



ENGINEERING
COLLEGE OF ENGINEERING
SEOUL NATIONAL UNIVERSITY
서울대학교공과대학

Department of Materials Science and Engineering

열역학 계산의 기초 및 응용

CALPHAD Thermodynamic Database and Applications to Steelmaking process and Alloy design

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- Review of Engineering Thermodynamics
- Computational thermodynamic database
 - Development of CALPHAD thermodynamic database
- Applications to Steelmaking process

REVIEW OF ENGINEERING THERMODYNAMICS

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

2. Chemical reaction between pure compounds (No solution)

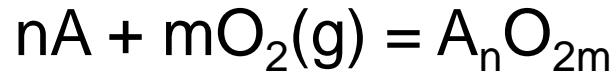


$$\begin{aligned}\Delta G_{rxn}^o &= G_{A_nB_m}^o - (nG_A^o + mG_B^o) \\ &= \Delta H_{rxn}^o - T\Delta S_{rxn}^o\end{aligned}$$

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

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

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

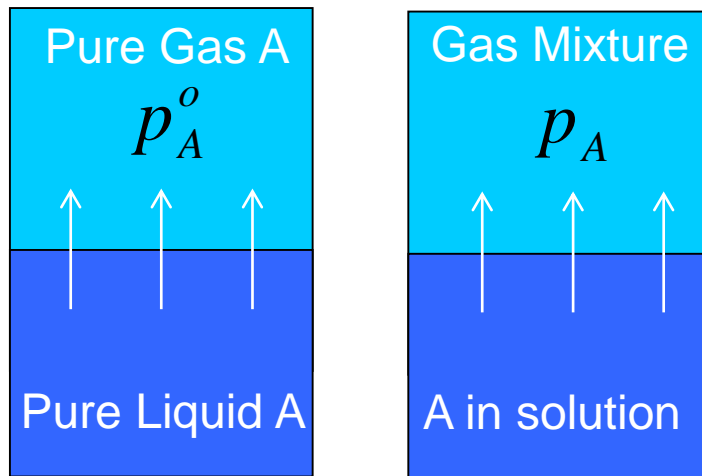
K_{eq} : Equilibrium constant

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

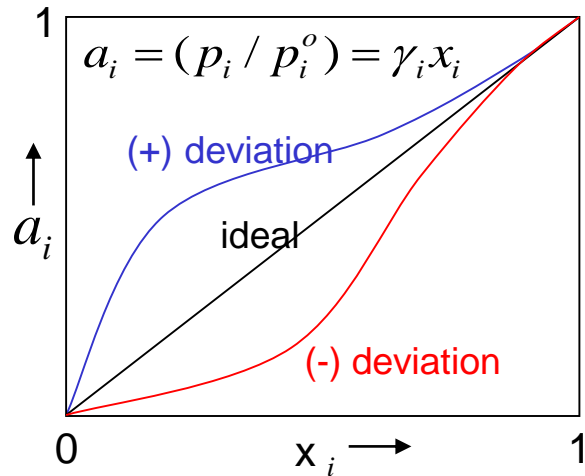


$$a_A = \frac{P_A}{P_A^{\circ}} = \gamma_A x_A$$

\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
 $\rightarrow a_i > x_i$: more active chemical reaction of i

(-) deviation: attraction between i and other species
 $\rightarrow a_i < x_i$: 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

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

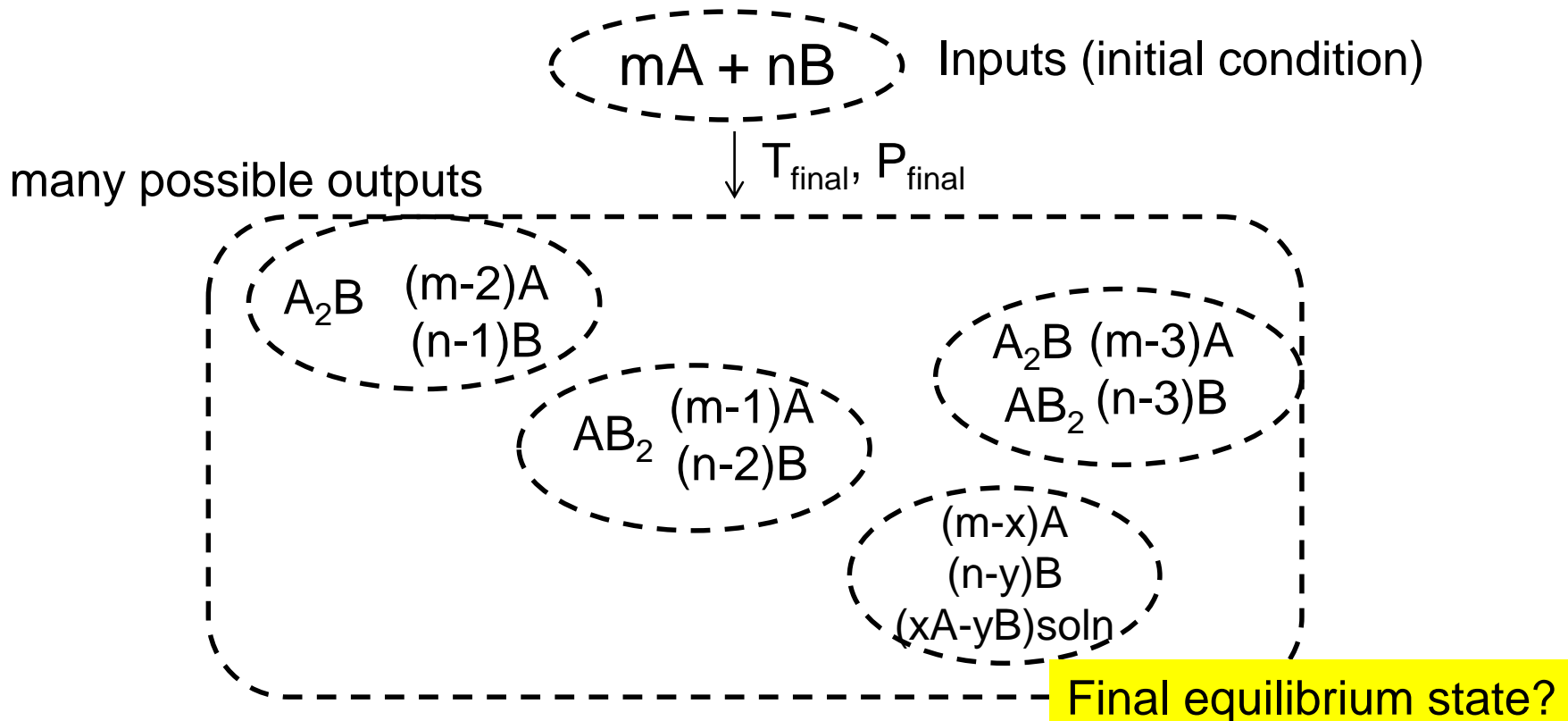
* FactSage solution database contains the model and model parameters to calculate G_i and eventually get a_i

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)

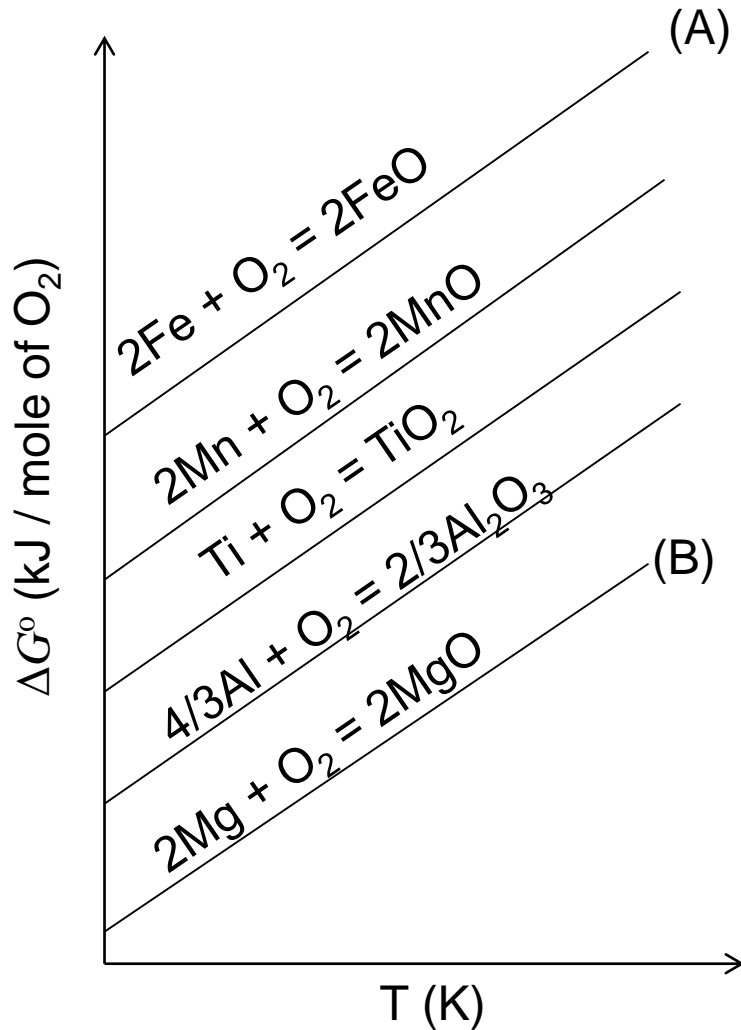
- We have to find out which phase assemblage is the most stable at given T_f and P_f with respect to the mass balance.
- Gibbs energy minimization routine: ChemSage, Solgas-mix, etc.

The most stable phase assemblage has the lowest Gibbs energy.

In FactSage

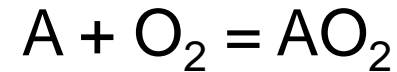
- Put inputs amount
- Select all possible phases (solid compounds, solid solutions, liquid solutions, gases)
- Set T_{final} and P_{final}
- Calculation (Gibbs energy minimization routine)
- Equilibrium phase assemblage

Ellingham Diagram



- Collection of ΔG° for oxidation reaction
 $m\text{A} + \text{O}_2 = \text{A}_m\text{O}_2$ (reference: 1 mol of O_2)

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



$$\Delta G = \Delta G^\circ + RT \ln \frac{(a_{\text{AO}_2})}{(a_{\text{A}}) (p_{\text{O}_2})}, (\Delta G = 0: \text{Equilibrium})$$

$$\Delta G^\circ = RT \ln p_{\text{O}_2}$$

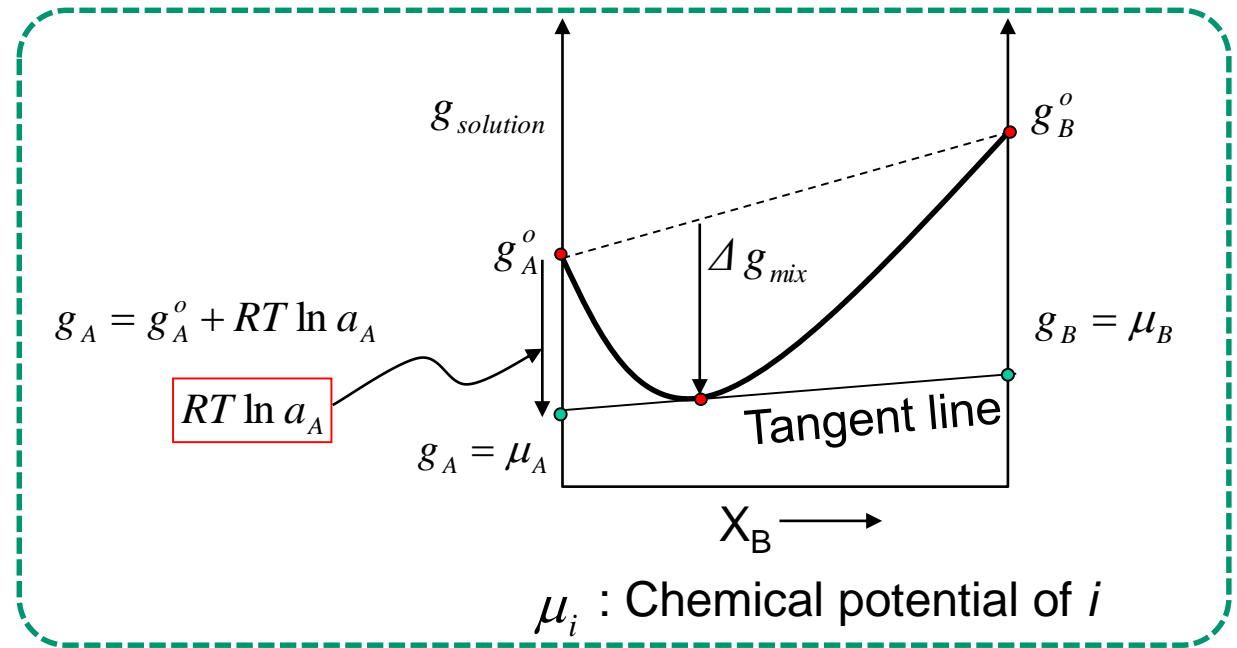
$$\Delta G^\circ = (R \ln p_{\text{O}_2}) \times T$$

Solution thermodynamics

A-B solution, (Solid or Liquid solution)

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

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



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

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: $RT \ln \gamma_A = \Omega_{AB} x_B^2$ 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: $\gamma_A = f(x, T)$

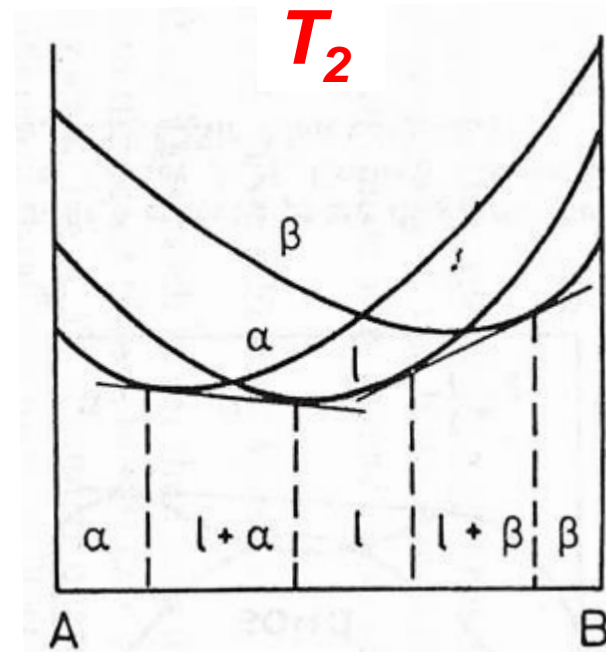
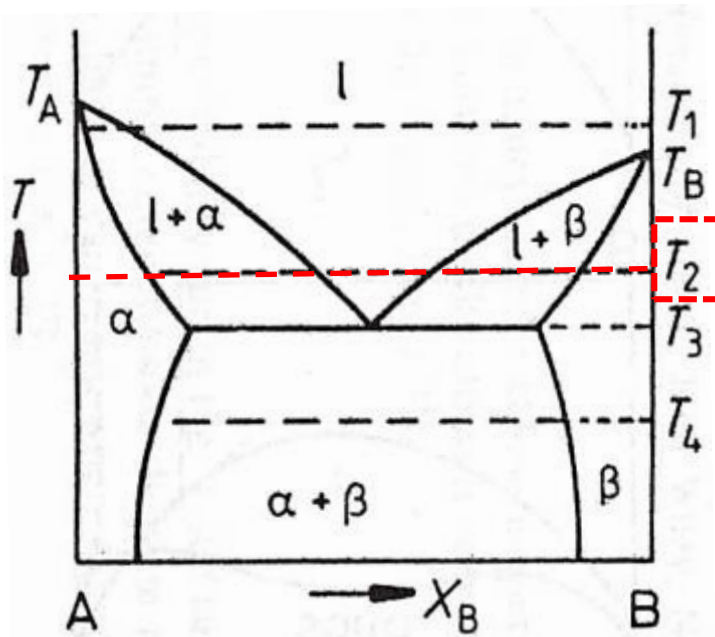
$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}$$

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

* 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.

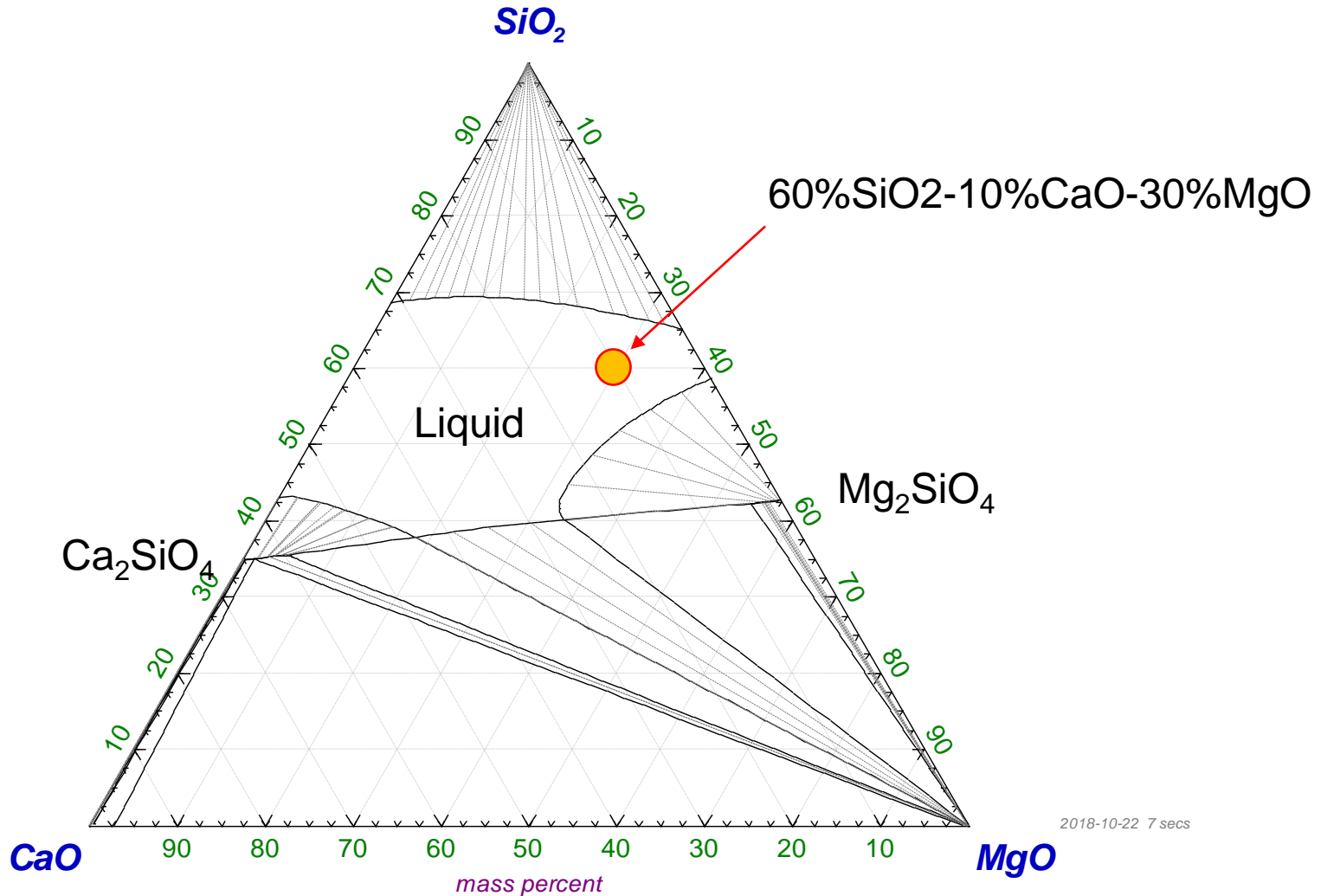


Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2nd Ed. CHAMAN & HALL (1992)

Ternary phase diagram: isothermal phase diagram

CaO - MgO - SiO₂

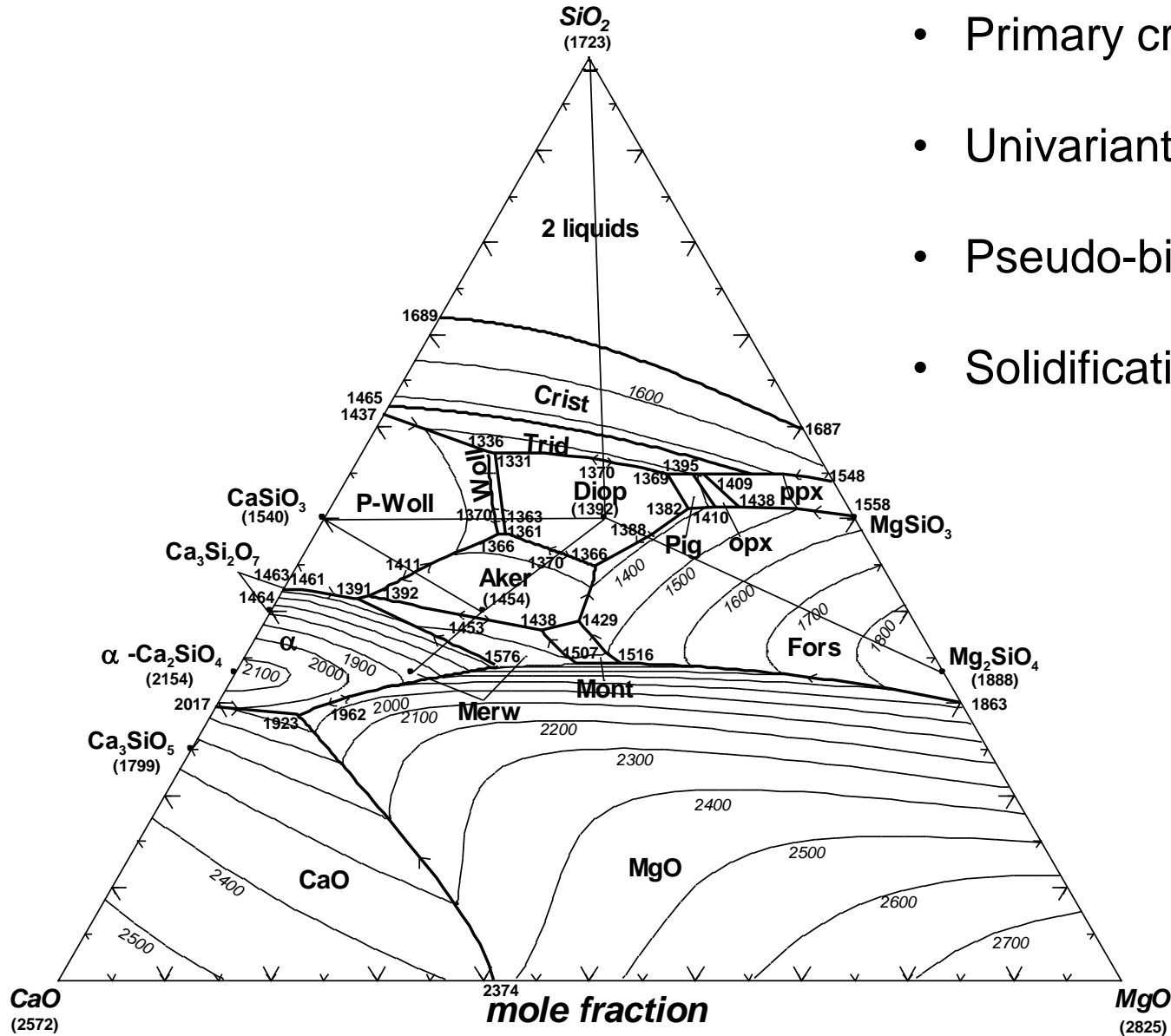
1600°C, 1 atm



2018-10-22 7 secs

Ternary phase diagram: Liquidus projection

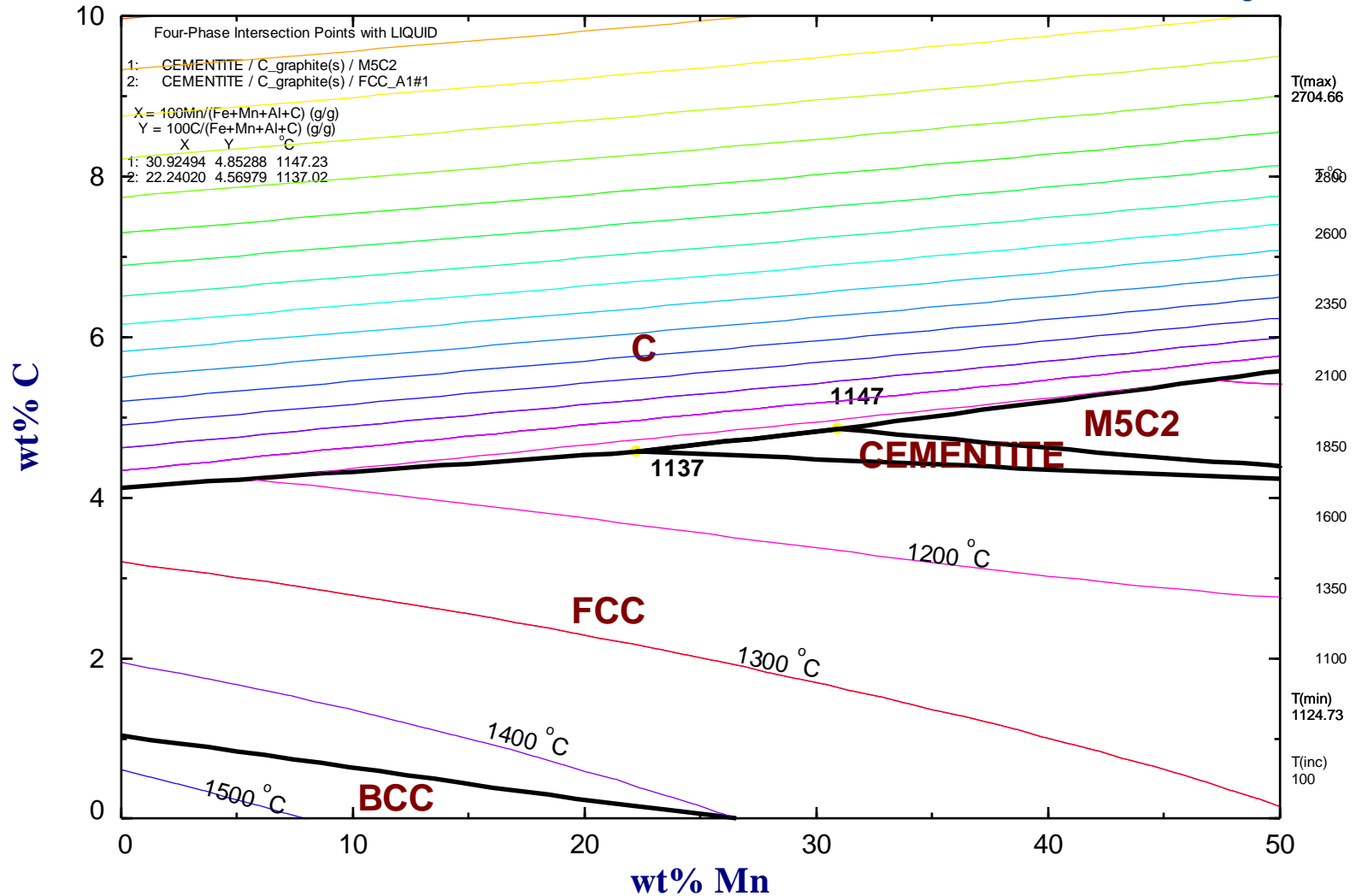
- Primary crystalline phase
- Univariant line
- Pseudo-binary phase diagram
- Solidification pass



Quaternary phase diagram: Liquidus projection

Fe - Mn - Al - C

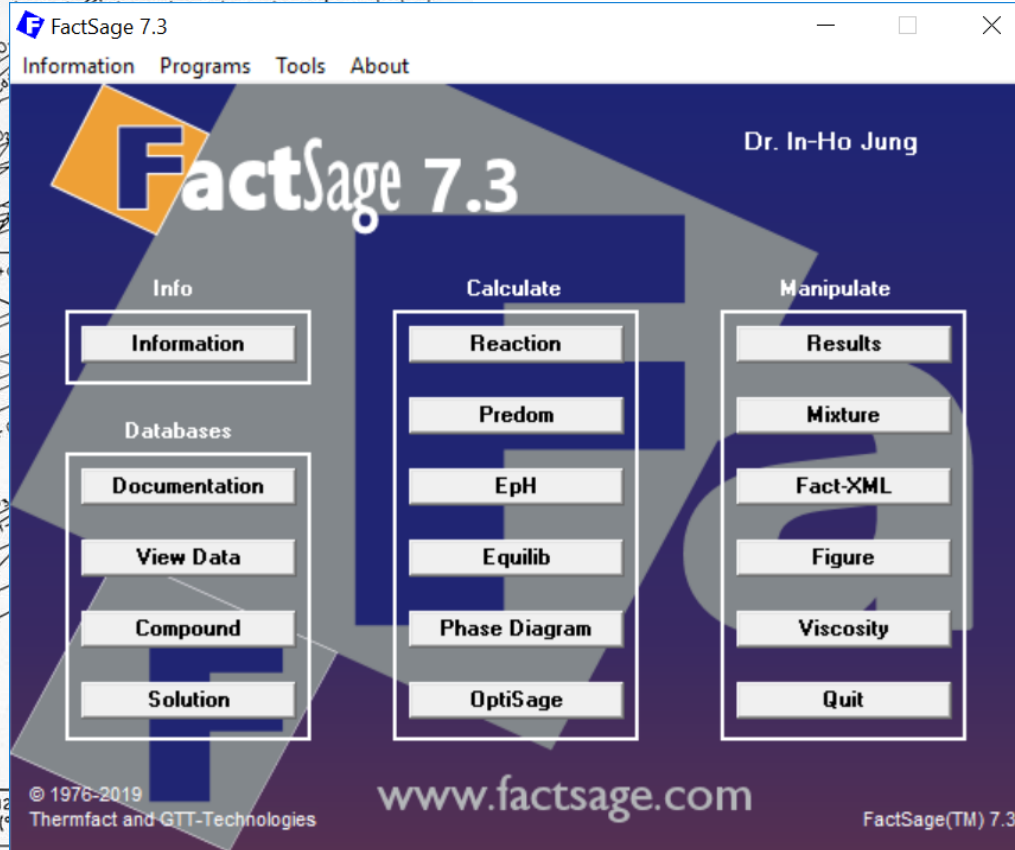
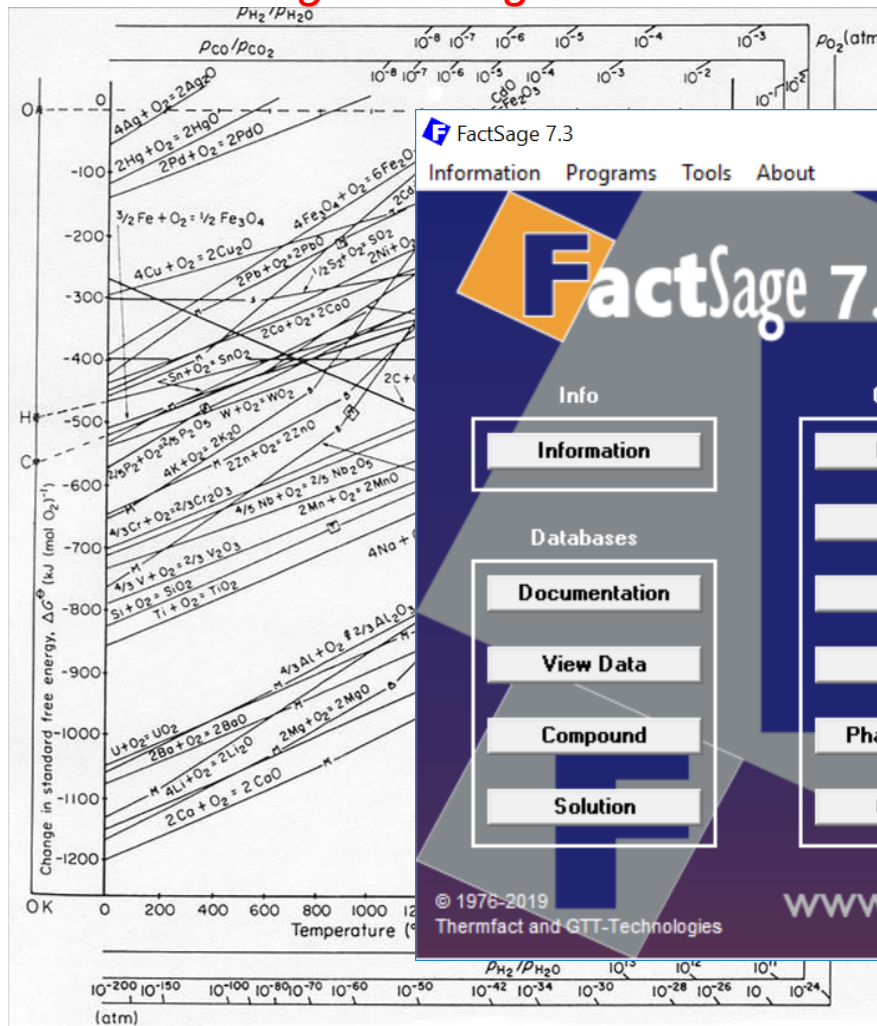
1.5 wt.% Al



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+]

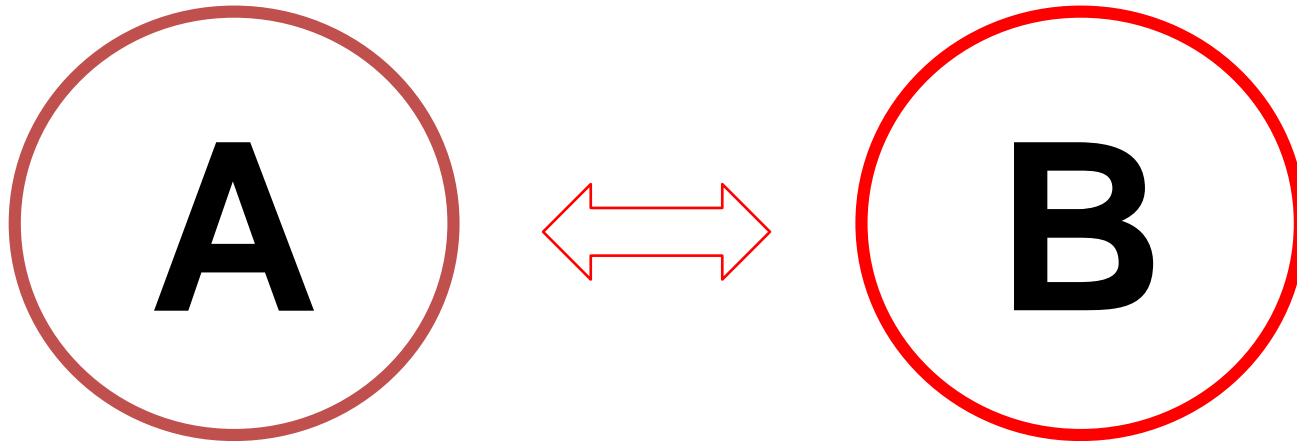
+ 5.7638 gram AMonoxide#1
 (5.7638 gram, 0.13398 mol)
 (1600 C, 1 atm, a=1.0000)
 (0.10016 wt.% CaO
 + 91.310 wt.% MgO
 + 0.18976 wt.% Al₂O₃
 + 8.3998 wt.% Cr₂O₃

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

CALPHAD THERMODYNAMIC DATABASE

- Thermodynamic models
- Database development

Development of Thermodynamic Database



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

→ Thermodynamic Database



CALPHAD

Phase diagram data

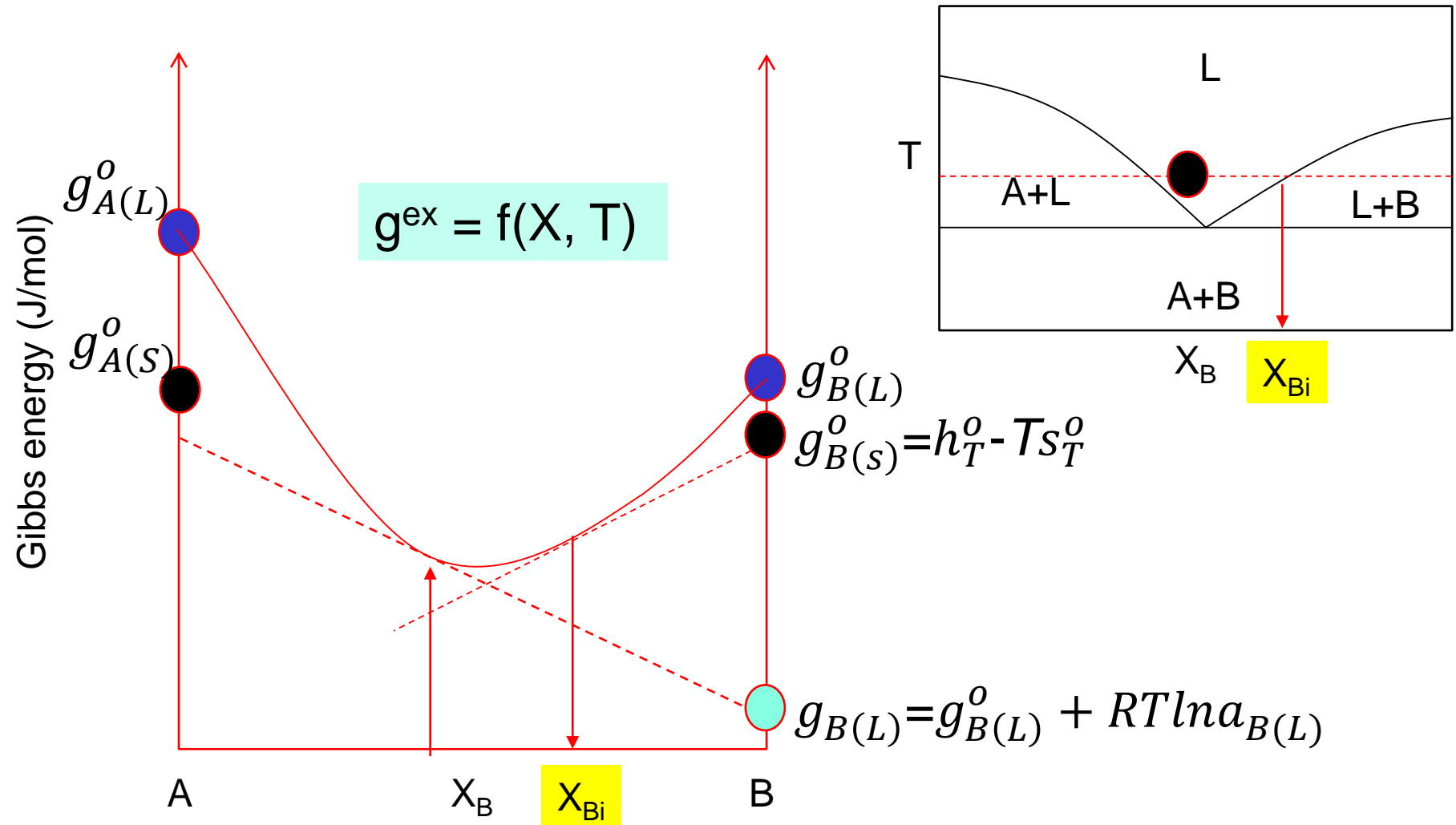
- Phase diagram
- S/L/G phase equilibria

Crystal Structural data

Thermodynamic data

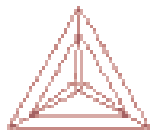
- Calorimetric data: Heat capacity, H of mixing, H of melting, etc.
- Vapour pressures
- Chemical Potentials: activity

CALPHAD type thermodynamic modeling



Commercial software and databases

FactSage™



Thermo-Calc Software



1970'

1980'

1990'

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

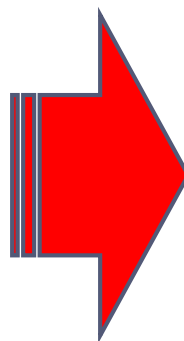


**Thermodynamic
database**

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

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

**Physical Property
database**

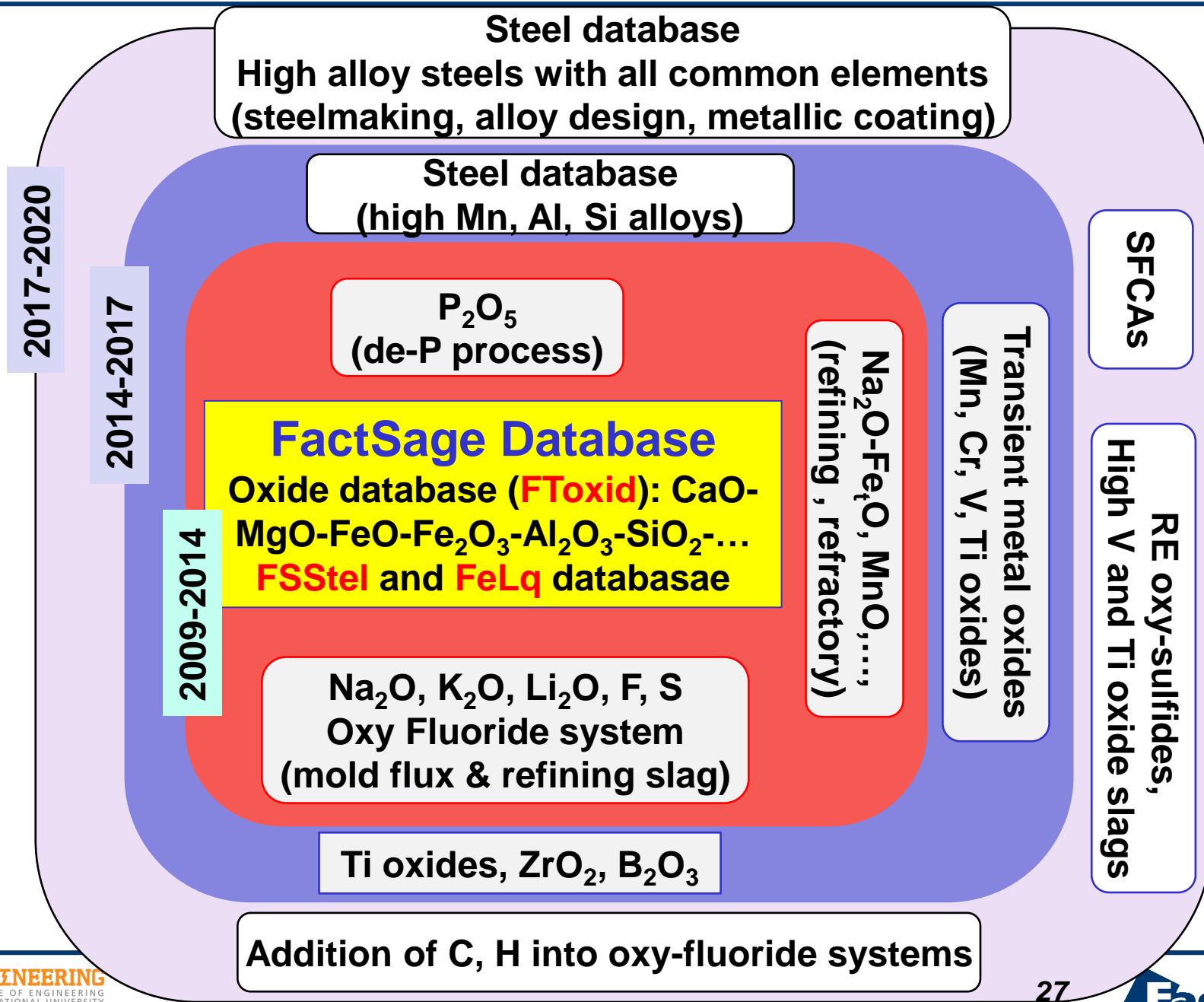


**Kinetic Process
Simulation models
(EERZ Concept)**

- Secondary Refining Units
- Continuous Casting Process

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

Steelmaking Consortium project (2009 ~ 2020)



Pure compound

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

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

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

$$C_p = a + bT + cT^2 + \dots$$

- Calorimetry
- emf
- Knudsen cell
- Vapor pressure

Solution

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



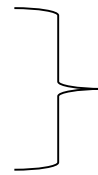
$$G_i = G_i^o + RT \ln a_i$$

Binary solution

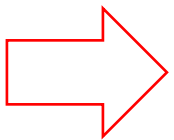
$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

$$= (x_A G_A^o + x_B G_B^o) - T\Delta S^{conf} + G^{ex}$$

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



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



Expression of S^{conf} and G^{ex} is dependent on the thermodynamic (solution) model

Bragg Williams Random Mixing Model (BWRMM)

$$G^L = X_A G_A^{o,L} + X_B G_B^{o,L} + RT(X_A \ln X_A + X_B \ln X_B) + G^{ex}$$

$$G^{ex} = \sum q_{AB}^{mn} X_A^m X_B^n$$

- Bad description of entropy of solution
 - Strong temperature dependence terms are required
- Many excess parameters in high order systems
- No proper interpolation technique:
 - Only using **Muggianu interpolation technique**

Solution model (2): Quasi-chemical Model

Modified Quasichemical Model (MQM)

$$(A - A) + (B - B) = 2(A - B) : \Delta g_{AB}$$

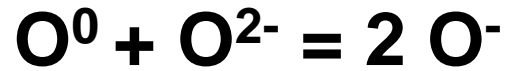
$$G = (n_A G_A^o + n_B G_B^o) - T\Delta S^{config} + n_{AB} (\Delta g_{AB} / 2)$$

$$\begin{aligned} \Delta S^{config} = & -R(n_A \ln X_A + n_B \ln X_B) \\ & - R[n_{AA} \ln(X_{AA} / Y_A^2) + n_{BB} \ln(X_{BB} / Y_B^2) \\ & + n_{AB} \ln(X_{AB} / 2Y_A Y_B)] \end{aligned}$$

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i \geq 1} g_{AB}^{i0} (X_{AA})^i + \sum_{j \geq 1} g_{AB}^{0j} (X_{BB})^j$$

- Good description of entropy \rightarrow less T dependent parameters
- Can use **proper interpolation technique**
- **Liquid Slags and Salts (oxide, fluoride, ...), Liquid alloys**

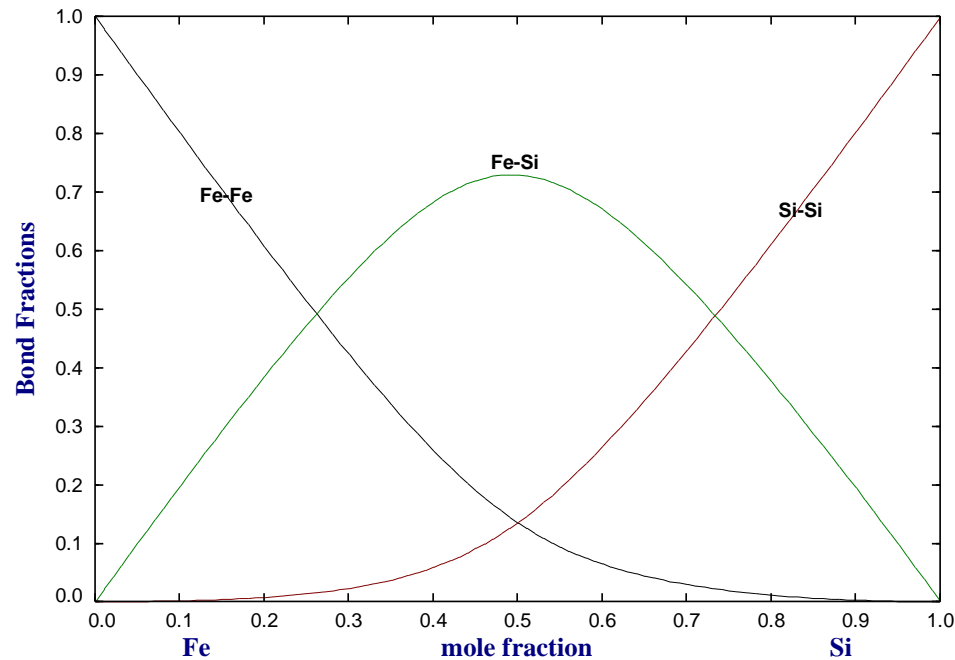
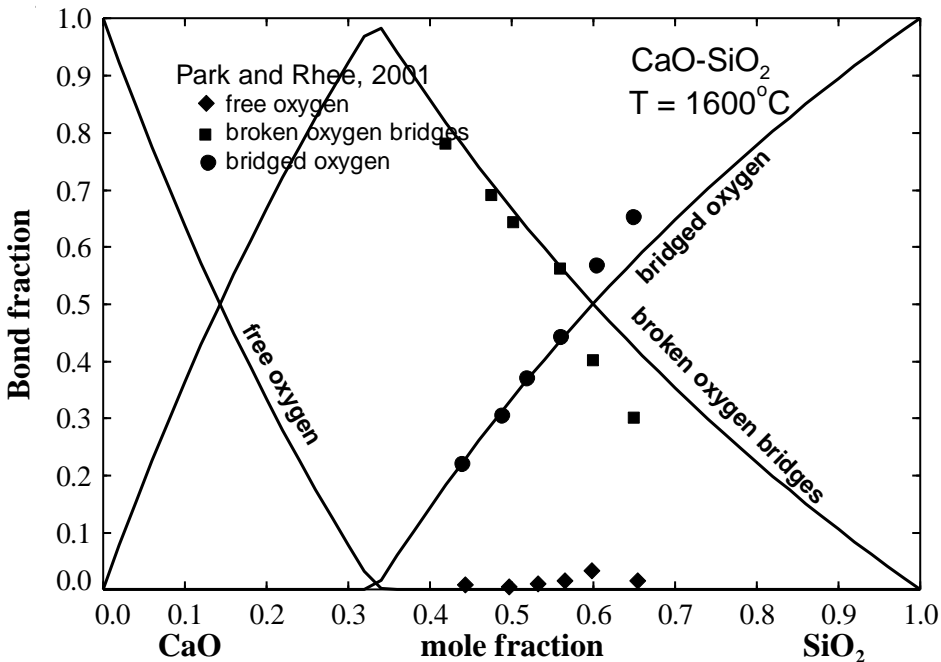
Solution model (2): Quasi-chemical Model



Calculated bonding in liquid silicates

Liquid Fe-Si solution

T=1600C



Bond fraction → Structure → Physical property models

Unified (Wagner) Interaction parameter model

$$a_{i(H)} = f_i x_i \quad \ln f_i = \varepsilon_i^i x_i + \varepsilon_i^j x_j + \varepsilon_i^k x_k + \dots$$

$$a_{i(\text{wt.}\%)} = f_i x_i \quad \log f_i = e_i^i [\text{wt}\% i] + e_i^j [\text{wt}\% j] + e_i^k [\text{wt}\% k] + \dots$$

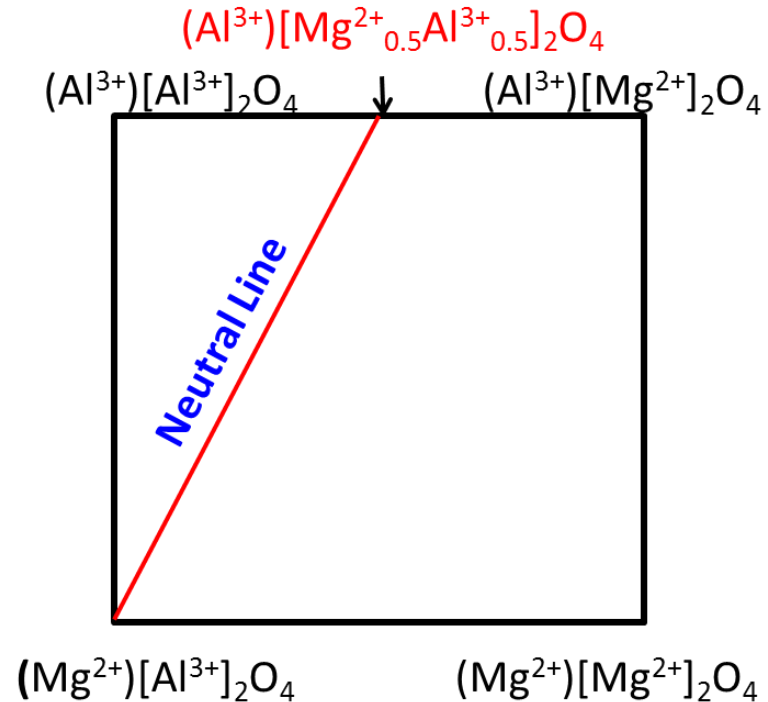
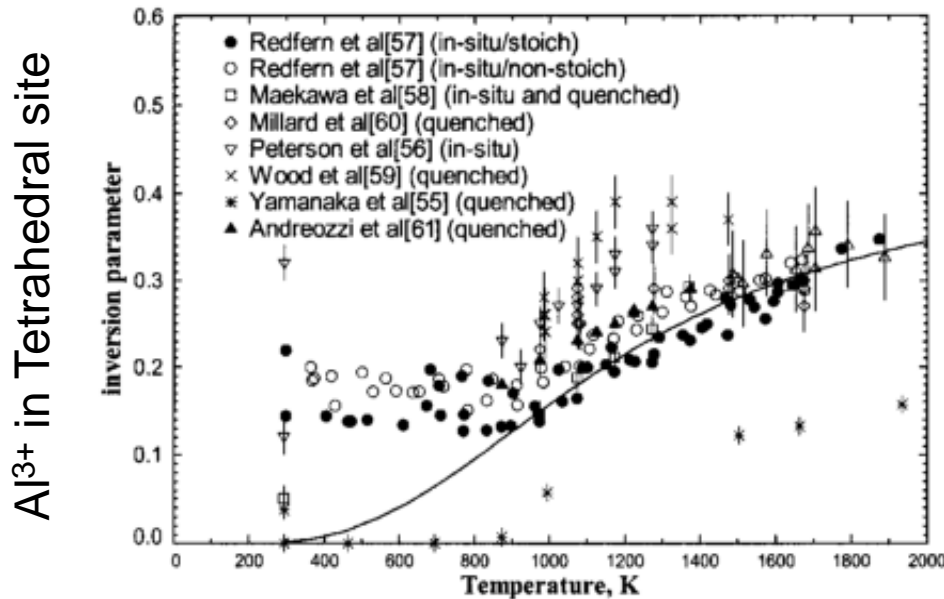
Gibbs energy of Fe-M-O system

$$\begin{aligned} G = & (n_{\underline{Fe}} g_{\underline{Fe}}^o + n_{\underline{M}} g_{\underline{M}}^o + n_{\underline{O}} g_{\underline{O}}^o) \\ & + RT(n_{\underline{Fe}} \ln X_{\underline{Fe}} + n_{\underline{M}} \ln X_{\underline{M}} + n_{\underline{O}} \ln X_{\underline{O}}) \\ & + RT(n_{\underline{Fe}} \ln f_{\underline{Fe}} + n_{\underline{M}} \ln f_{\underline{M}} + n_{\underline{O}} \ln f_{\underline{O}}) \end{aligned}$$

- Limited to dilute solution
- Many interaction parameters with increasing elements
- No interpolation technique implemented

Solid solution (4): Compound Energy Formalism (CEF)

MgAl₂O₄ spinel: (Mg²⁺, Al³⁺)^T[Mg²⁺, Al³⁺]^O₂O₄



$$G = \sum_i \sum_j Y_i^T Y_j^O G_{ij} - TS^{config} + G^{excess}$$

$$S^{config} = -R \left(\sum_i Y_i^T \ln Y_i^T + 2 \sum_j Y_j^O \ln Y_j^O \right)$$

where Y_i is site fraction of i in given site.

Many solid solutions are described using CEF.

Solid solution (4): Compound Energy Formalism (CEF)

Many solid solutions in Steel database and Oxide database are described using the CEF in consideration of the structure of each solution phase.

FCC: (Fe, Mn, Ni, Cr,)[Va, C, N, ...]

BCC: (Fe, Mn, Ni, Cr,)[Va, C, N, ...]₃

...

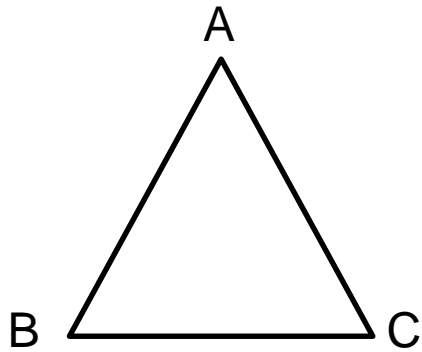
Spinel: (Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺)^T[Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺]₂^OO₄

Olivine: (Mg²⁺, Fe²⁺, Mn²⁺)^{M2}(Mg²⁺, Fe²⁺, Mn²⁺)^{M1}O₄

...

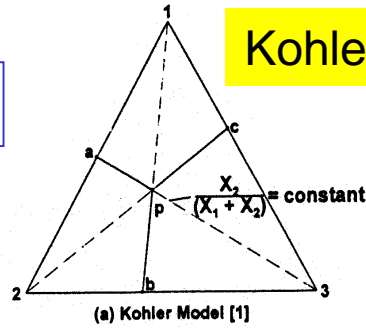
Interpolation technique for the prediction of Gibbs Energy

First approximation of ternary or higher order Gibbs energy from binary parameters



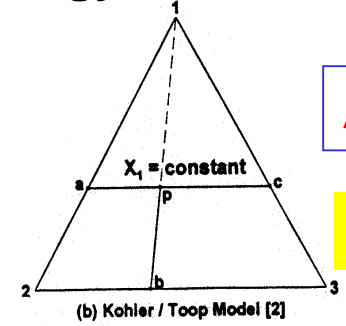
$$A = B = C$$

Kohler



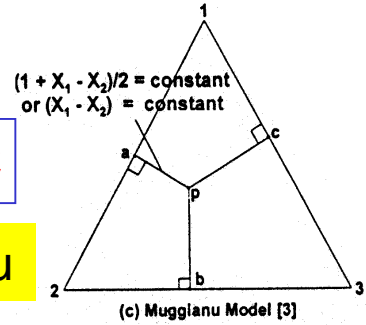
$$A = B / C$$

Toop

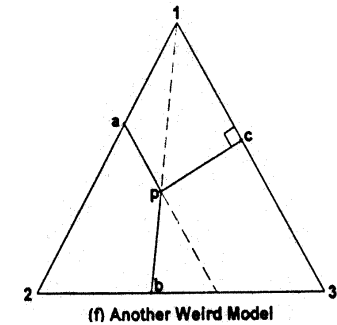
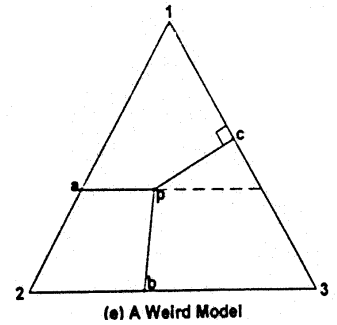
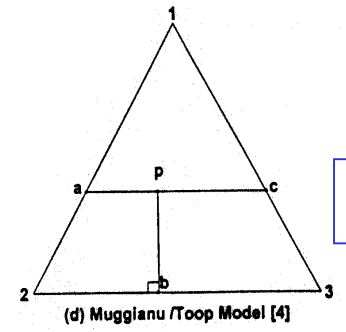


$$A \sim B \sim C$$

Muggianu

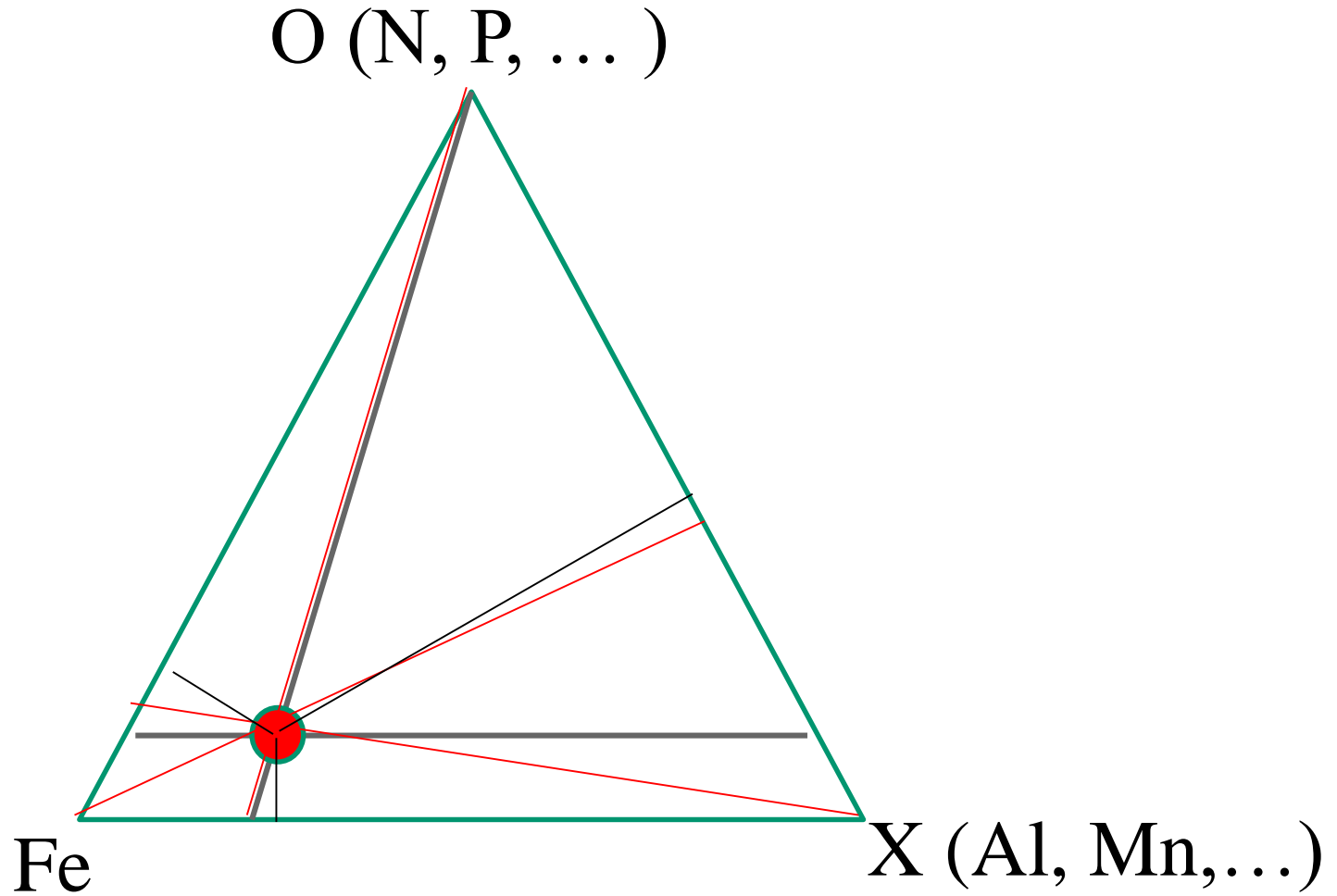


$$A \sim B / C$$



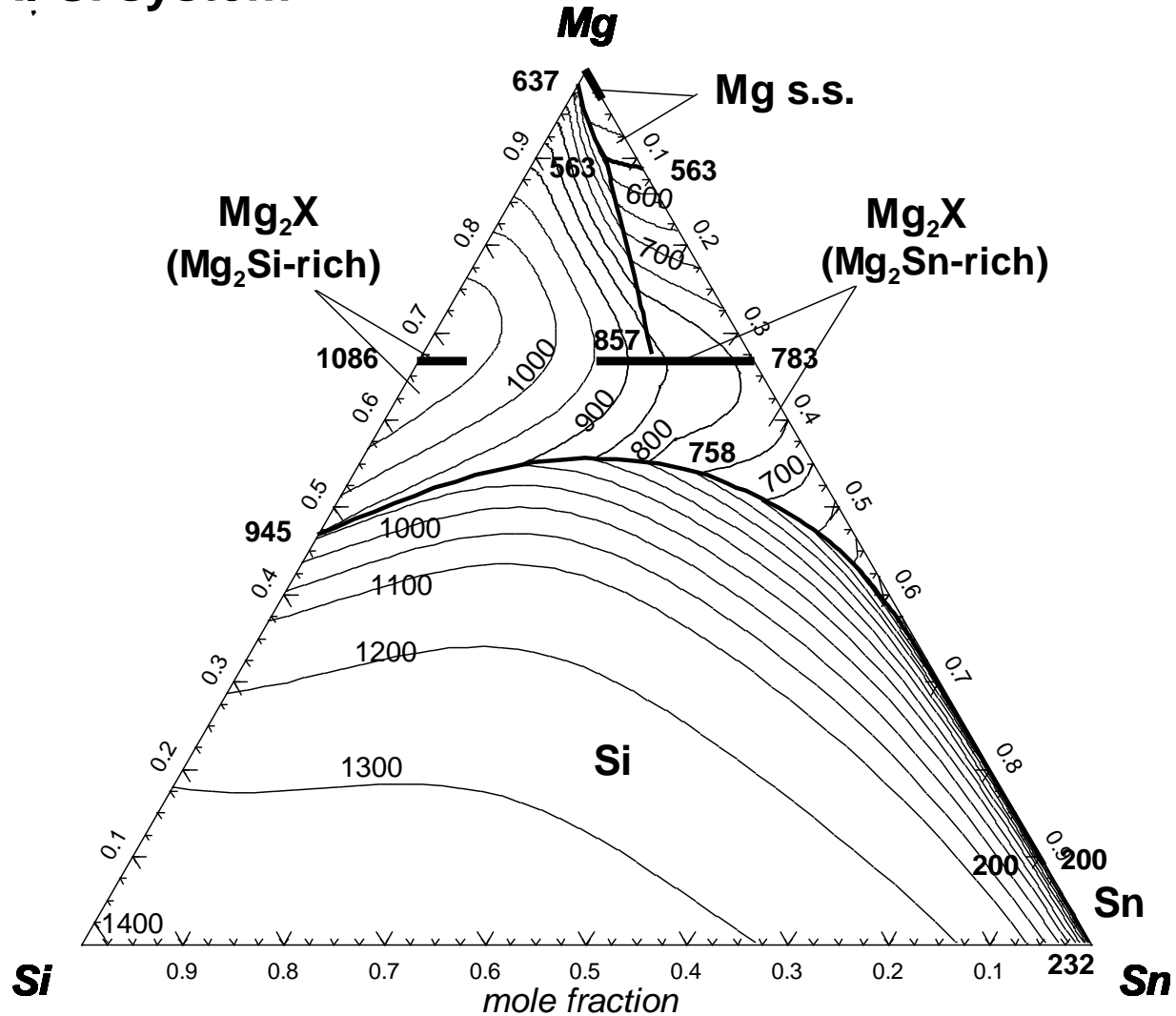
Theoretically, flexible interpolation technique can be applied to both MQM and BWRMM

Interpolation technique: Dilute solute elements



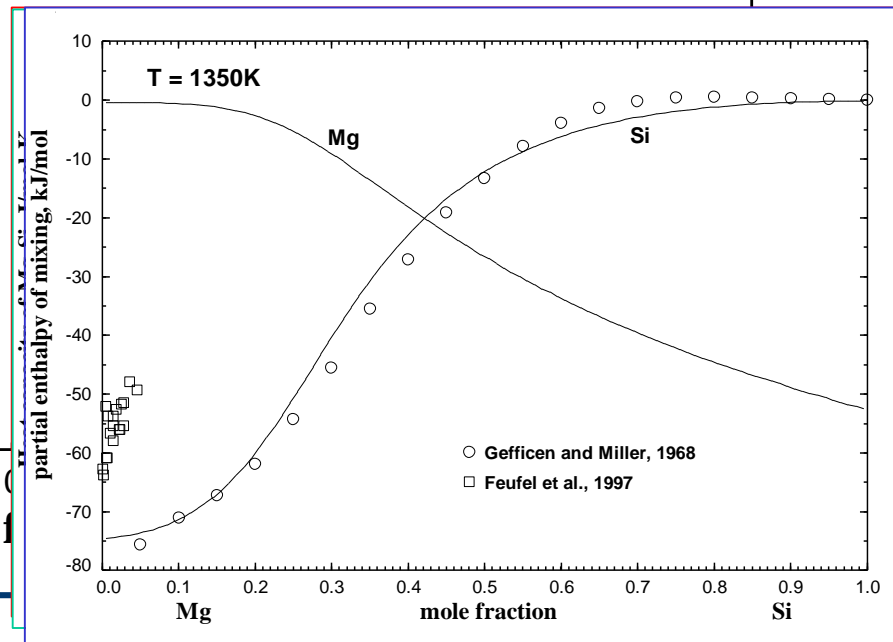
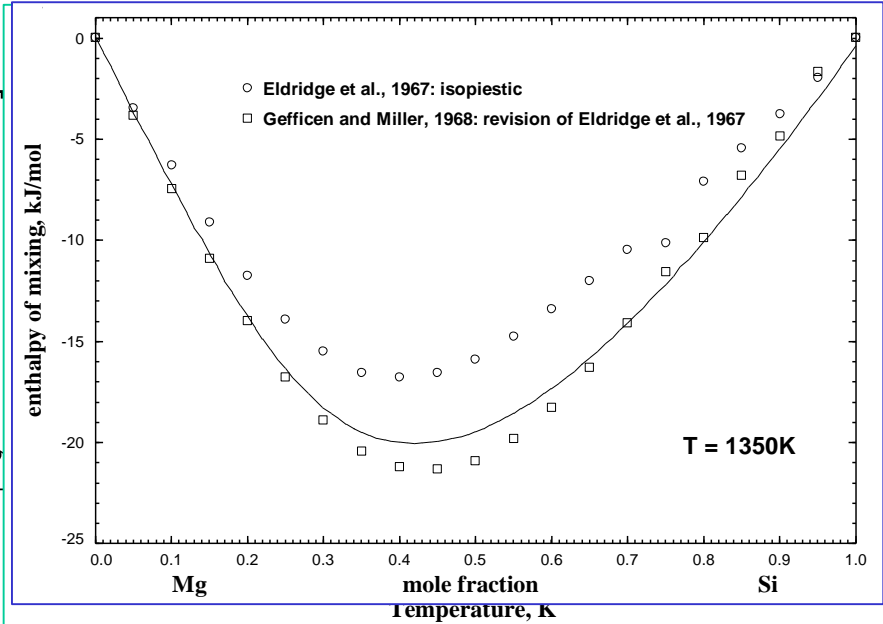
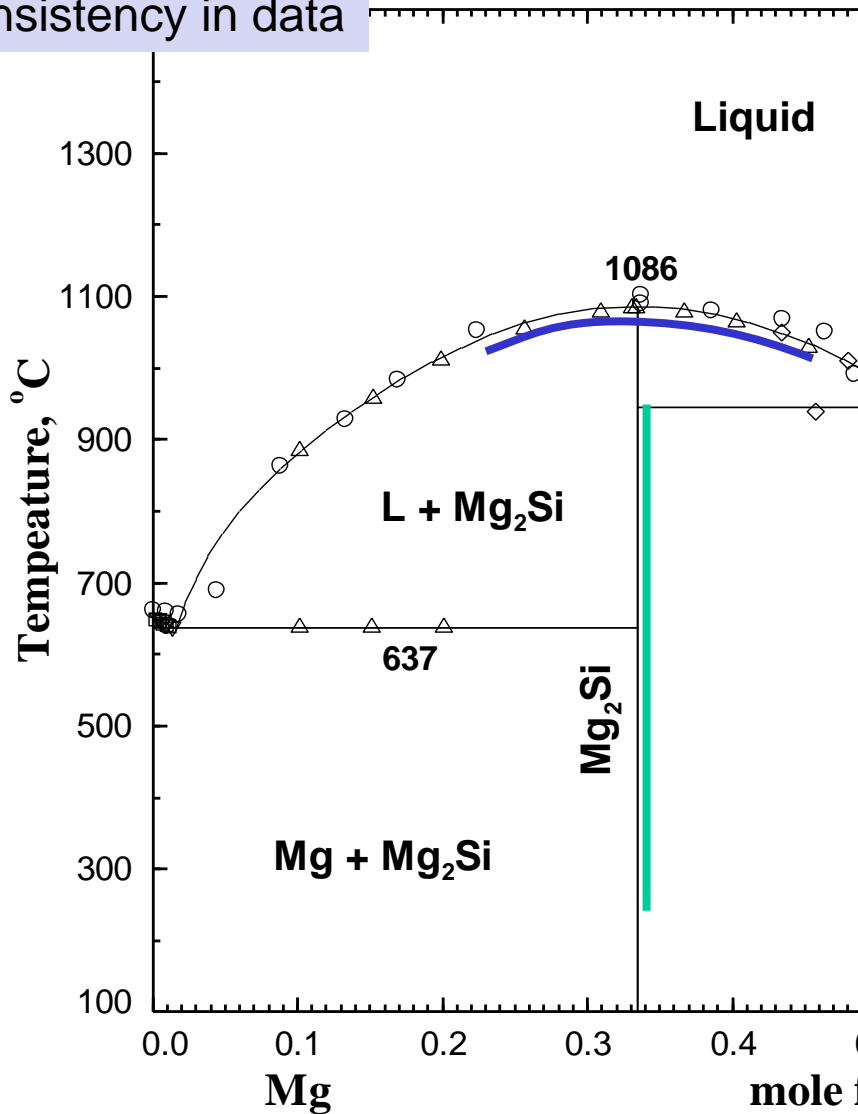
Database development for ternary system

Ternary Mg-Al-Si system

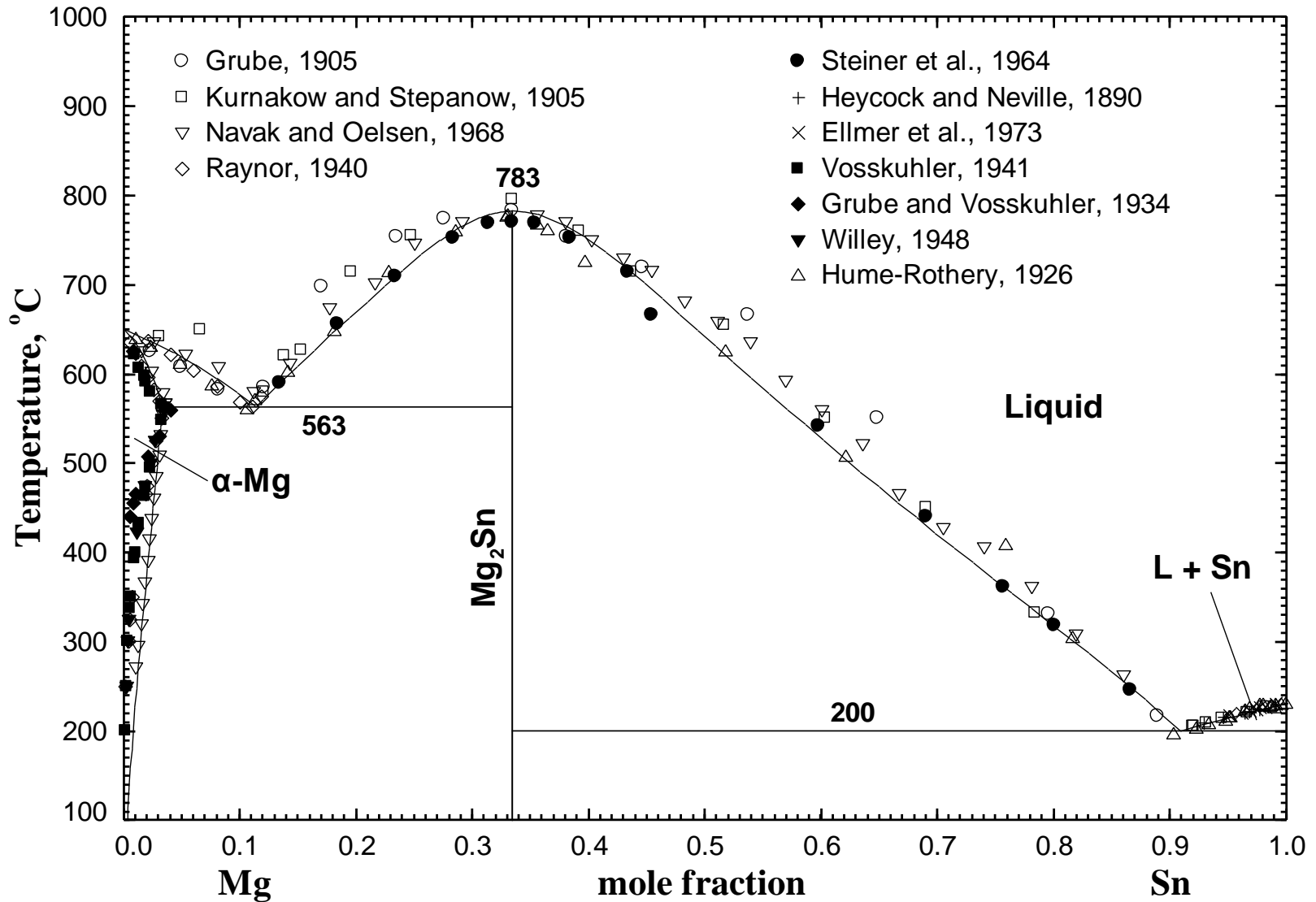


Thermodynamic Modeling: Mg-Si-Sn system

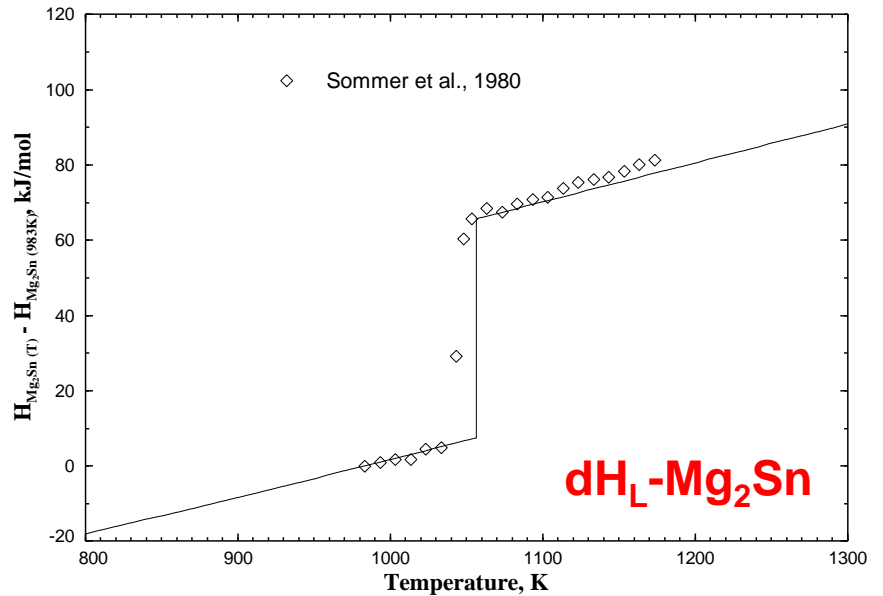
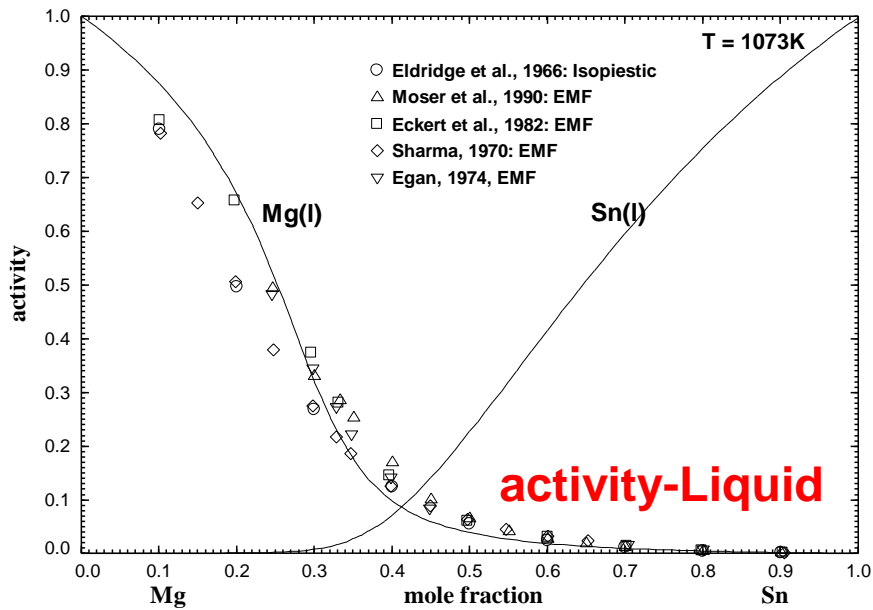
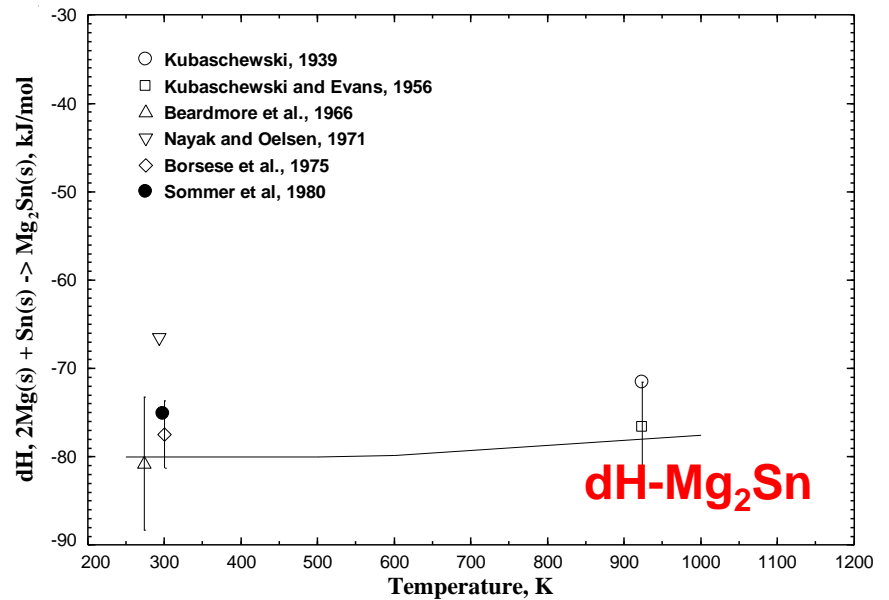
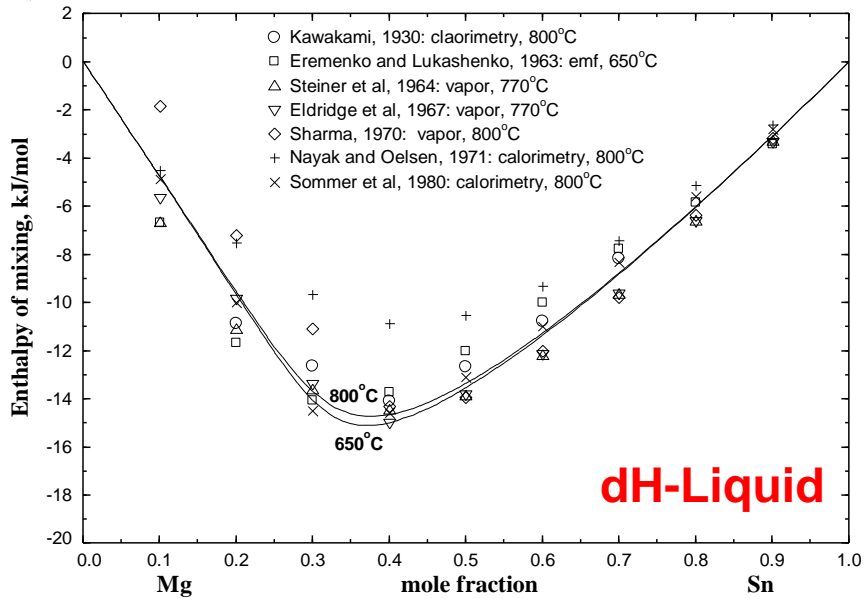
Consistency in data



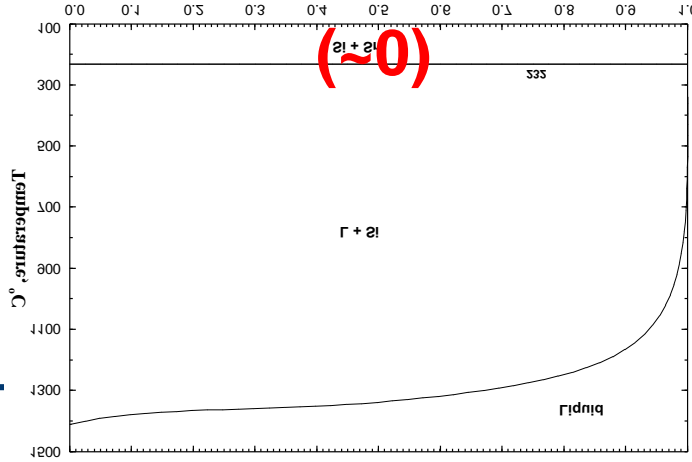
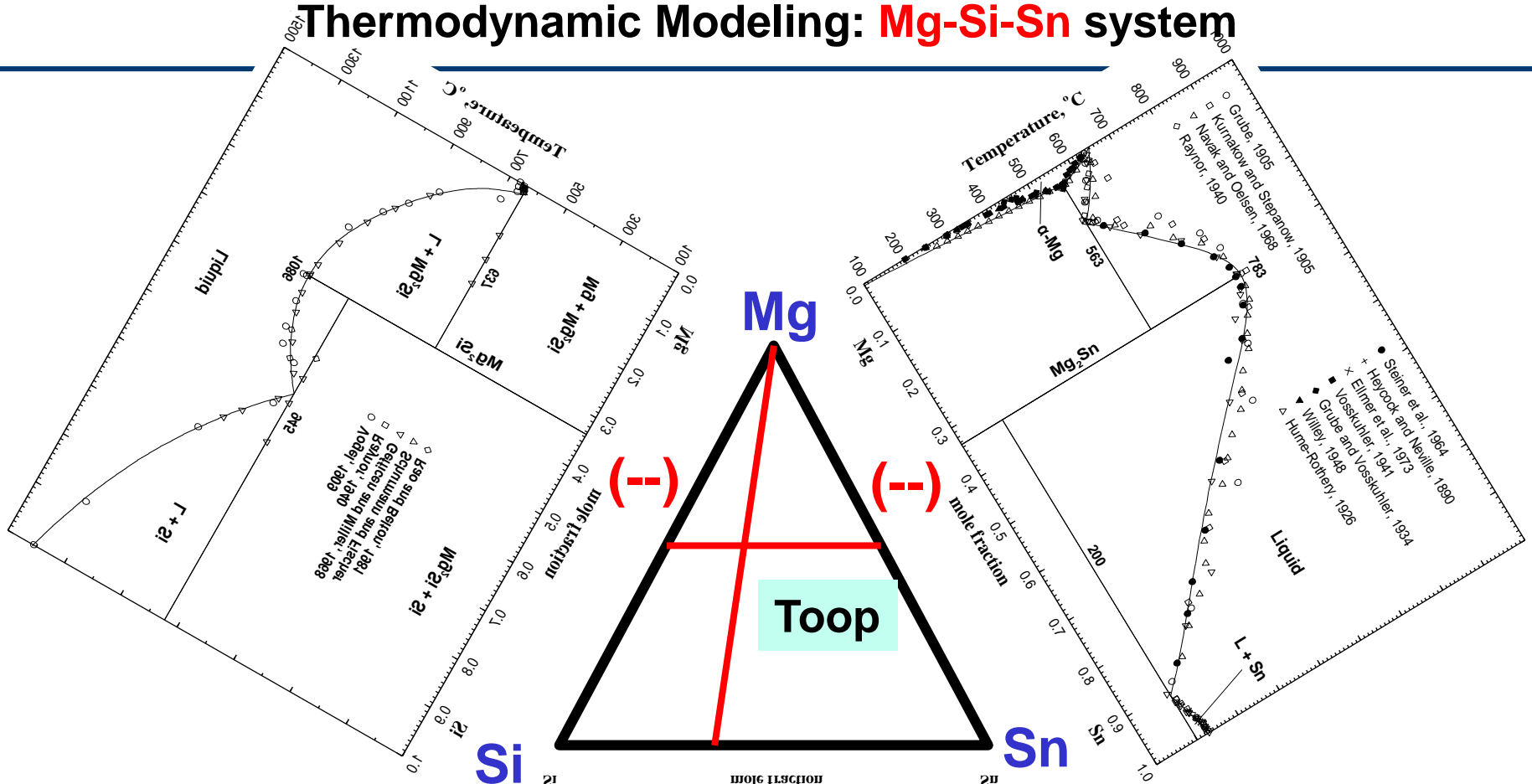
Thermodynamic Modeling: Mg-Si-Sn system



Thermodynamic Modeling: Mg-Si-Sn system

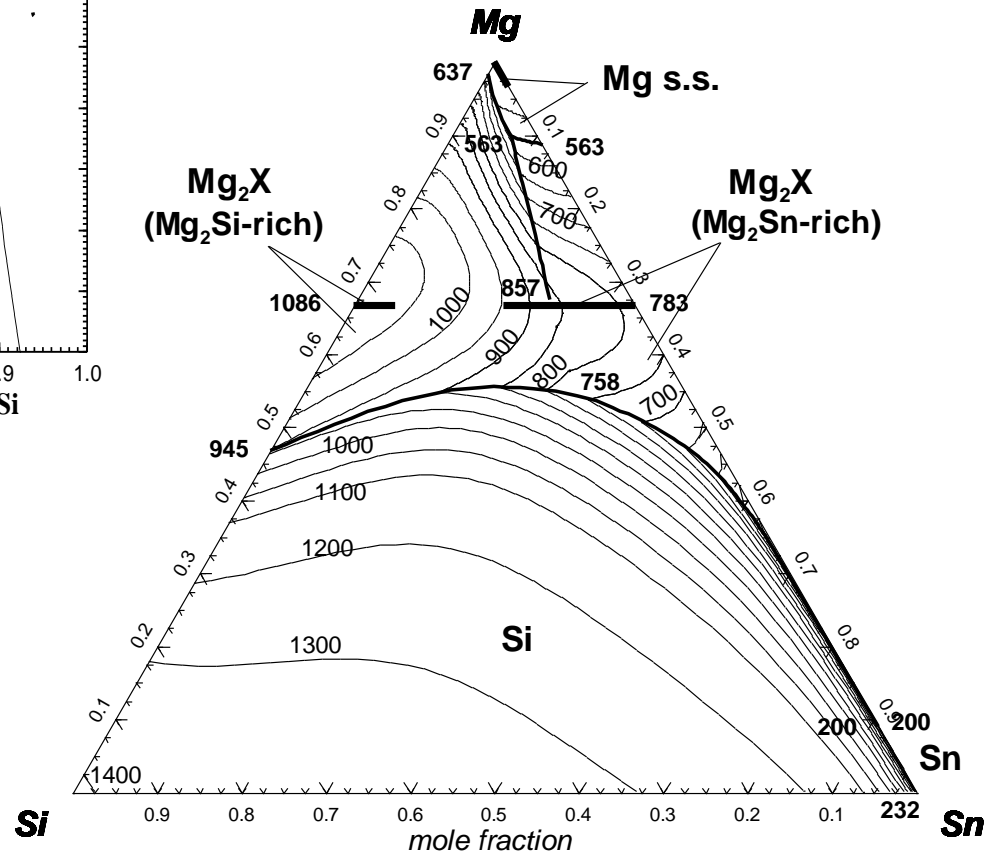
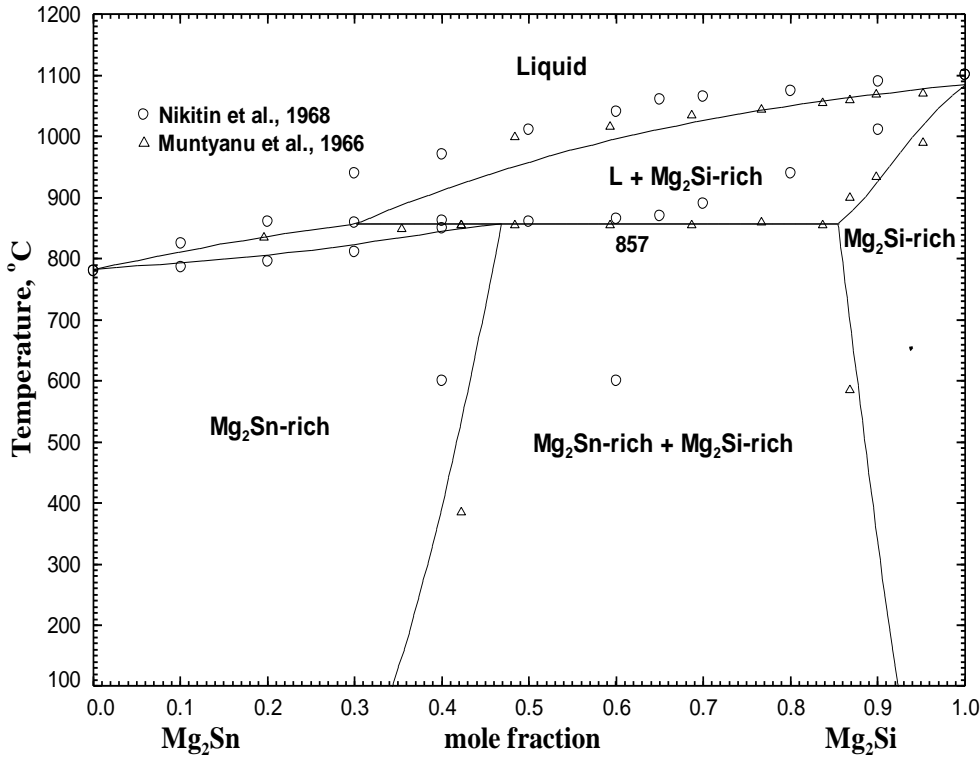


Thermodynamic Modeling: Mg-Si-Sn system



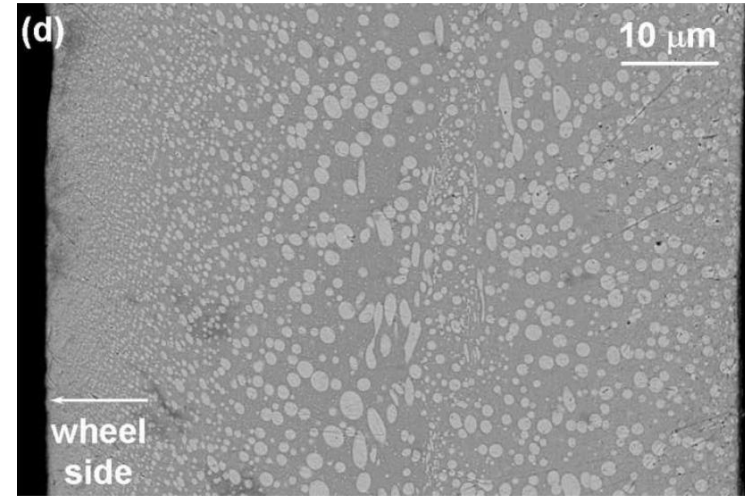
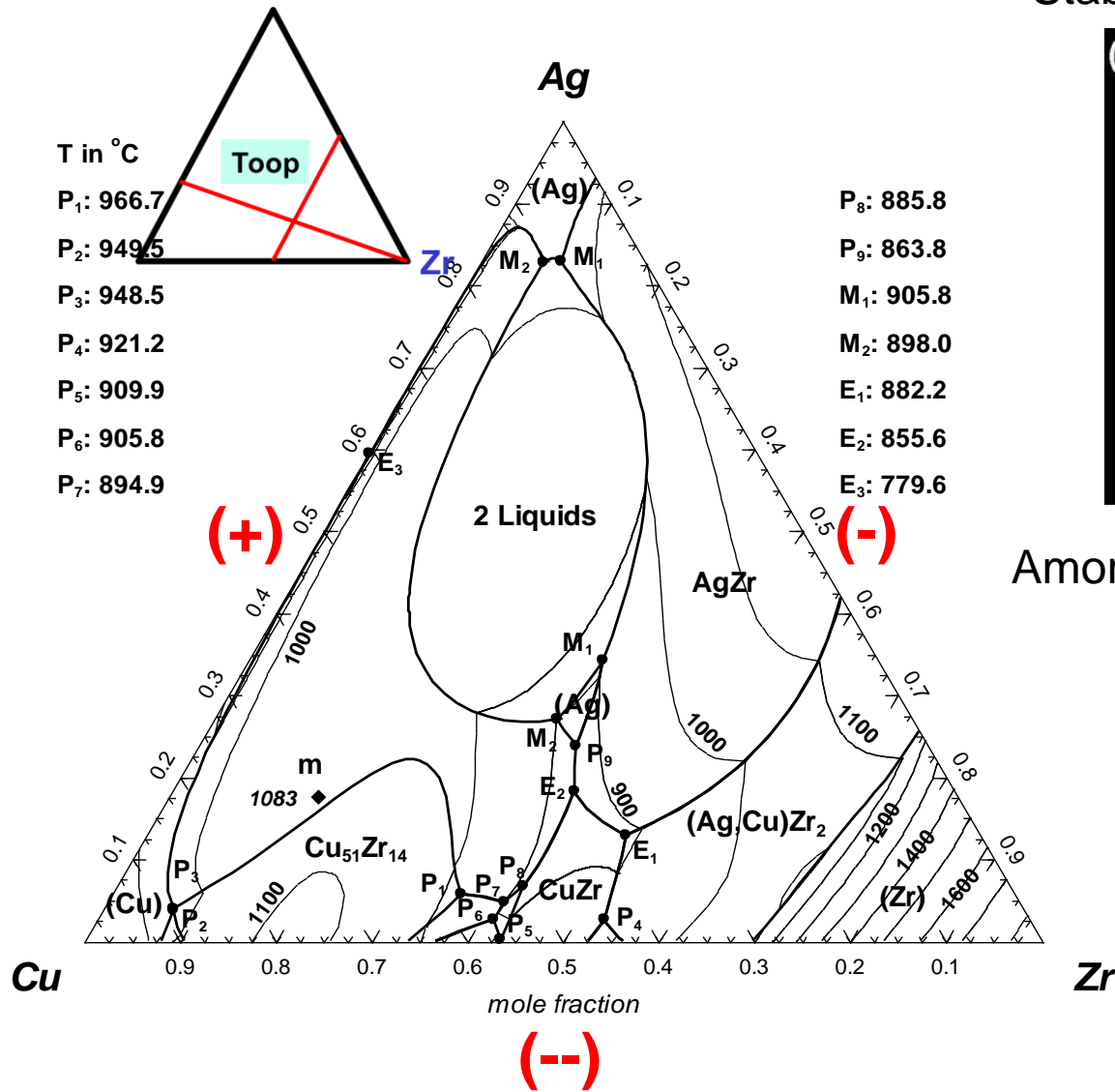
Thermodynamic Modeling: Mg-Si-Sn system

- Liquid solution: Two ternary excess terms
- Solid solution: $\text{Mg}_2(\text{Sn}, \text{Si})$

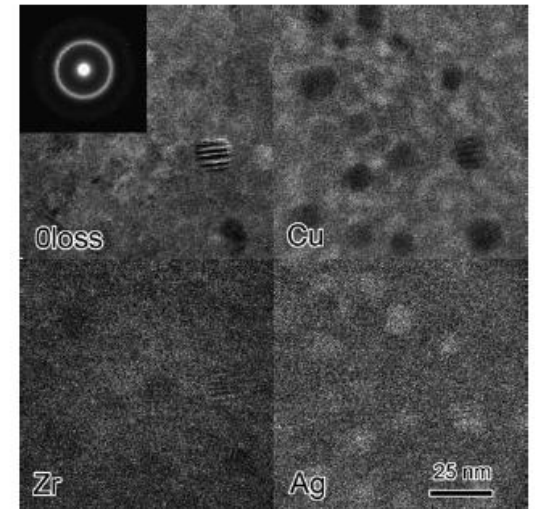


Thermodynamic Modeling: Ag-Cu-Zr system

Stable liquid miscibility gap (2 liquids)

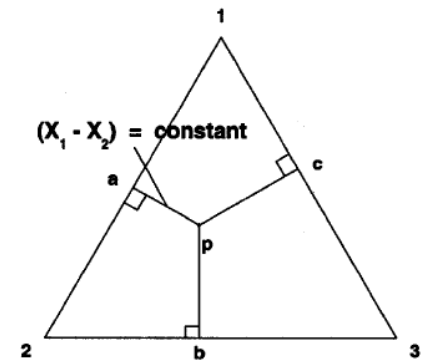


Amorphous phase – Ag-rich segregation



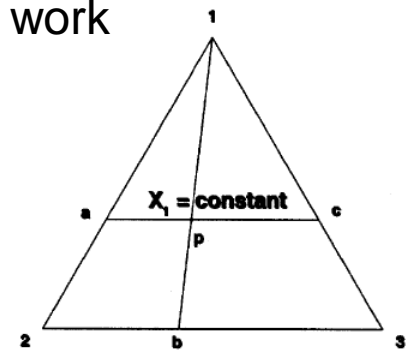
Thermodynamic modeling of Zn-Al-Fe system

- FactSage FSstel database
- Nakano et al. (2007)
- Luo et al. (2012)

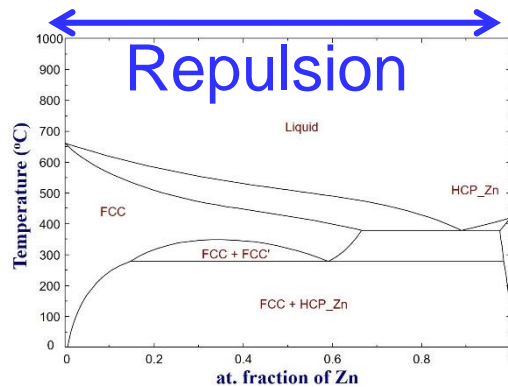
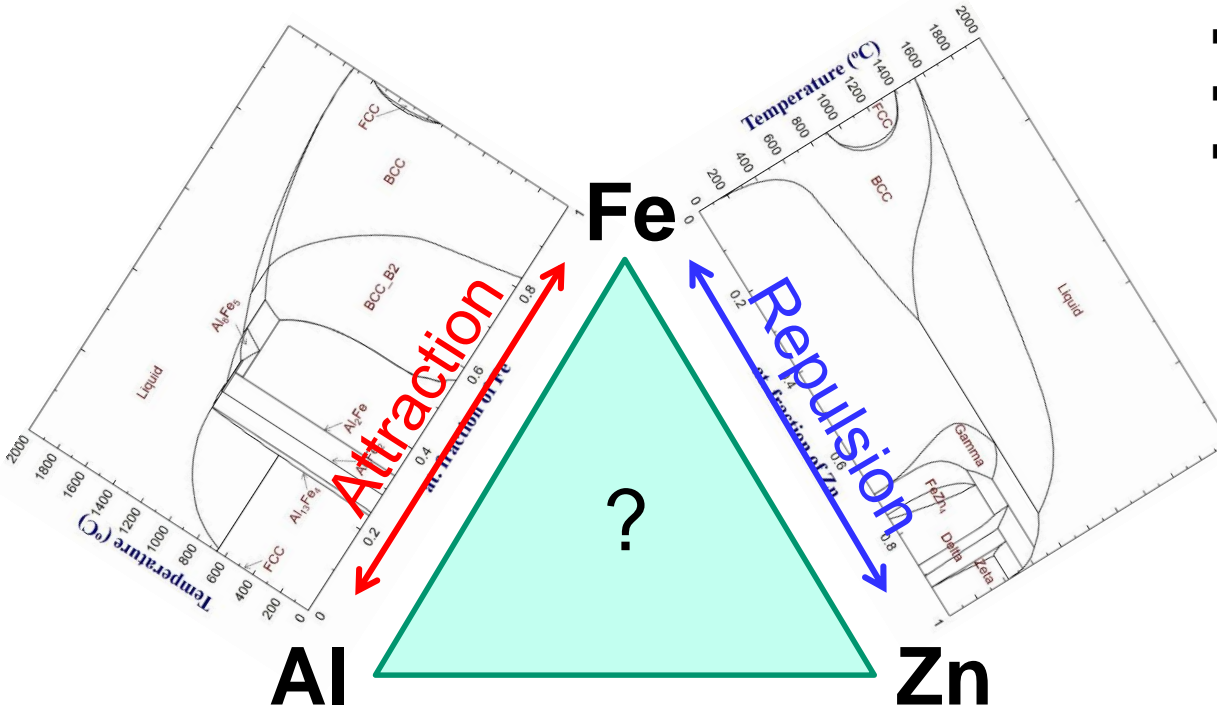


Muggianu Model [1975Mug]

- Present work



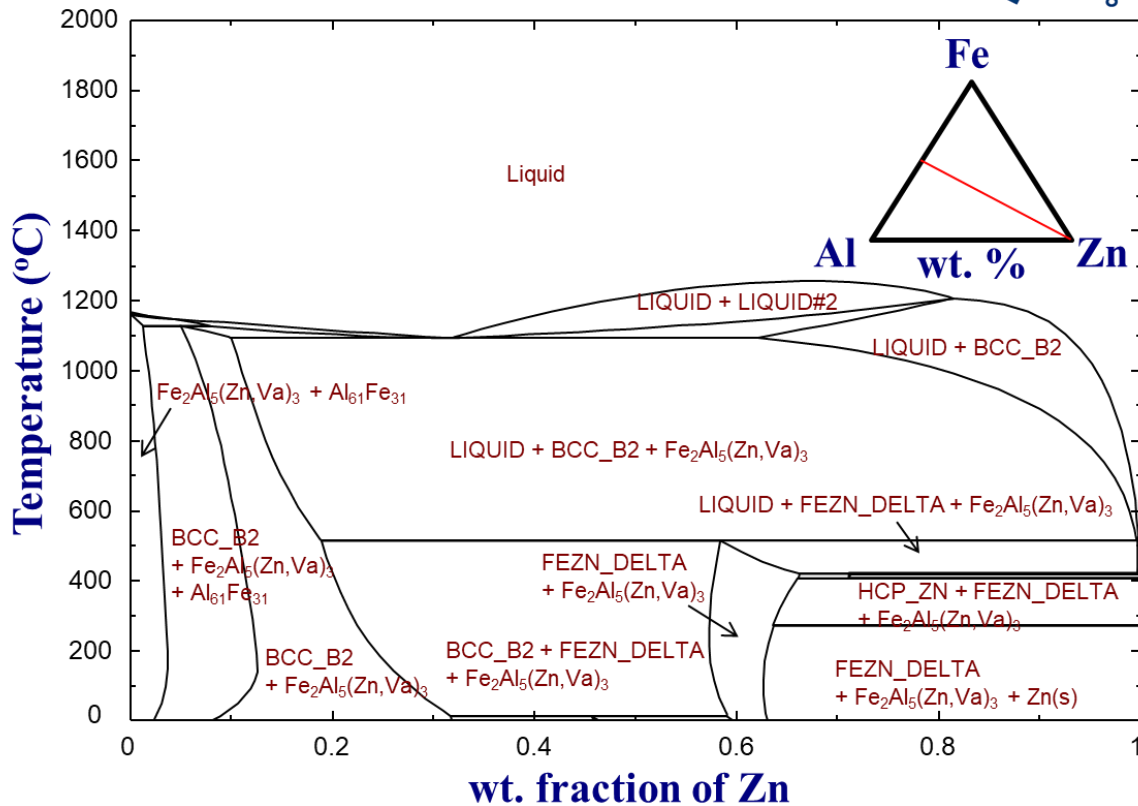
Kohler / Toop Model [1965Too]



Thermodynamic modeling of Zn-Al-Fe system

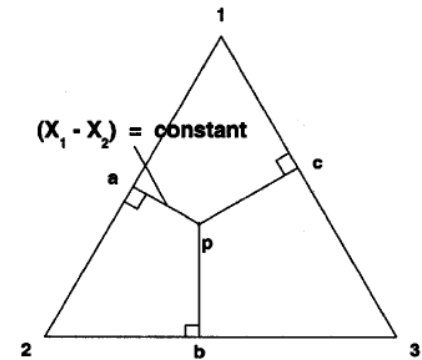
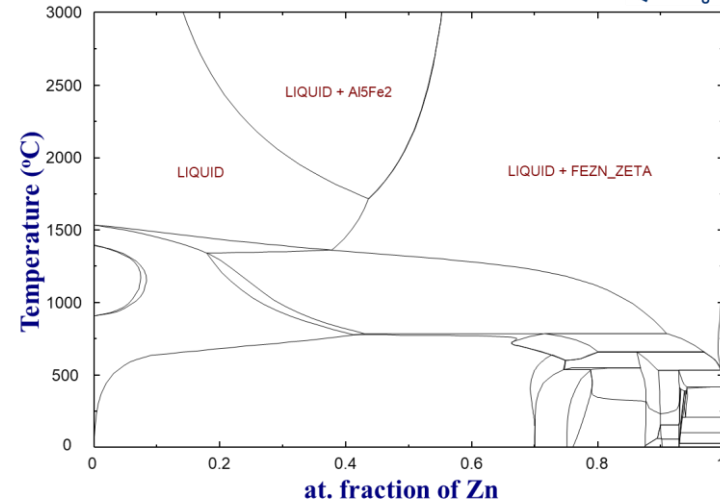
Random mixing model

Al - Zn - Fe



FSSStel 7.0

Fe - Zn - 0.000001Al

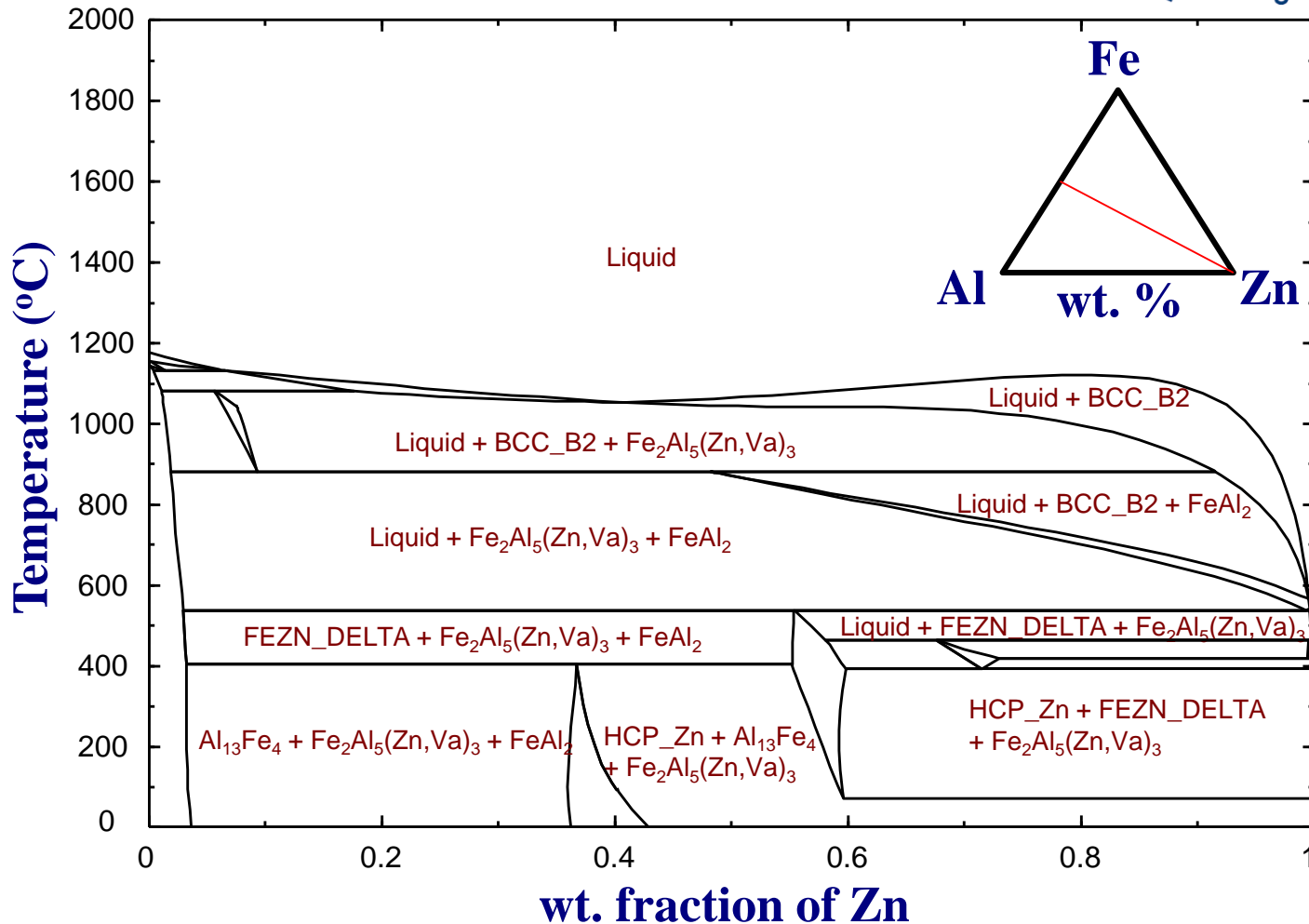
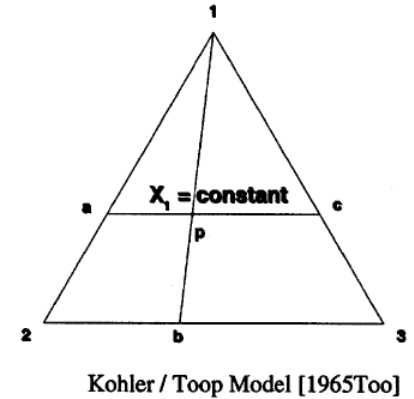


Muggianu Model [1975Mug]

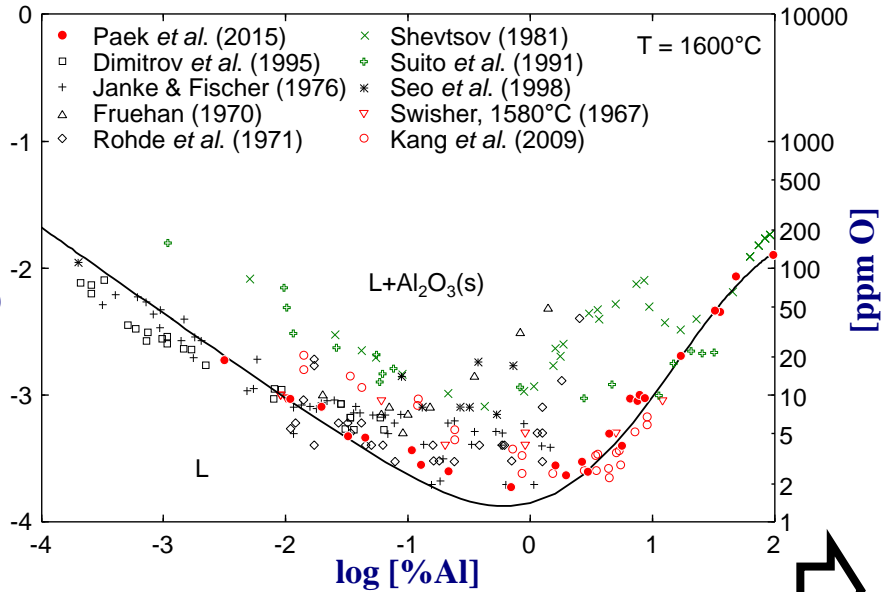
Thermodynamic modeling of Zn-Al-Fe system

New (MQM)

Al - Zn - Fe

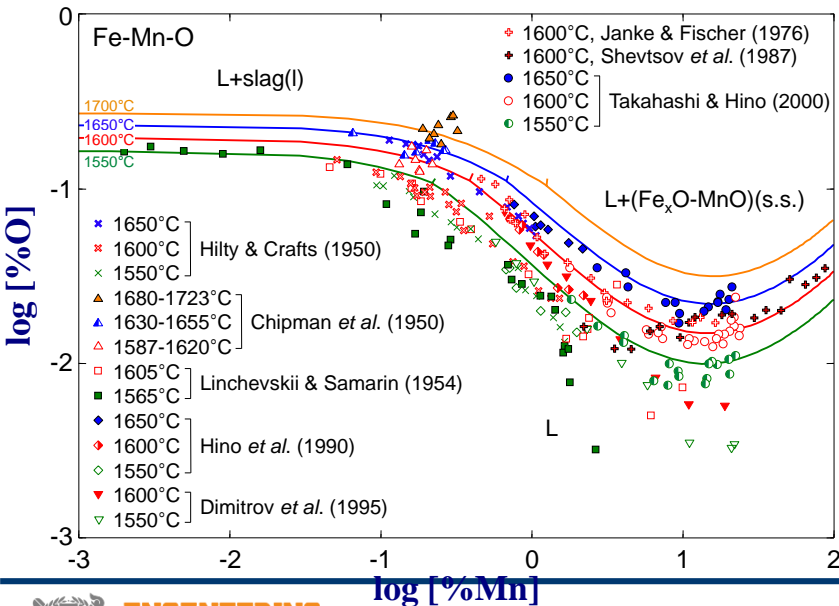
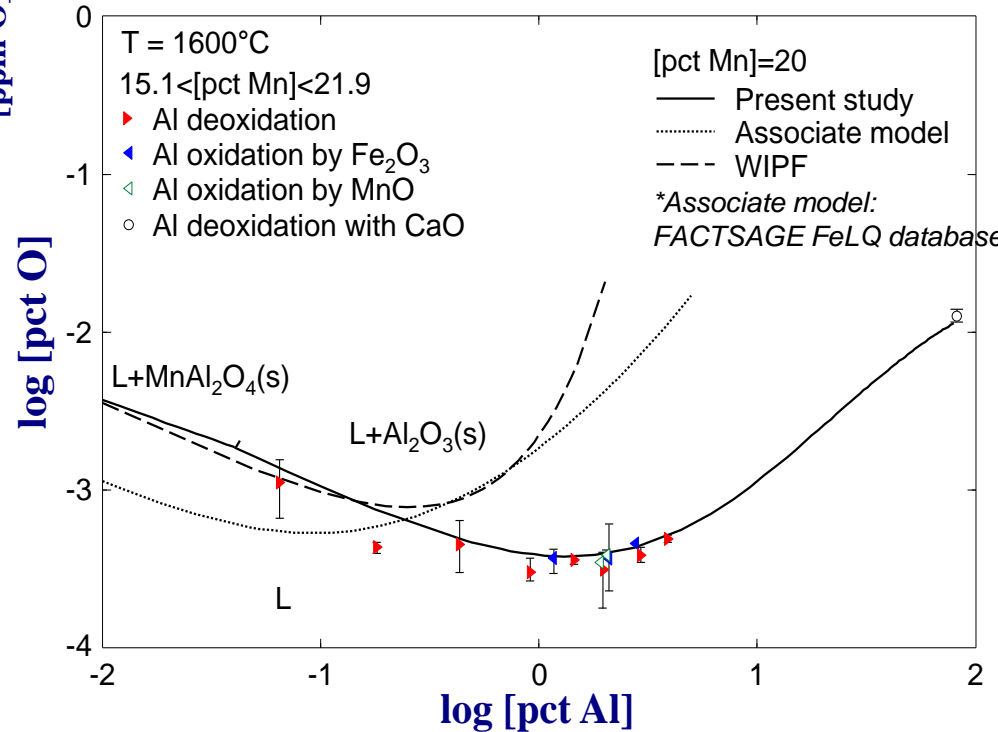


Predictive ability of Thermodynamic model



Present study: MQM

Predicted from Al- and Mn-deoxidation curve



Thermodynamic model should have good predictive ability !!

APPLICATIONS TO STEELMAKING PROCESS AND ALLOY DESIGN

- Simple calculations
- Advanced applications

Current thermodynamic databases for steel and Oxides

- **Steel database for alloy development:** Physical metallurgy
 - ✓ Thermo-Calc: TCFE database
 - ✓ FactSage: FSStel database (up to 72 version)
 - Bragg Williams Random Mixing Model (sub-regular solution models):
Liquid solution
 - Compound Energy Formalism: Solid solutions
- **Dedicated database for Molten steel for refining process**
 - ✓ FactSage: FTmisc FeLq database
 - Unified Interaction parameter model (Modified Wagner model)
- **New steel database – MQM for liquid solution**
 - ✓ **FactSage: FSStel database for steel (73 version)**
FTlite database for Al and Mg alloys
- **FTOxid database (FactSage):**
Oxide database containing
 - ✓ CaO-MgO-Al₂O₃-SiO₂-FeOx-MnO-TiOx-CrOx-P₂O₅...S...F...

Accuracy of new database: Fe-Mn-Si-Al-C system

Persoly et al., IOC conf. Series, vol. 119, 2016, 012013.

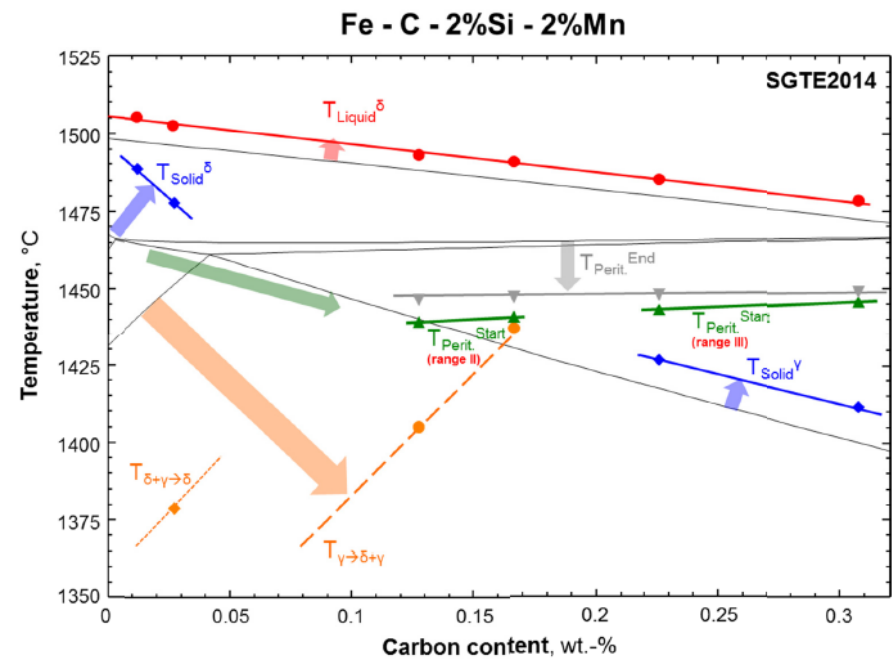
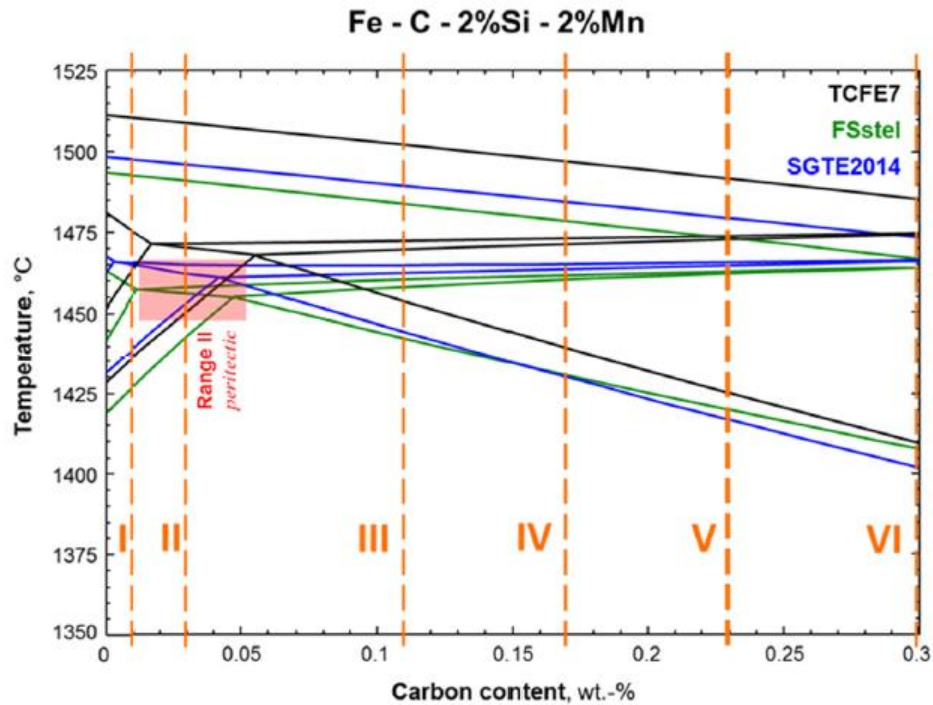
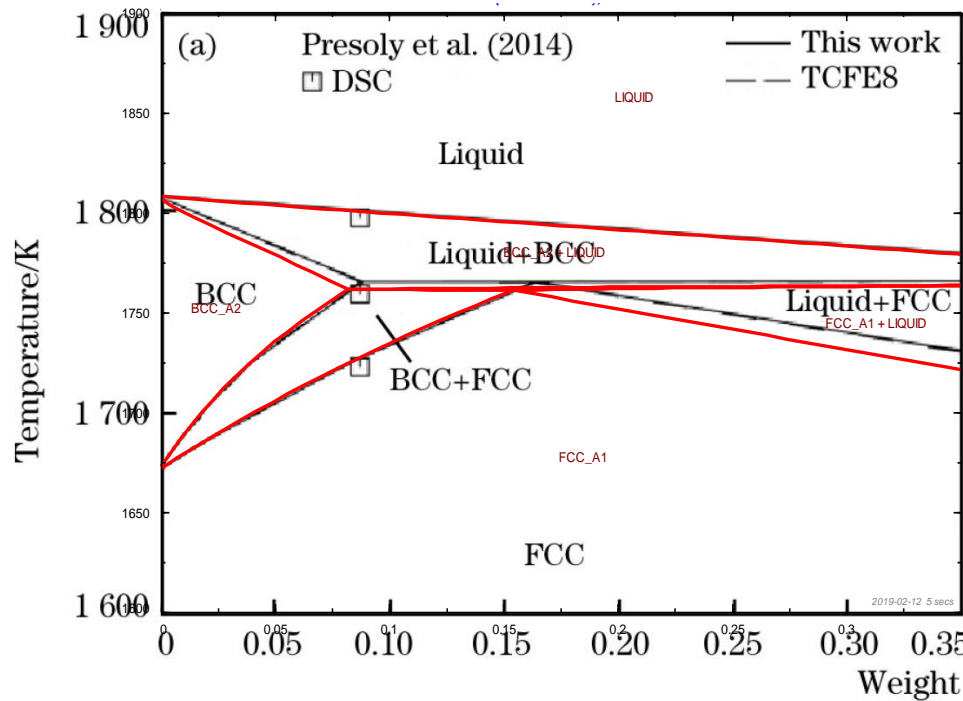
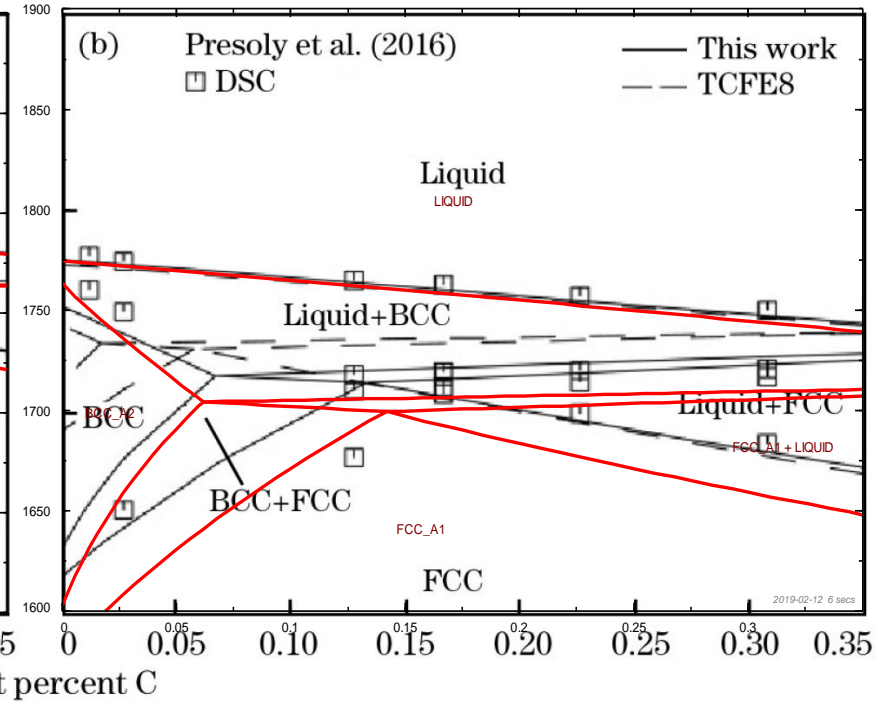


Figure 5. First measurement results of the Fe-C-2%Si-2%Mn.

Fe-C-0.37Mn-0.07Si

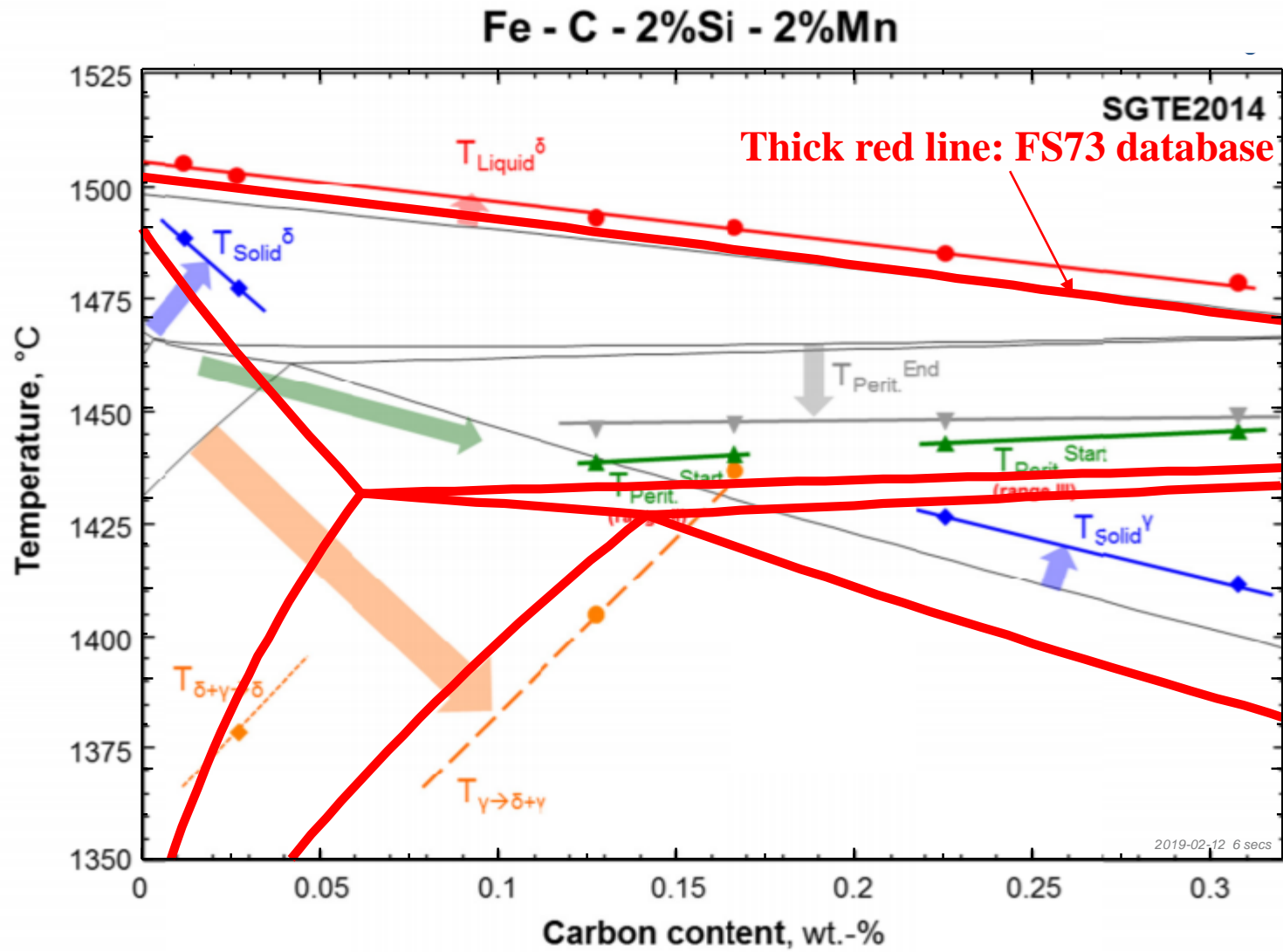


Fe-C-2Mn-2Si



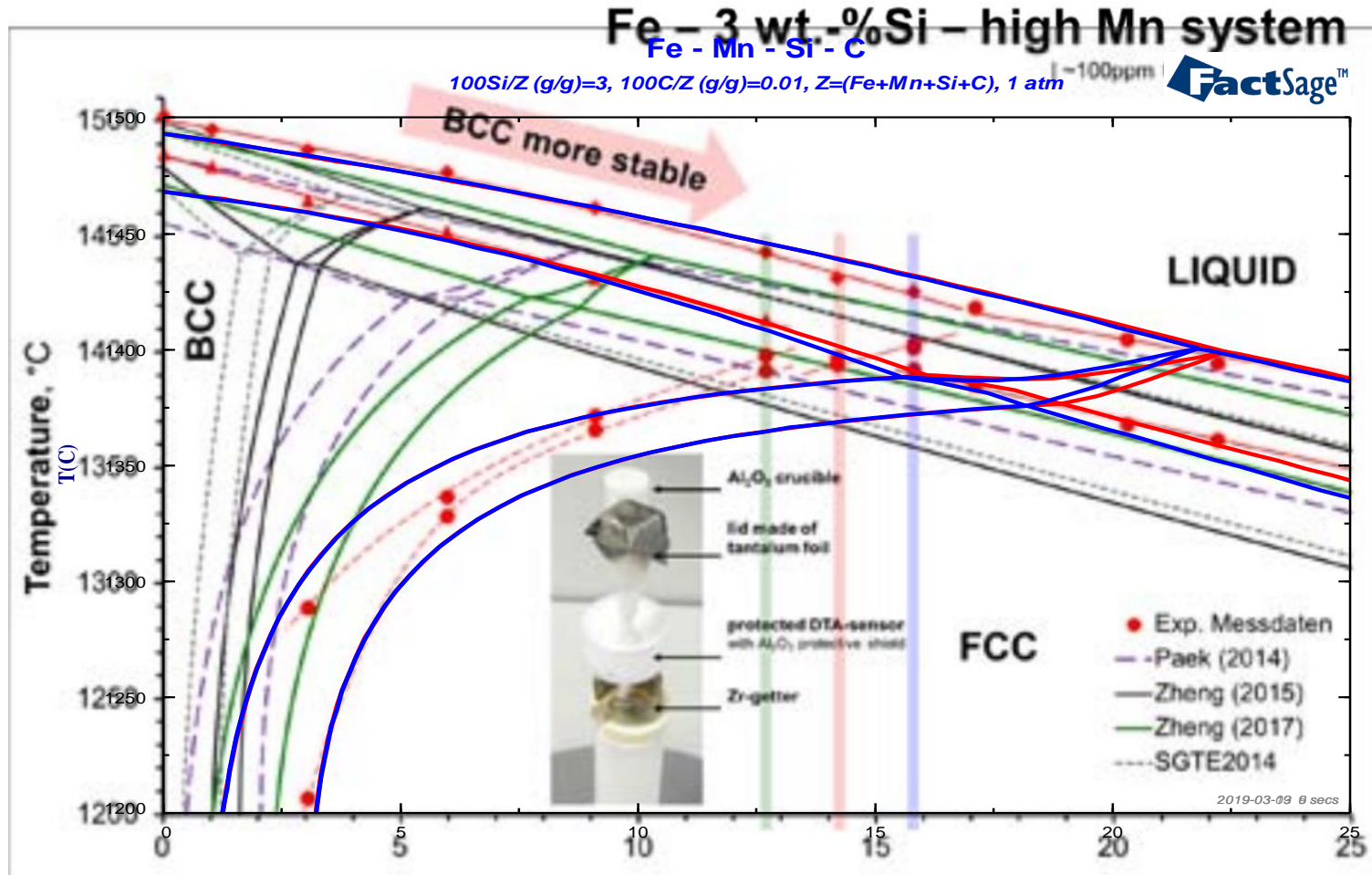
Red-line is new FS73 database;

I believe this assessment work by Chinese group (labeled as this work) is more or less taken by ThermoCalc-TCFE9



Data from Presoly et al. (DTA; 2016~2017); Our group (Minkyu Paek now at Aalto Univ.) performed the same DSC experiments for a couple of samples and confirmed these data

Data from Presoly et al. (DTA; 2016~2017); Our group (Minkyu Paek now at Aalto Univ.) performed the same DSC experiments for a couple of samples and confirmed these data



Previously database cannot reproduce the liquidus and solidus & BCC/FCC transition

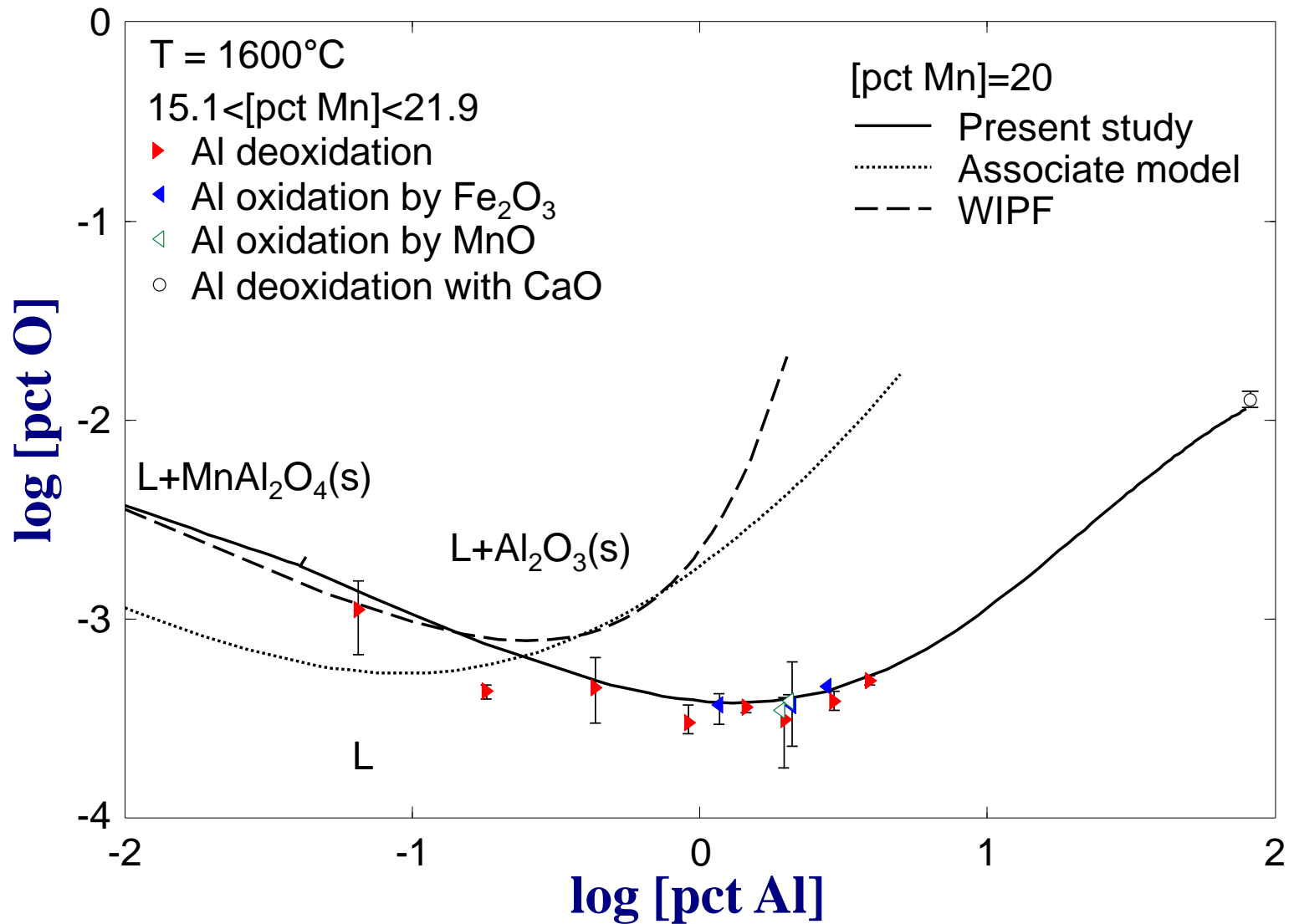
Secondary Steelmaking Process

- Ladle – Deoxidation
- LF – Mn alloying process
- RH – Degassing (gas removal – N, H, ...)
- Refractory of ladle

Casting

- Solidification: Liquidus projection, Scheil cooling, ...
- Defect control: AlN formation

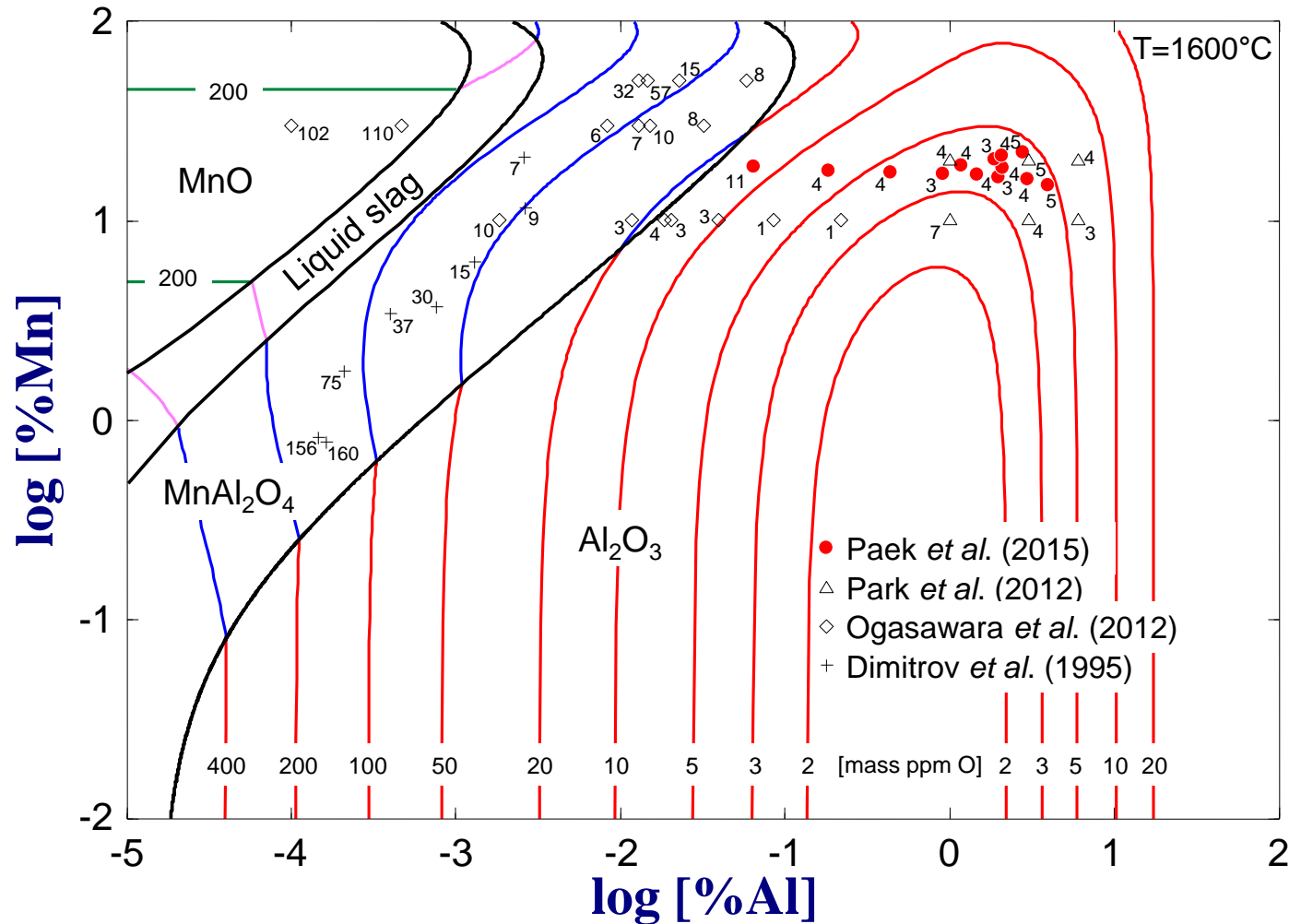
Al deoxidation equilibria in Fe-Mn-Al-O melt



Al deoxidation equilibria in Fe-Mn-Al-O melt

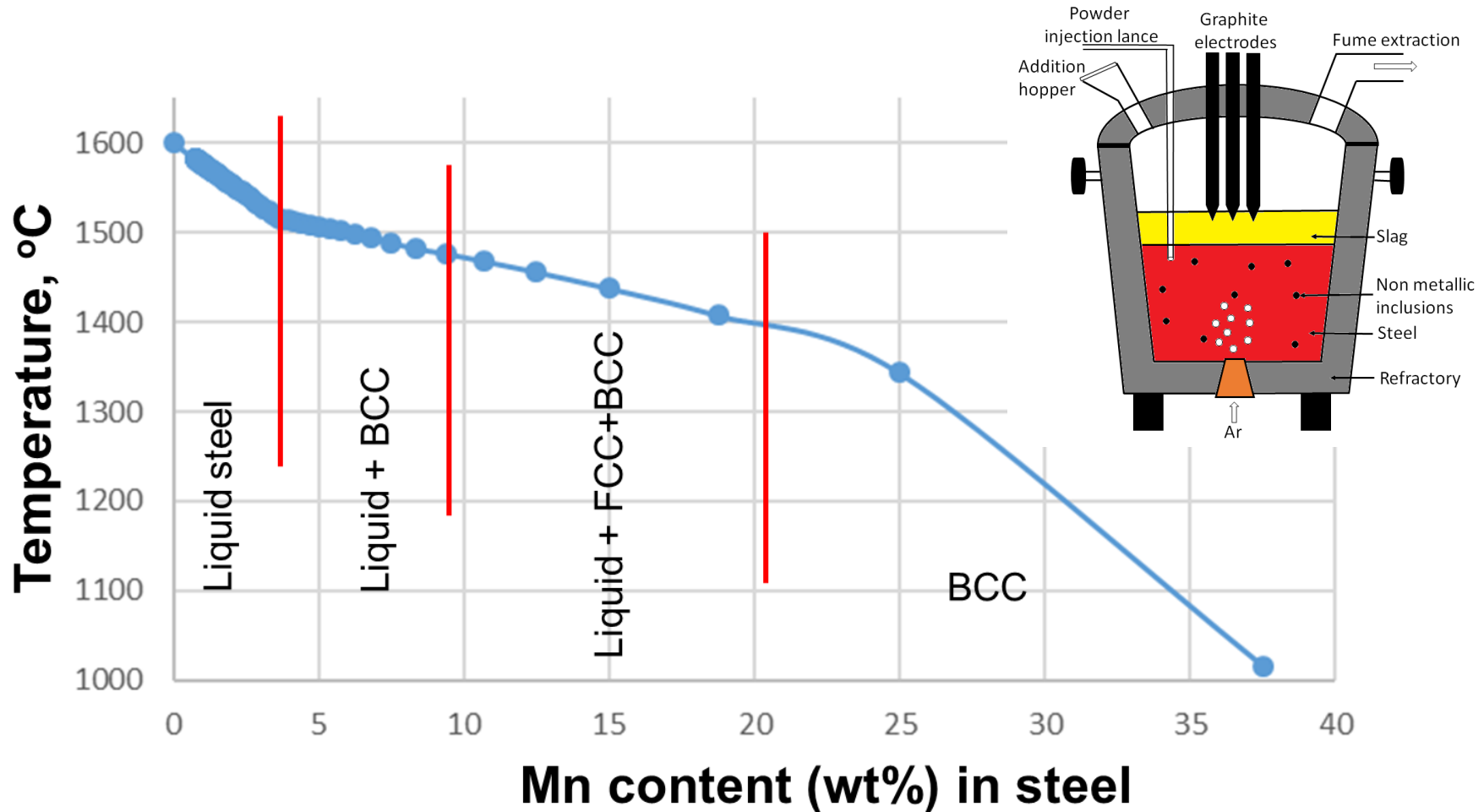
● Stability diagram (MQM)

New steel database

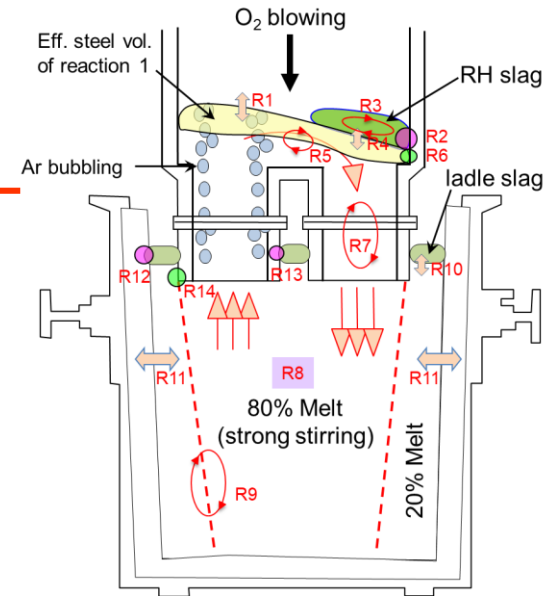
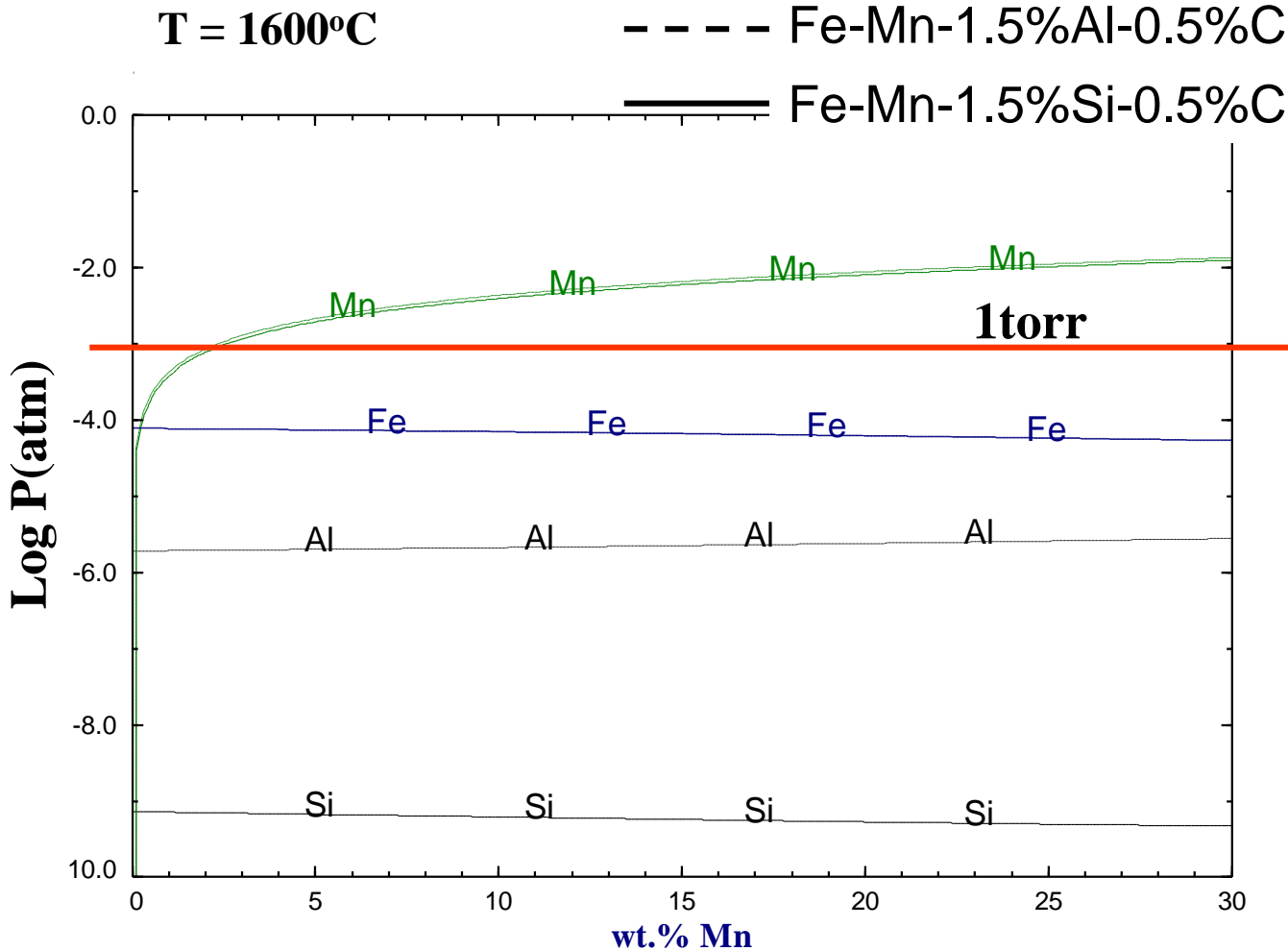


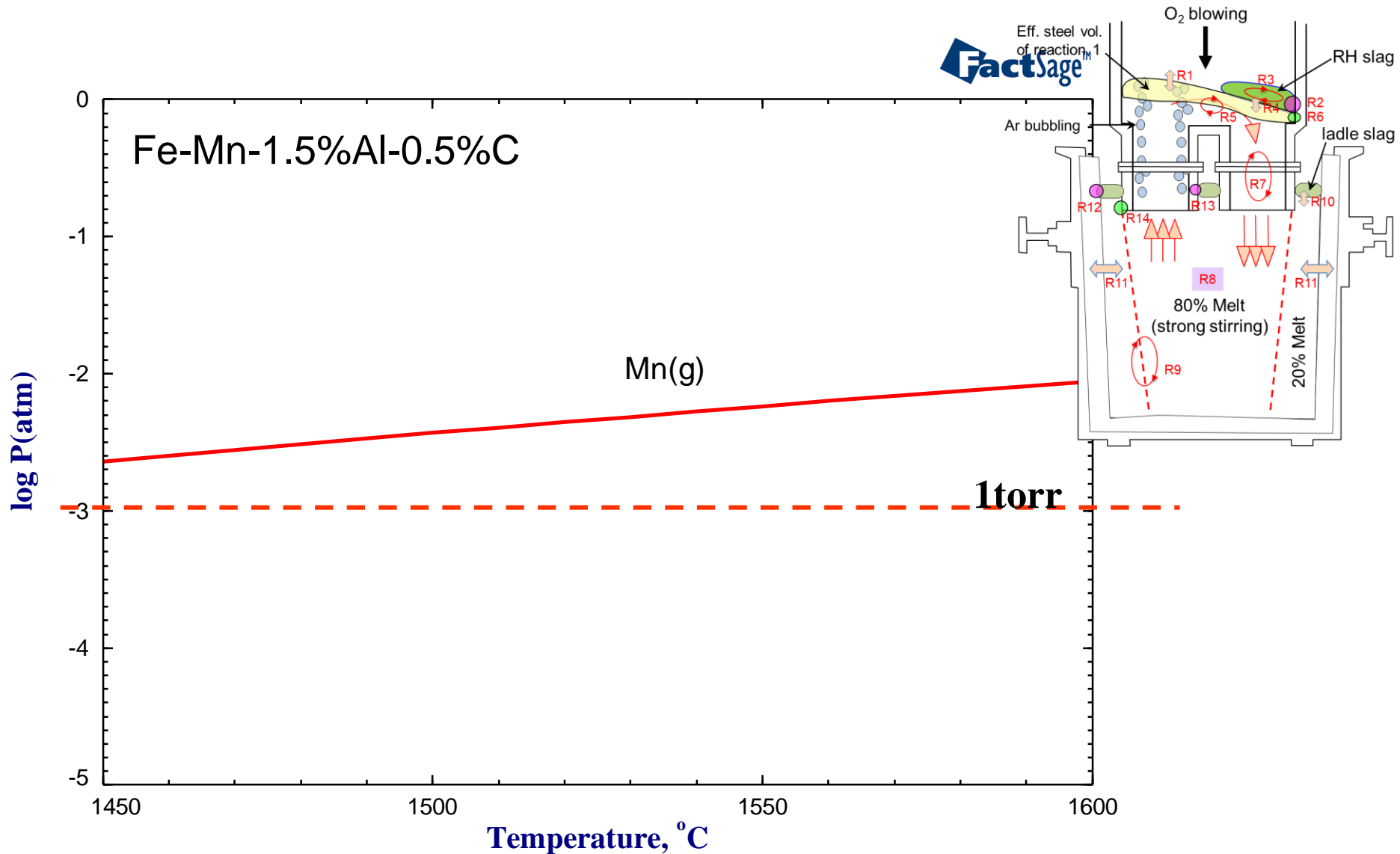
LF – addition of FeMn alloy

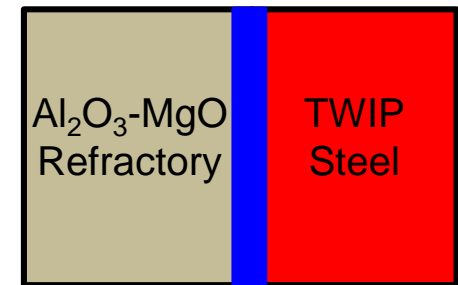
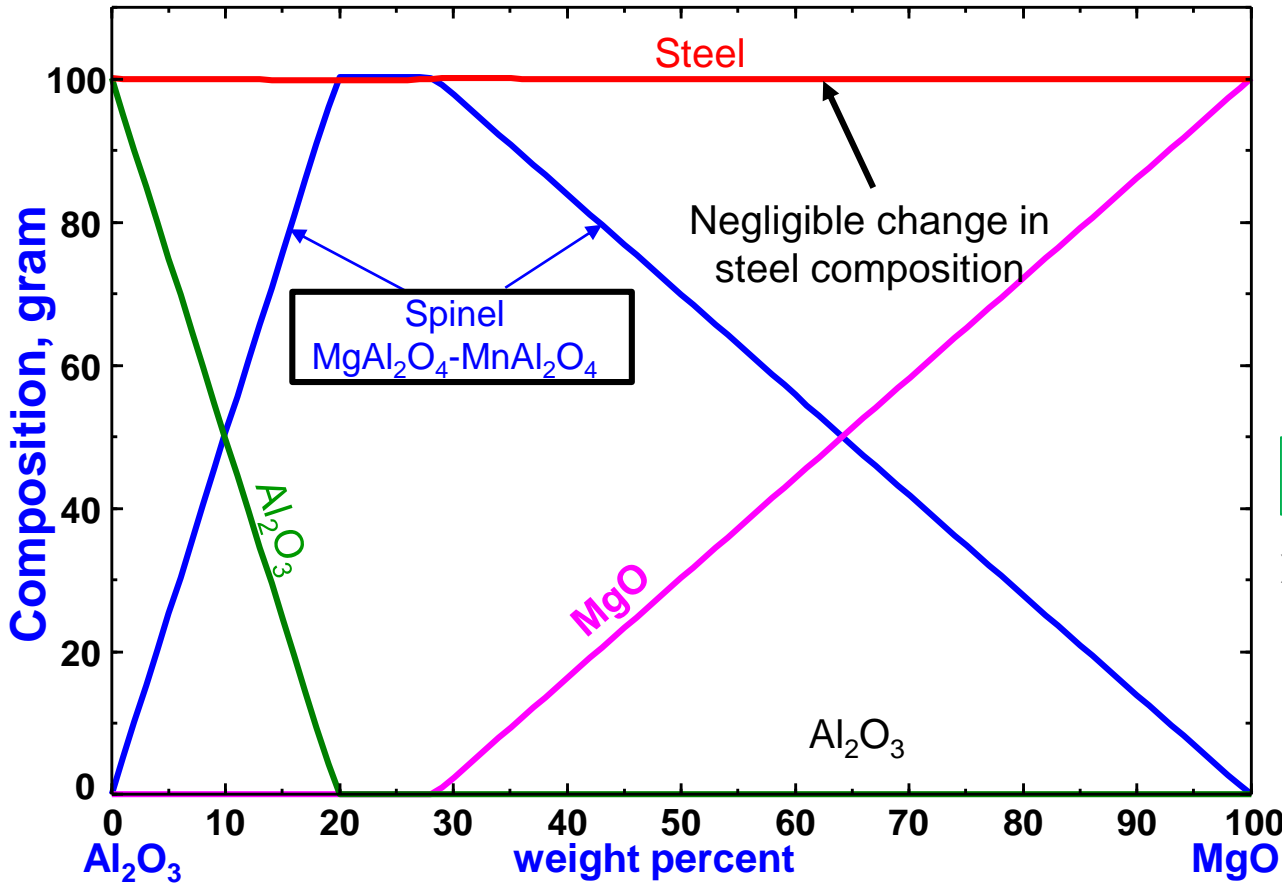
Liquid Fe at 1600C + FeMn (75%Mn-24%Fe-1%C) at 25 °C



High vapor pressure of Mn → Degassing limit ??







Stable spinel layer

Thermodynamic Calculation

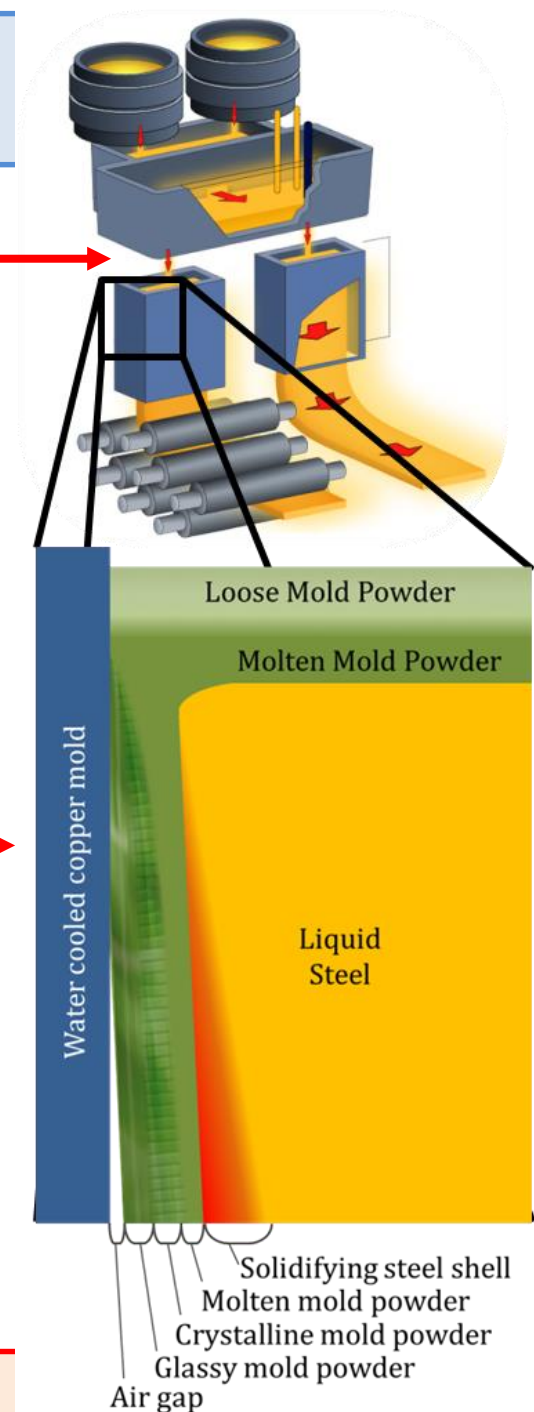
- Enhancement of spinel matrix
 $MgAl_2O_4 \longrightarrow MgAl_2O_4-MnAl_2O_4$
- High alumina spinel castable
 (90%Al₂O₃-10%MgO)

Submerged Entry Nozzle (SEN)

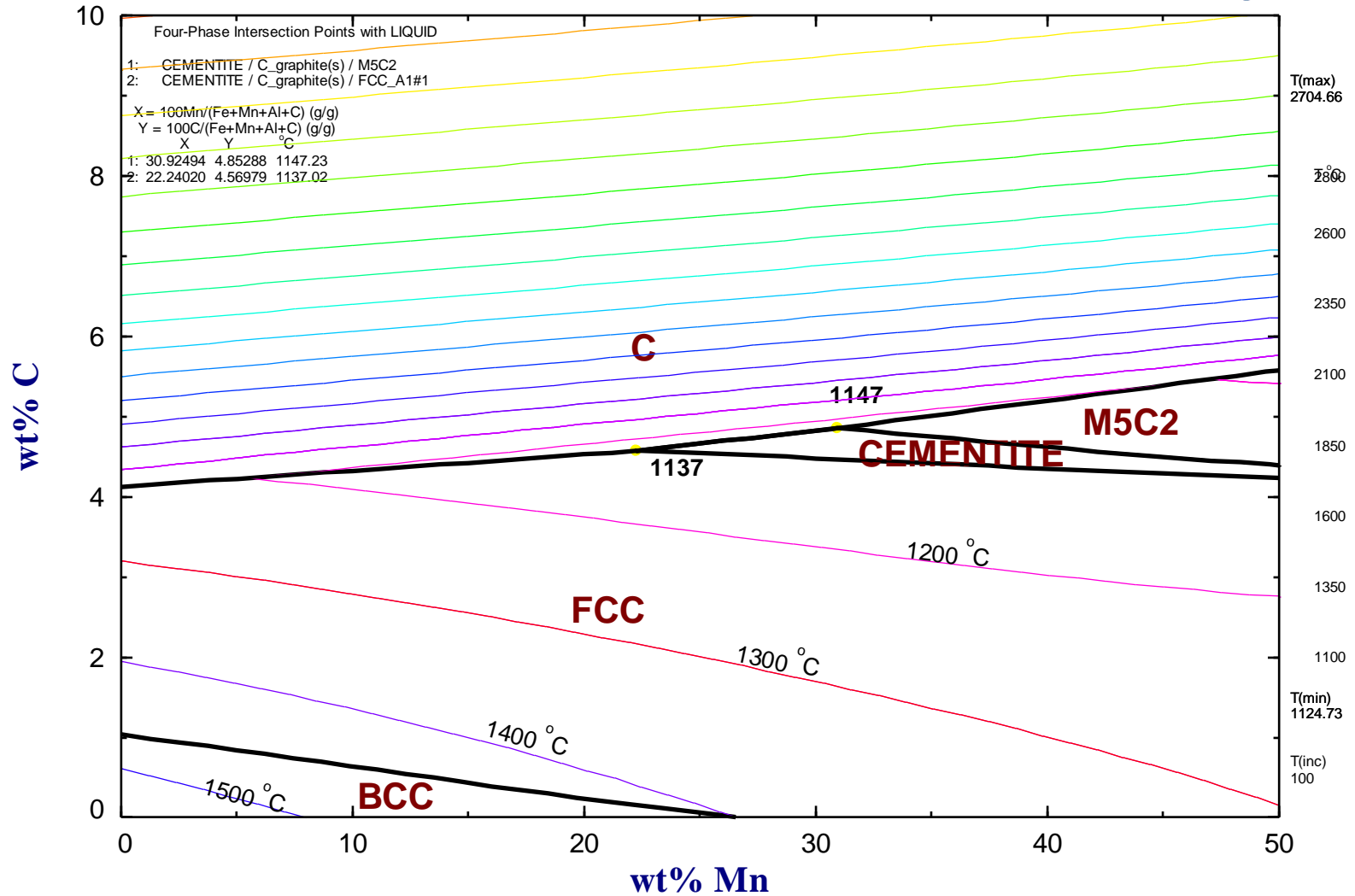
- Reoxidation of liquid steel

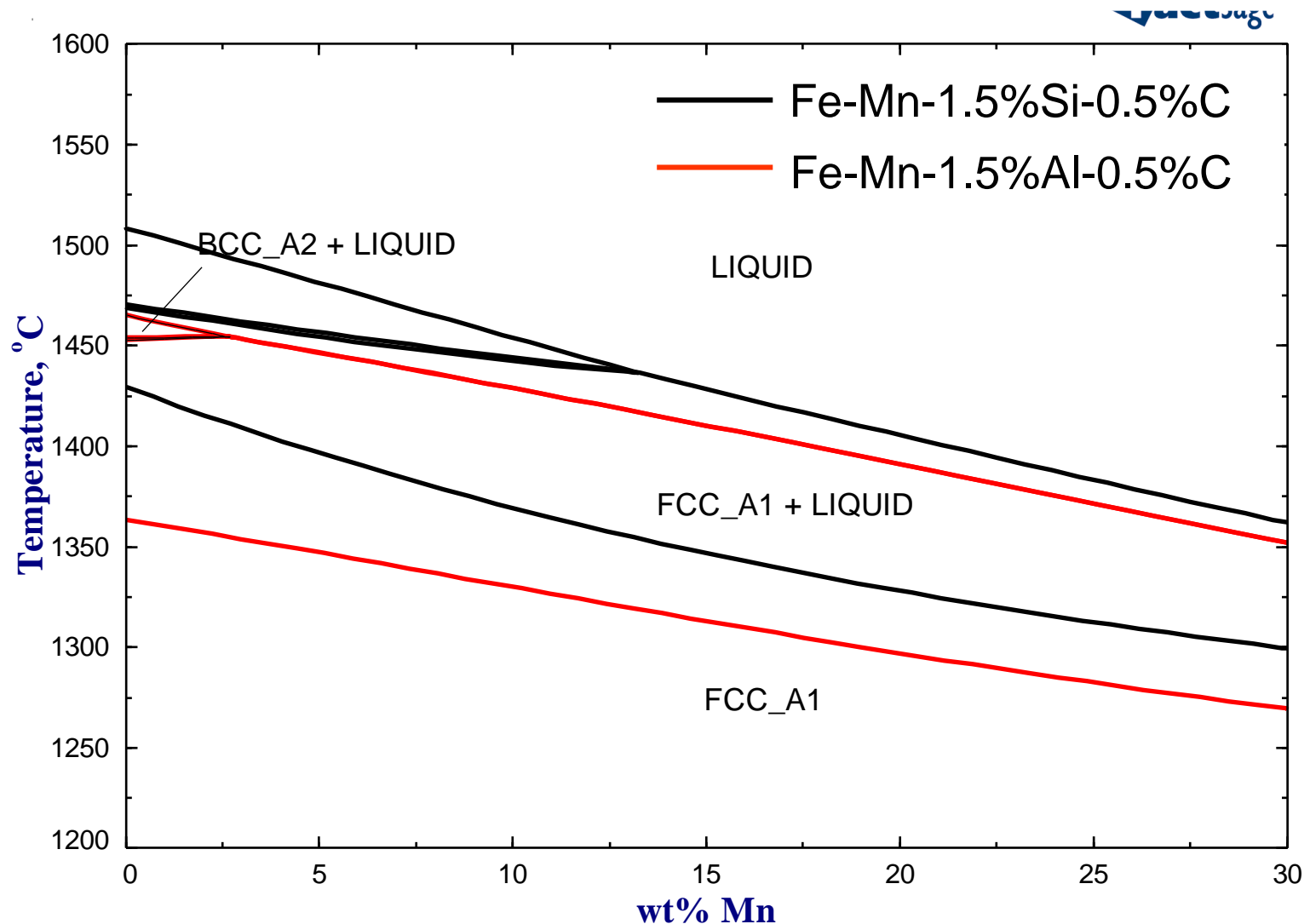
Mold

- Solidification range of steel
- Mold flux design
- Surface quality (AIN)

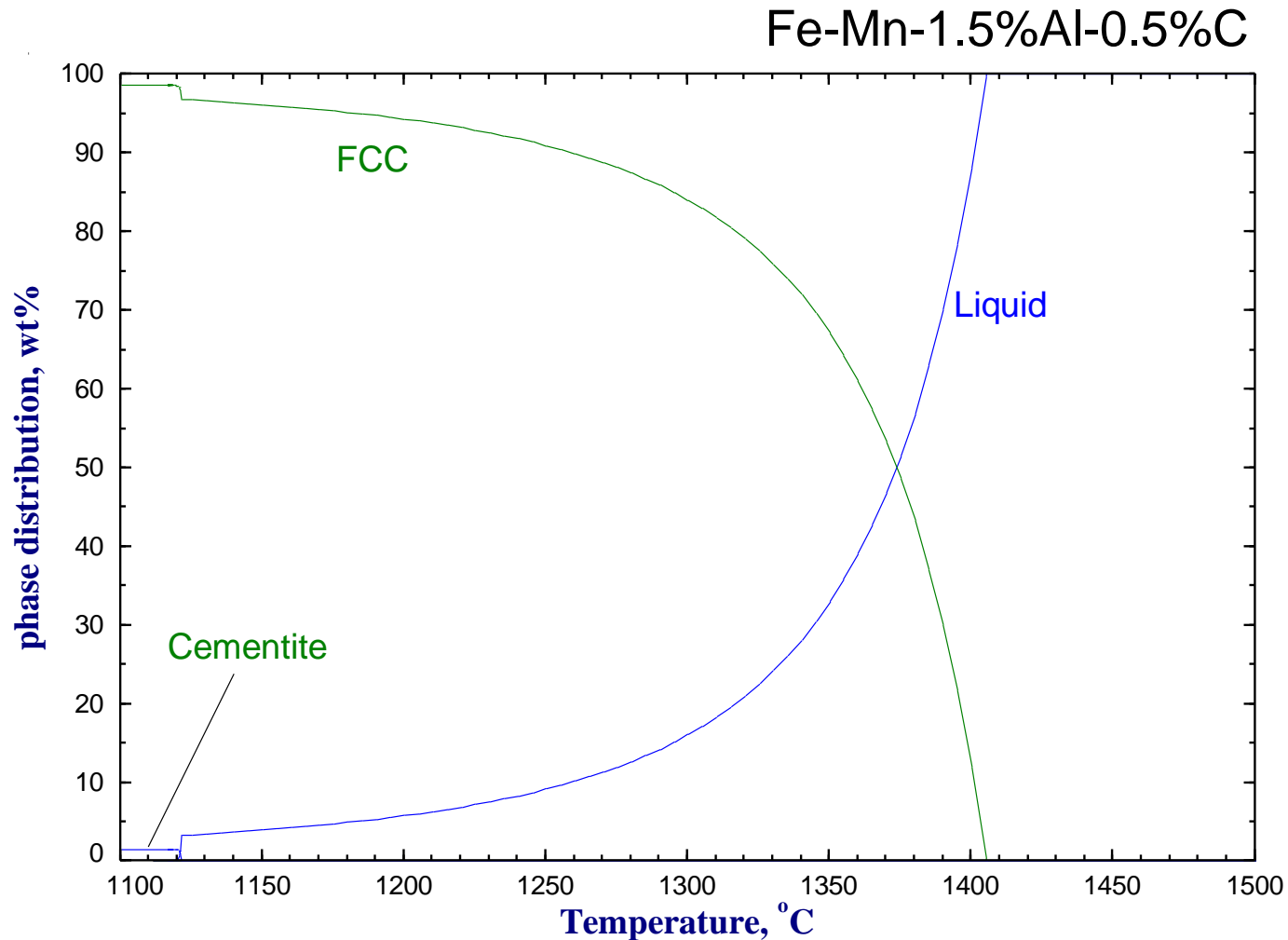


Fe - Mn - Al - C
1.5 wt.% Al





Scheil cooling: complete diffusion in liquid and no diffusion in solids

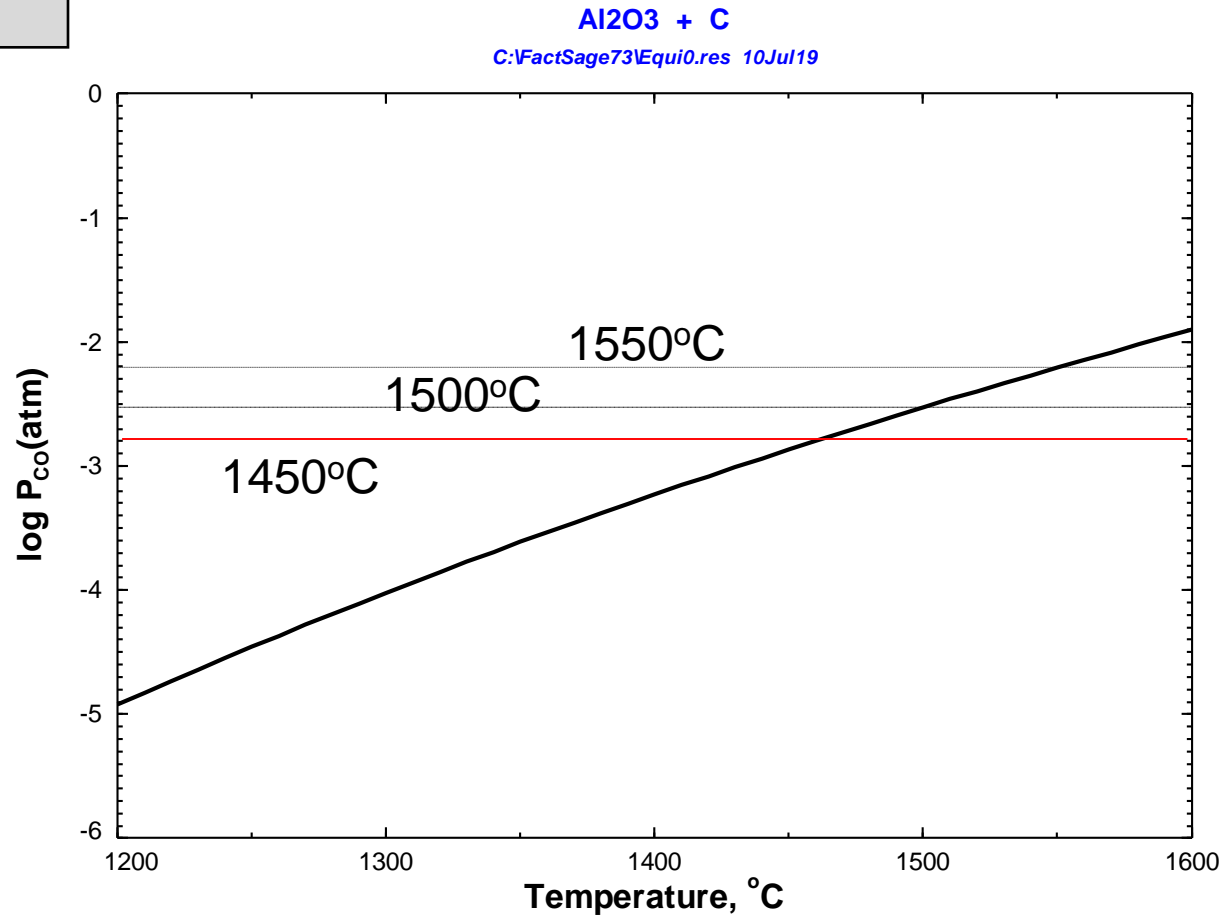
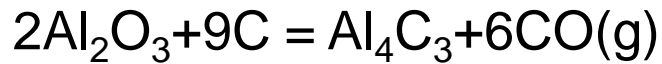
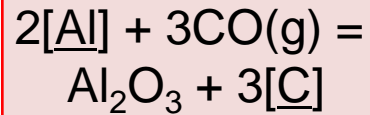


Liquid steel
(Al-killed)

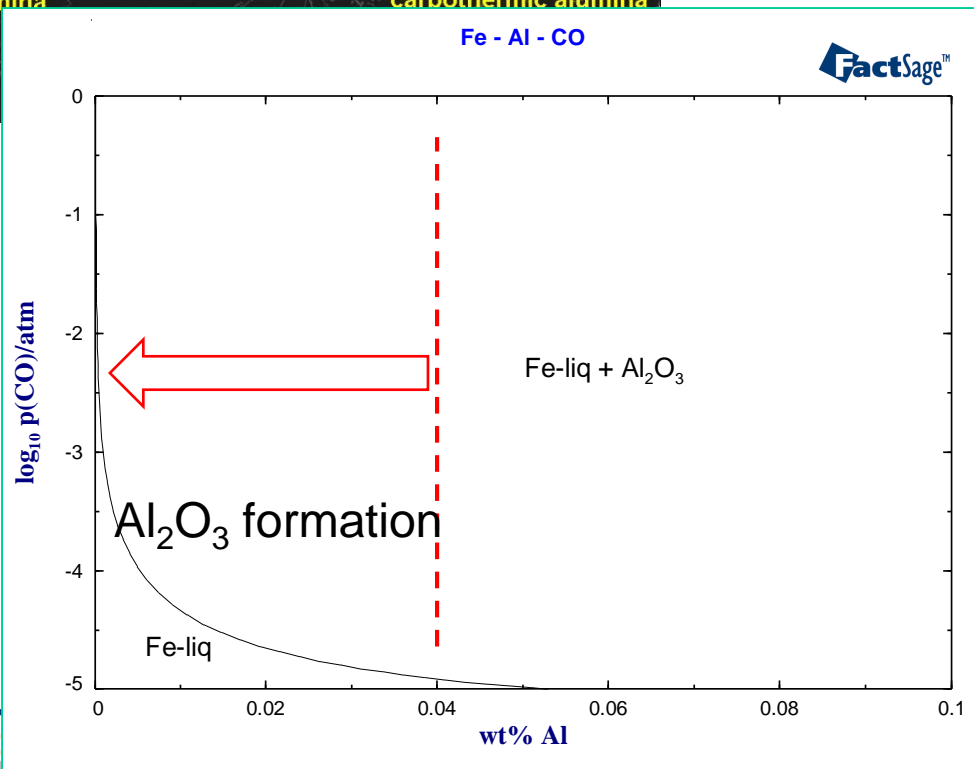
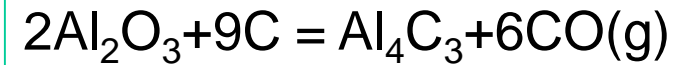
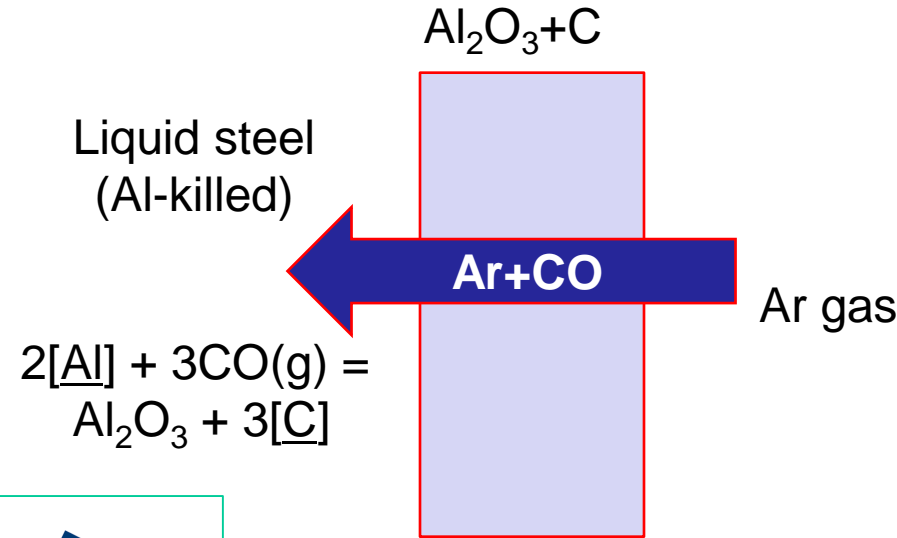
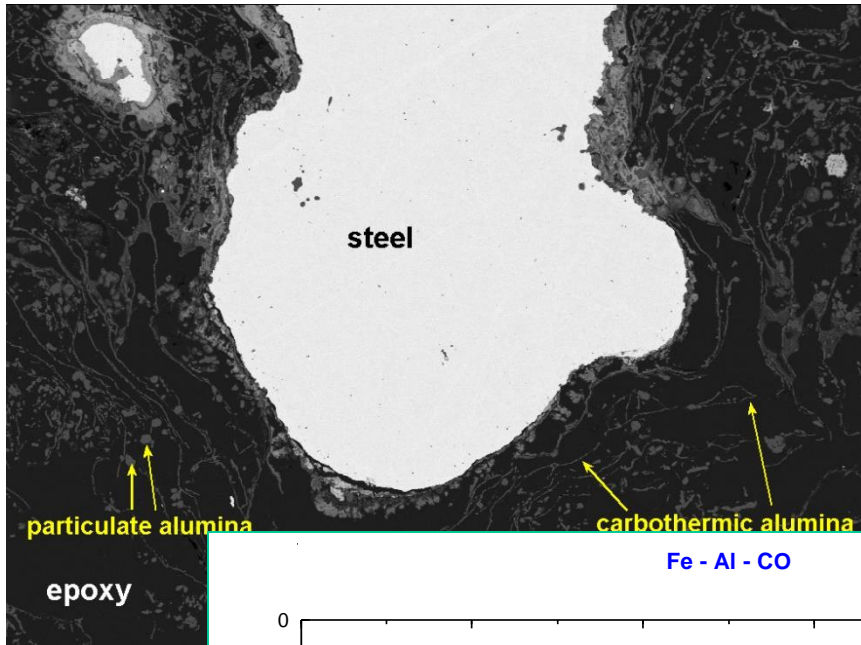
$\text{Al}_2\text{O}_3 + \text{C}$

Ar gas

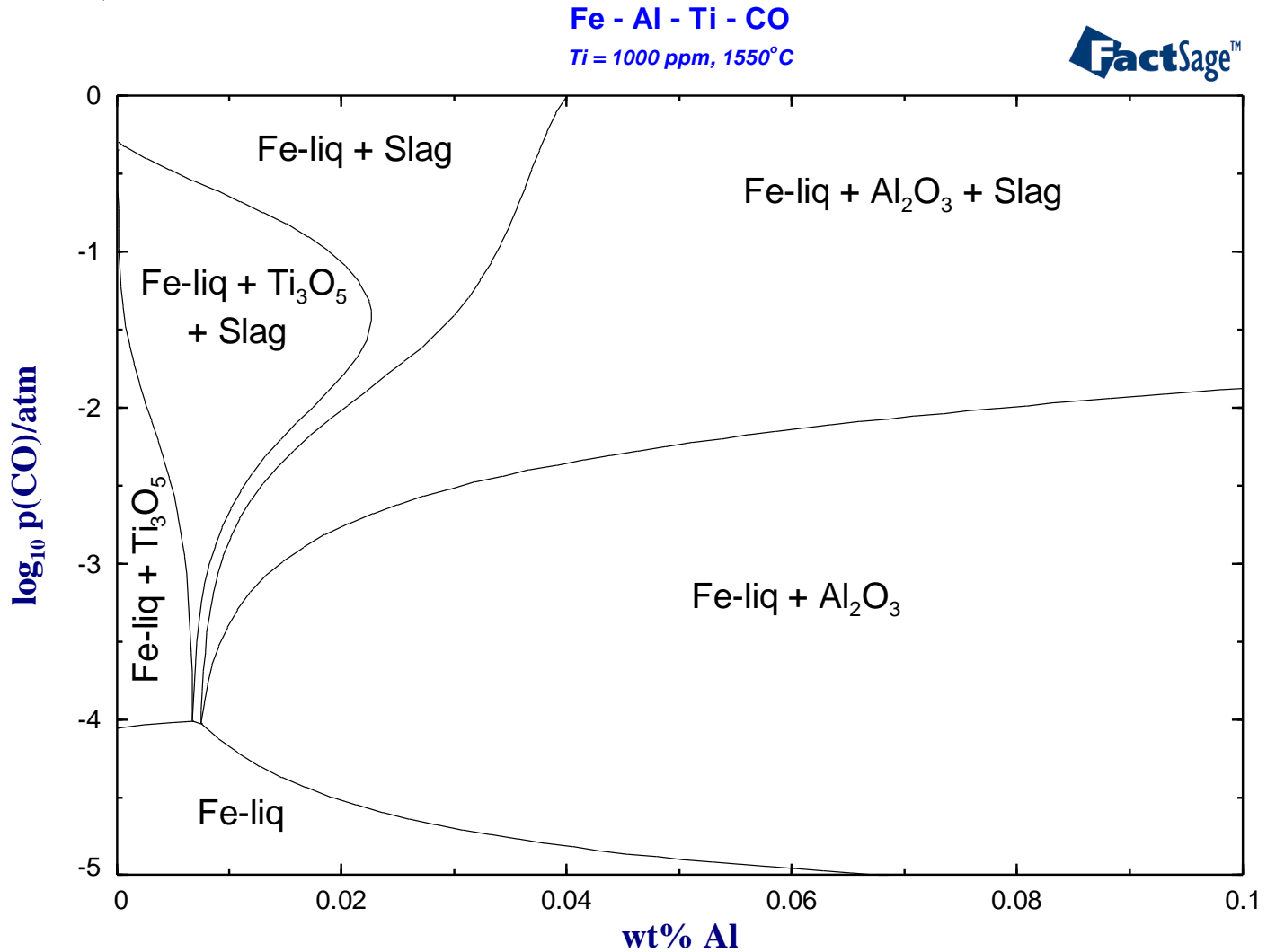
Ar+CO



Formation of Al₂O₃ in Nozzle: Al killed steel



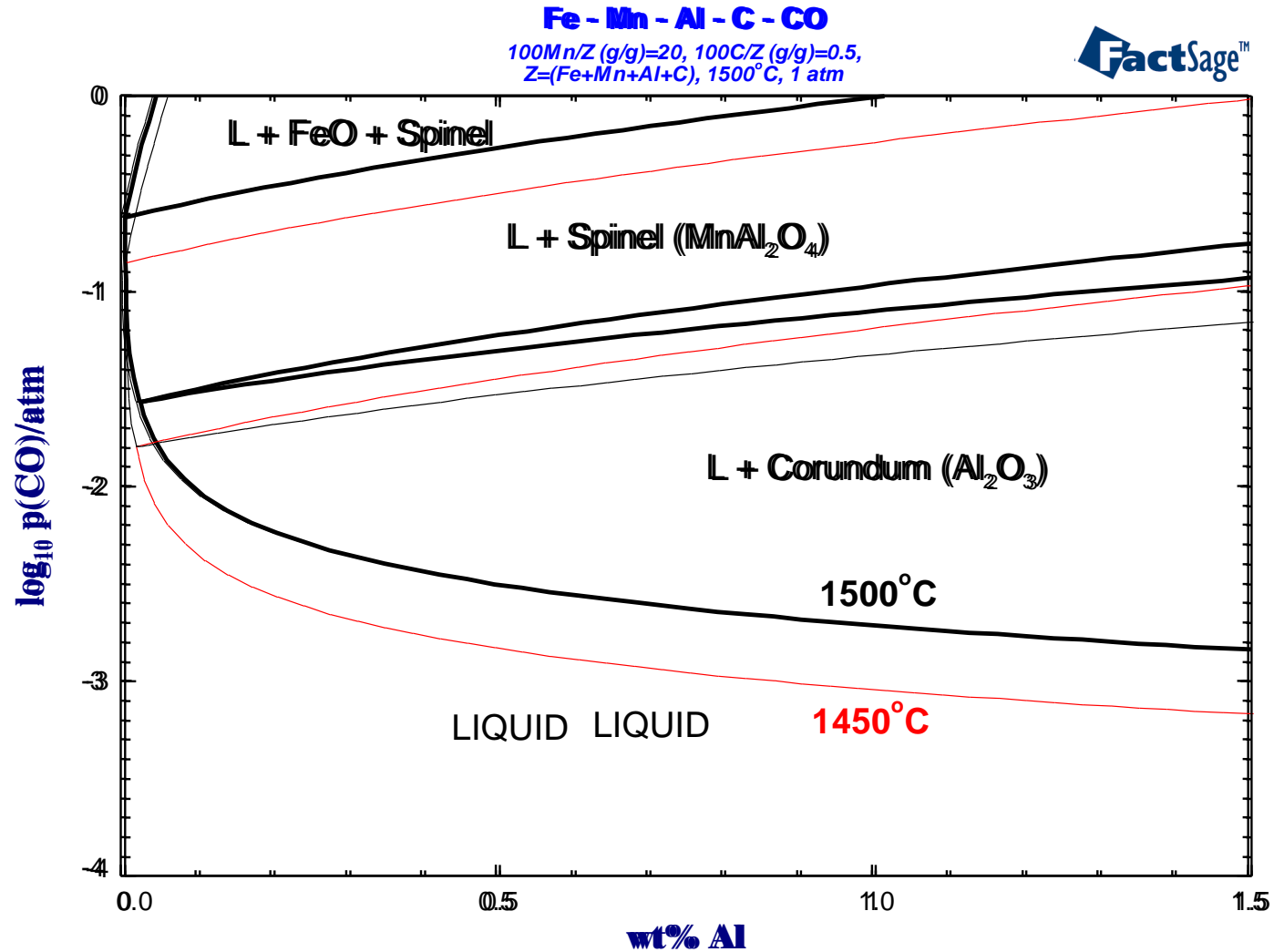
Nozzle clogging in Al-Ti killed steel



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

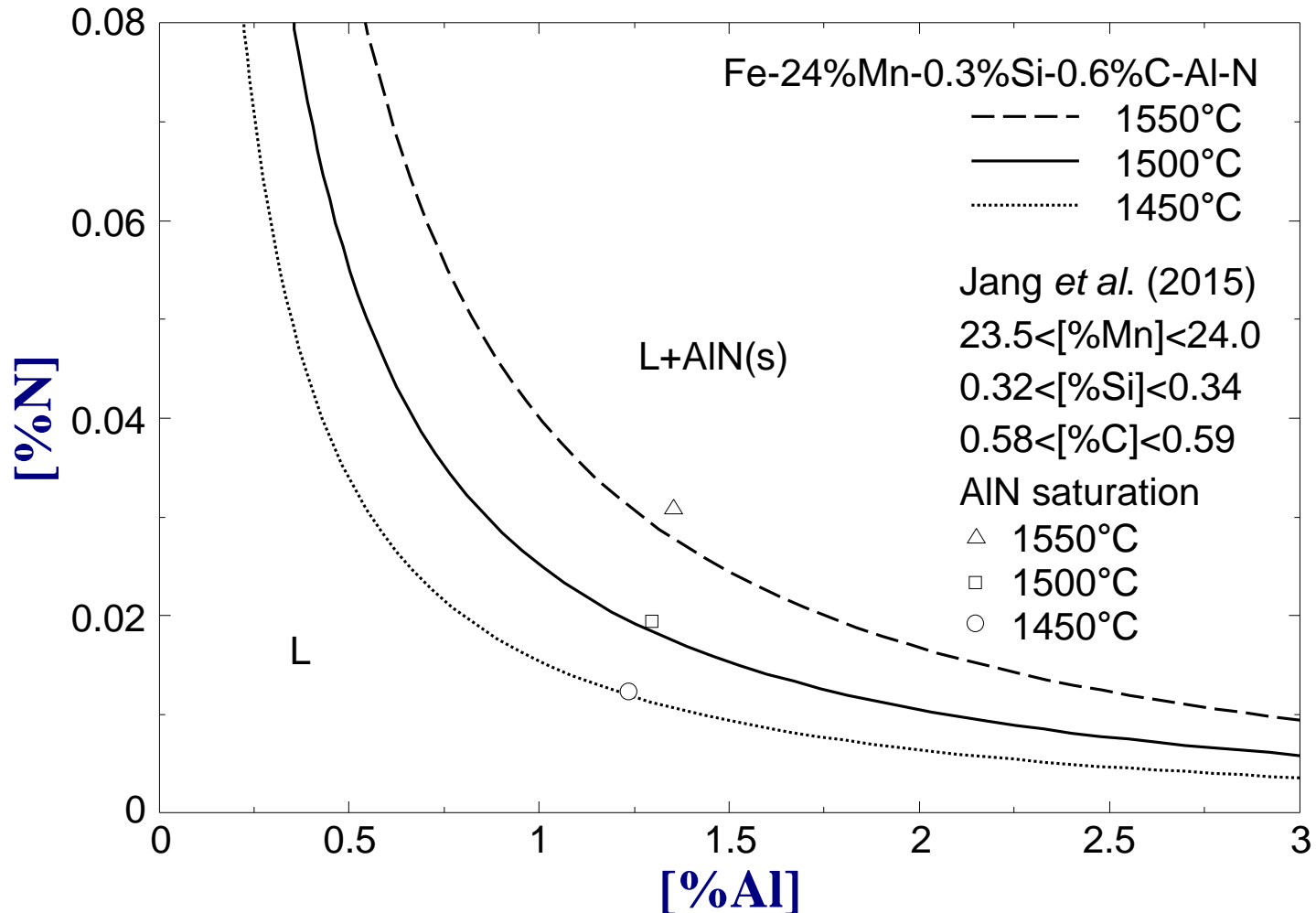
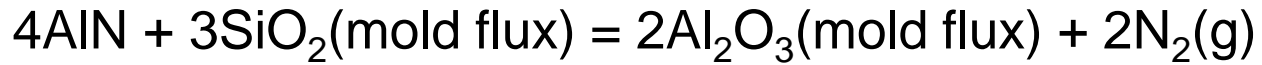
Nozzle clogging in high Mn Steel

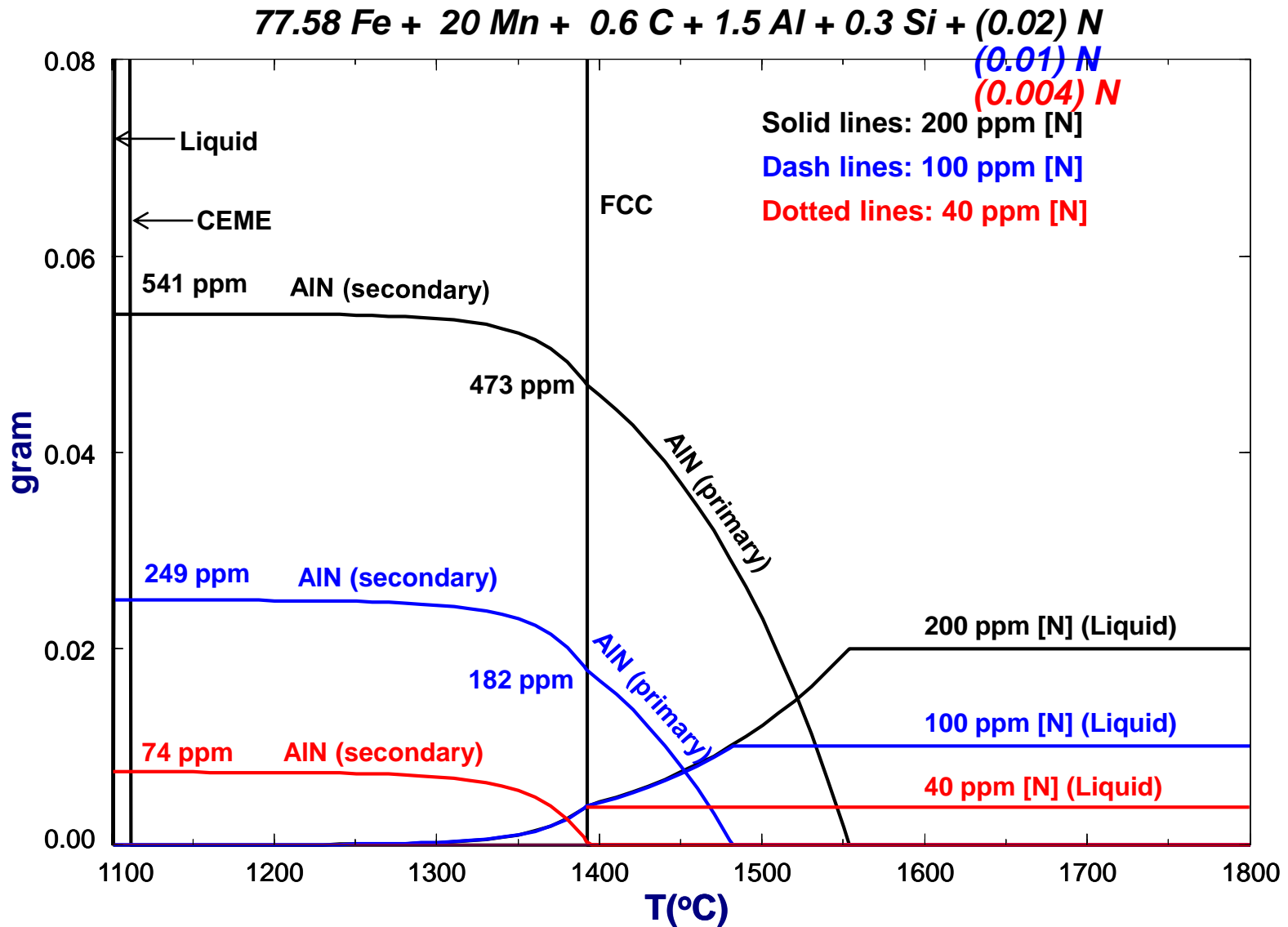
Fe-20wt%Mn-1.5%Al-0.5%C

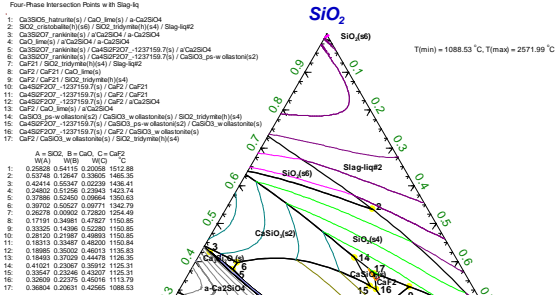


AlN solubility product in TWIP steel

AlN: bad for surface quality





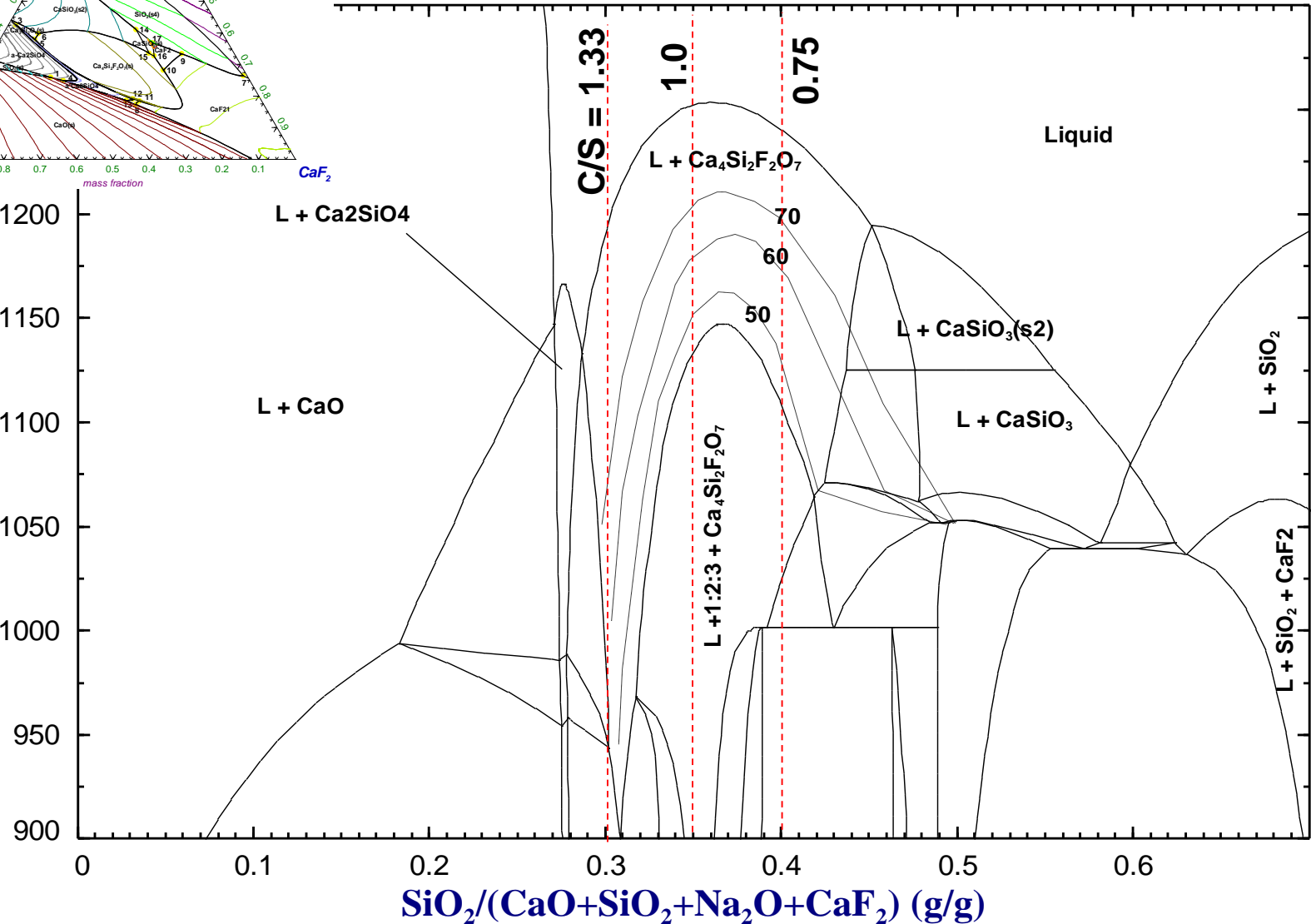


Mold flux design

CaO - SiO₂ - Na₂O - CaF₂
 Na_2O/Z (g/g) = 0.1, CaF_2/Z (g/g) = 0.2,
 $Z=(CaO+SiO_2+Na_2O+CaF_2)$

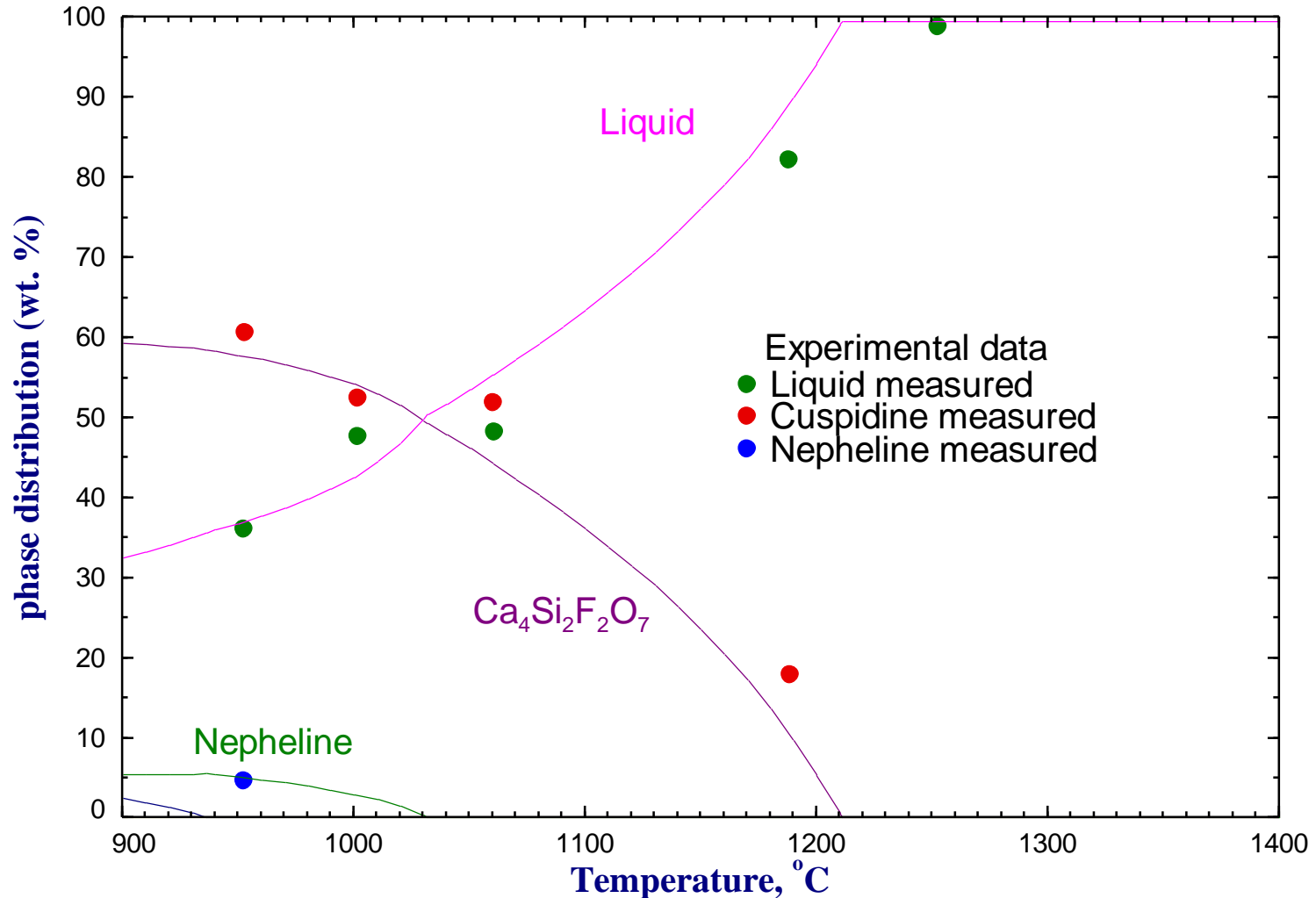


Temperature, °C

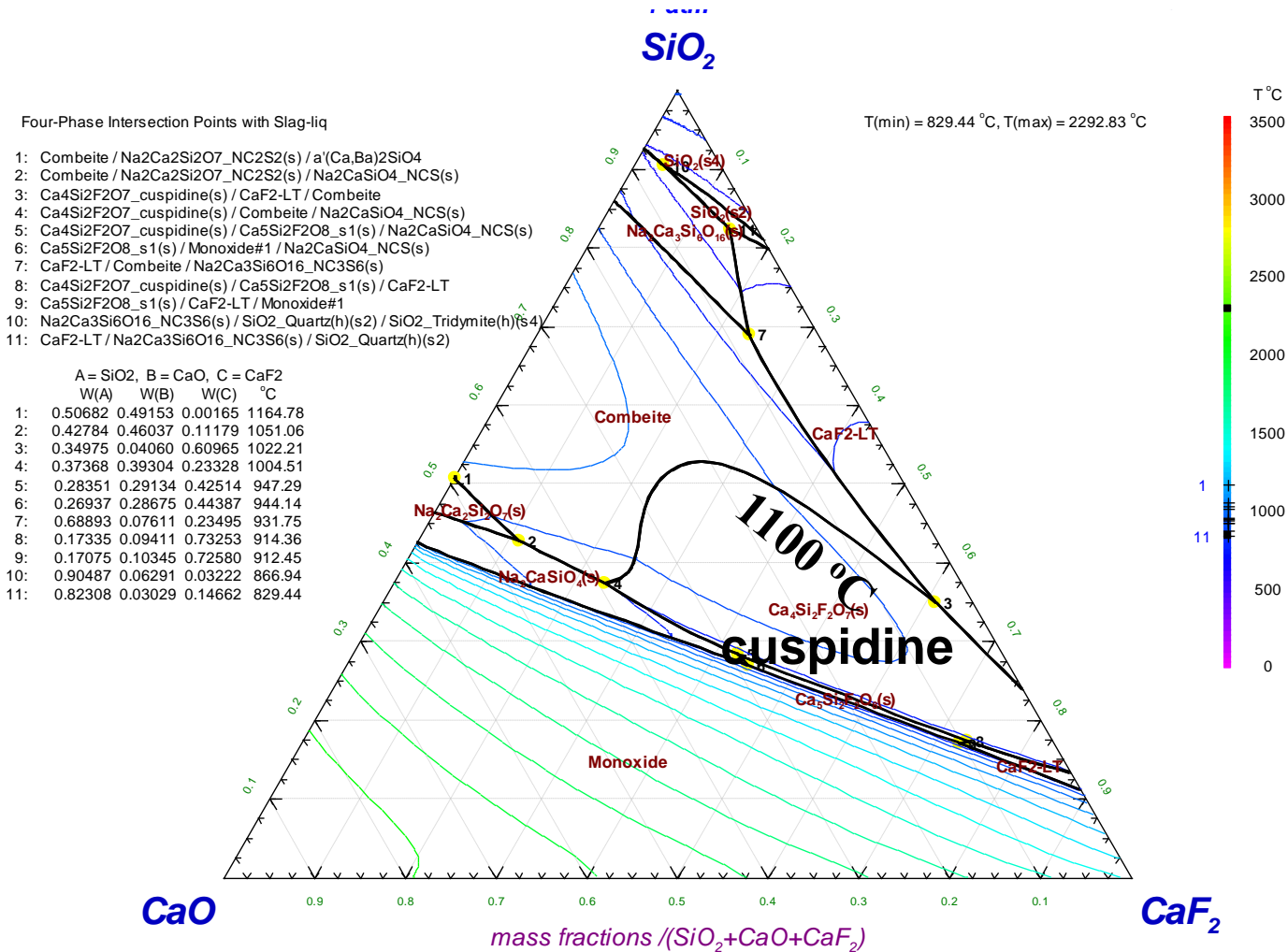


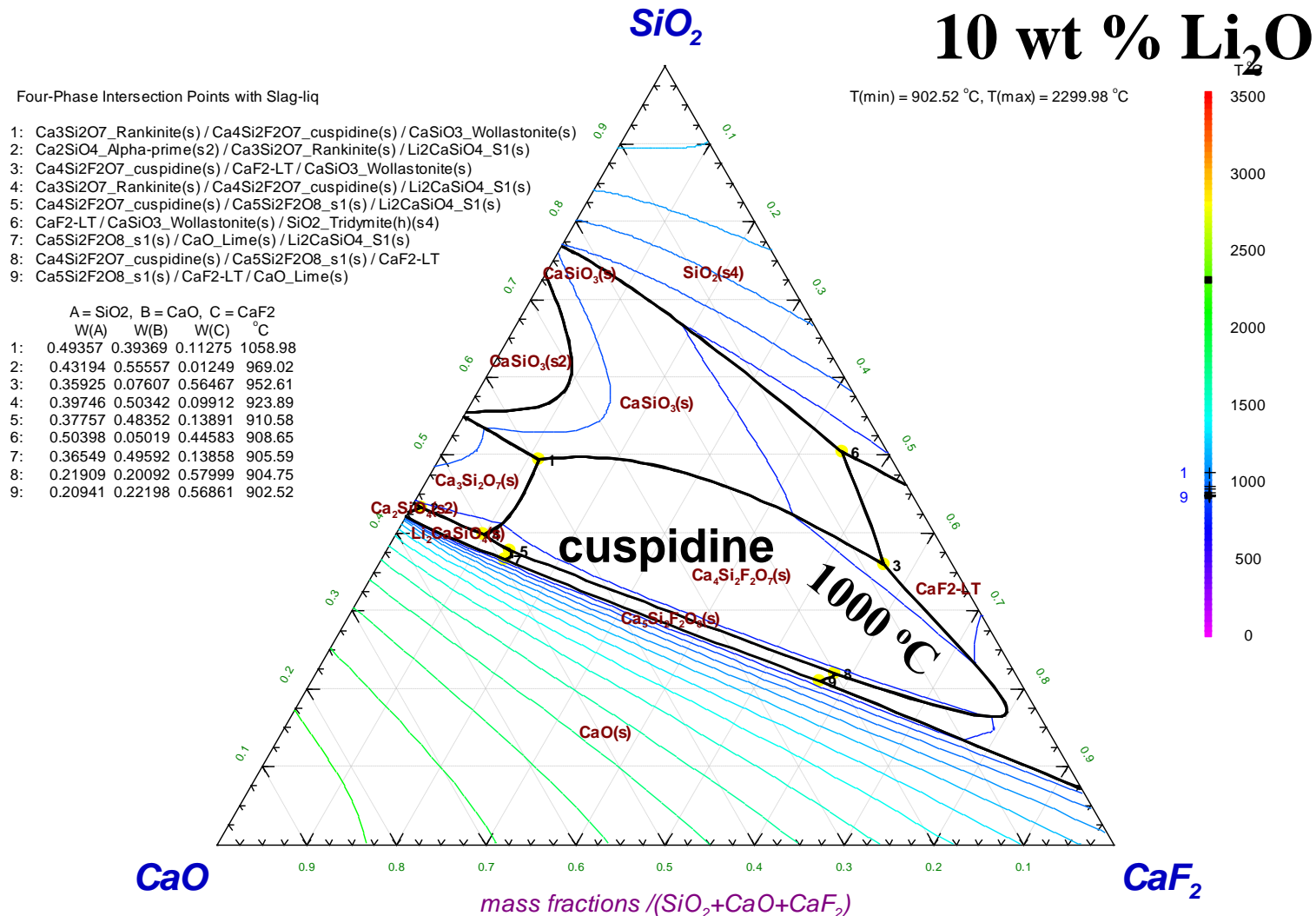
Mold flux: Equilibrium solidification

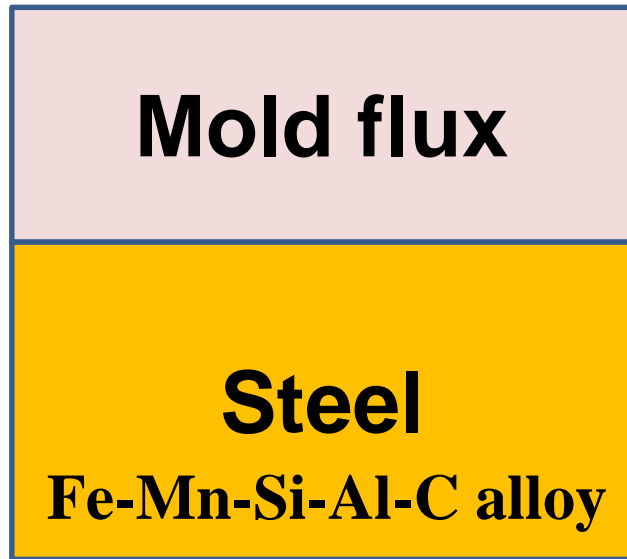
22.3 CaF₂ + 9.2 Na₂O + 4.4 MgO + 3.8 Al₂O₃ + 33.6 SiO₂ + 26.2 CaO



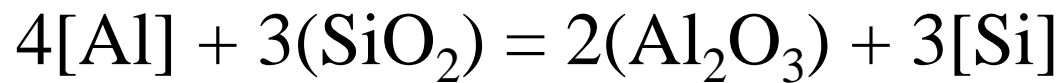
20 wt % Na₂O







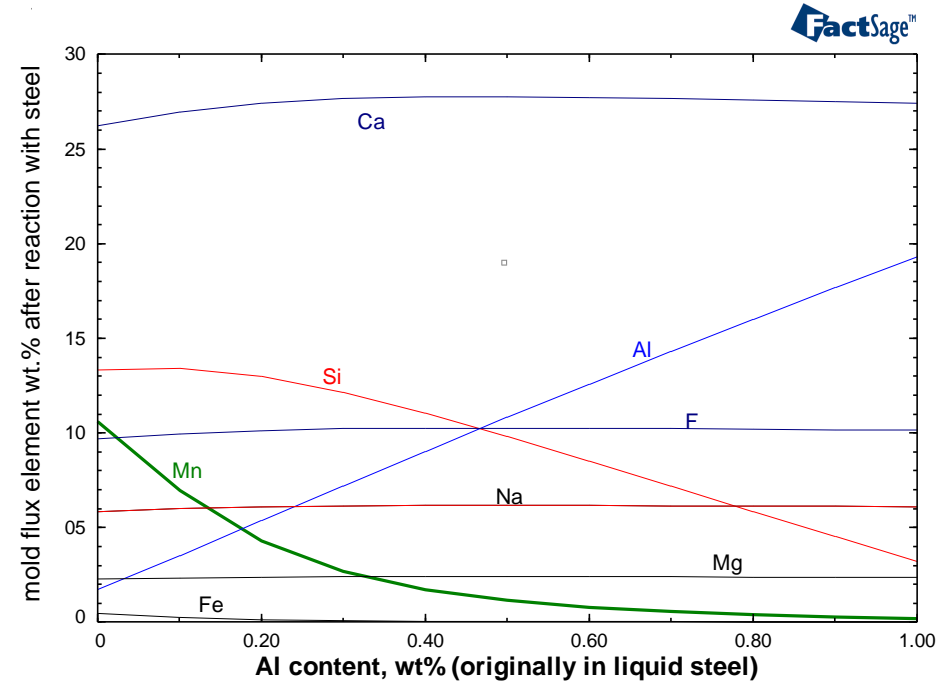
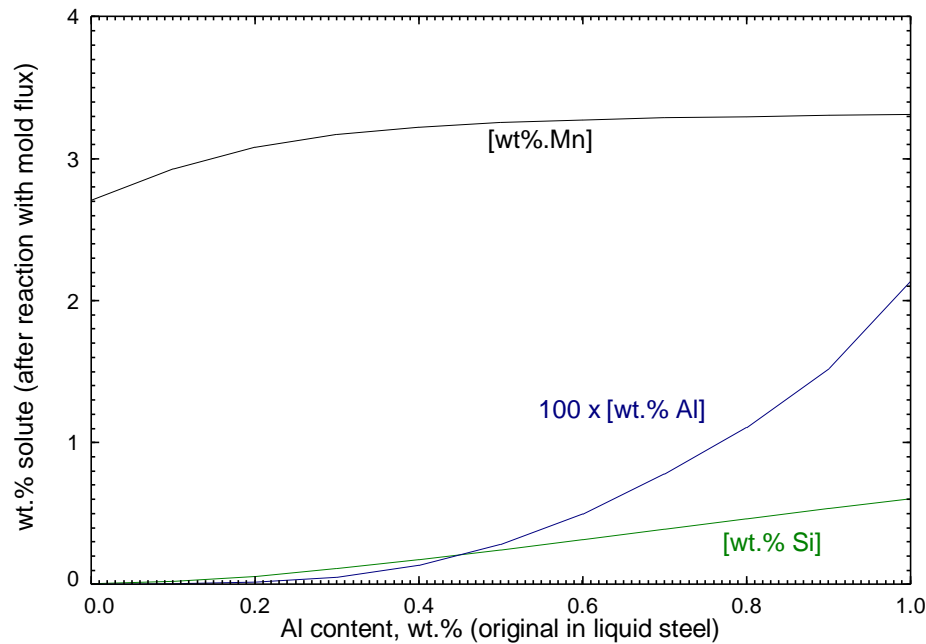
Typical mold flux:
 $\text{CaO-SiO}_2\text{-Na}_2\text{O-CaF}_2$



Addition of MnO_2 to minimize the change of mold flux chemistry

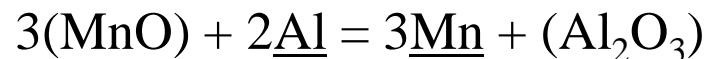
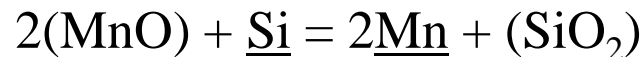
Typical mass ratio between mold flux and liquid steel = 1:20 ~ 1:10

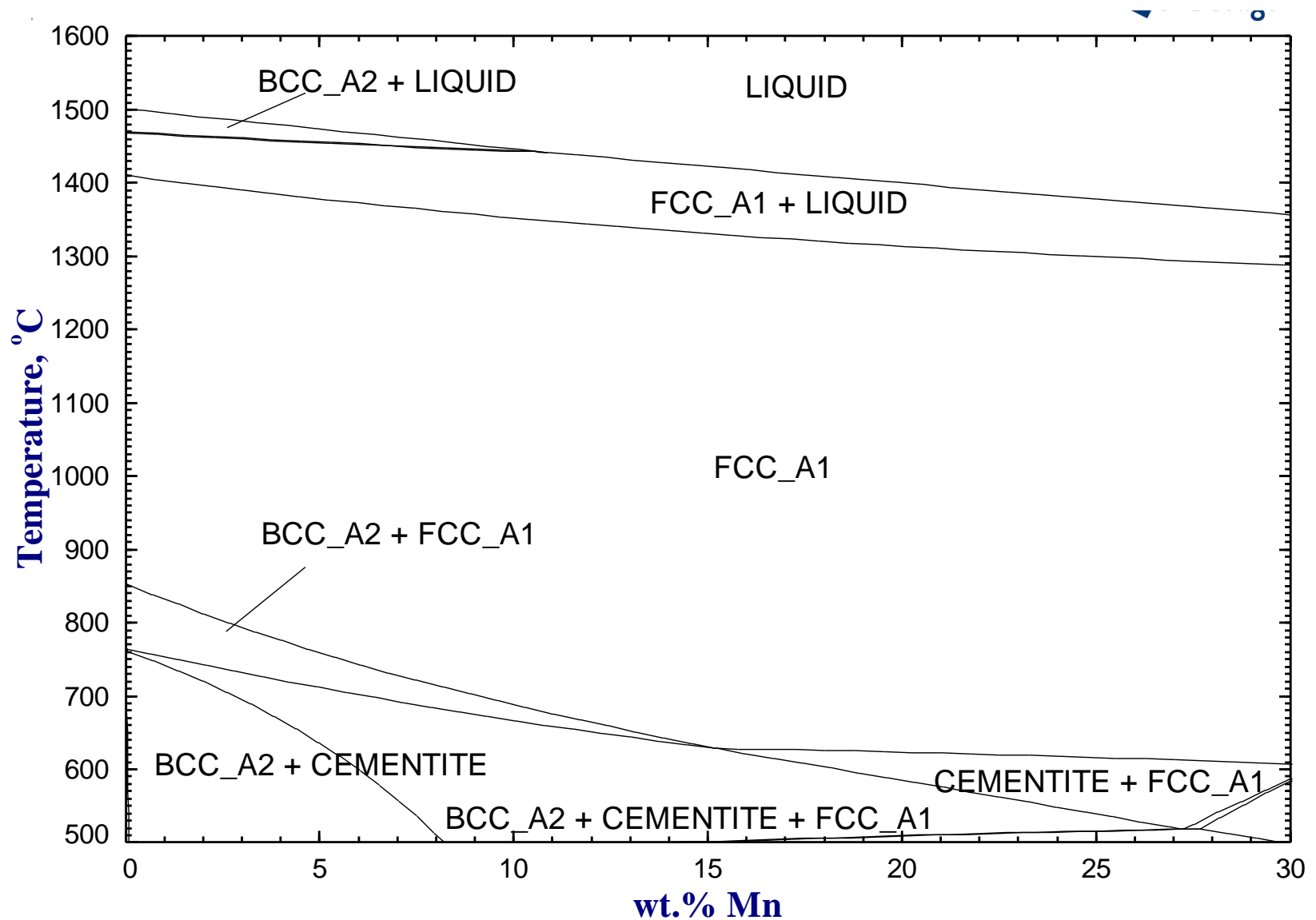
100 gram of liquid steel (Fe-3%Mn-xAl) + 5 gram of mold flux + 0.5 gram of MnO₂



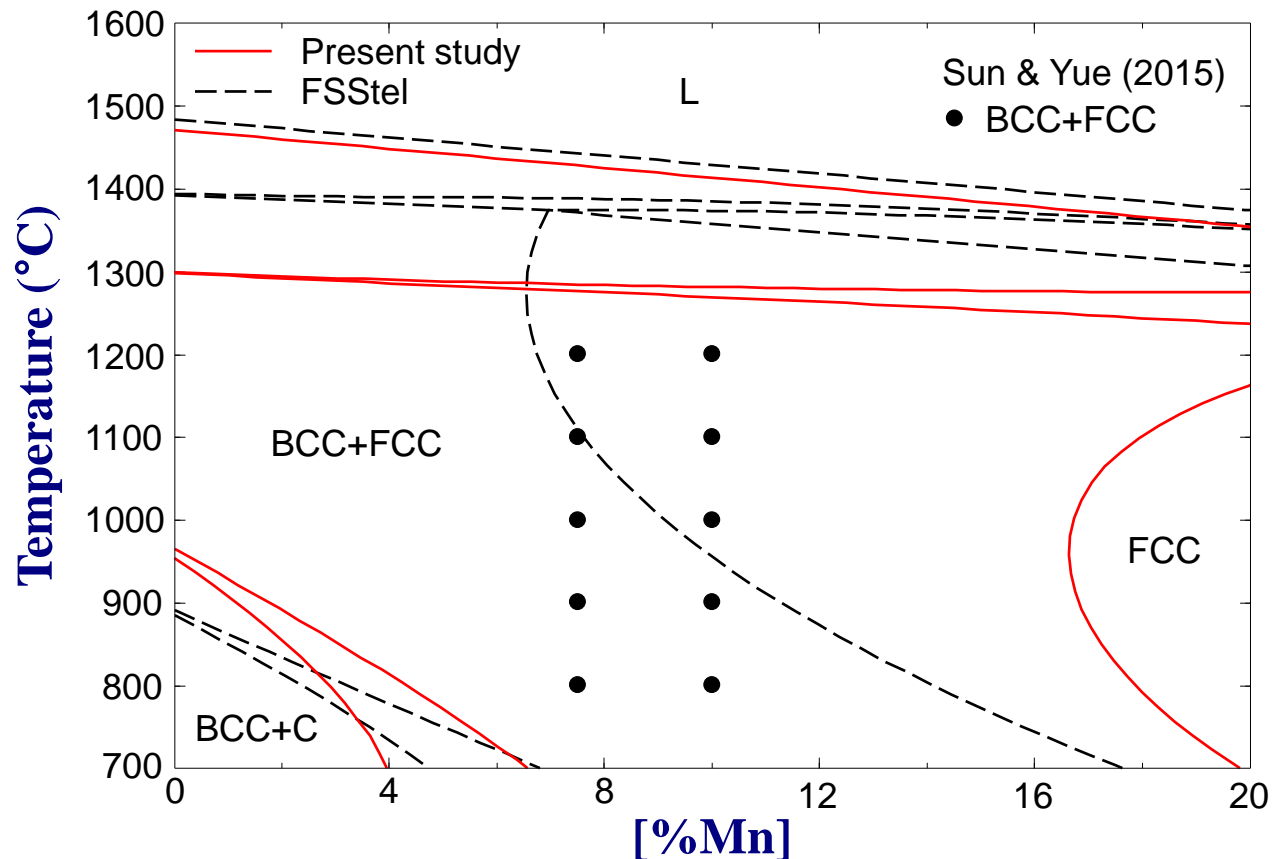
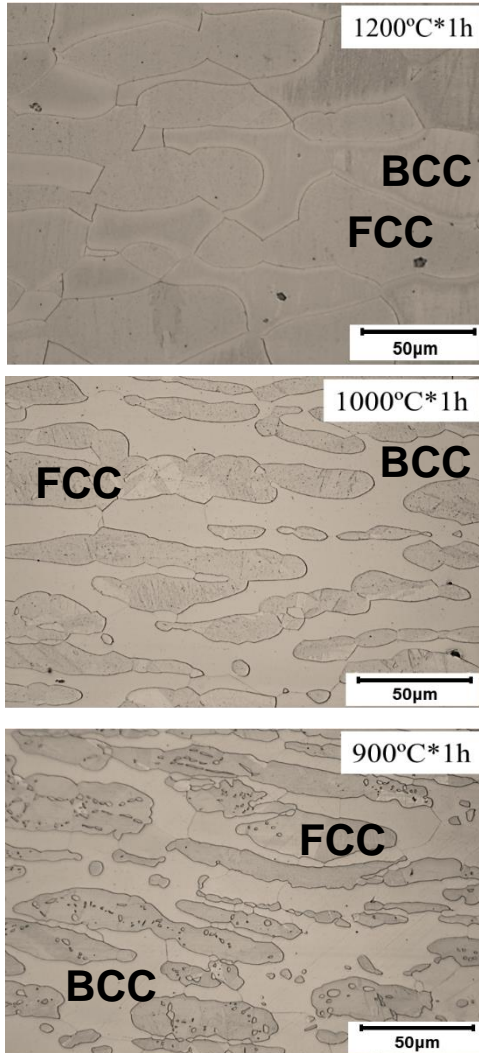
→ Before MnO₂ (MnO) is completely consumed by Al, reduction of SiO₂ begins

Simply due to the equilibrium of:

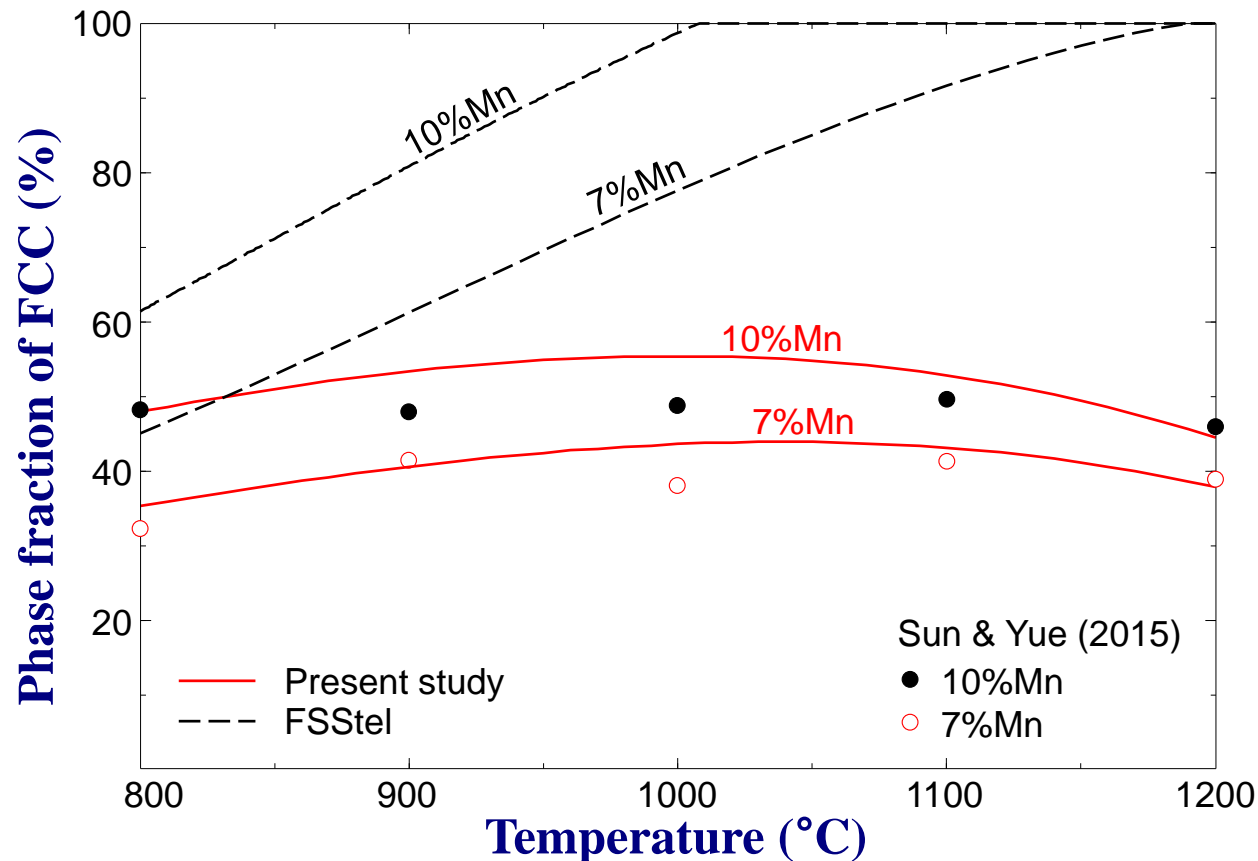
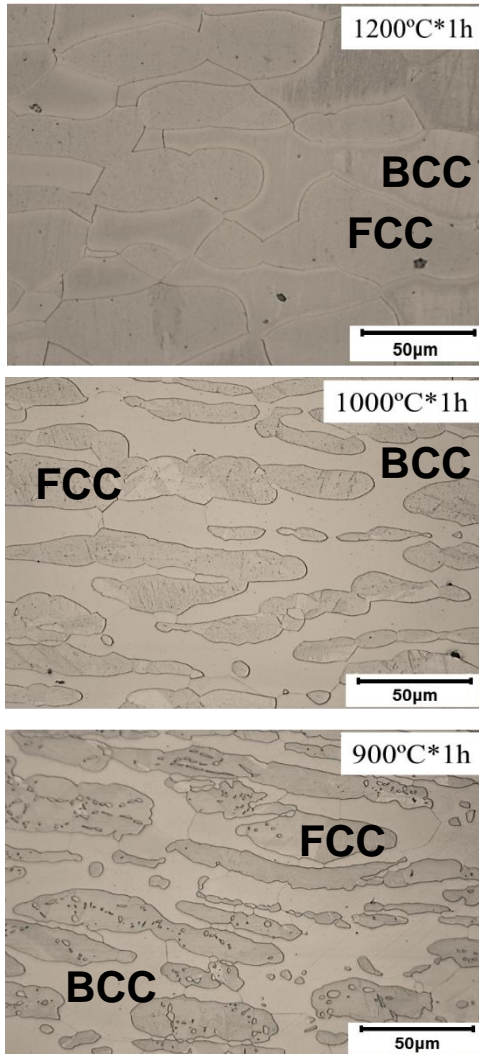




Fe-X%Mn-3Al-3Si-0.2C (X= 7.5 & 10)



Fe-X%Mn-3Al-3Si-0.2C (X= 7.5 & 10)

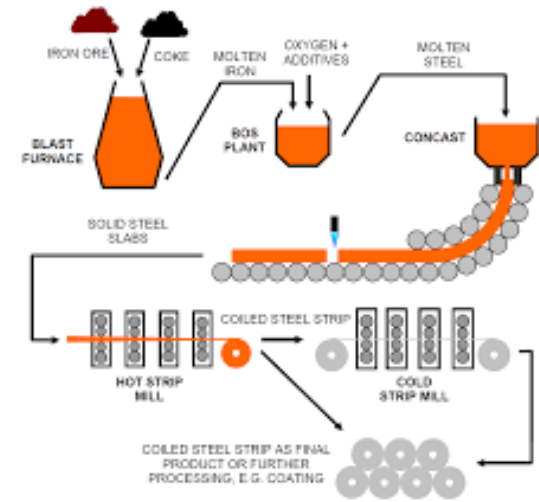


Metastable phase transformation at rolling process

Deformation of γ -austanite

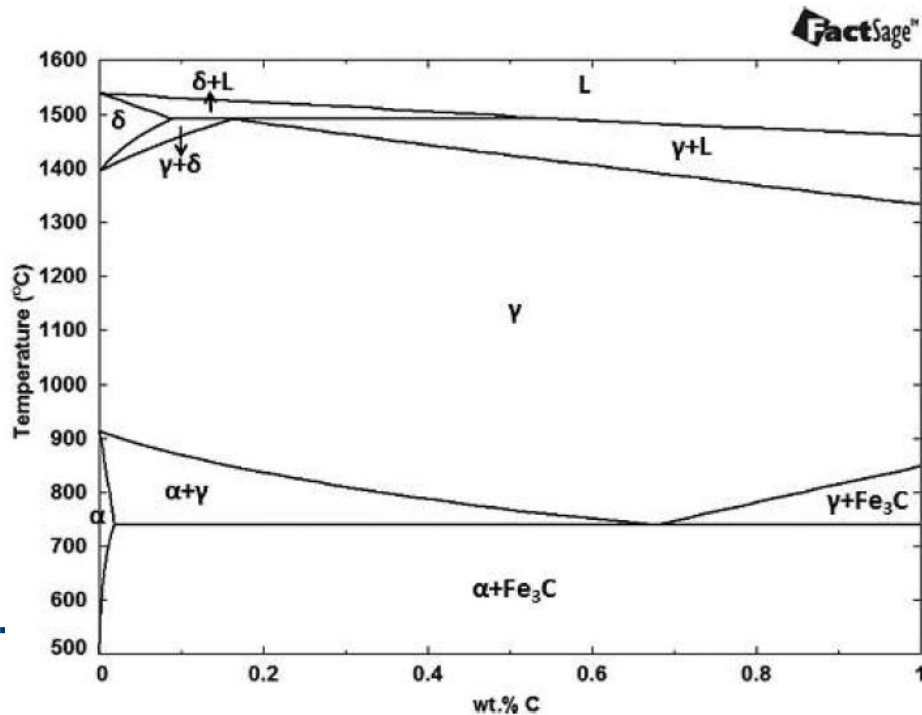
→ Shear accommodation + Dilatation energy to γ -austanite

→ de-stabilization of γ -austanite

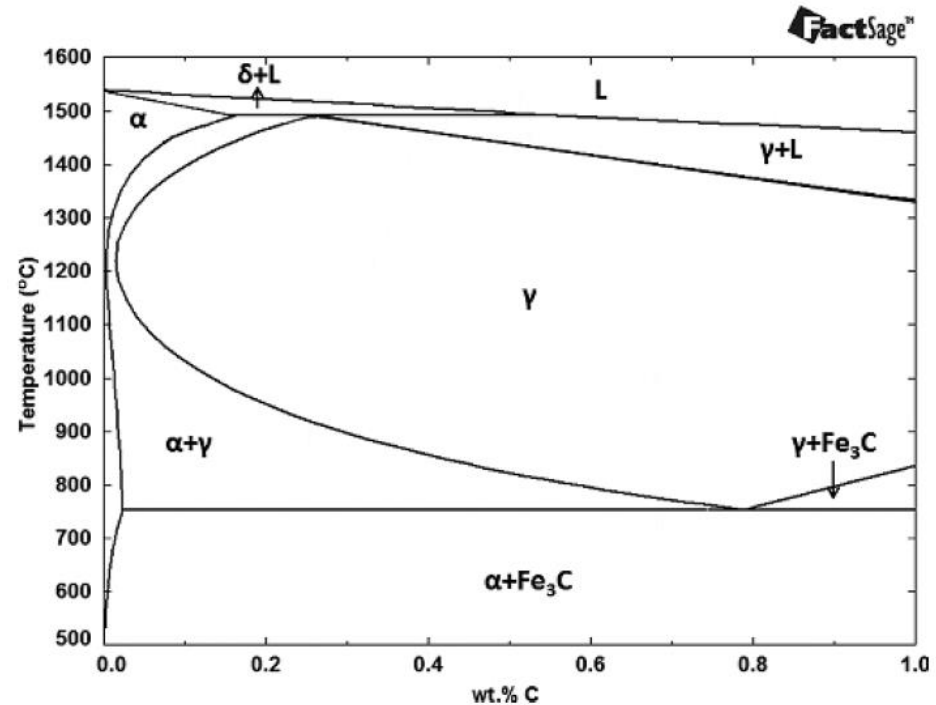


Jonas et al. Materials Science Forum, 2017, vol. 879, p. 29-35

Static condition: Equilibrium

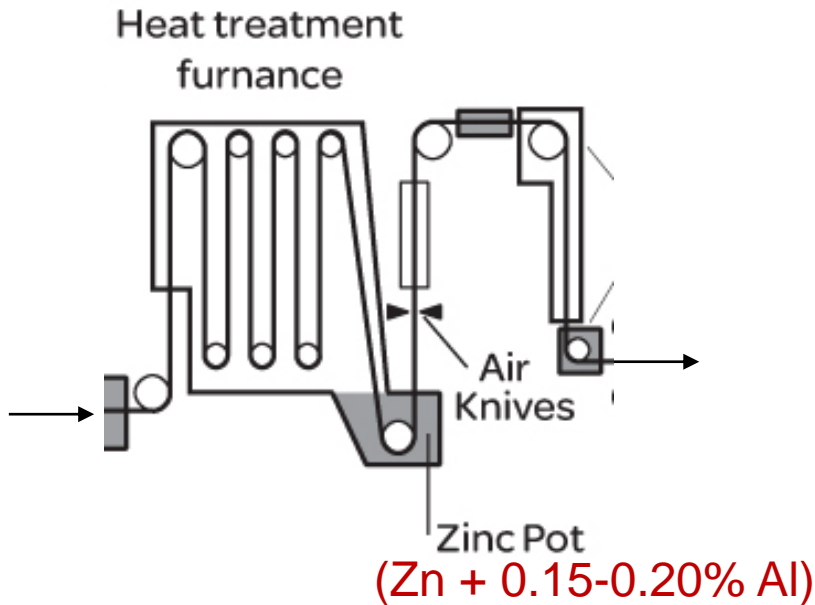


Dynamic condition: Non-equilibrium



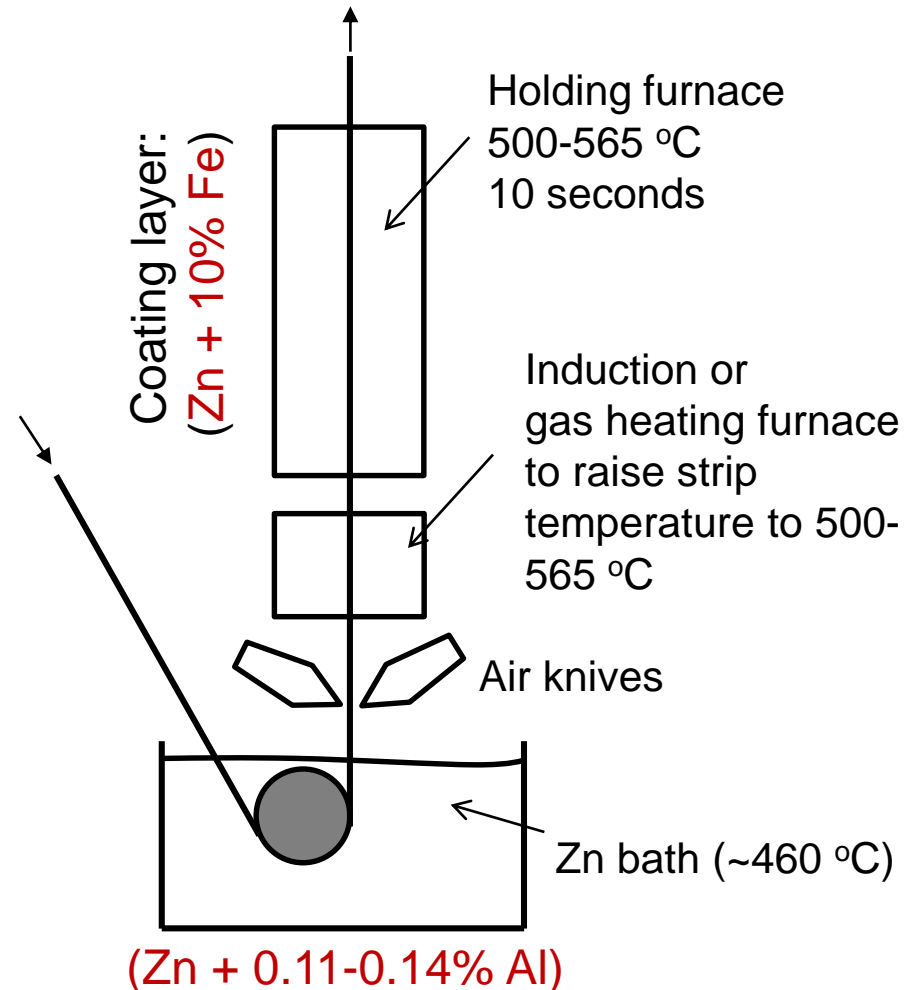
Continuous galvanizing and galvannealing line

Galvanizing process

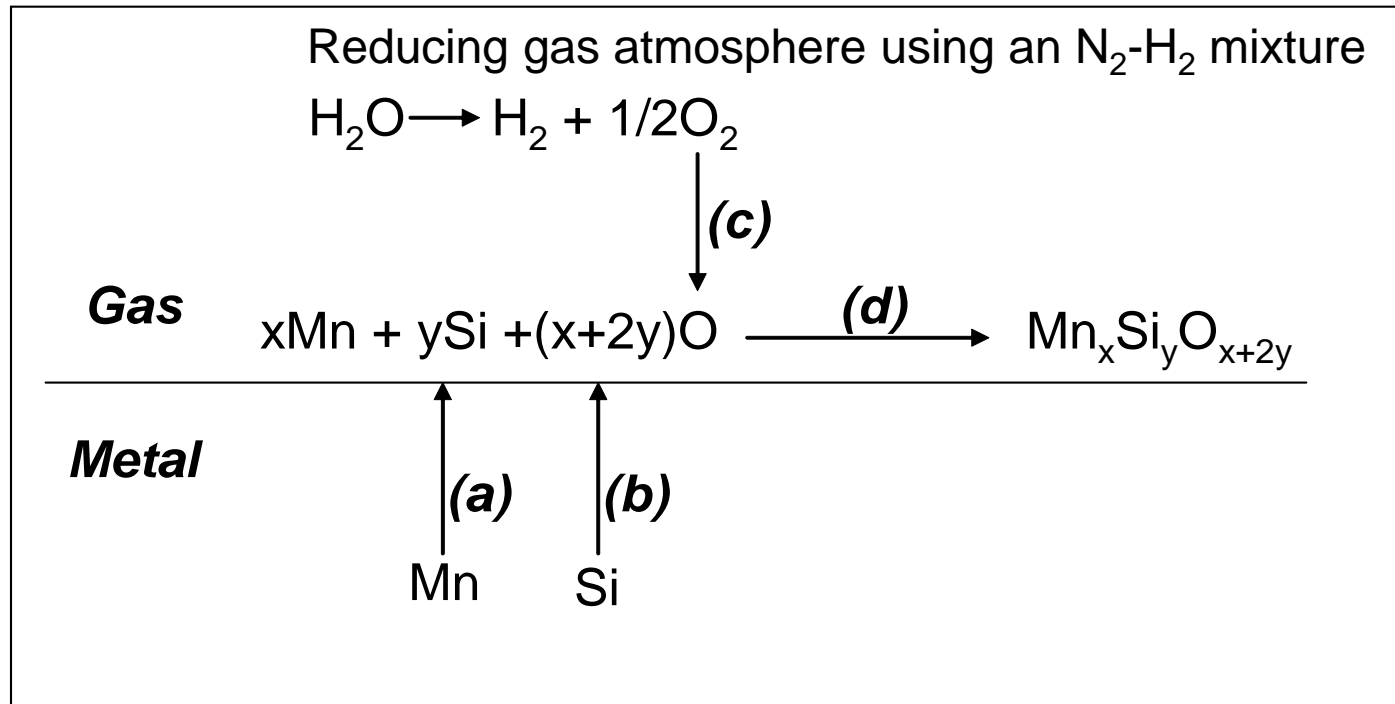


- Zn bath temperature: ~460 °C typically 463-465 °C
- Line speed: up to 200 m min⁻¹
- Immersion time: 2-8 seconds

Galvannealing process



Annealing furnace: Oxidation of steel in reducing condition



In the early stage of the internal/external oxidation :

- Mn and Si contents are enough to form oxides on the surface of steel

Oxidation reaction can be controlled by

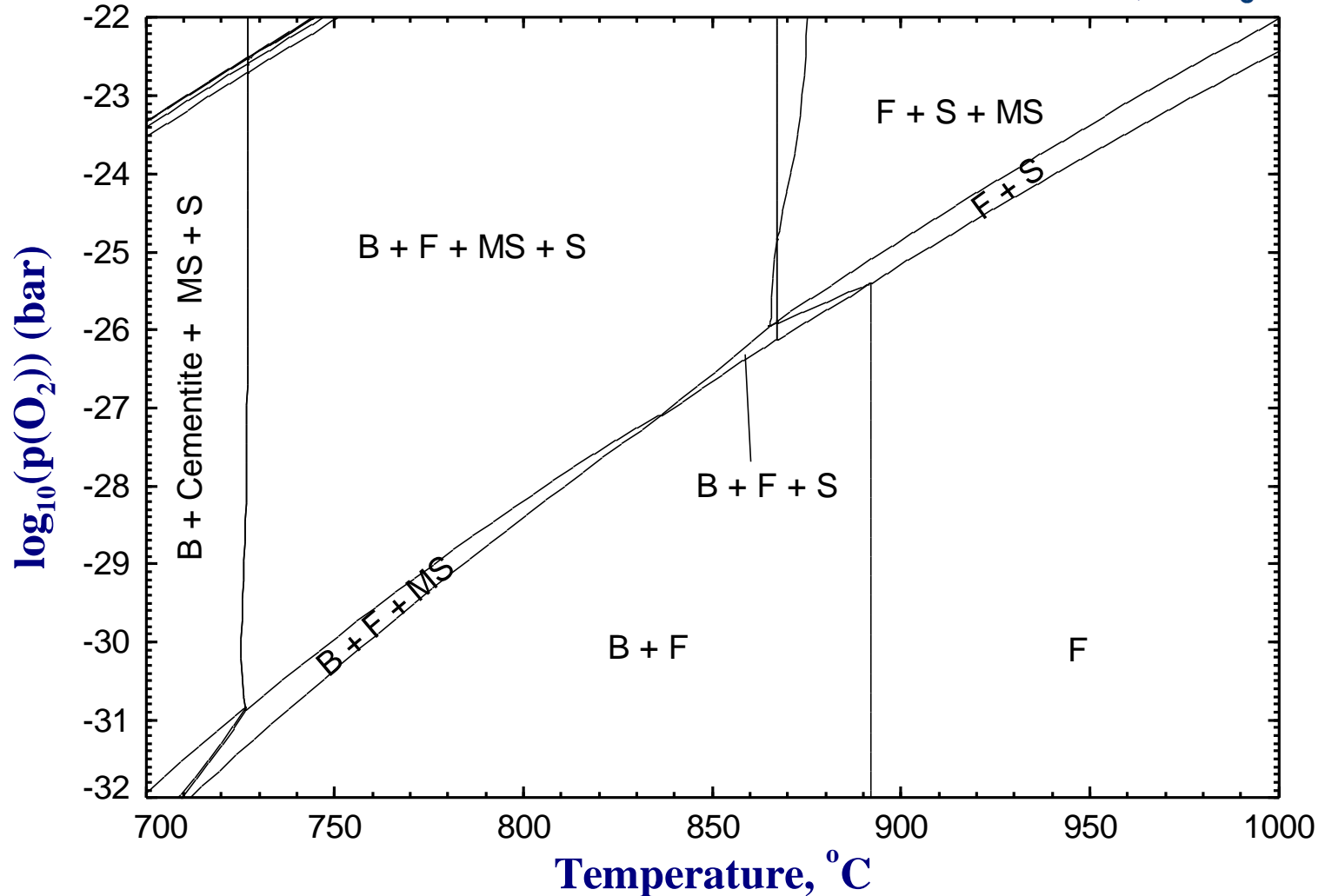
(1) supply of O₂ gas (c)

(2) formation of $\text{Mn}_x\text{Si}_y\text{O}_{x+2y}$ oxides on the steel surface (d)

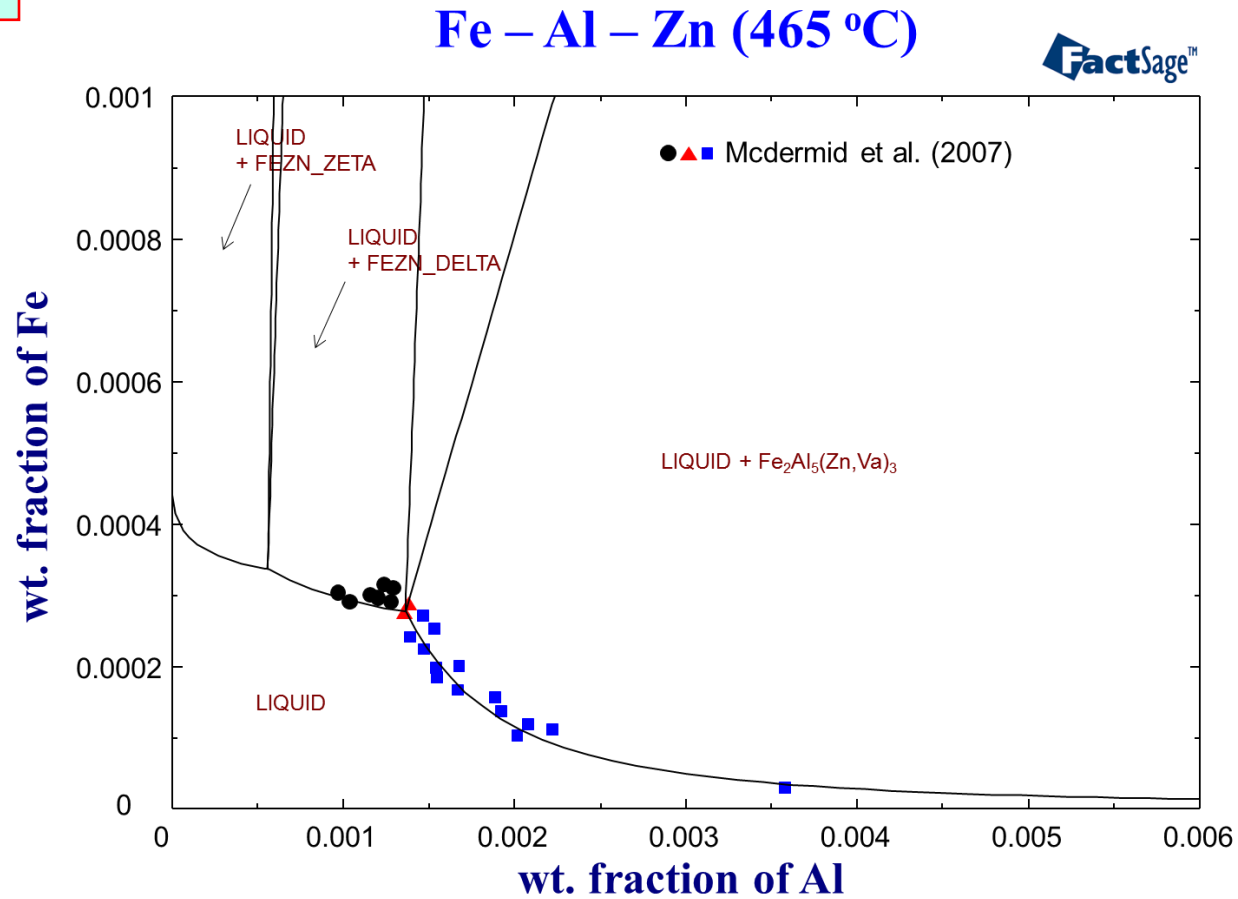
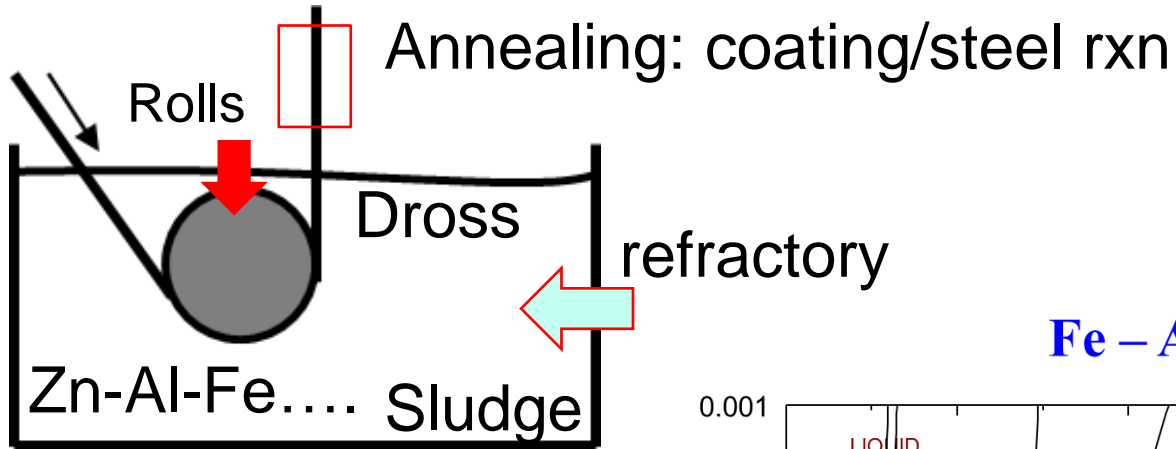
Oxidation of steel: PO₂-Temperature diagram

Fe-C-1.5%Mn-1.5%Si-0.08%C

B, F, MS and S stand for BCC, FCC, MnSiO₃ and SiO₂

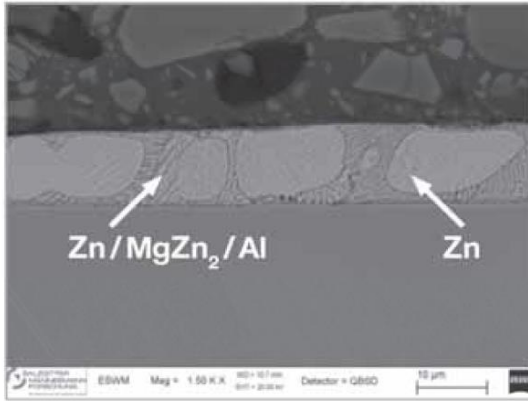


Dross and Sludge formation



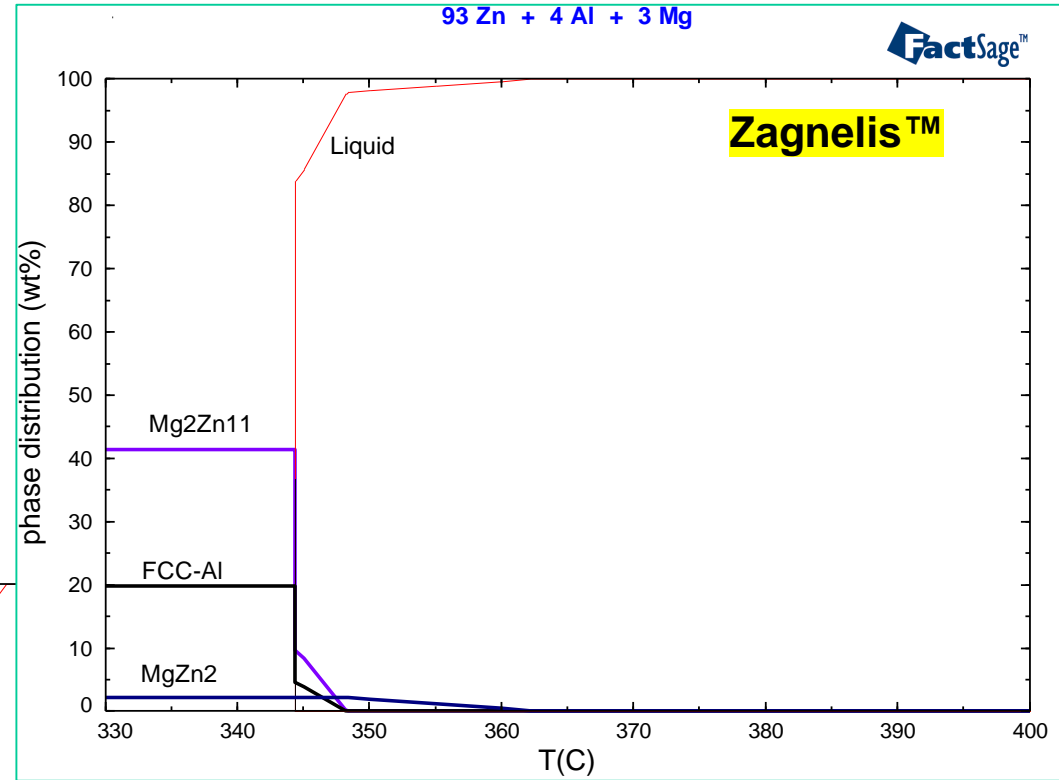
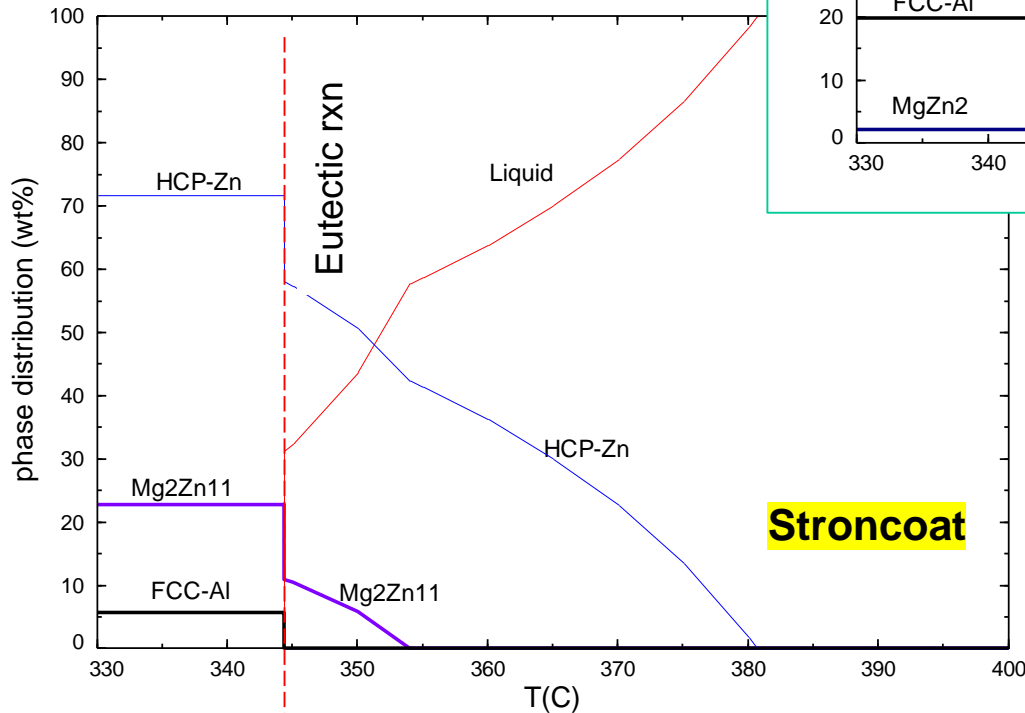
New coating system: ZincMagnesium coating Zn-Mg-Al

ZM Stroncoat® in Salzgitter



T. Koll: 18th Galvanising & Coil Coating Conf., 2013

97 Zn + 1.5 Al + 1.5 Mg



As cast microstructure
 → Scheil cooling calculation

LETTER

doi:10.1038/nature14144

Brittle intermetallic compound makes ultrastrong low-density steel with large ductility

Sang-Heon Kim¹, Hansoo Kim¹ & Nack J. Kim¹

“Here we show that an FeAl-type brittle but **hard intermetallic compound (B2)** can be effectively used as a strengthening second phase in high-aluminium low-density steel, while alleviating its harmful effect on ductility by controlling its morphology and dispersion.”

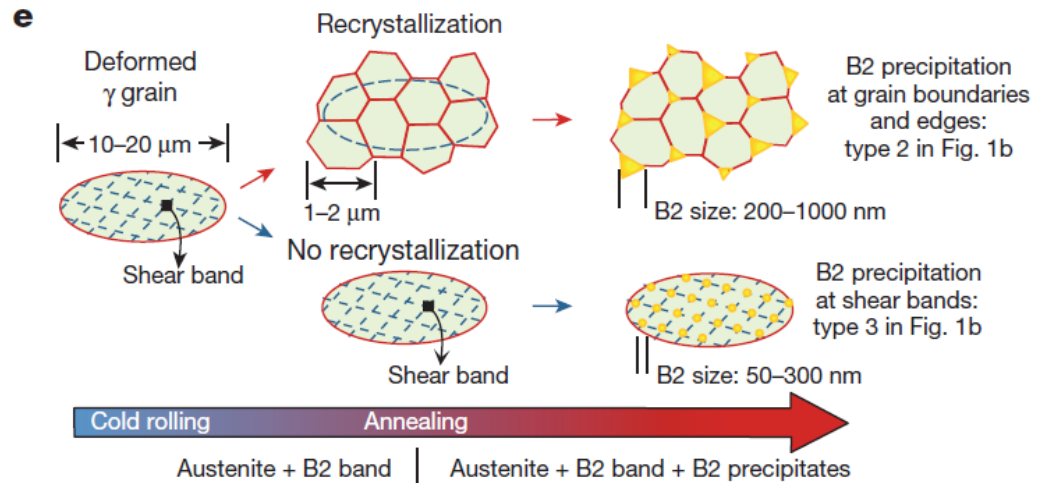
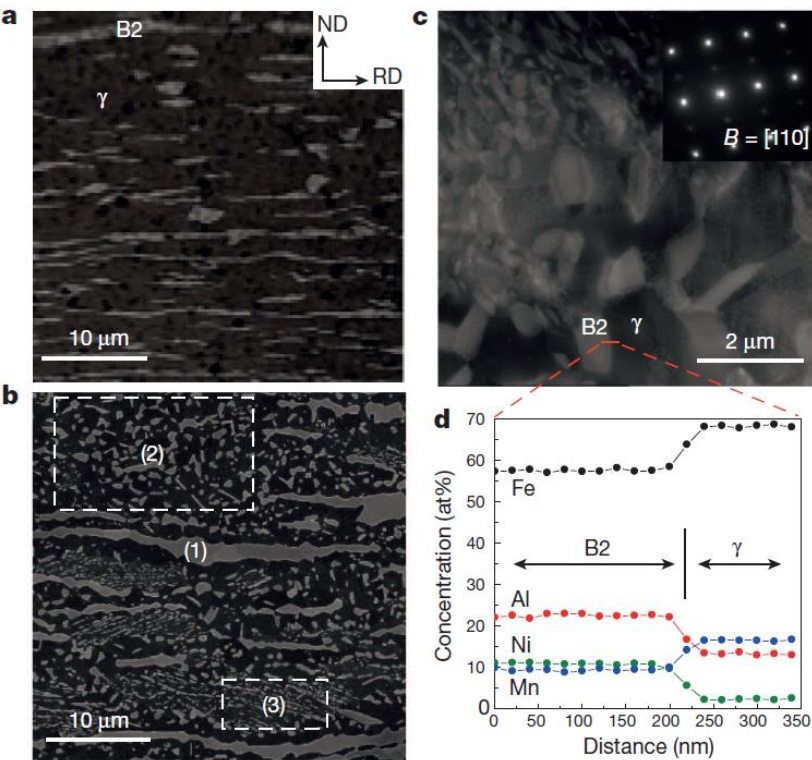
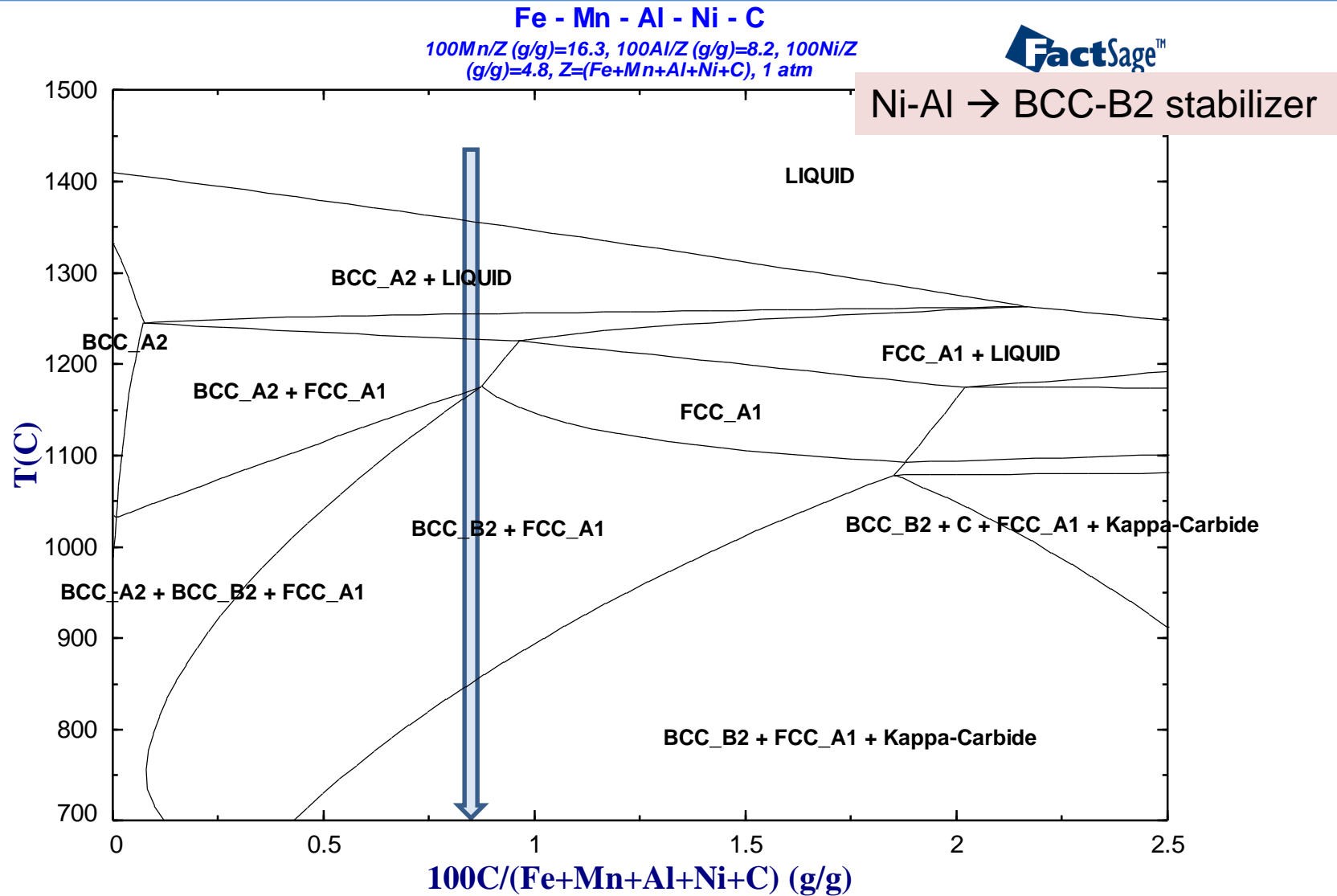
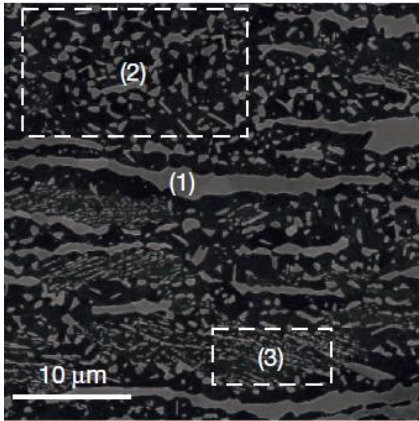


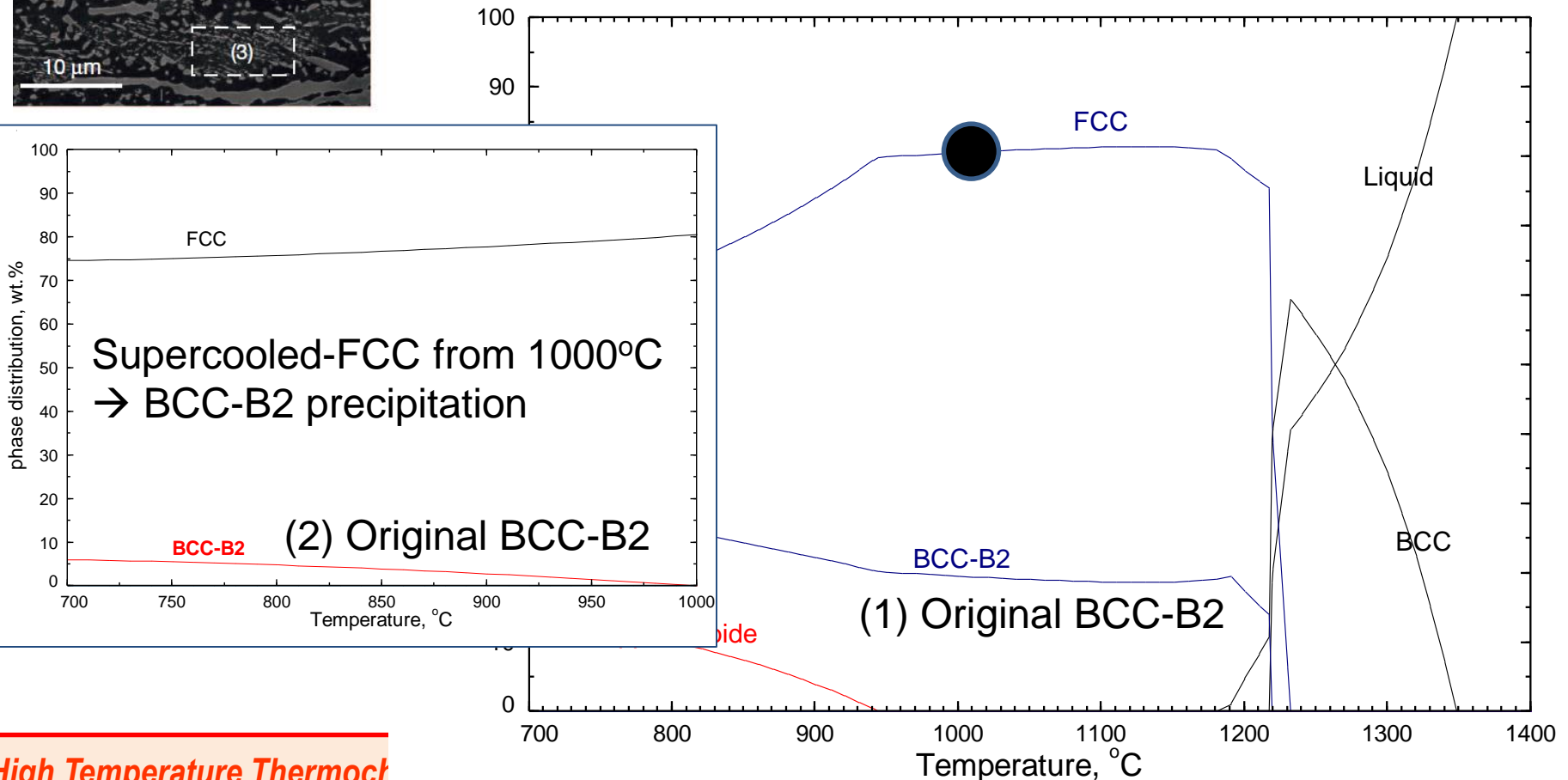
Figure 1 | Precipitation of B2 particles during annealing of cold rolled Fe-10%Al-15%Mn-0.8%C-5%Ni (weight per cent) high-specific-strength





- (1) Original BCC-B2 phase
- (2) BCC-B2 precipitates from FCC

68.14 Fe + 16 Mn + 5 Ni + 10 Al + 0.86C in wt.%



Process simulation

EERZ model: mass transfer + thermodynamics

- **EAF, BOF, RH degassor, LF, Powder injection, Tundish, mold flux**

Solidification

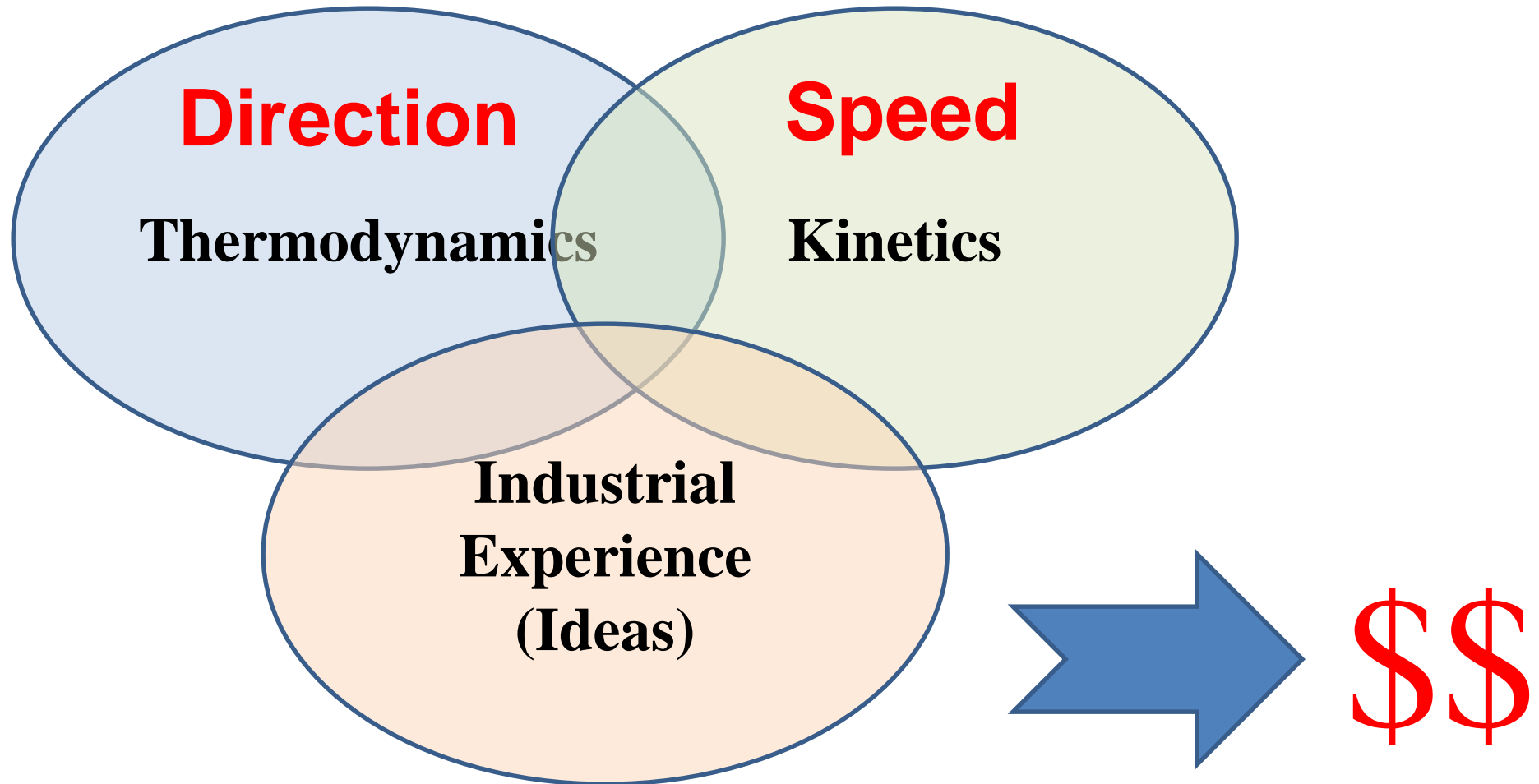
Solidification model: Back diffusion in solid steel

Solid state transformation

Solid state phase transition and precipitation: Diffusion and precipitation kinetics

- **Dictra, Prisma**

Summary



Acknowledgement

Steelmaking consortium project (2009~2020) – 2019 Annual meeting, July 9-11, Seoul, Korea



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