Thermo-Calc Software

A “high entropy” alloy database TCHEA2

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EUROMAT 2017

EUROPEAN CONGRESS AND EXHIBITION ON ADVANCED MATERIALS AND PROCESSES

17-22 SEPTEMBER 2017
THESSALONIKI, GREECE
CONFERENCE CULTURAL CENTER
“THESSALONIKI CONCERT HALL”

HELLENIC METALLURGICAL SOCIETY (HMS)
HELLENIC SOCIETY FOR THE SCIENCE & TECHNOLOGY OF CONDENSED MATTER (HSSTCM)

EURO MAT 2017

Thermo-Calc Software

1. Calphad and TCHEA2

2. Models and modeling

3. Prediction of Phase formation

4. Application in alloy design

Why Calphad?

- **Empirical rules** (Hume-Rothery rule and the like)
- **Theoretical first principles method**
- **Semi-empirical Calphad method**

Calphad+++

- **Considering** specific systems, specific structures, specific compositions, various intermetallics, solutions bases on intermetallics
- **Predicting**
  - which SSSs to form, and its composition and temperature ranges
  - if, when and where it orders
  - if, when and where it decomposes
  - which intermetallics to form and the phase amounts
  - the coexistence and competitions of several SSSs
  - the promising/coherent/semicoherent intermetalics
  - ...
  - **Aided by** theoretical first principles method

Calphad+++

Thermo-Calc Software

Crystallography

Ab-initio calculations
(electron configuration)

Phase equilibria

Assessments

Advanced phase model
Model parameters

Modeling

Gibbs energy descriptions

Thermodynamic databases

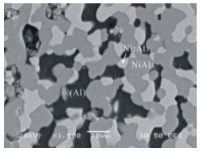
Database development

Calculation

Thermodynamic properties,
H, S, G, Cp, α, μ

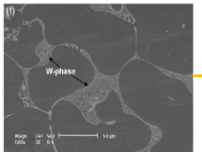
Phase equilibria
All sorts of phase diagrams

Solidification simulation



equilibrium

Phase formation, fraction, composition, transformation temperature, solidification sequences, eutectic, peritectic…



as-cast

Calphad: Thermodynamics & kinetics

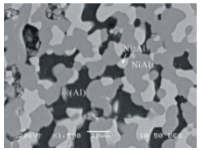
Thermo-Calc Software

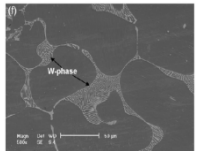
Thermodynamic Database

Thermo-Calc

Equilibrium calculation
Solidification simulation

Phase formation, fraction, composition, solidification sequences, eutectic…

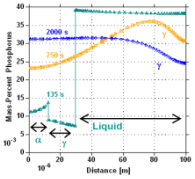


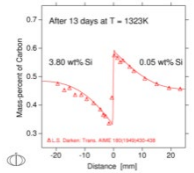


Mobility Database

DICTRA

Diffusion-controlled phase transformations



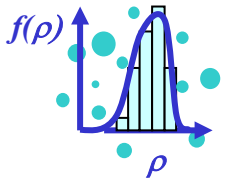


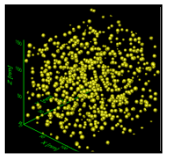
Property Database

TC-PRISMA

Nucleation, growth, coarsening

Multi-particle precipitation kinetics





Interfacial energy
Volume

Elastic constants
Viscosity
...

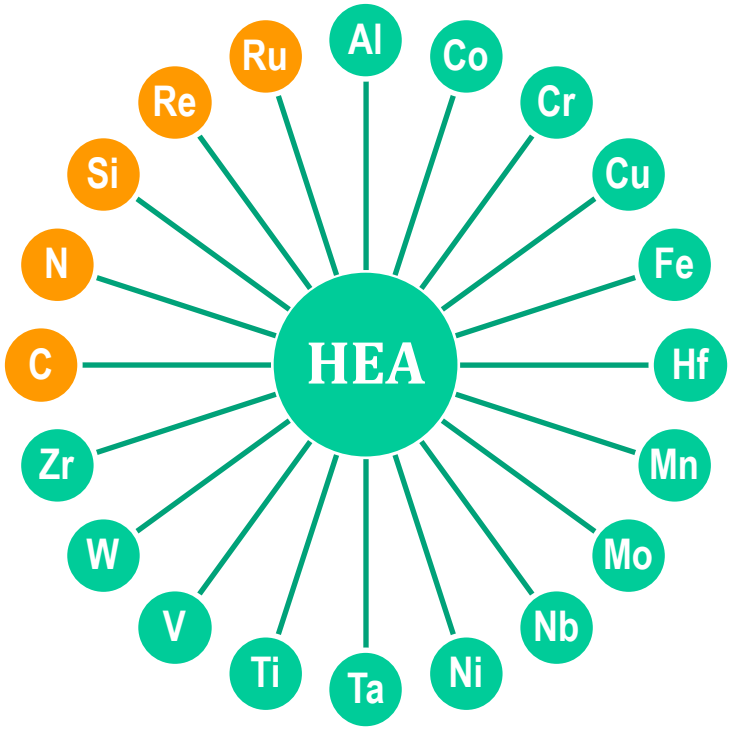
Ultimate goal: microstructure evolution and materials proerties

TCHEA: CCAs/MPEAs, inkl. HEAs

Thermo-Calc Software

TCHEA1
2016a

TCHEA2
2017a



TCHEA2

- 20 element framework
- 185 binaries assessed
- 443 ternaries assessed
- ALL solid phases in assessed systems

Raymundo Arroyave

(Texas A & M University)

- 216 HEAs
- 85 % on target

Highlight

- Compounds of the same structure are modelled as the same phase and the mutual solubility considered, e.g. Sigma
- Partitioning models for BCC and FCC (order/disorder)

Thermo-Calc Software

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Thermodynamic models

Thermo-Calc Software

- **Substitutional phases**
  - Liquid, Fcc_A1, Bcc_A2, Hcp_A3, & more

$$G^{\emptyset} = \sum_{i}^{n} x_i G_i^{\emptyset} + RT \cdot \sum_{i}^{n} x_i \ln(x_i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j L_{ij} + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^{n} x_i x_j x_k L_{ijk} \qquad \text{(Eq 1)}$$

- To reliablby extrapolate into
  - high-order systems
  - metalstable compositional ranges
- Bin. & Tern. interaction parameters are crucial

Thermodynamic models

Thermo-Calc Software

- **Sublattice models**
  - Intermetallic compounds & solutions based on them
  - Most with 2SL and 3SL models

$$
\begin{aligned}
G^{\emptyset} = & \sum_{i=1}^{m}\sum_{j=1}^{n} y_i^{(1)} y_j^{(2)} G^{\emptyset}_{i:j} + RT \\
& \cdot \left(2 \cdot \sum_{i}^{m} y_i^{(1)} \ln(y_i^{(1)}) + \sum_{i}^{n} y_i^{(2)} \ln\left(y_i^{(2)}\right) \right) \\
& + \sum_{i=1}^{m-1}\sum_{j=i+1}^{m}\sum_{k}^{n} y_i^{(1)} y_j^{(1)} y_k^{(2)} L_{ij:k} \qquad \text{(Eq 2)} \\
& + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\sum_{k}^{m} y_k^{(1)} y_i^{(2)} y_j^{(2)} L_{k:ij} \\
& + \sum_{i=1}^{m-1}\sum_{j=i+1}^{m}\sum_{k=1}^{n}\sum_{l=k+1}^{n-1} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} L_{ij:kl}
\end{aligned}
$$

Thermodynamic models

- **Partitioning models**
  - Fcc_L12 + Fcc_A1
  - Bcc_B2 + Bcc_A2

$$G_m = G_m^{dis}(x_i) + G_m^{ord}(y_i^s) - G_m^{ord}(x_i) \qquad \text{(Eq 3)}$$

Gibbs energy of disordered structure

Contribution from ordering parameters

Thermodynamic models

- **Non-disorder partitioning model**
  - Sigma, …

$(A, B, \ldots)10\ (A, B, \ldots)4\ (A, B, \ldots)16$

$2a + 8i_2$ $\quad 4f$ $\quad 8i_1 + 8j$

$(A, B, \ldots)$

hypothetical sigma solution

$$G_m = G_m^{dis}(x_i) + G_m^{ord}(y_i^s) \qquad \text{(Eq 4)}$$

Gibbs energy of the fictitious disordered structure

Contribution from ordering parameters

Molar volume

- **molar volume** and its temperature and composition dependence
- **experimental data** of densities, lattice parameters, and thermal expansivity and/or **theoretical values**
- **recalculation of** volume & volume fraction, density, expansivity, shrinkage during casting, lattice parameters & lattice misfit

$$V = V_0 \cdot exp\left(\int_{T_0}^{T} 3\alpha dT\right)$$

Redlich-Kister expansion

$$V_m = x_A V^A + x_B V^B + x_A x_B \cdot V^{A,B}$$

$$V_m = x_A V^A + x_B V^B$$

Vegard's law

$$V_m = \sum_{i=A}^{B}\sum_{j=A}^{B} y_i^{(1)} y_j^{(2)} V^{i:j} + \sum_{i=A}^{B} y_i^{(1)} y_A^{(2)} y_B^{(2)} \cdot V^{i:A,B} + \sum_{j=A}^{B} y_A^{(1)} y_B^{(1)} y_j^{(2)} \cdot V^{A,B:j}$$

Sublattice model

1. Calphad and TCHEA2

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Prediction of Phase formation

Thermo-Calc Software

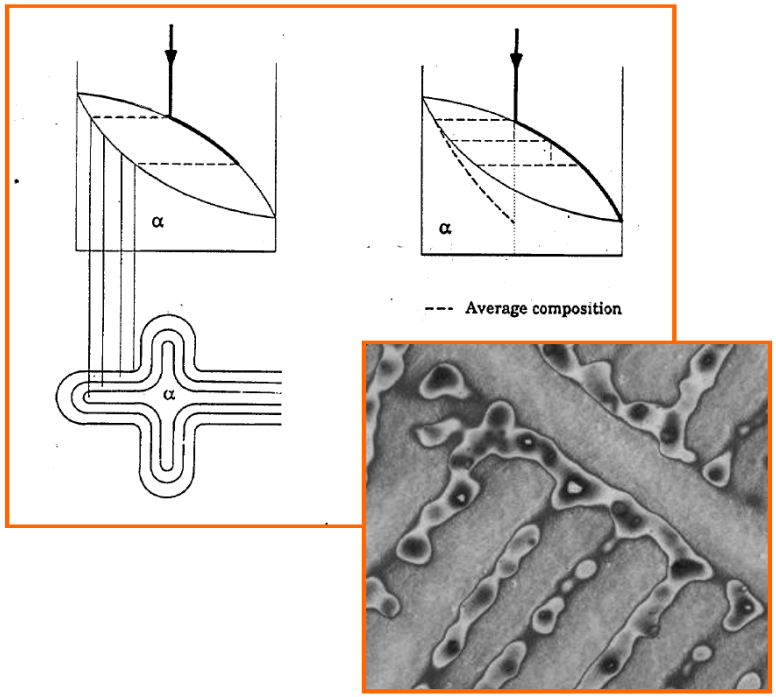
- **Heat treatment (homogenization, aging, etc.)**
- **Solidification**

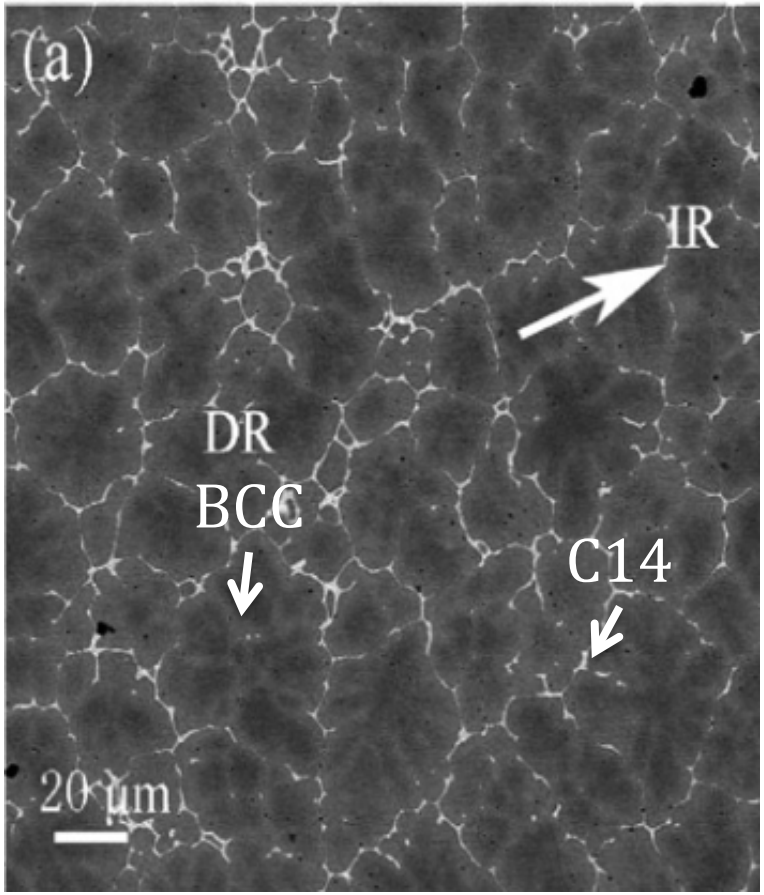
- Phases
- Phase formation sequence
- Phase fractions
- Phase compositions
- Phase reactions
- Phase transition temperatures
- Composition microsegregation

Solidification simulations

- **Using TCHEA and Thermo-Calc**
  - Equilibrium calculation
  - Scheil (non-equilibrium) calculation

Assumption for Scheil: the diffusion in liquid is extremely fast while that in solid phases is extremely slow



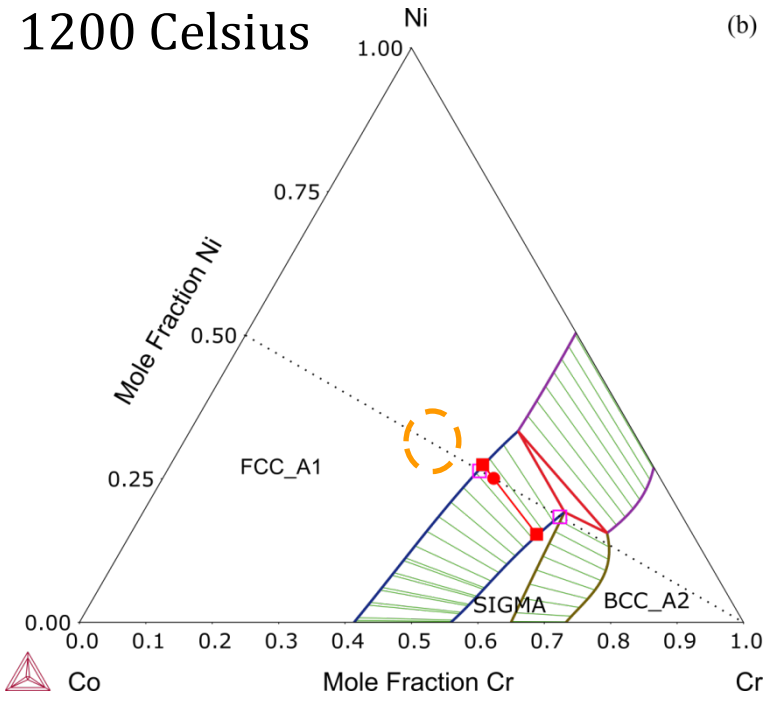


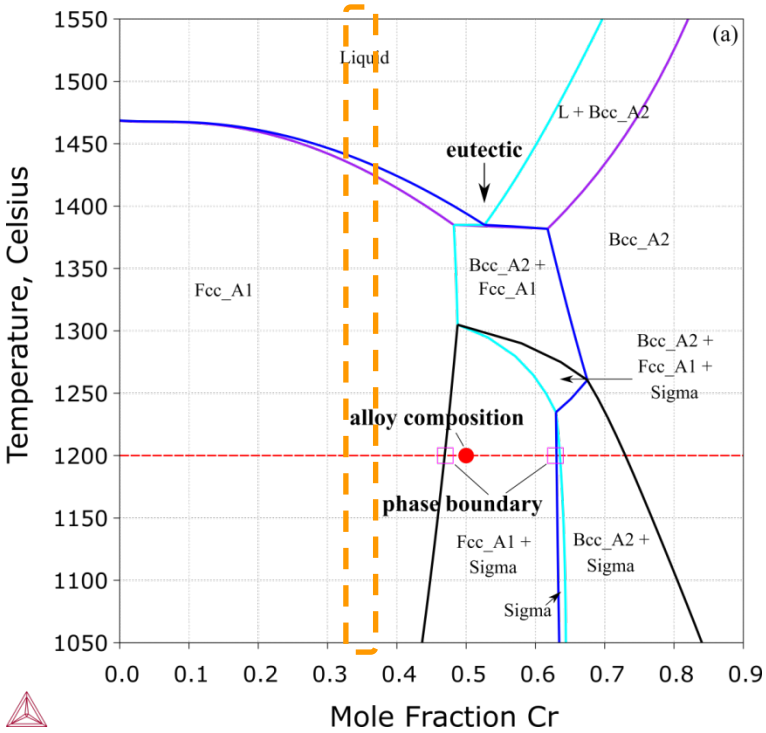
2012MaSG-MSEA480, Arc melt

AlCoCrFeNi-0.10Nb

Co-Cr-Ni

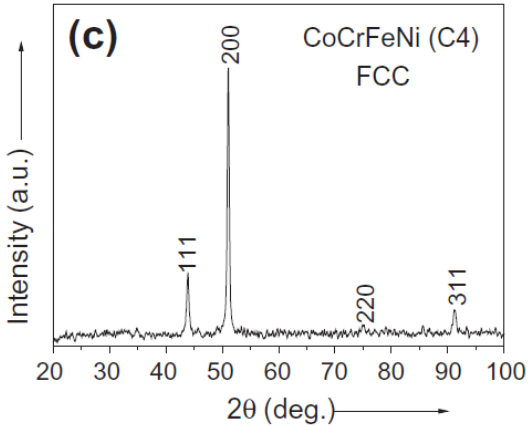
- **Fcc_A1 @ Co1Cr1Ni1**
  - Competition from Sigma
  - Competition from Bcc_A2

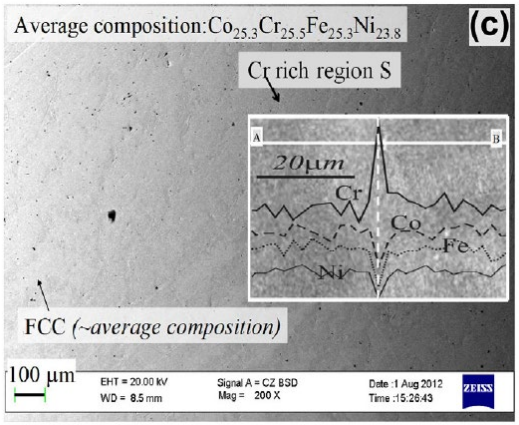


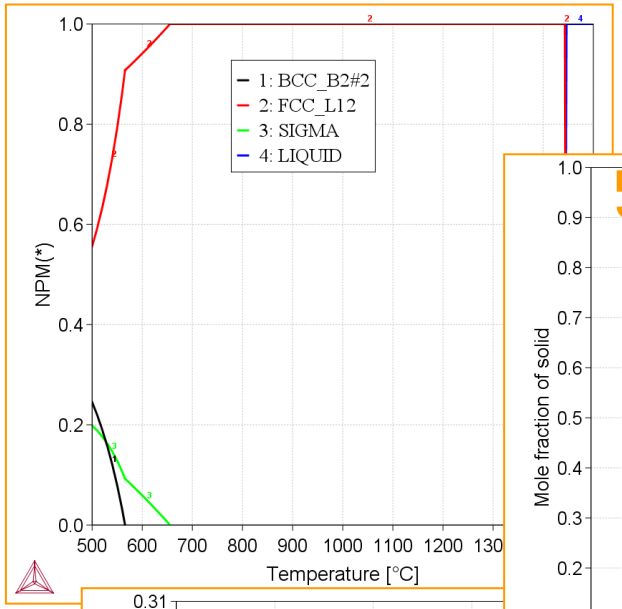


CoCrFeNi

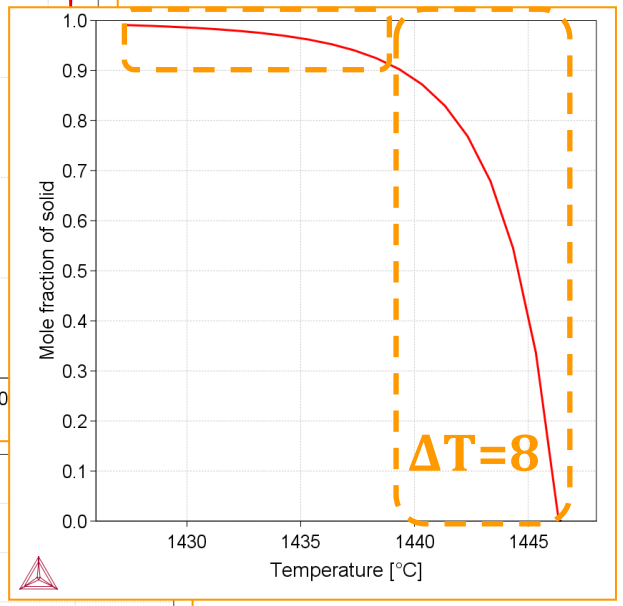
- **Fcc_A1 single @ Co1Cr1Ni1Fe1**
  - As-cast Hsu (2005)
  - 850 °C, 24 h Singh (2014)

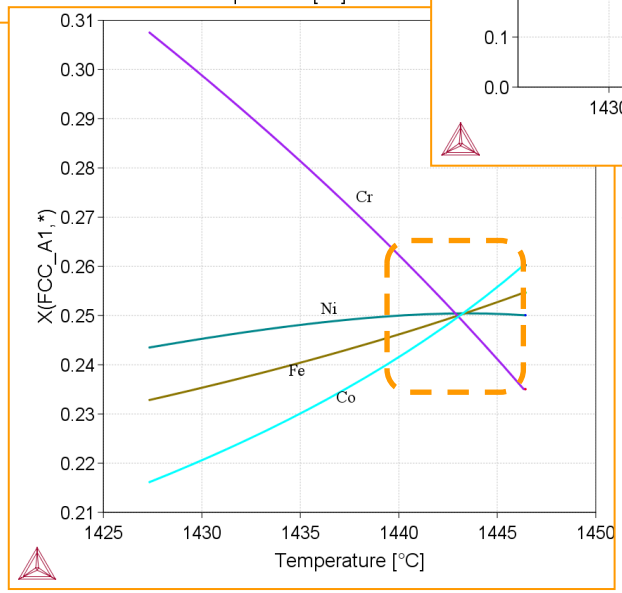




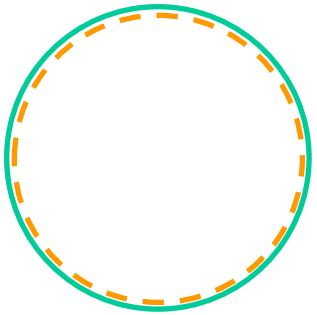


⇦equilibrium calculation





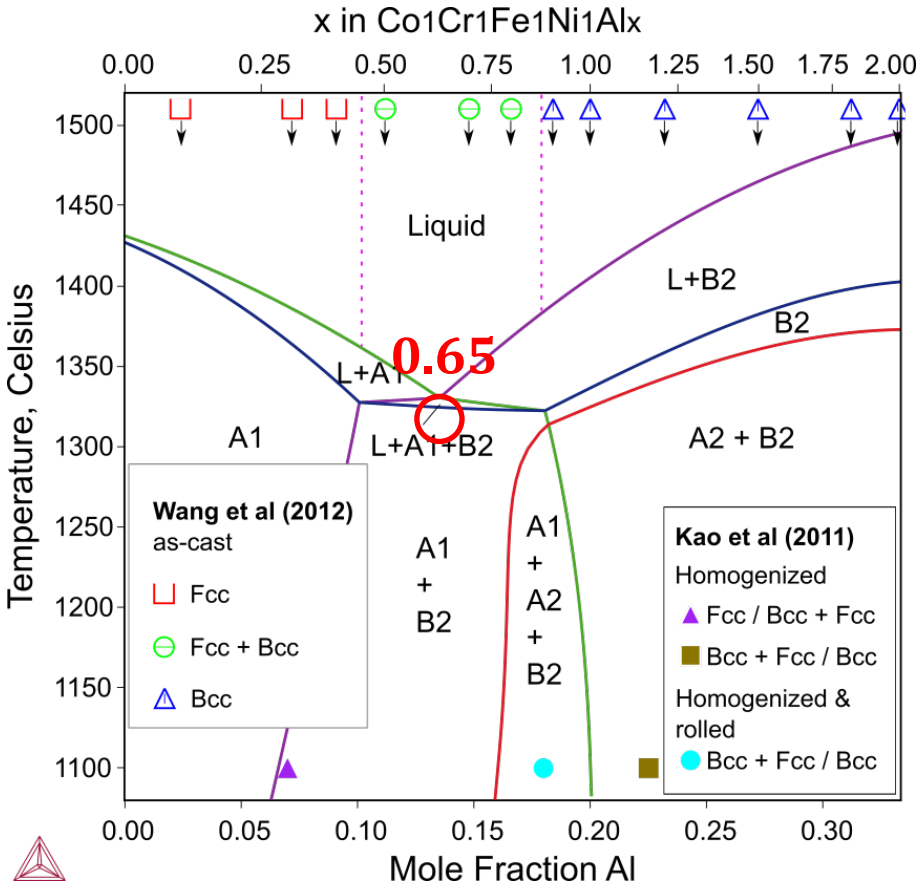
⇦ ⇧Scheil calculation



Hsu et al., Mater. Chem. Phys. 92 (2005) 112.
Singh, J. Alloys Compd. 587 (2014) 113.

CoCrFeNi-Al

- The phase formation depends on experimental conditions, especially cooling rate and heat treatment.



2009Chou-MSEB184

as-cast alloys, heated @ +10 C/min to 1100 C, stayed for 24 h.

- x = 0-0.375 FCC
- x = 0.5-1.0 FCC+BCC
- x = 1.25-2.0 BCC

2009Kao-JAlloyComp57

as-cast alloys, heated @ +20 C/min to 1100 C, stayed for 24 h.

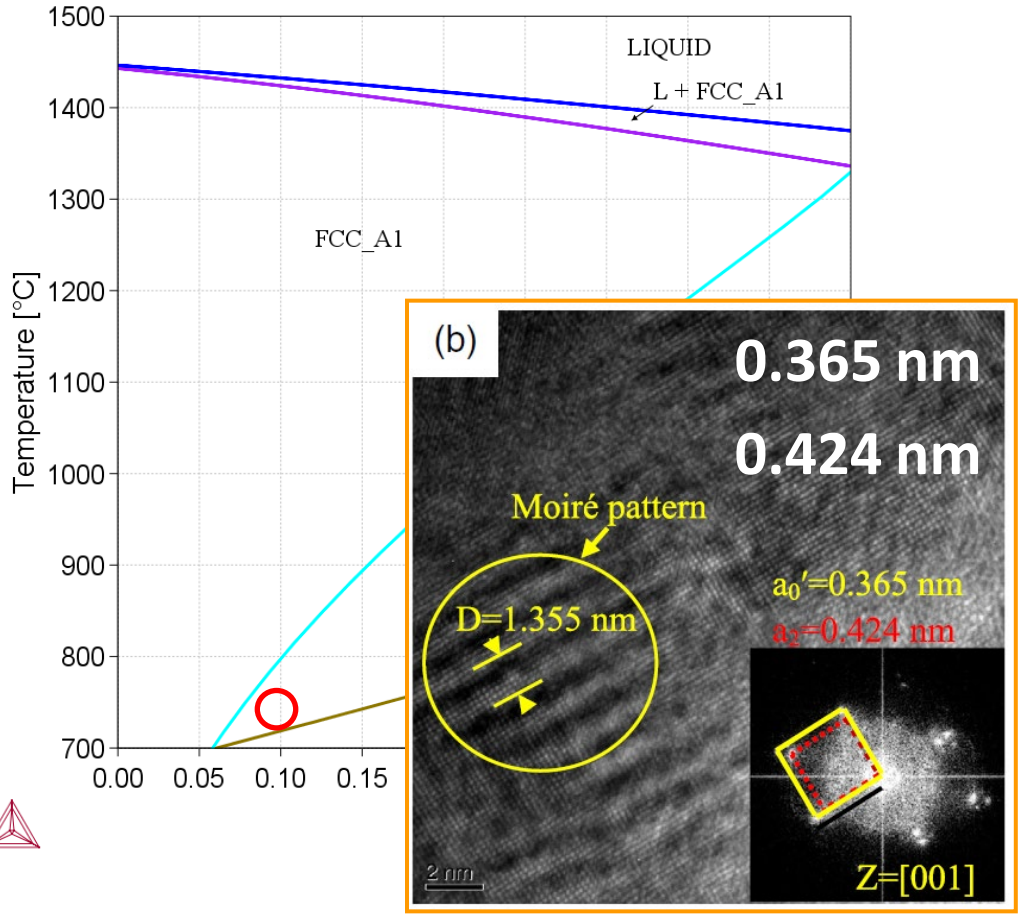
- x = 0-0.375 FCC
- x = 0.5-0.75 FCC+BCC
- x = 0.875-2.0 BCC

2008Zhang-AdvEngMater534

FCC in as-cast Al0.5CrFeCoNi

CoCrFeNi-0.1Al

- **He (2017)**
  - Single Fcc_A1 is metastable @ 750 °C
  - Decomposition after 800 h (2nd FCC)



- **Calculation: 2.65% Bcc_A2 instead of a 2nd A1**

NI 2.85033E-01

AL 2.26551E-01

CR 7.66706E-02

CO 2.27997E-01

FE 1.83749E-01

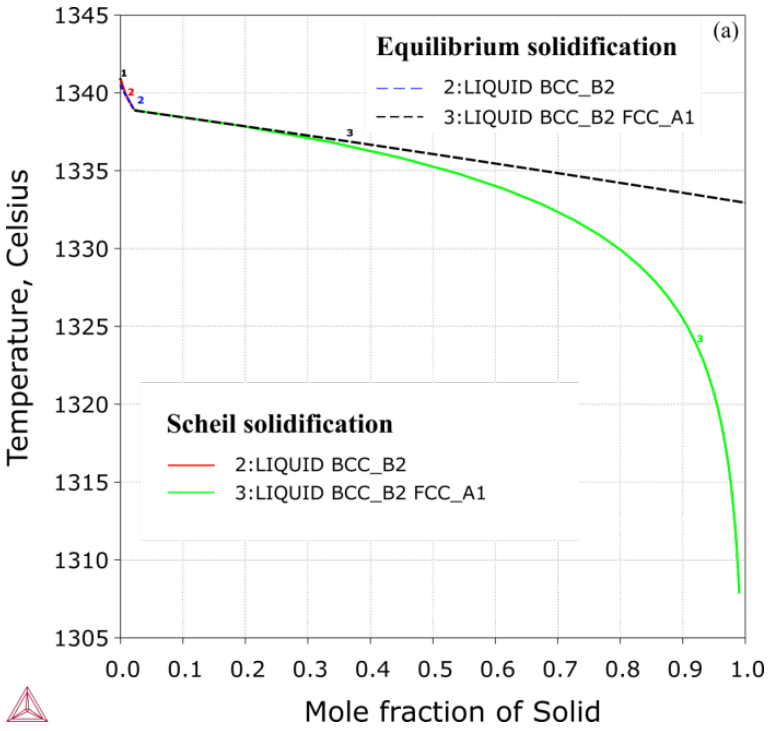
- **Not in miscibility gap**
- **0.3670 nm A1**
- **0.2924 nm A2**

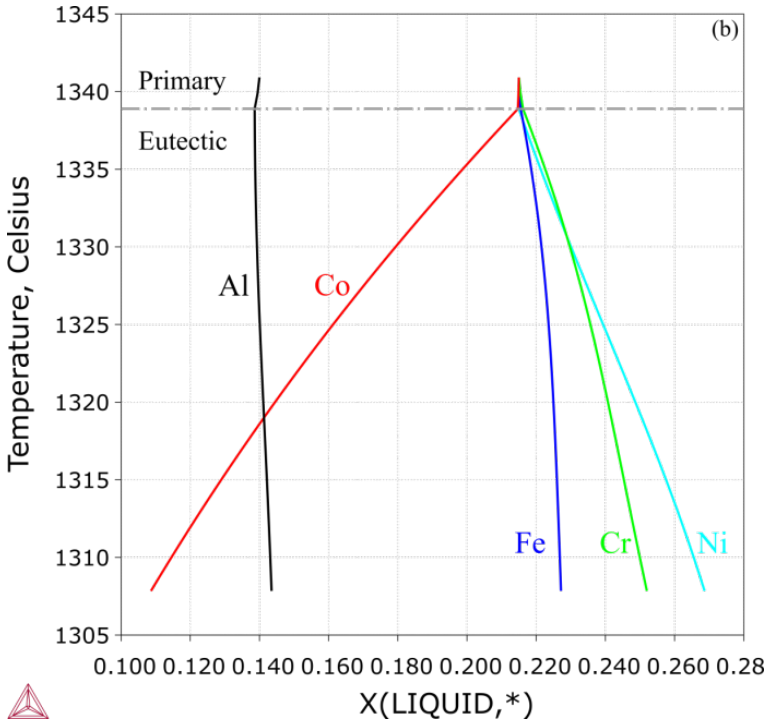
$$\sqrt{2} \cdot a = 0.413 \text{ nm}$$

- He et al., Scr. Mater. 126 (2017) 15-19

CoCrFeNi-0.65Al (13.98 at.% Al)

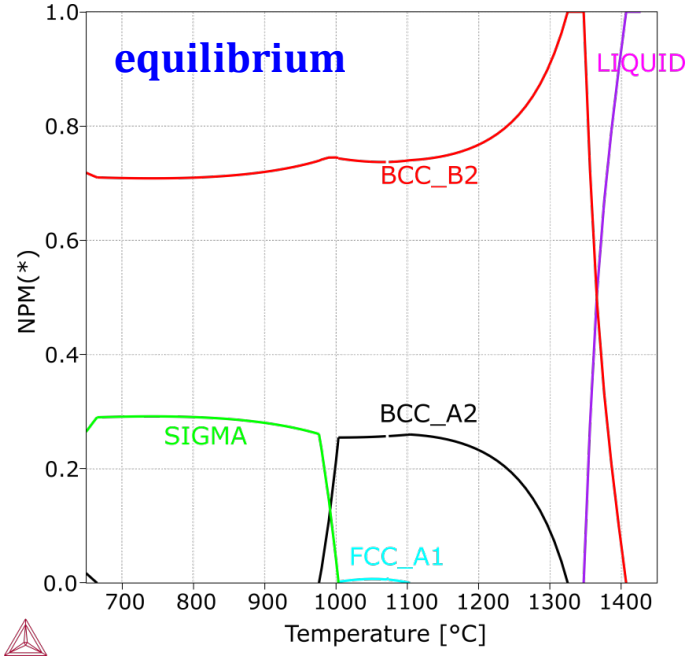
- 2-phase eutectic reaction is not invariant
- Segregation can be significant

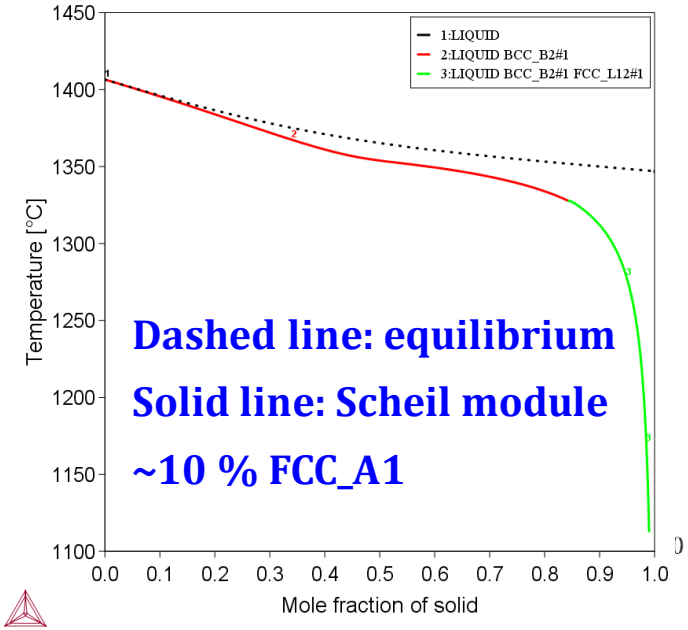




Solidification simulation of the eutectic alloy $Co_1Cr_1Fe_1Ni_1Al_{0.65}$: (a) phase formation sequence and solid phase fractions from equilibrium (in dashed line) and Scheil simulation (solid line); and (b) liquid phase composition from Scheil simulation

CoCrFeNi-1Al





2012Wang-Intermetallics44

- As-cast: BCC_B2

2009Chou-MSEB184

+10 C/min to 1100 C, held for 24 h

- BCC + FCC

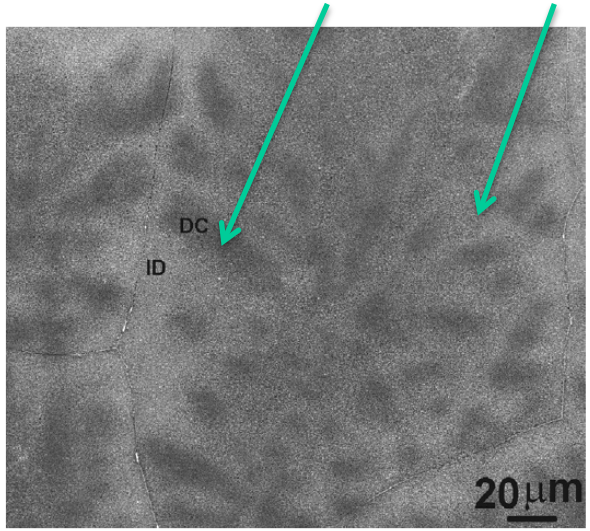
2009Kao-JAlloyComp57

+20 C/min to 1100 C, held for 24 h

- BCC

2016Munitz-JAlloysCompd683

- As-cast: BCC_B2 + BCC_A2

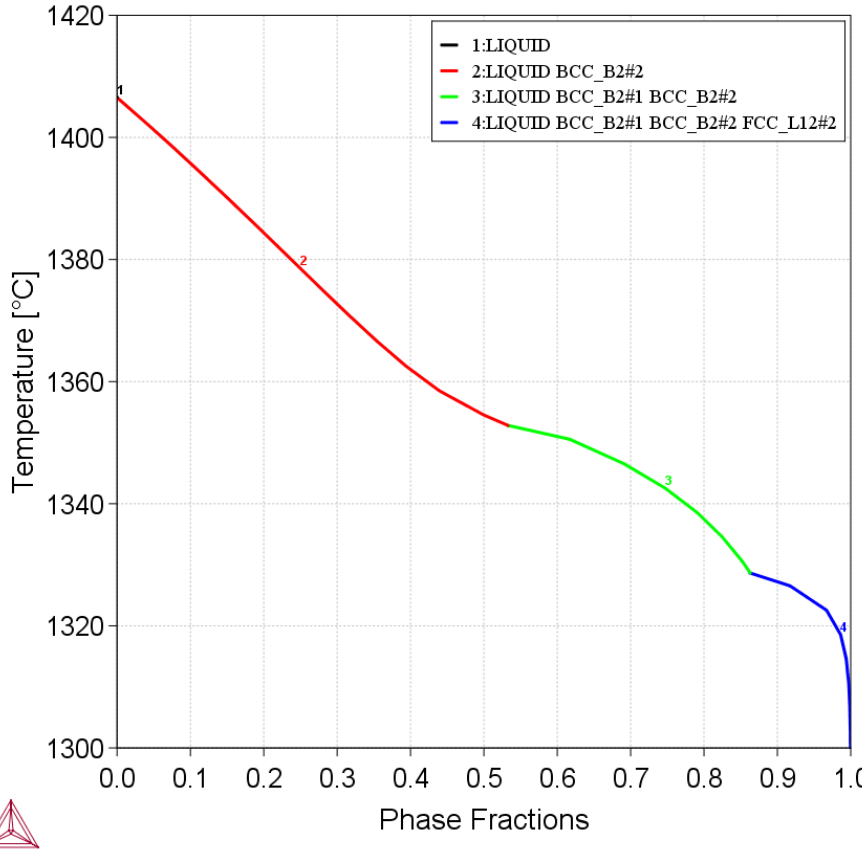


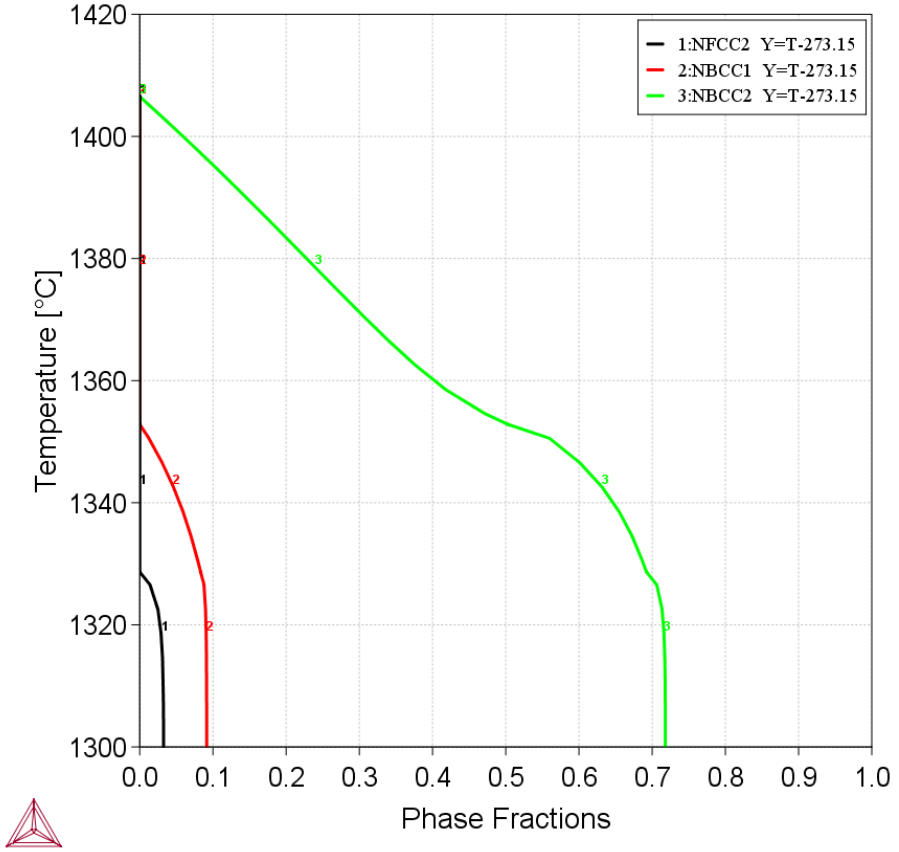
Simplifications

- Back diffusion in Bcc_B2
- Composition segregation in liquid

CoCrFeNi-1Al

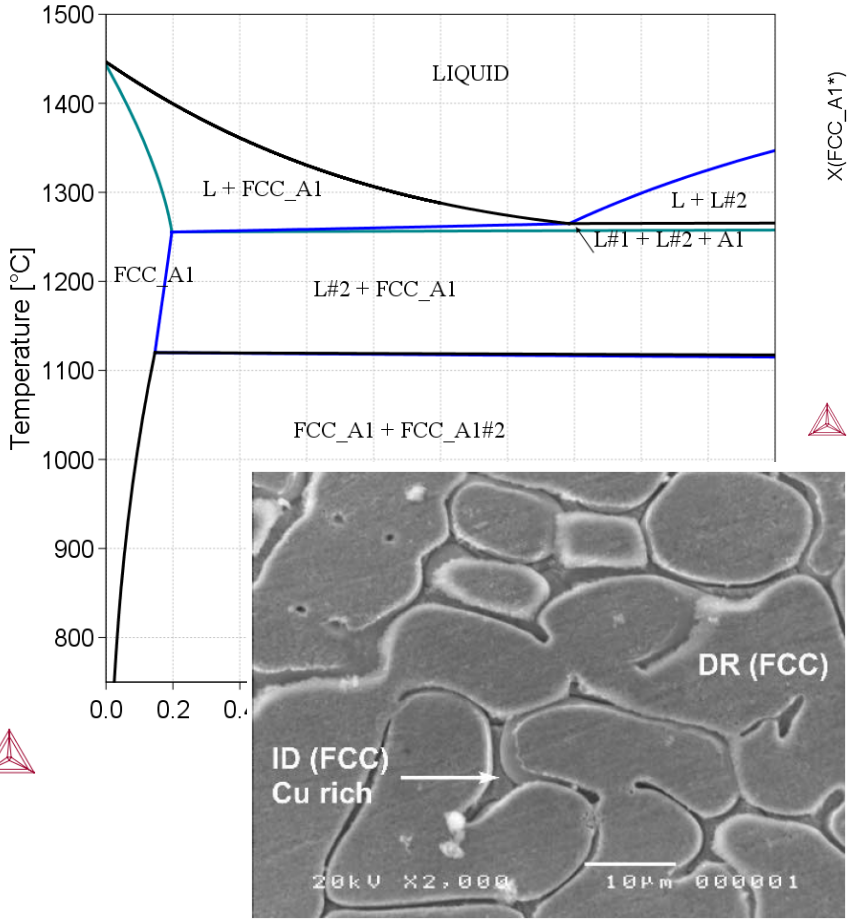
- **Step-by-step Scheil simulation**
  - Step size: 4 K

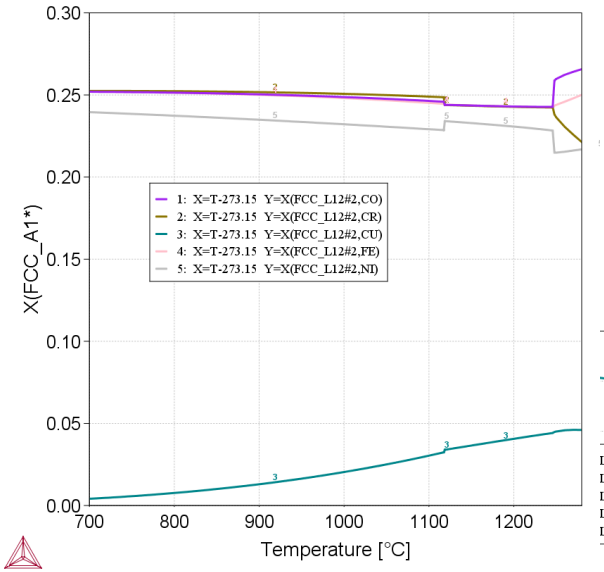


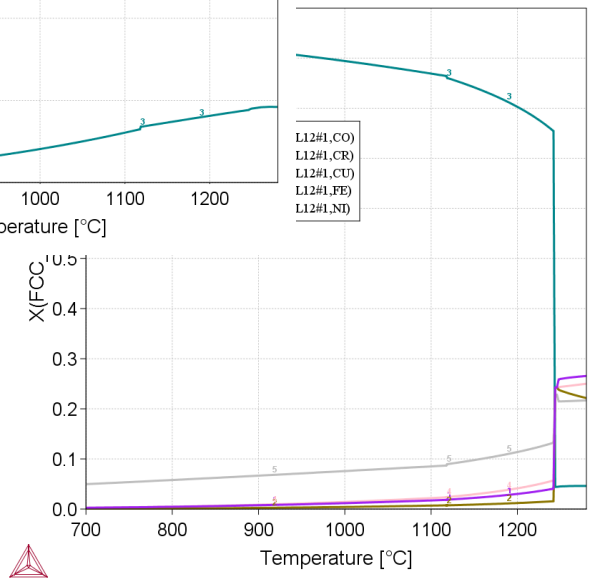


CoCrFeNi-Cu

- **2005Tong-MetMaterTransA881**
- **2 Fcc_A1 phases @ Co1Cr1Cu1Fe1Ni1**
  - as-cast, 1 to 10 K/s







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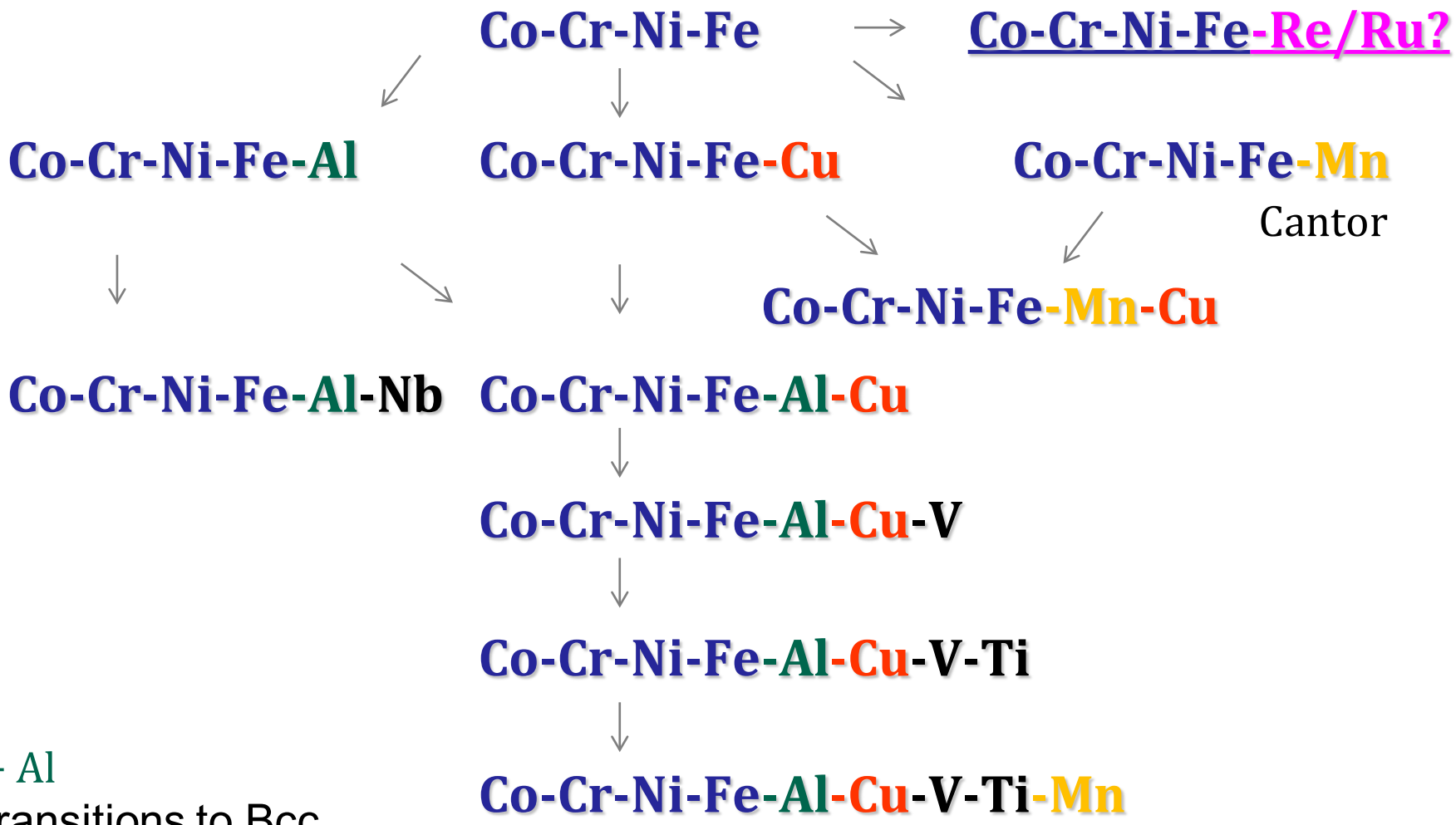
Alloy composition map

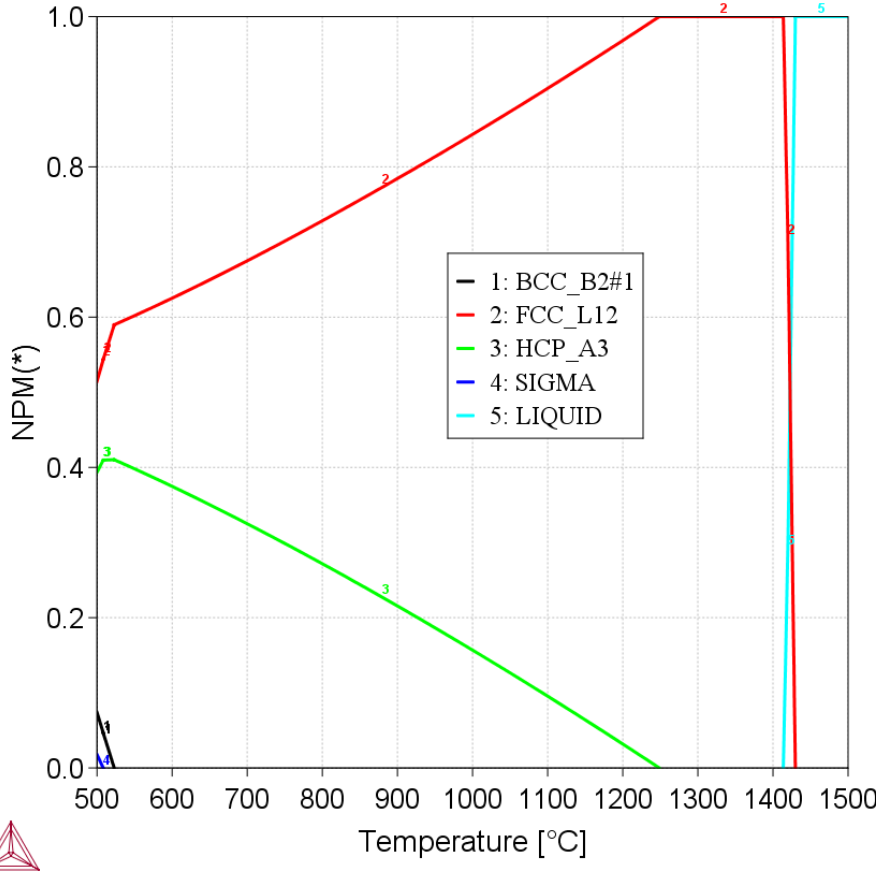


+ Al
transitions to Bcc
+ Cu
causes decomposition

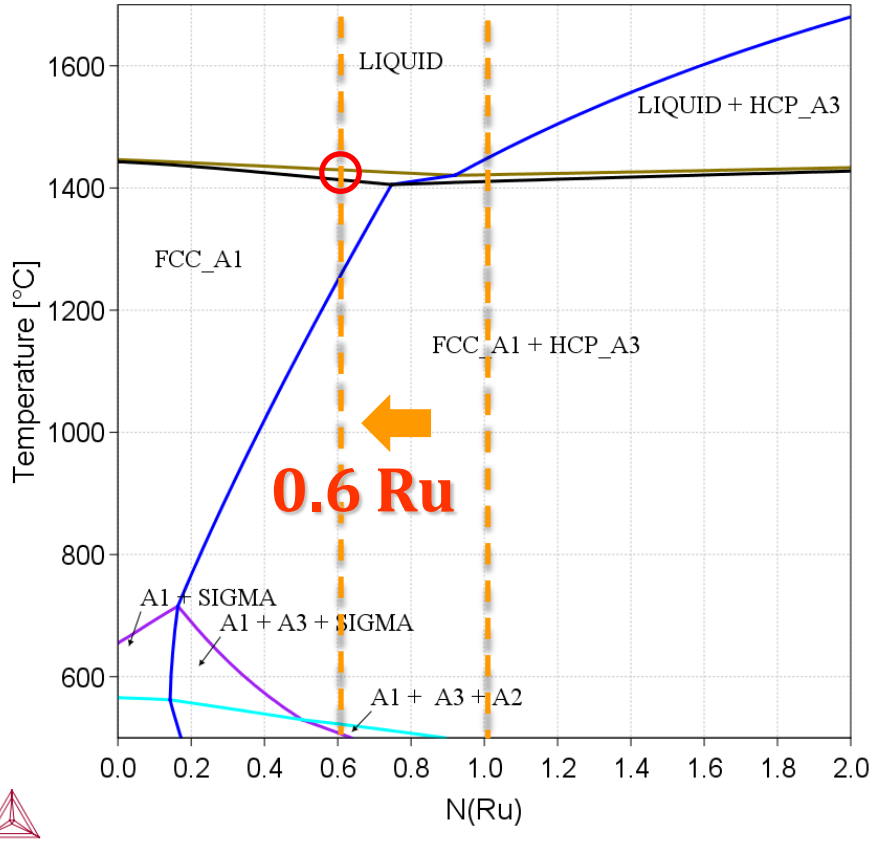
CoCrFeNi + Re vs Ru

- Fcc_A1 to Hcp_A3

2017.09.15.13.39.52
TCHEA2: CO, CR, FE, NI, RU
N(CO)=1., N(CR)=1., N(FE)=1., N(NI)=1., N(RU)=0.6, P=1E5

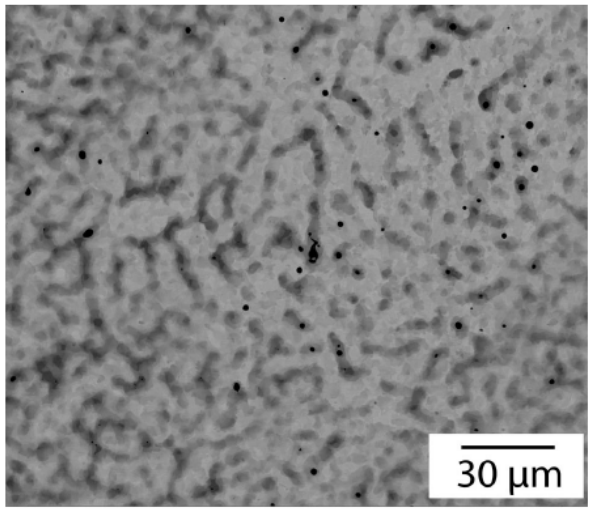


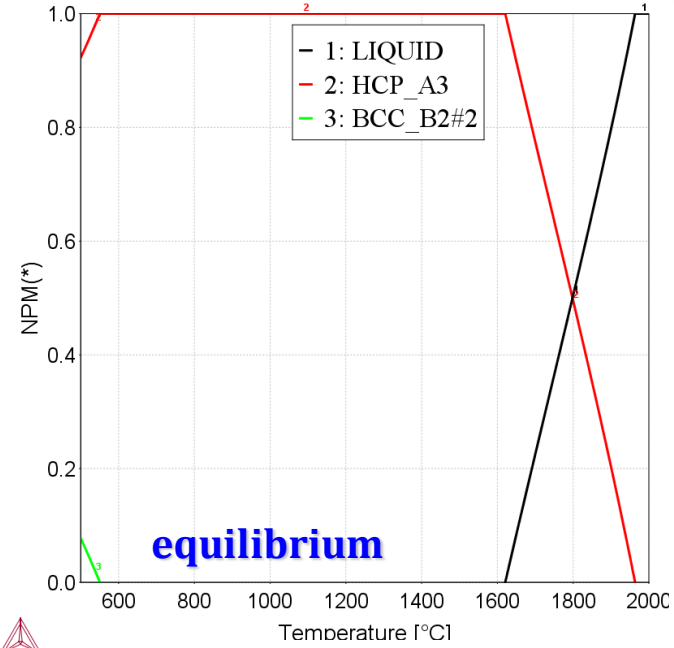
2017.09.15.13.21.10
TCHEA2: CO, CR, FE, NI, RU
N(CO)=1, N(CR)=1, N(FE)=1, N(NI)=1, P=1E5

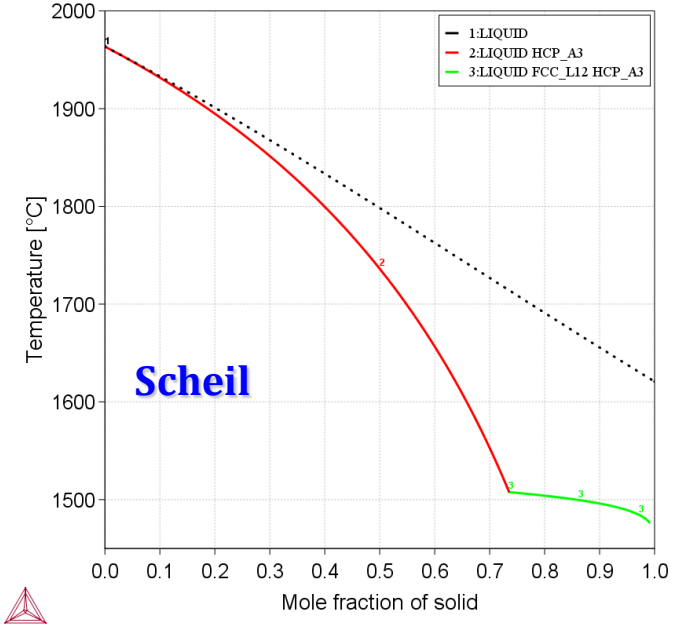


CoFeReRu

- 2016Gao-MMTA47
  As-cast

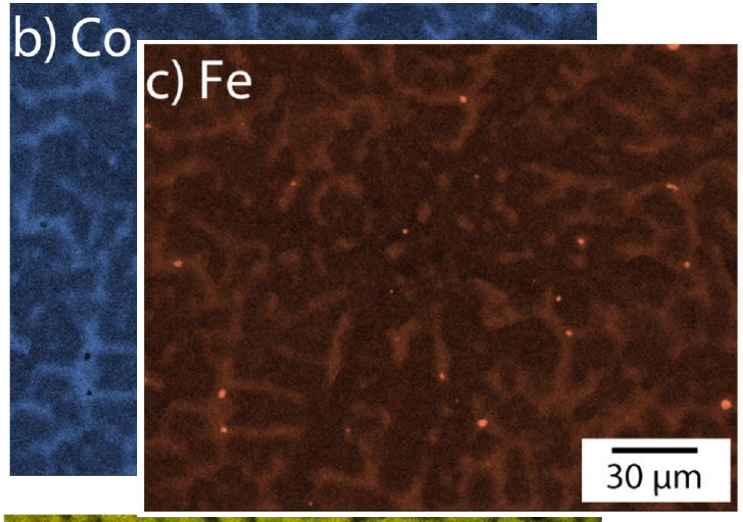


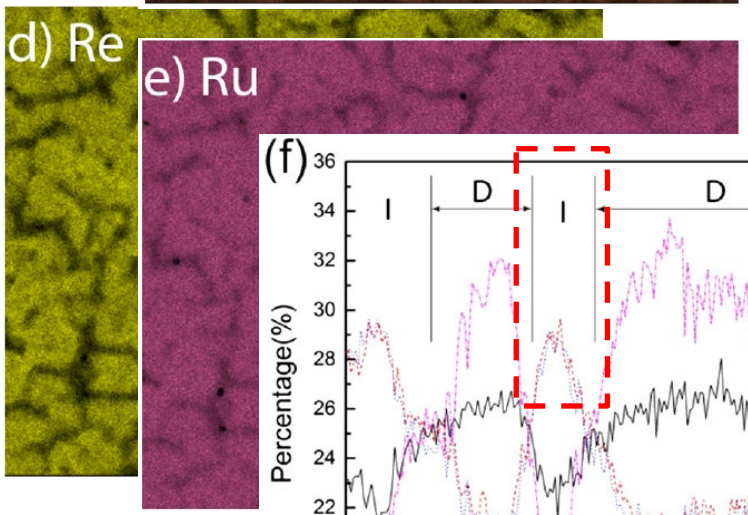


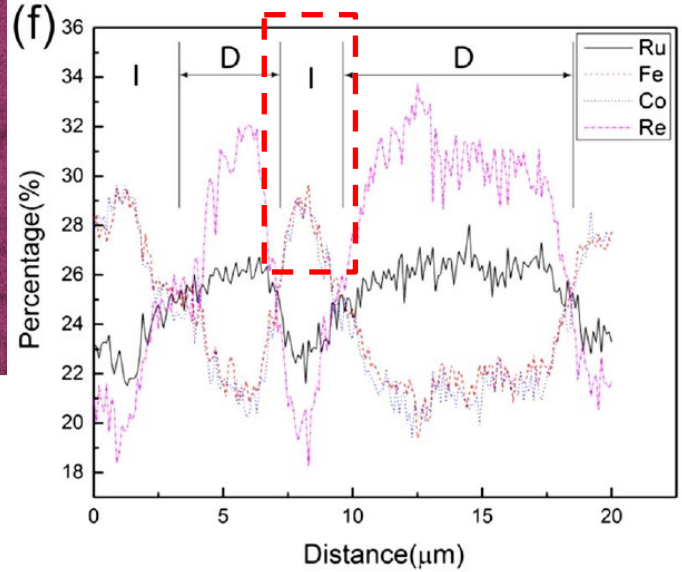


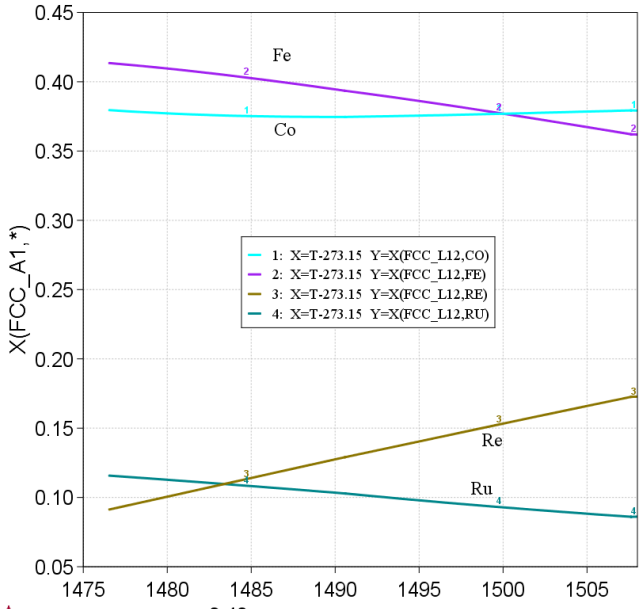
Co-Fe-Re-Ru

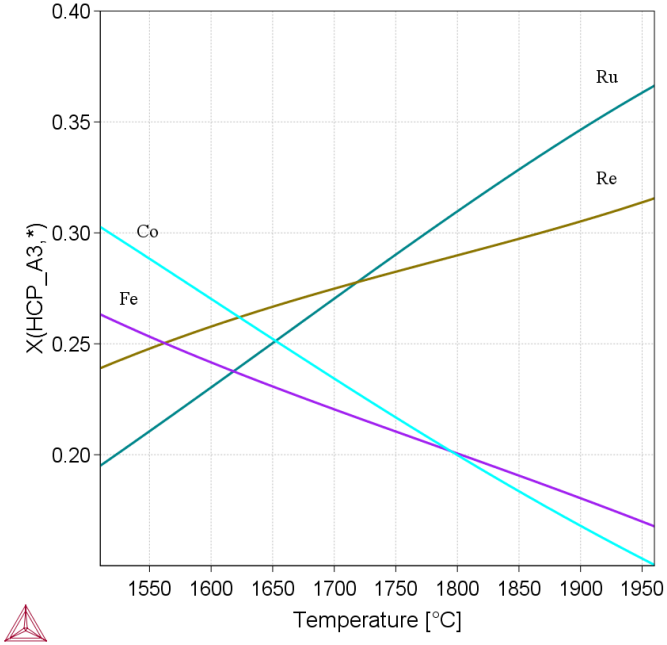
- 2016Gao-MMTA47



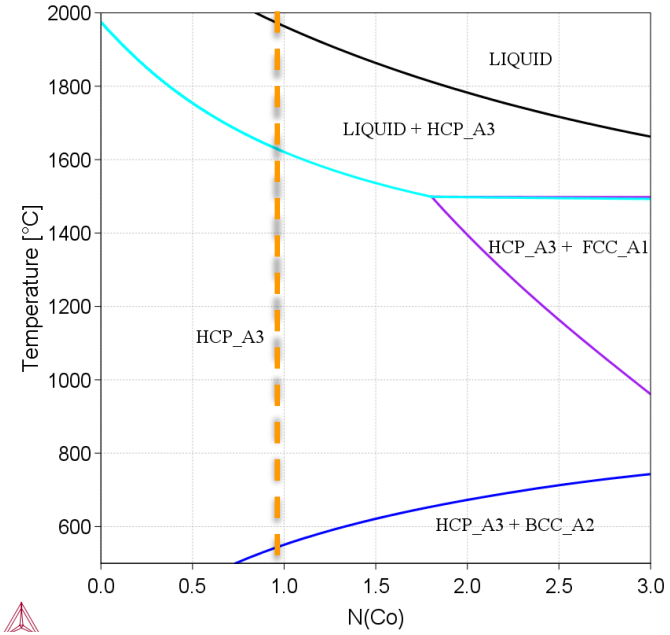


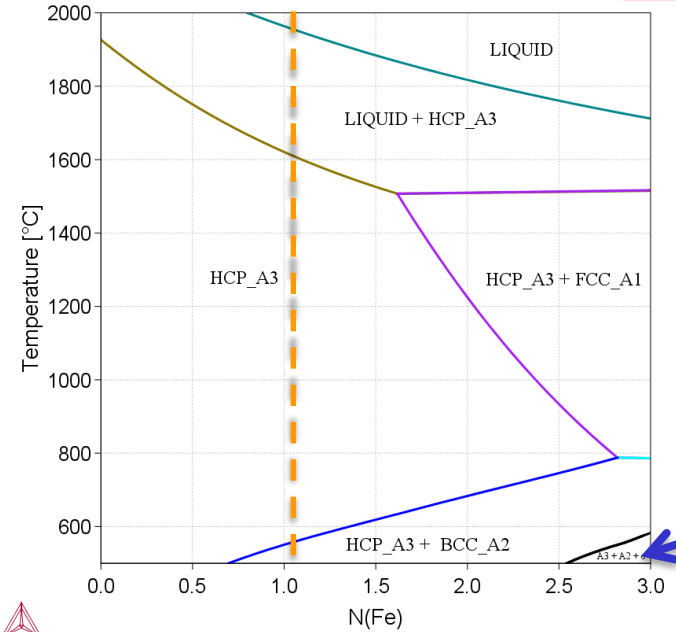




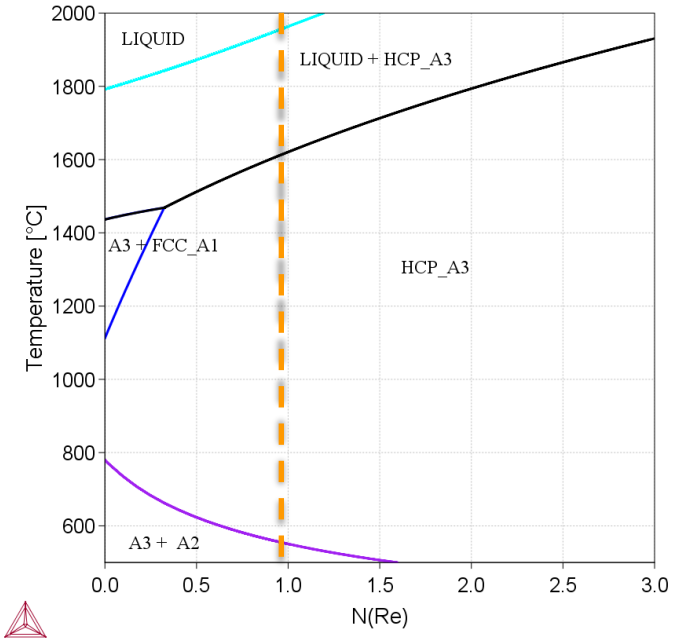


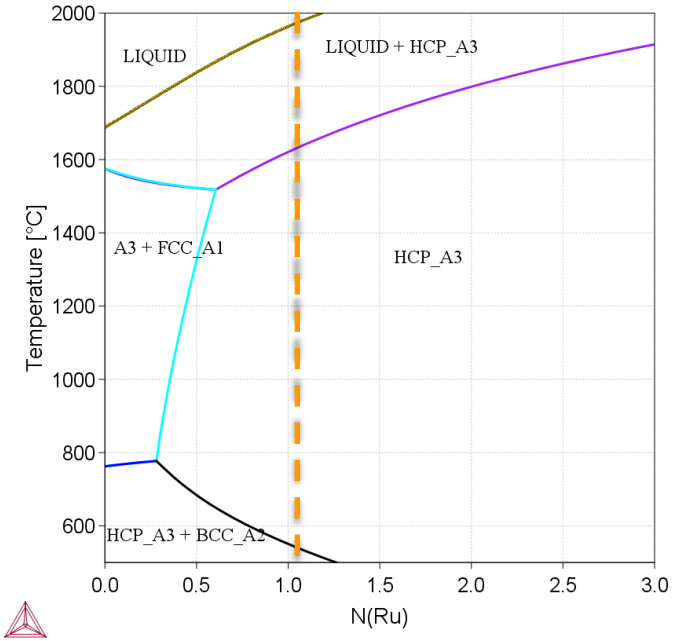
Co-Fe-Re-Ru





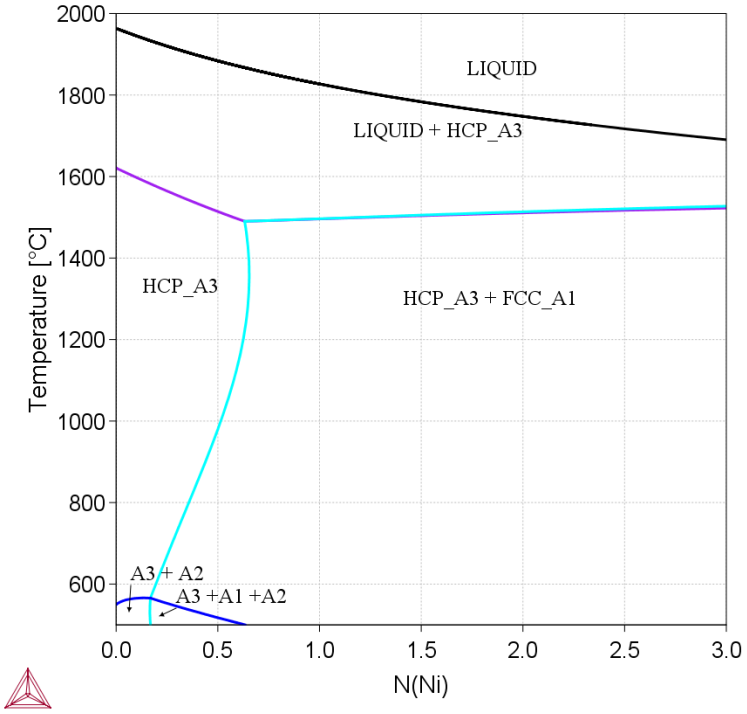
sigma

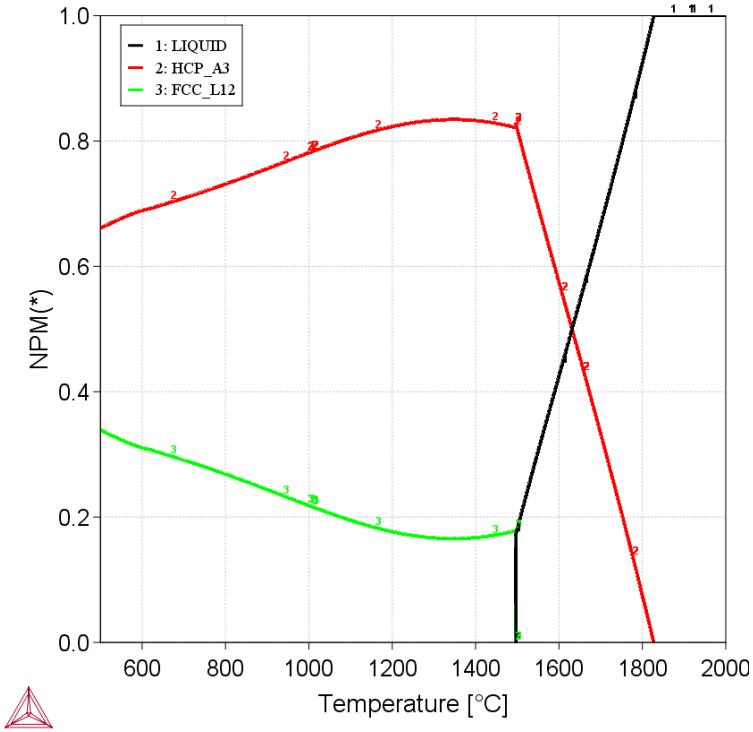




Co-Fe-Re-Ru-X

- **No experimental investigations**
  - Ni



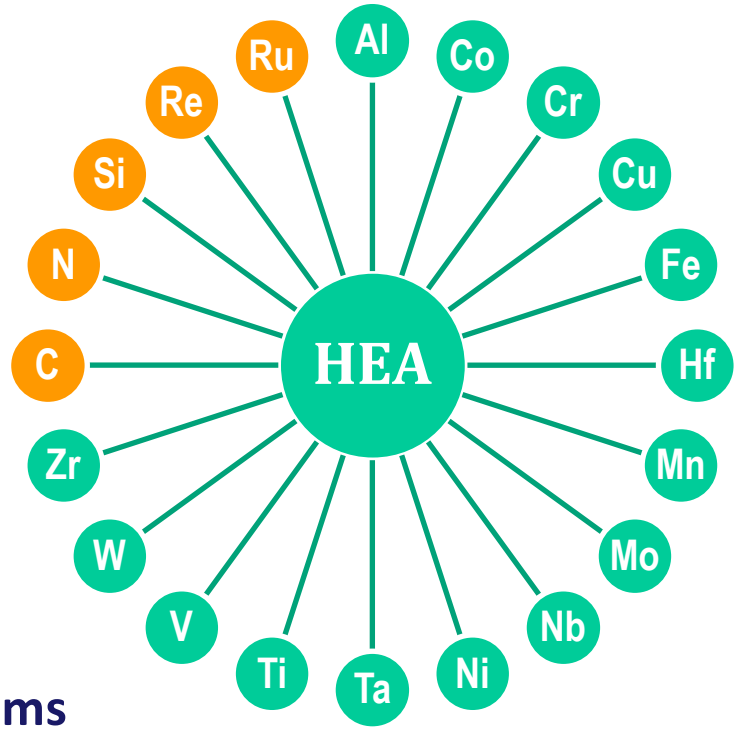


Summary

Thermo-Calc Software

TCHEA1
2016a

TCHEA2
2017a



- 185 binaries assessed
- 443 ternaries assessed
- ALL solid phases in assessed systems