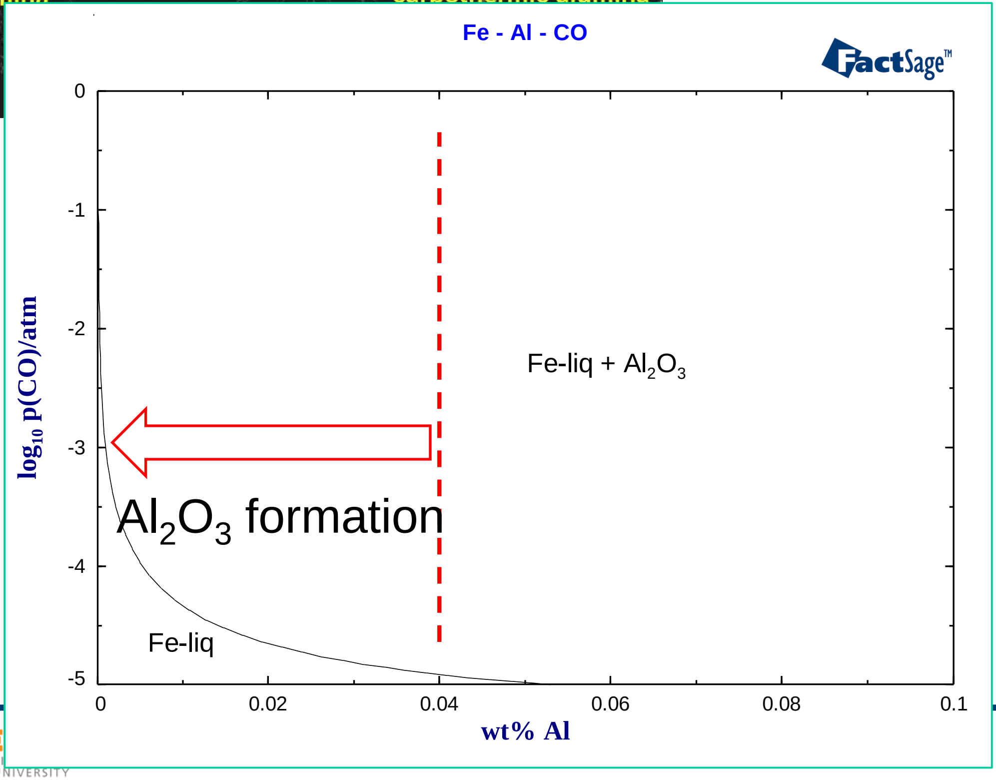




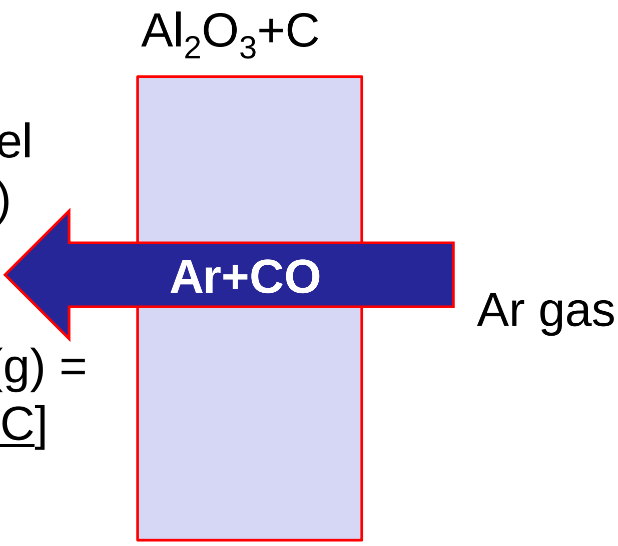
Ar gas injection can effectively reduce CO partial pressure
→ Carbothermal reduction of ZrO_2 to ZrC is possible.

Formation of Al_2O_3 in Nozzle: Al killed steel





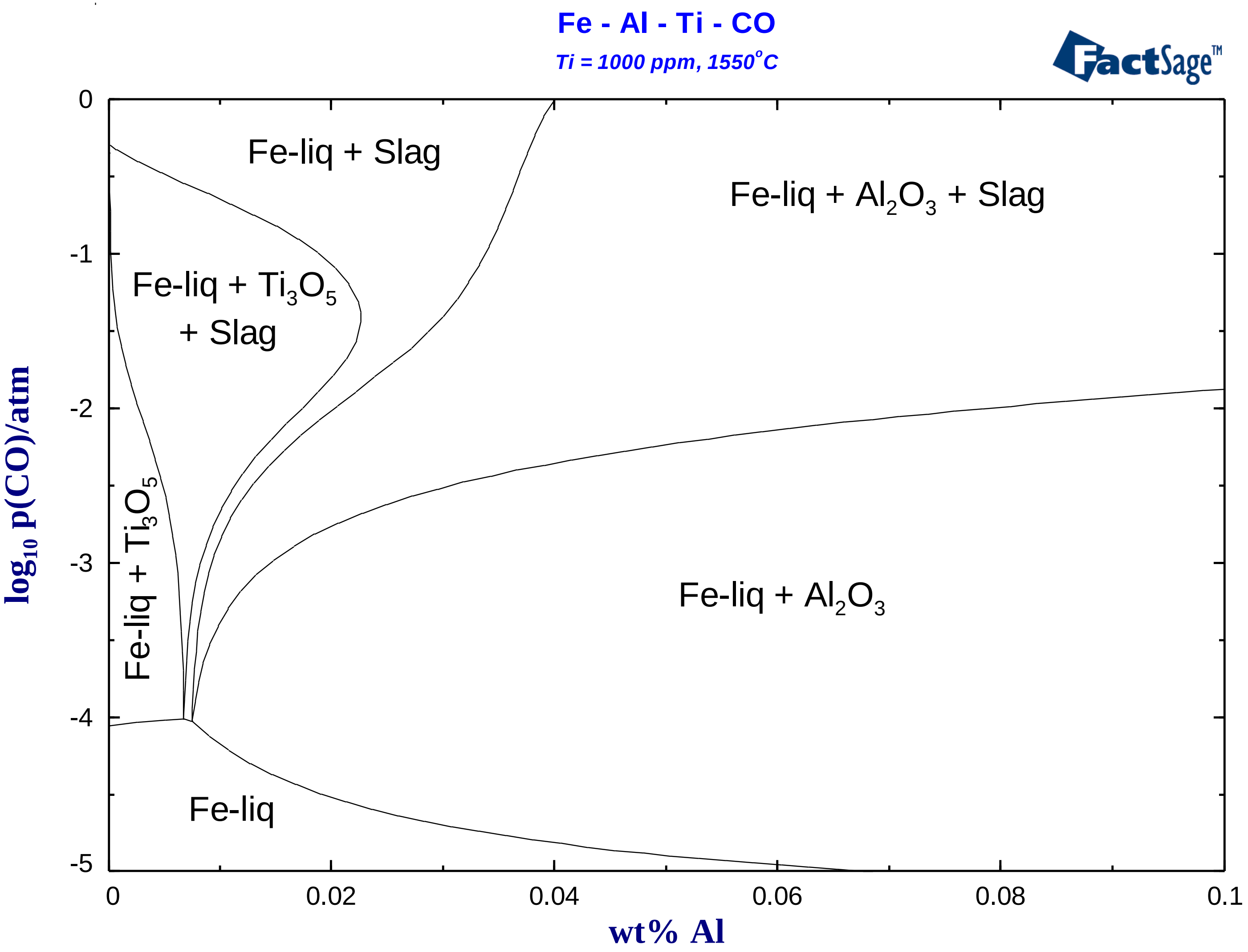
Liquid steel
(Al-killed)



$$2[\underline{Al}] + 3CO(g) = Al_2O_3 + 3[\underline{C}]$$

$$2Al_2O_3+9C = Al_4C_3+6CO(g)$$

Nozzle clogging in Al-Ti killed steel

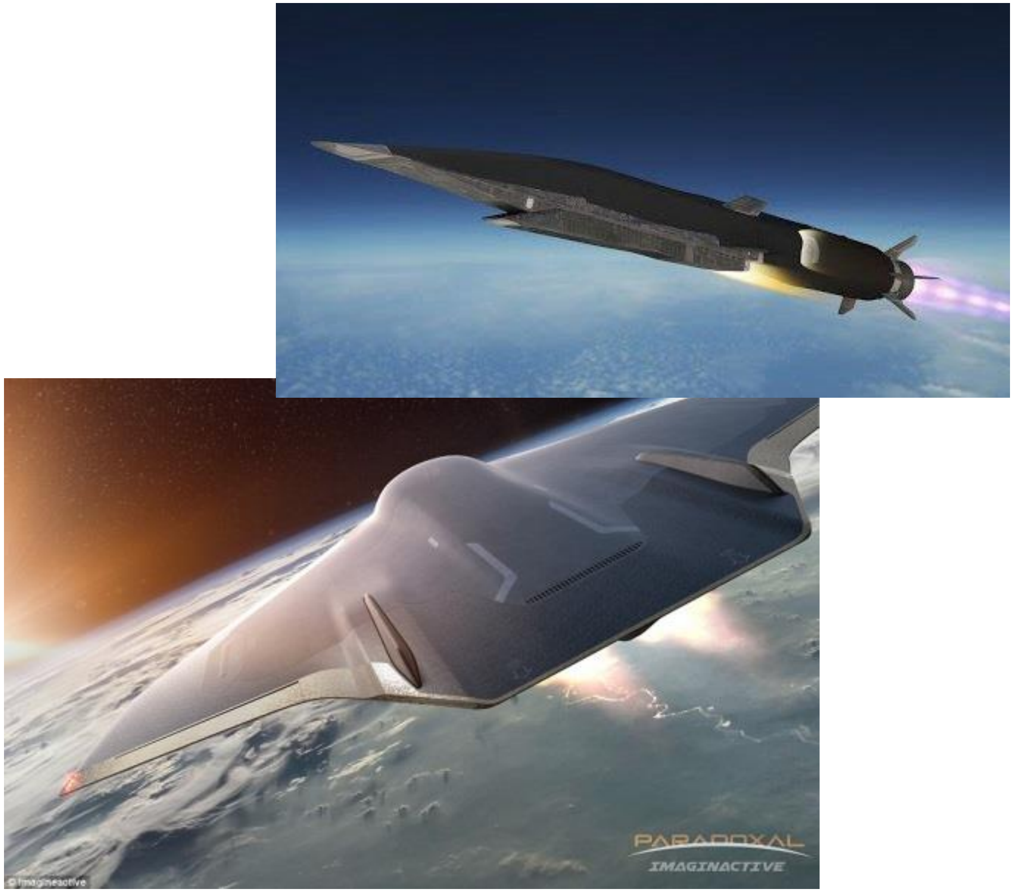


Reoxidation of steel by CO gas through ceramic nozzle to form slag(Al-Ti-O) and Al_2O_3

Ultra High Temperature Ceramics

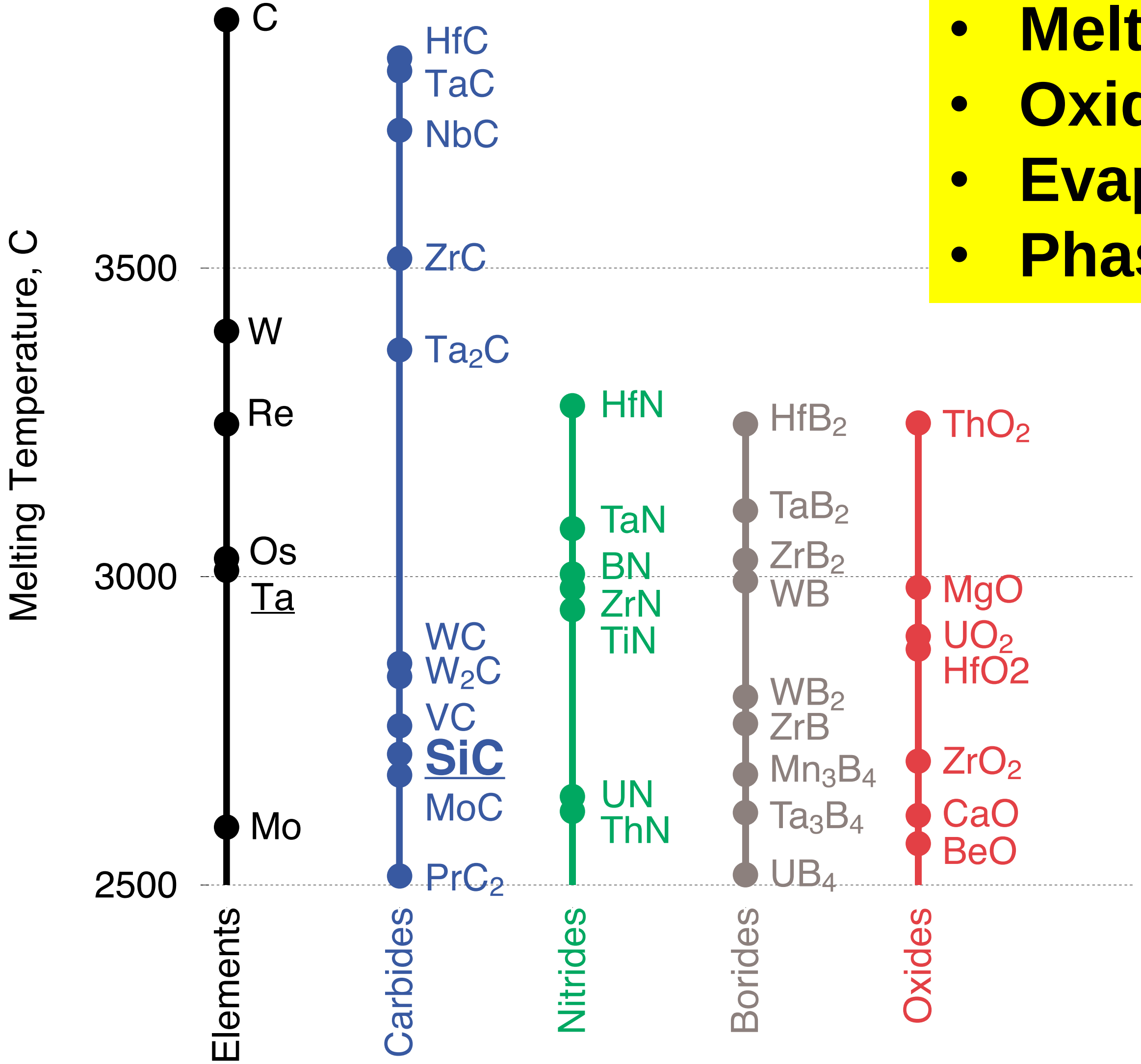
- **Ceramic Matrix Composites (CMC)**
- **TBC coating: ZrO_2 stabilized by CaO, Y_2O_3, etc.)**
- **Self-healing materials**

LEAP, GE9X Engine



Ultra High Temperature Ceramics

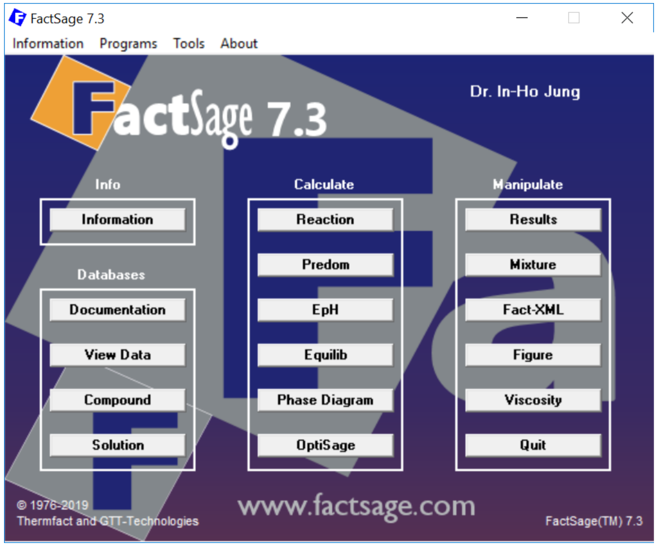
- **Melting**
- **Oxidation**
- **Evaporation**
- **Phase transition**



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

Available Thermodynamic Database – Ultra high T ceramics

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
- ZrO_2-CaO, MgO, ….
- ZrO_2-RE_2O_3 are not available – in progress

Applications of phase diagram: Case Study

Oxidation

- Carbide → Oxides
- ZrC, HfC, SiC

Evaporation

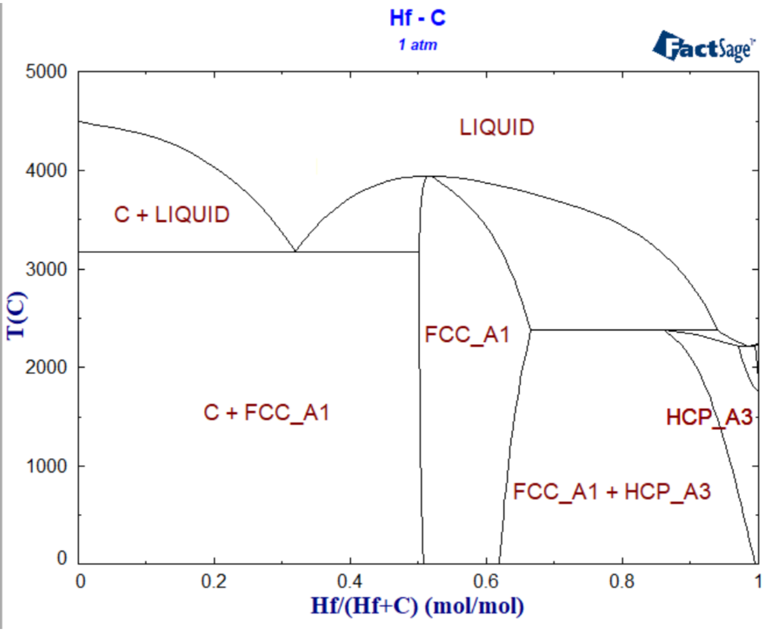
- SiO_2 → SiO gas

CMC

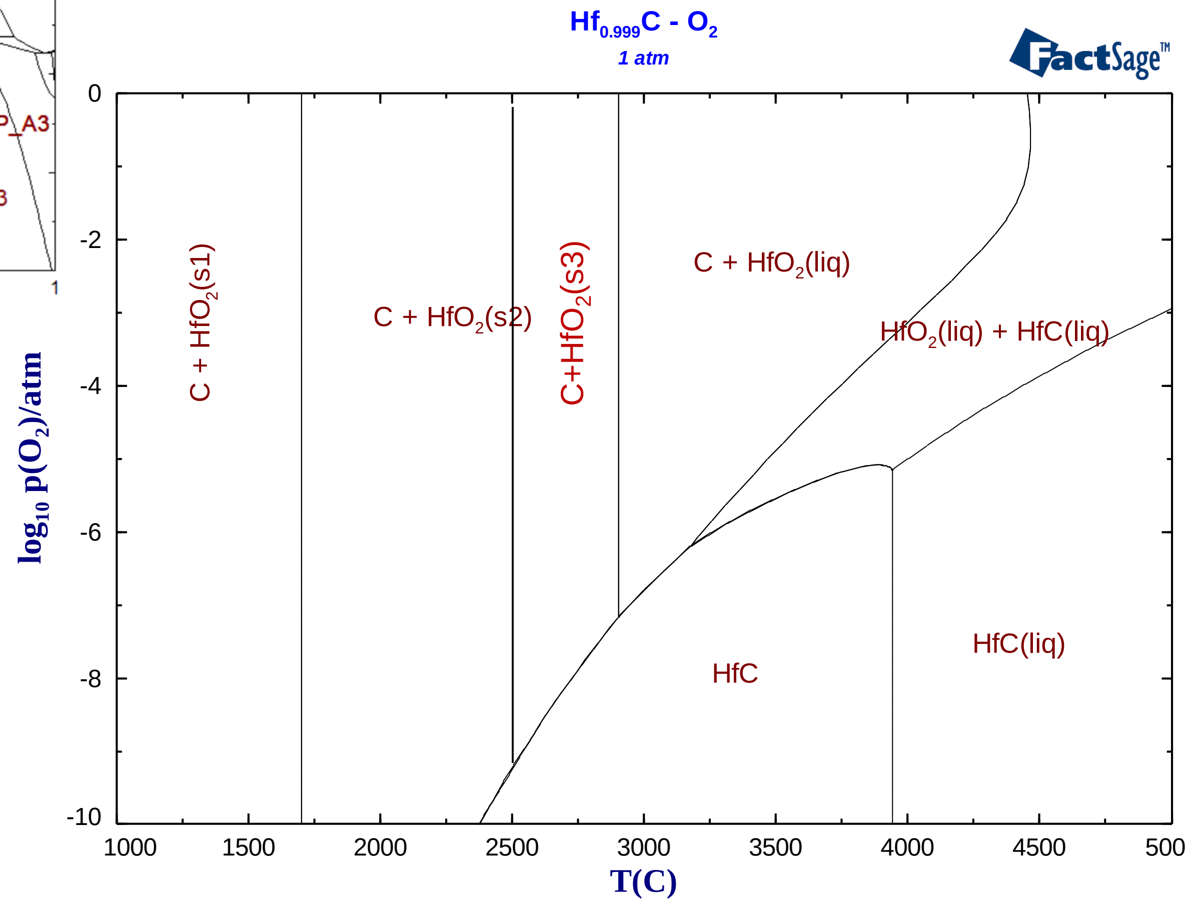
- SiC/SiC_f
- Self healing CMC

ZrO_2-CaO and ZrO_2-RE_2O_3

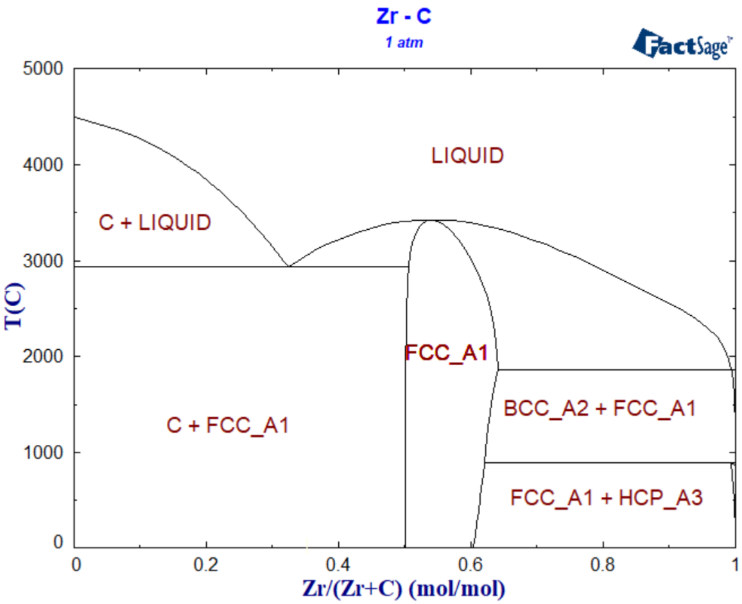
Oxidation: HfC



HfO_2
S3: Cubic
S2: Tetragonal
S1: Monoclinic



Oxidation: ZrC

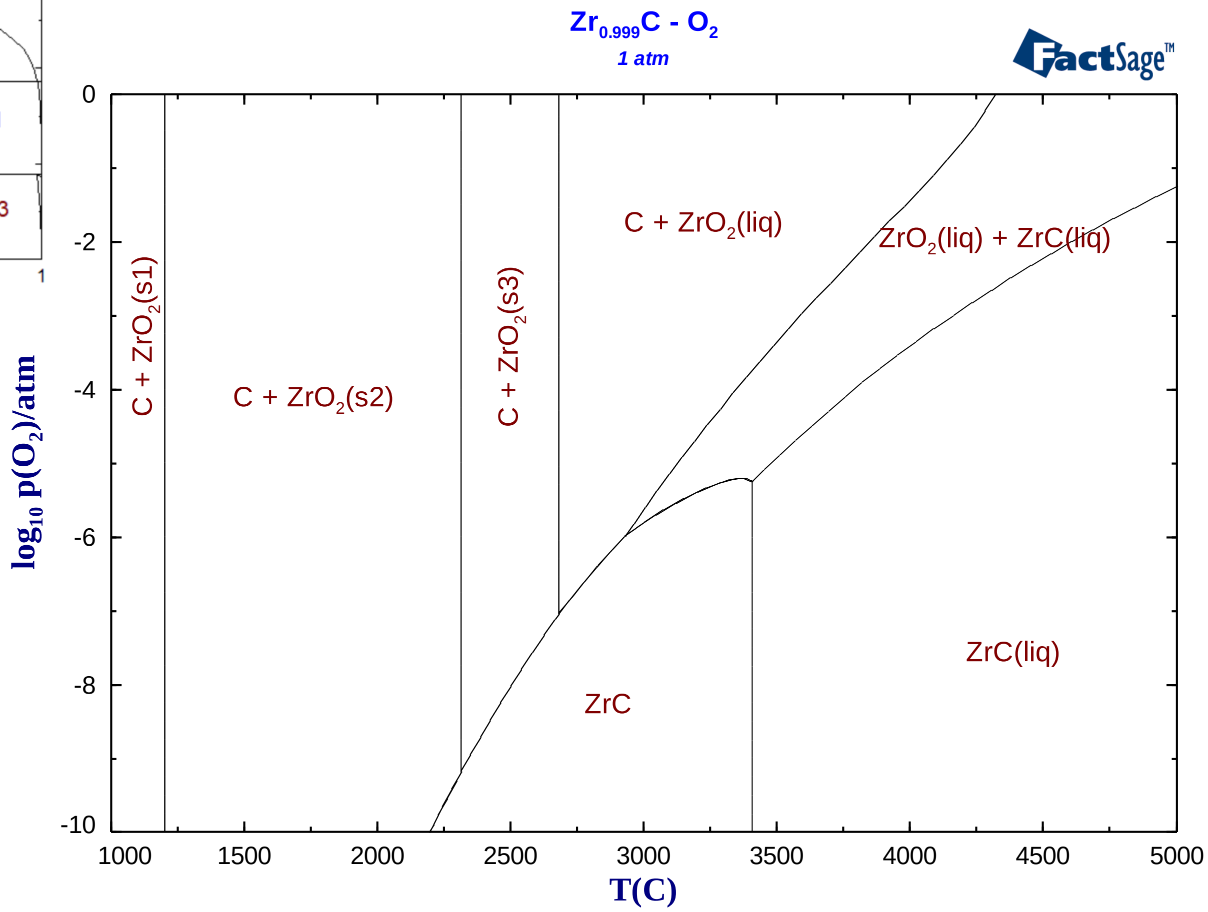


ZrO_2

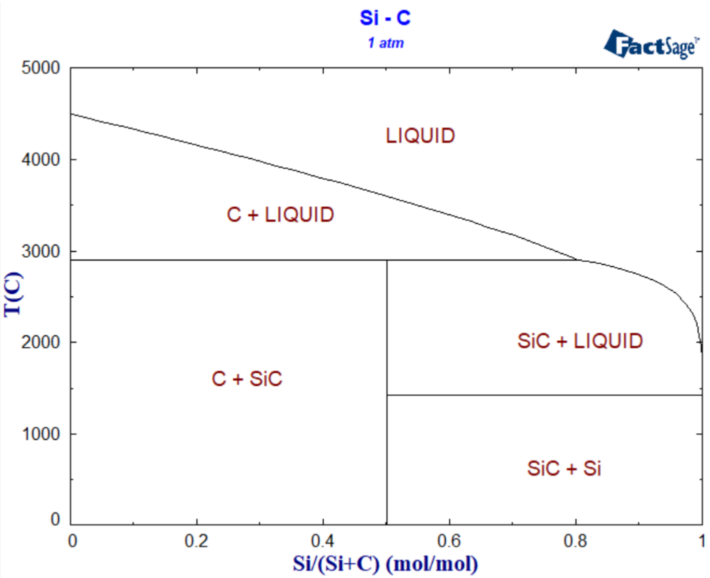
S3: Cubic

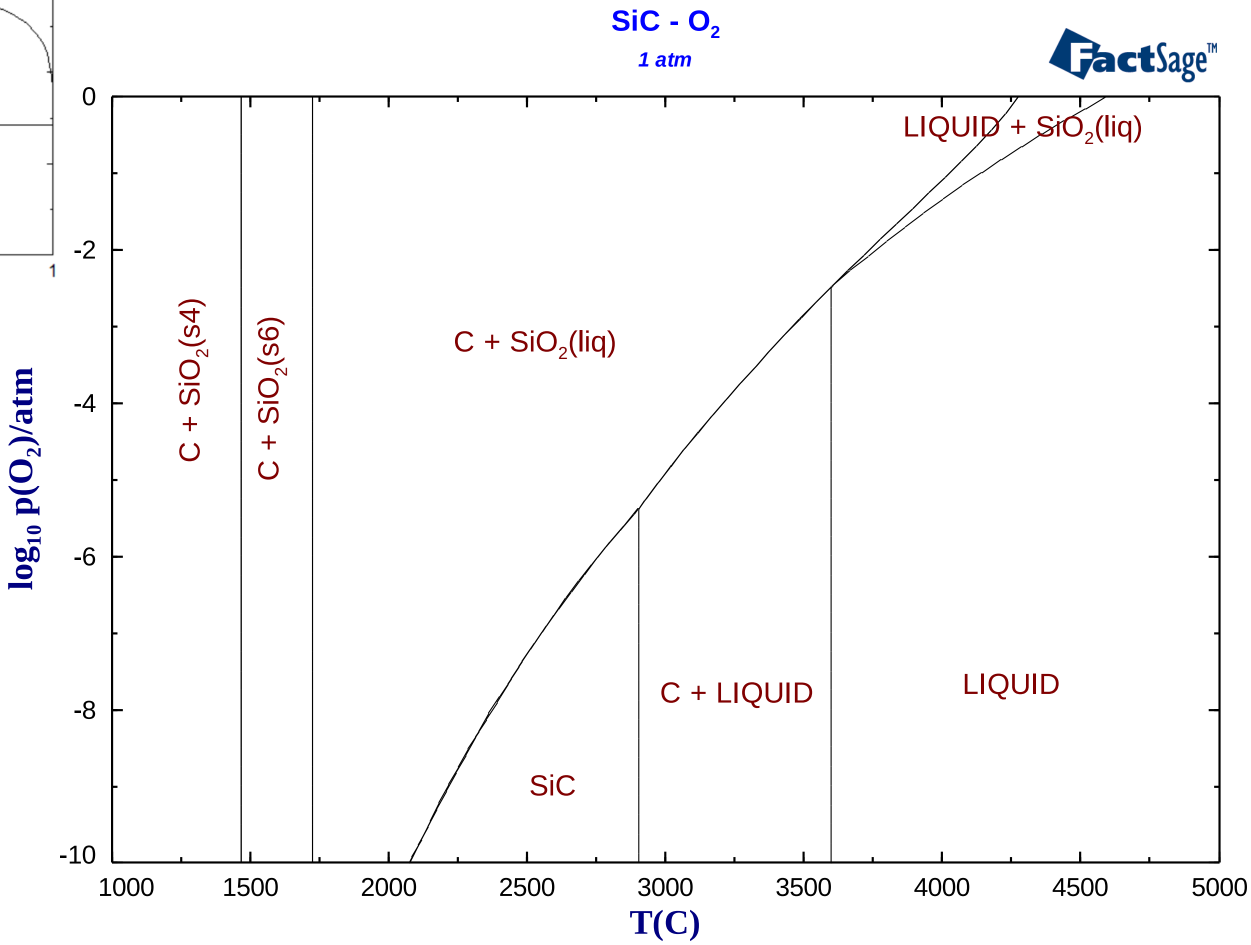
S2: Tetragonal

S1: Monoclinic



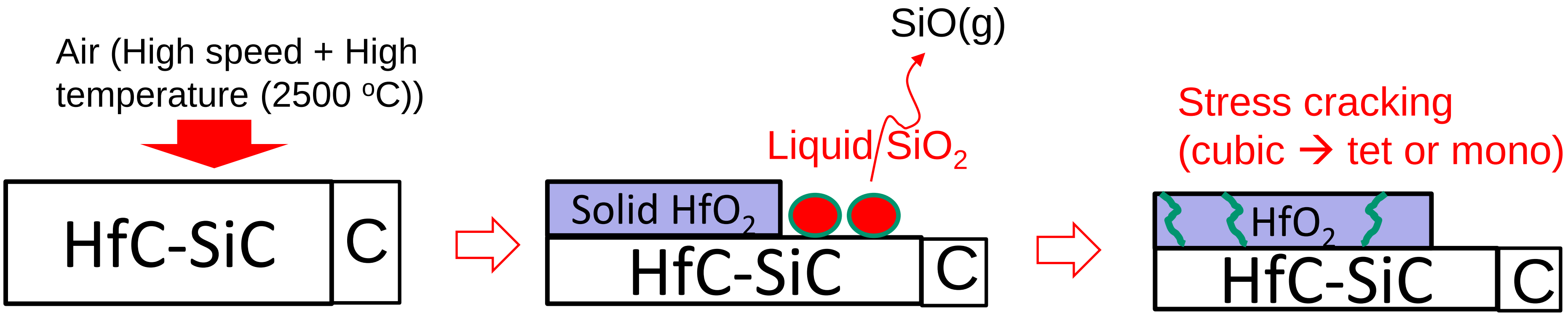
Oxidation: SiC





Oxidation of ZrC-SiC-C (CMC)

Definition of problem



Air (High speed + High temperature (2500 °C))

Stress cracking (cubic → tet or mono)

Solution: addition of xO, xC, yO, yC

Selection criteria of cubic HfO_2 stabilizer

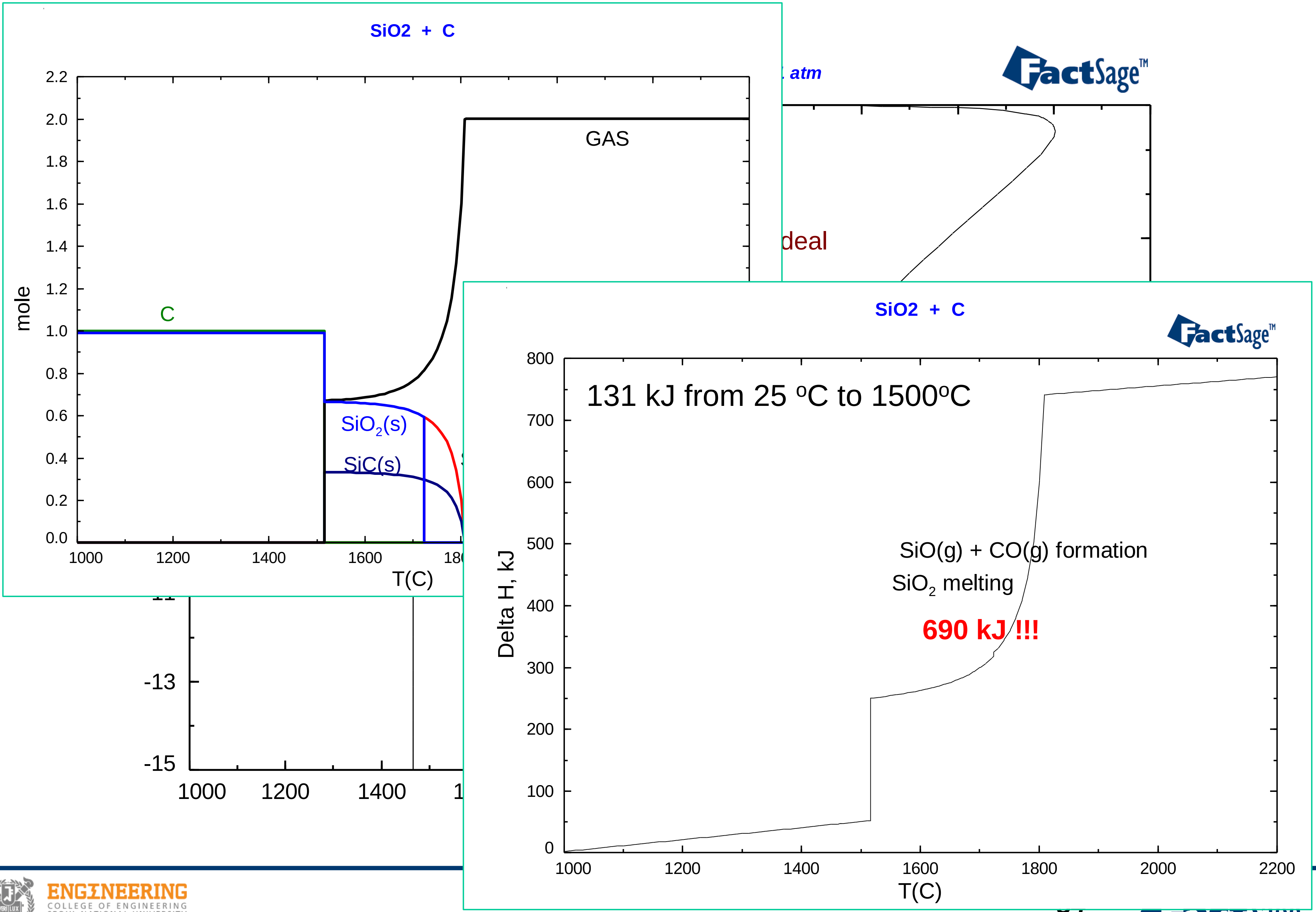
(i) No melting at 2500 °C

(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: $SiO_2(l) \rightarrow SiO(g)$



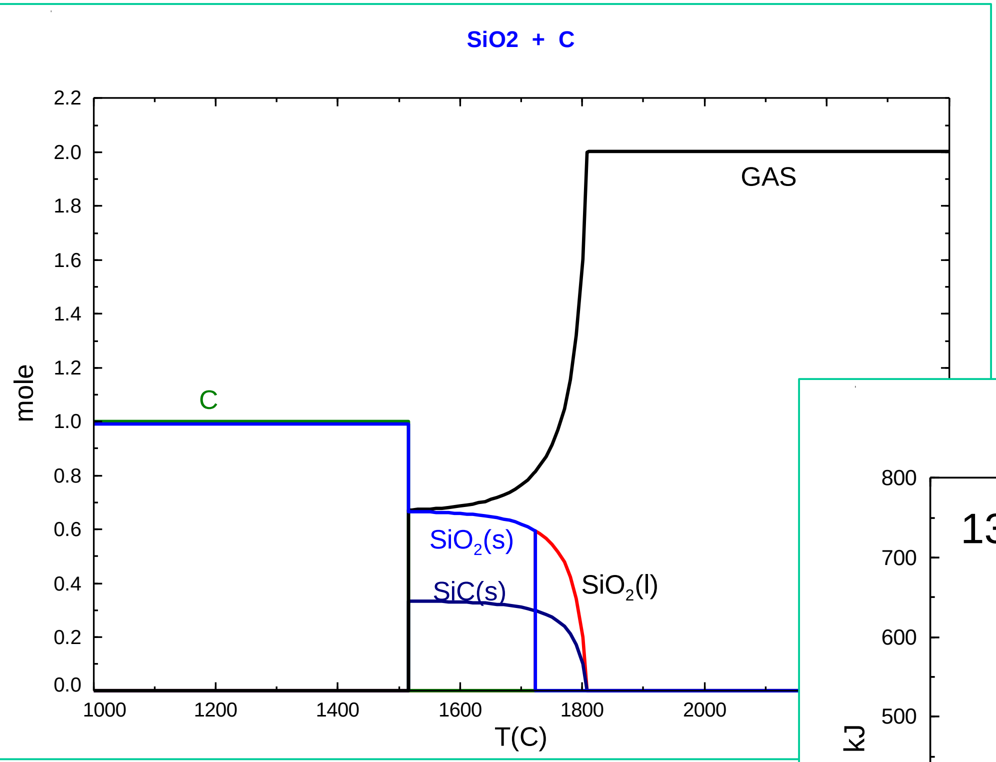
131 kJ from 25 ºC to 1500ºC

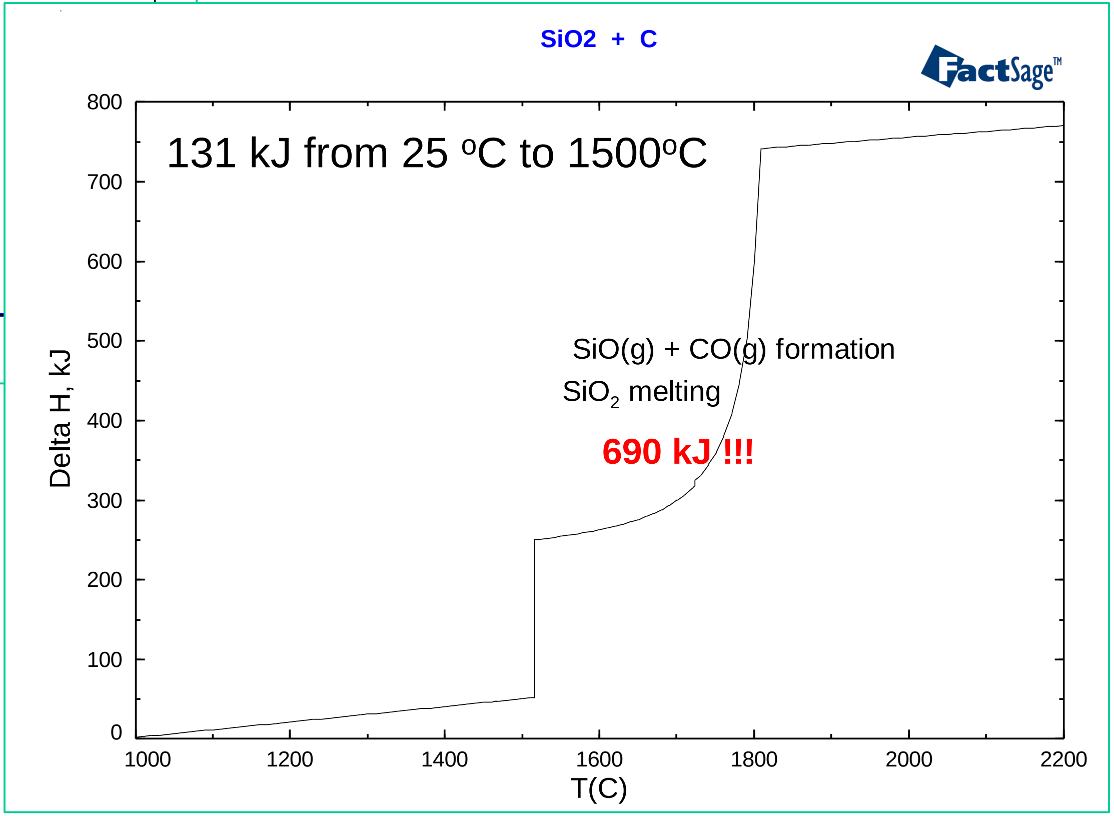
SiO(g) + CO(g) formation

SiO_2 melting

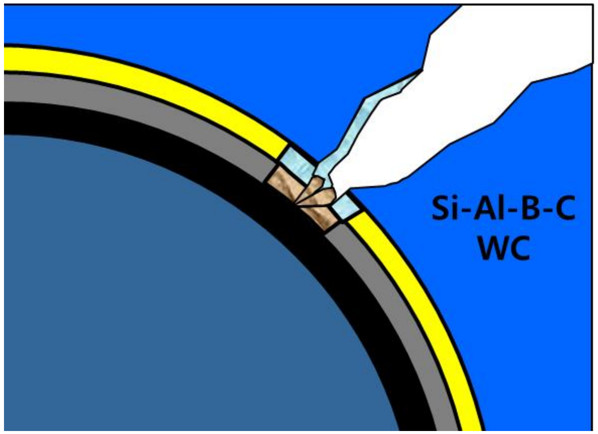
690 kJ !!!

Evaporation: $SiO_2 + C \rightarrow SiO(g) + CO(g)$





Self healing CMC



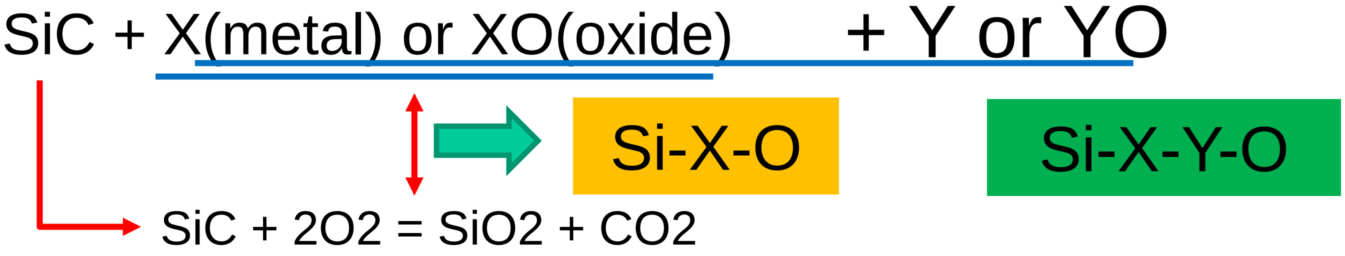
SiC + (Al-B)metal // C

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2$$

$$2Al + 2B + 3O_2 \rightarrow Al_2O_3 + B_2O_3$$

$$SiO_2 + Al_2O_3 + B_2O_3 \rightarrow \text{Liquid + Solid oxide}$$

(Liquid can fill up the gap)



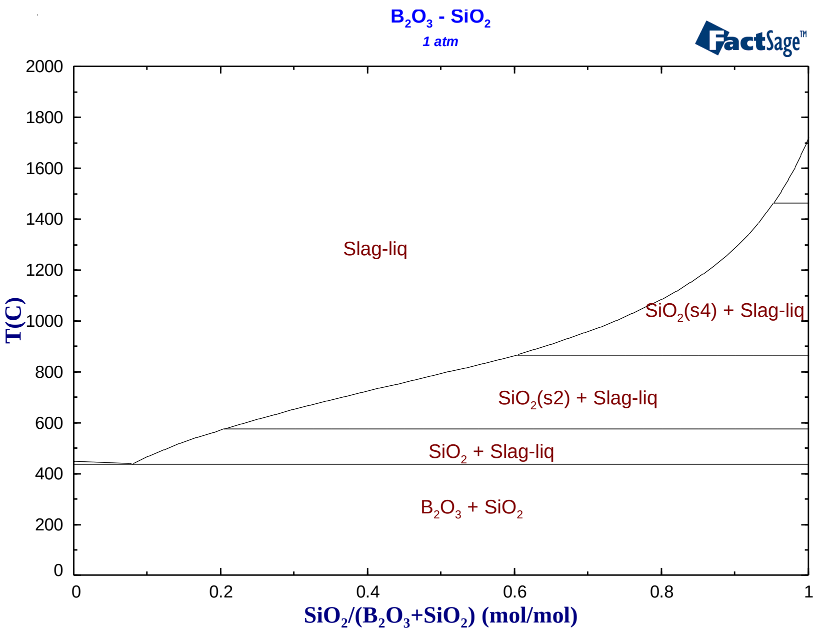
SiC + X(metal) or XO(oxide) + Y or YO

Si-X-O

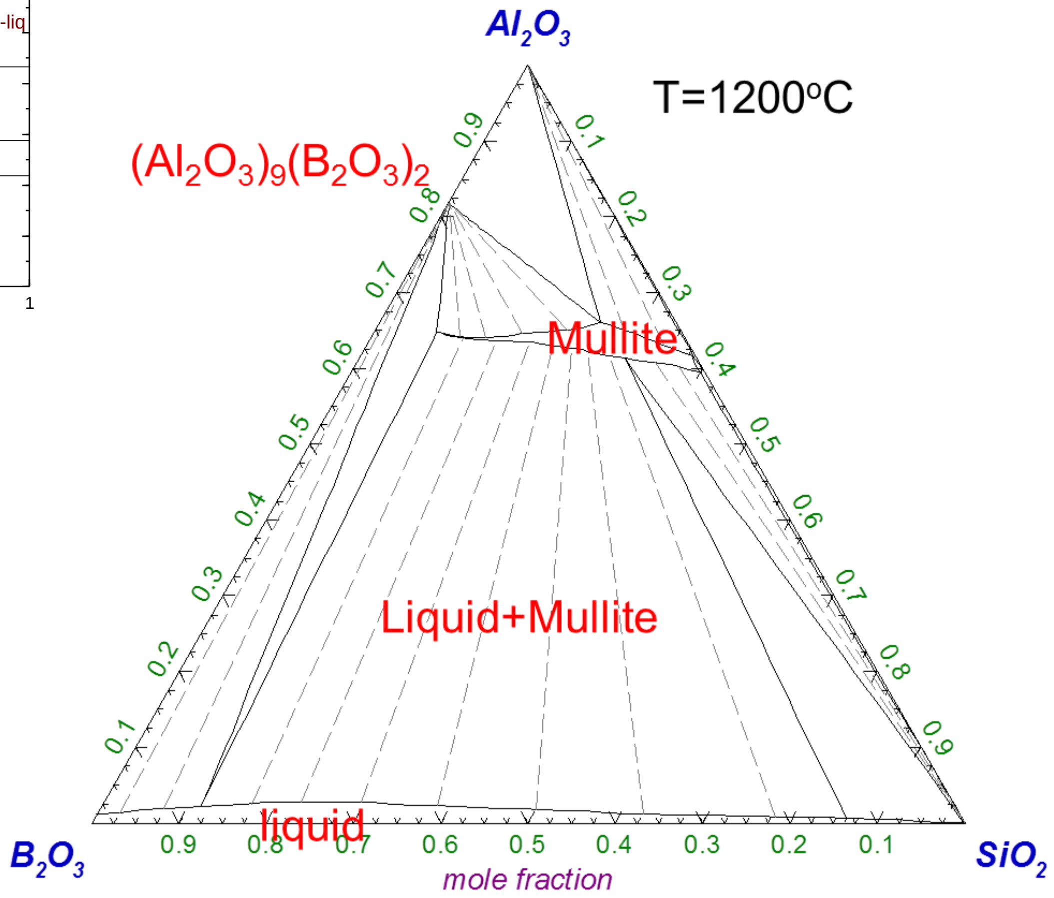
Si-X-Y-O

SiC + 2O2 = SiO2 + CO2

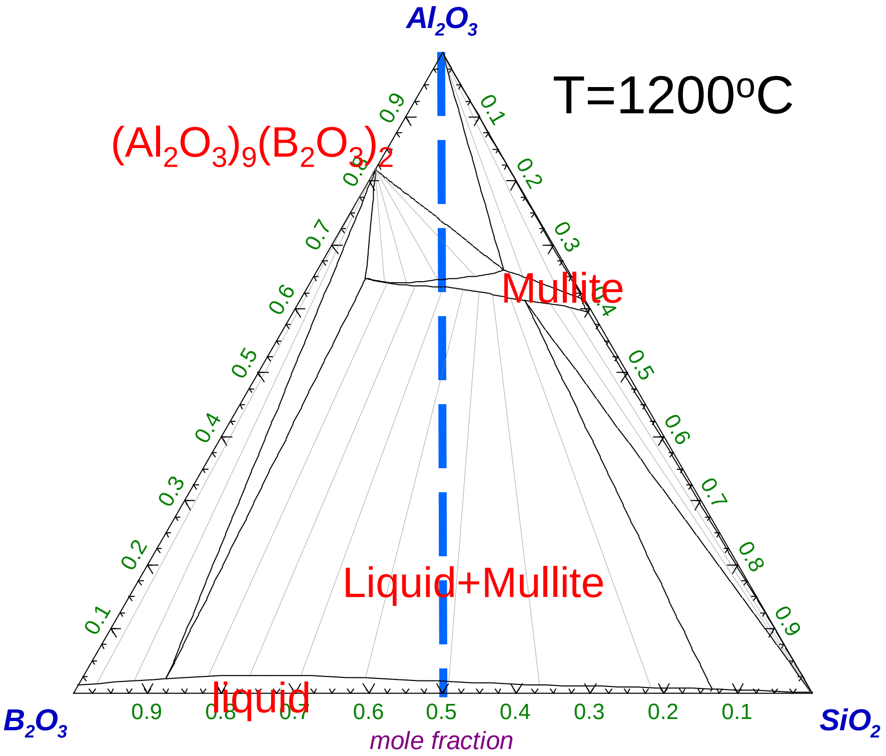
Self healing mechanism: Al_2O_3-B_2O_3-SiO_2 system



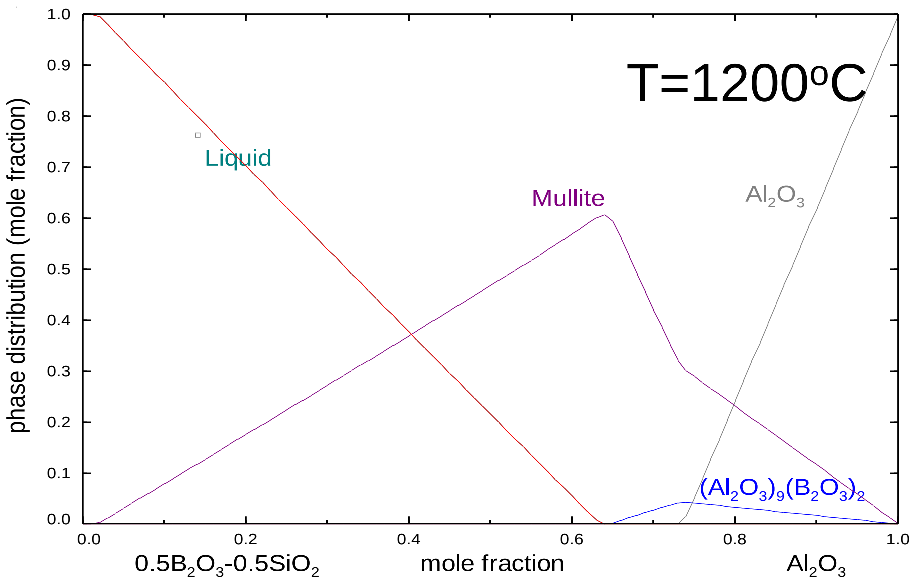
Liquid formation at low temperature



Self healing mechanism: Al_2O_3-B_2O_3-SiO_2 system

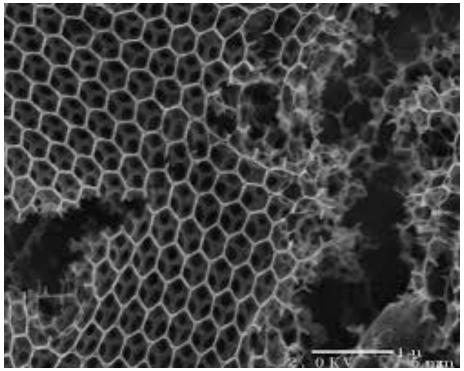


Increasing effective viscosity by forming liquid+solid mixture

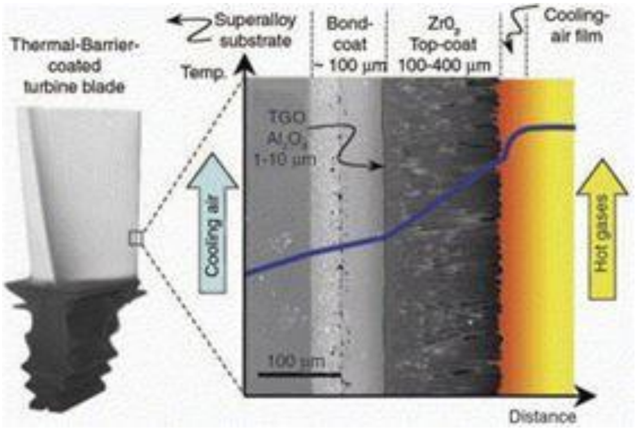


Materials Design and Structure Design

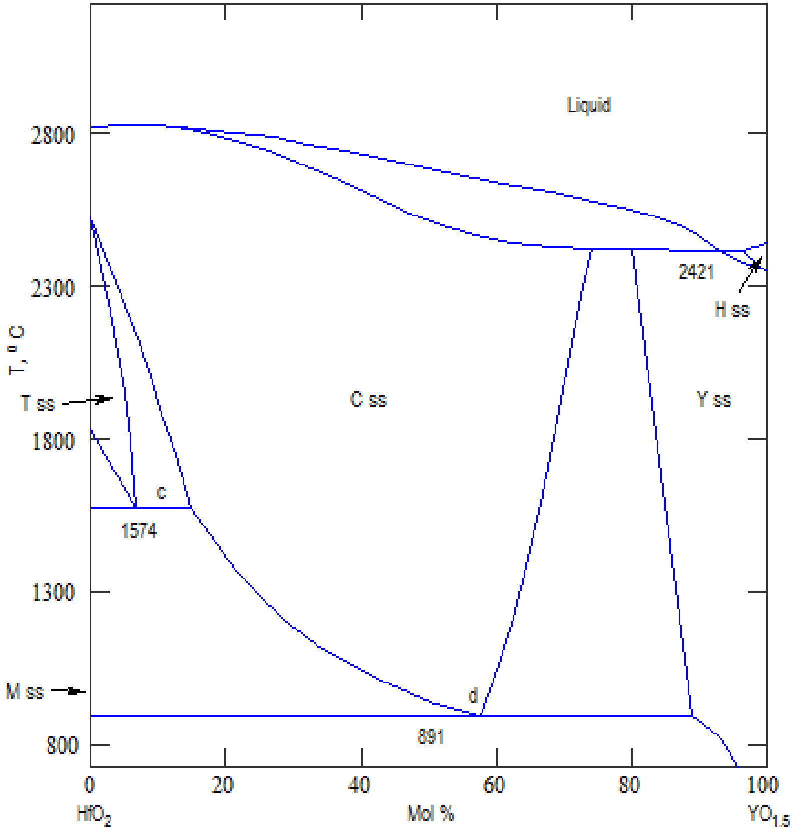
- Si–B–C + Al → not good at high temperature because Liquid can be pulled out.
- Si–B–C + porous Al_2O_3 → same chemistry but may be Good structure

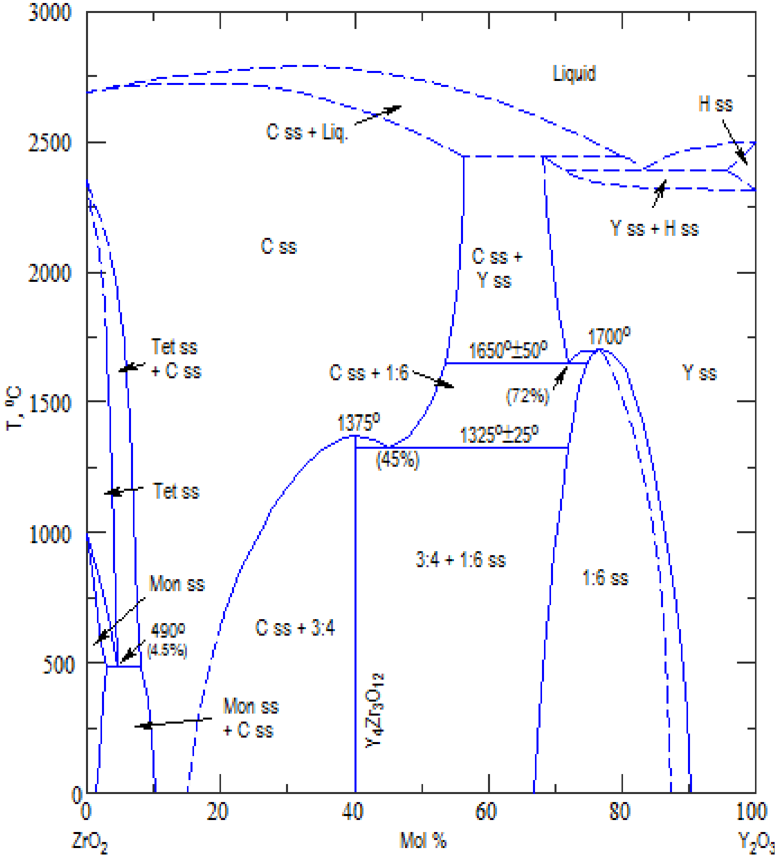


TBC coating: Cubic HfO_2 and ZrO_2 stabilization

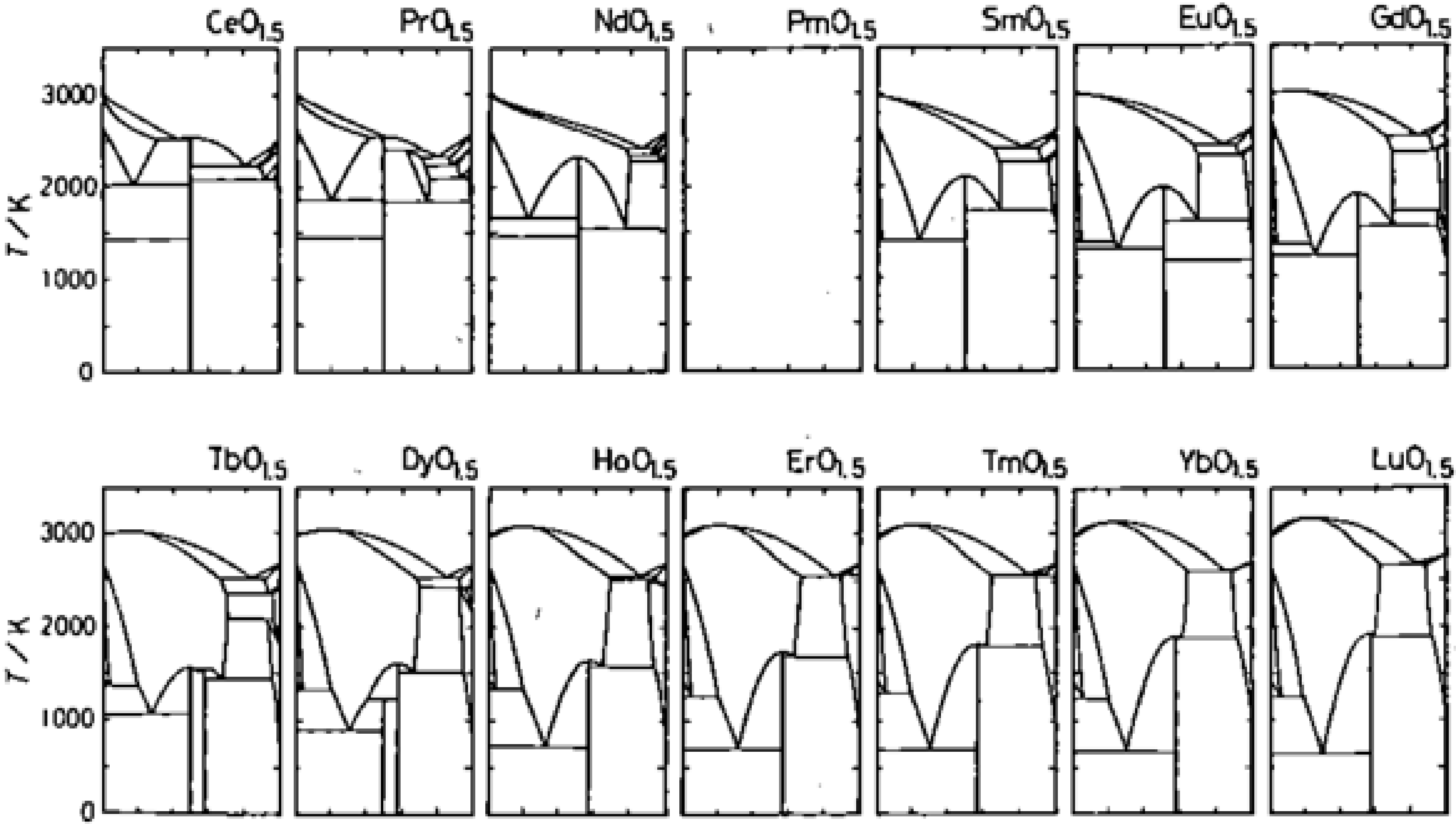


Cubic HfO_2 and ZrO_2 stabilization by additives



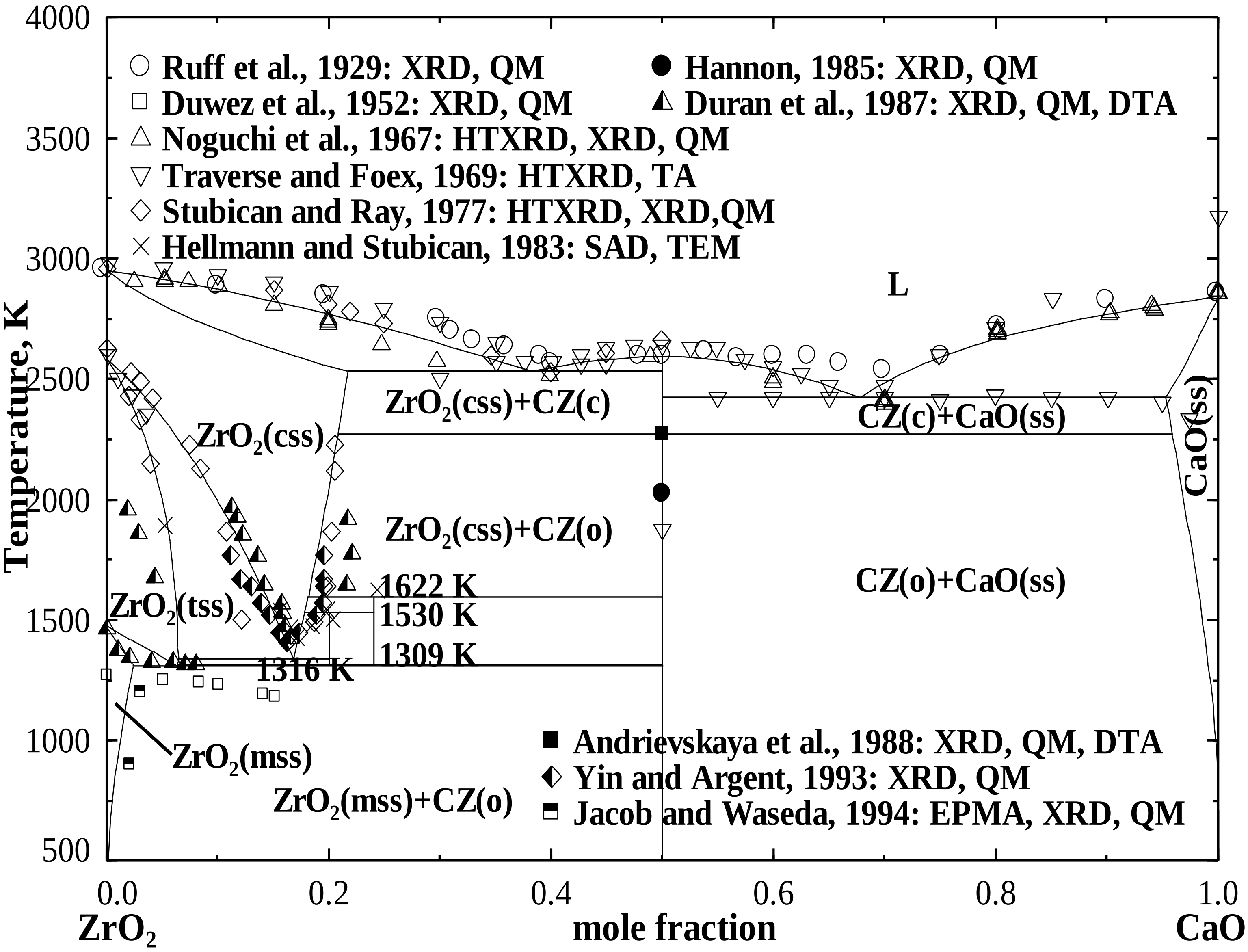


ZrO_2-Re_2O_3 phase diagram (Predicted)



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

ZrO_2-CaO



4000
3500
3000
2500
2000
1500
1000
500
Temperature, K
○ Ruff et al., 1929: XRD, QM
□ Duwez et al., 1952: XRD, QM
△ Noguchi et al., 1967: HTXRD, XRD, QM
▽ Traverse and Foex, 1969: HTXRD, TA
◇ Stubican and Ray, 1977: HTXRD, XRD,QM
× Hellmann and Stubican, 1983: SAD, TEM
● Hannon, 1985: XRD, QM
◭ Duran et al., 1987: XRD, QM, DTA
L
ZrO2(css)+CZ(c)
ZrO2(css)
CZ(c)+CaO(ss)
CaO(ss)
ZrO2(css)+CZ(o)
1622 K
1530 K
1309 K
1316 K
ZrO2(tss)
CZ(o)+CaO(ss)
ZrO2(mss)
ZrO2(mss)+CZ(o)
■ Andrievskaya et al., 1988: XRD, QM, DTA
◆ Yin and Argent, 1993: XRD, QM
▬ Jacob and Waseda, 1994: EPMA, XRD, QM
0.0
0.2
0.4
0.6
0.8
1.0
ZrO2
mole fraction
CaO

Summary

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

HYUNDAI STEEL

TATA STEEL

voestalpine

NUCOR

SeAH Besteel

posco

RHI

NIPPON STEEL & SUMITOMO METAL

JFE

DOOSAN

Doosan Heavy Industries & Construction

RioTinto

SCHOTT glass made of ideas