Calphad Database development for HEMs:

Challenges, progresses and prospects

Hai-Lin Chen, Huahai Mao, Qing Chen

November 8th, 2016

Thermo-Calc Software AB, Stockholm, Sweden

www.thermocalc.com

Outlines

1. Brief introduction to TCSAB & myself
2. Brief review & comments on HEAs
3. Database development & its challenges & strategies
4. Calculations (“free courses” & examples)
5. Future developments & next release

Introduction

Thermo-Calc Software

Thermo-Calc Software AB

- 1971: Sublattice model (Hillert & Staffansson @ KTH)
- 1977: Development of Thermo-Calc starts
- 1981: First version of Thermo-Calc
- 1984: First sale of Thermo-Calc Classic
- 1984: First sale of the TCFE database
- 1994: First sale of DICTRA
- 1997: The company Thermo-Calc Software was formed
- 2004: The subsidiary Thermo-Calc Software Inc. was formed
- 2011: First sale of TC-PRISMA
- 2013: Release of the new generation of Thermo-Calc
- 2015: Release of the Property Model Calculator

Thermo-Calc Software AB
Norra Stationsgatan 93
SE-113 64 Stockholm
SWEDEN

Thermo-Calc Software Inc.
4160 Washington Road
McMurray
PA 15317
USA

Hai-Lin Chen

Project Leader, Light Metal Alloy databases

hailin@thermocalc.se

- TCAL (0 to 4)
- TCMG (1 to 4)
- TCTI (0 to 1)
- involved in TCHEA1

High entropy alloys

- 5+ principal elements
- each PE 5-35 %
- + minor alloying elements
- Forming single solid solution / solutions / solution(s) + intermetallics

Forming SSSs instead of intermetallics

- Hume Rothery Rule (atomic size difference, valence electron concentration, electronegativity)
- enthalpy of mixing **regular, binary**
- entropy of mixing **ideal**

High entropy effect	Severe lattice-distortion effect
Sluggish diffusion effect	Cocktail effect

Typical criteria

$$Delta = \sqrt{\sum_{i=1}^{N} c_i (1 - r_i/\bar{r})^2}$$

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j$$

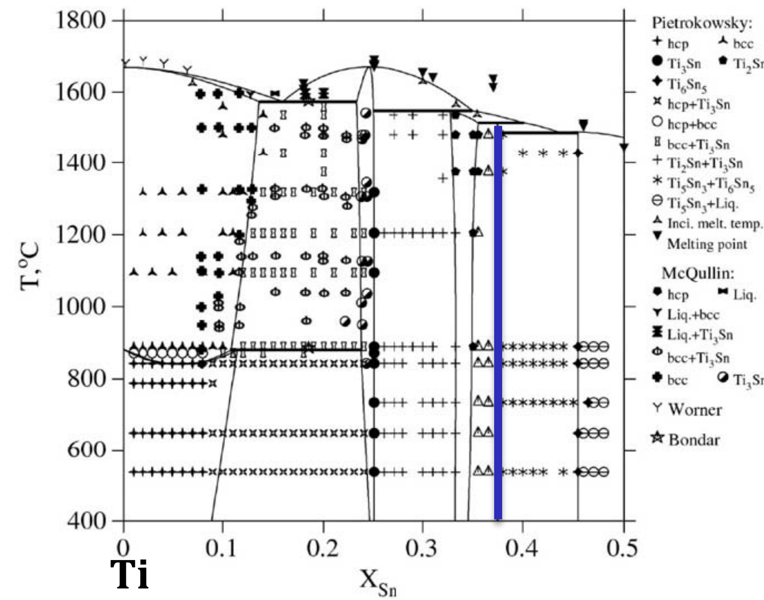
$$\Delta S_{mix} = -R \sum_{i=1}^{N} c_i Ln\, c_i$$

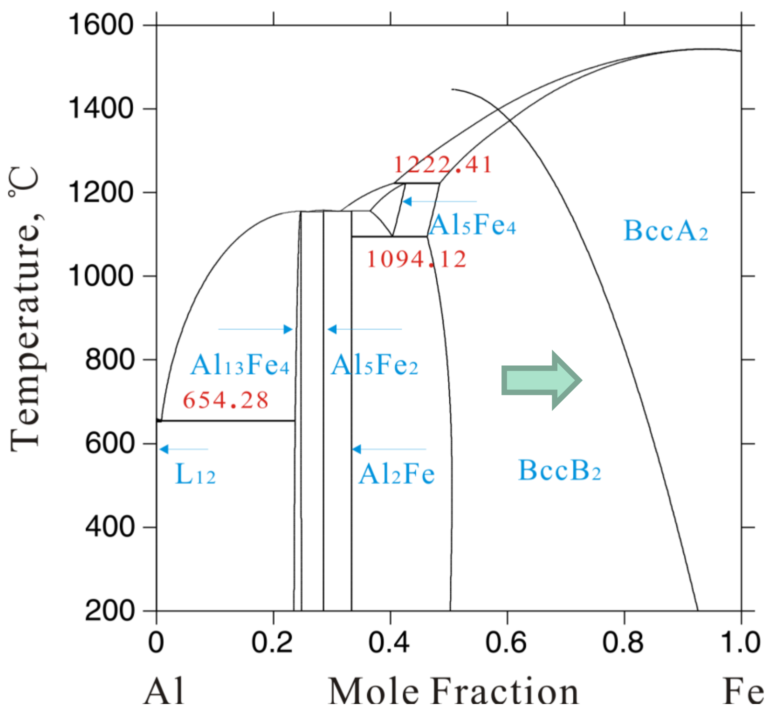
- $\delta \leq +8.5$
- $-22 \leq \Delta H \leq +7$
- $11 \leq \Delta S \leq +19.5$

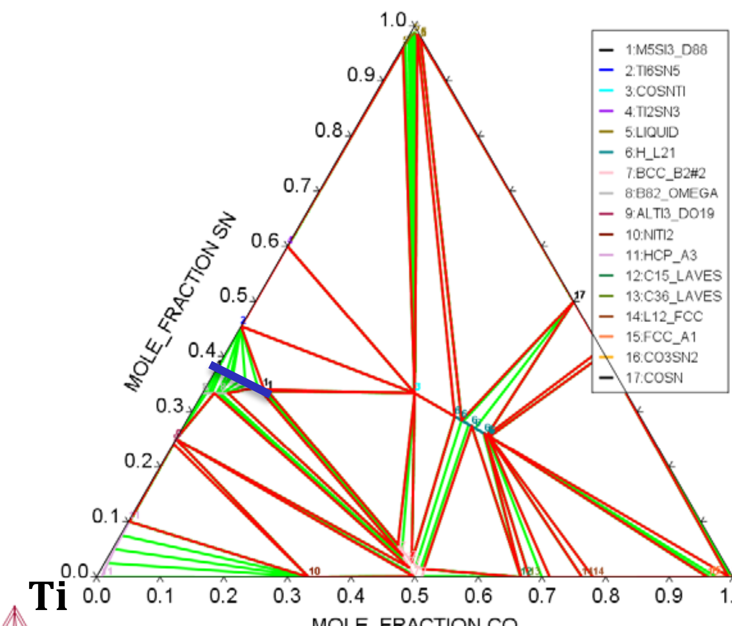
❖ Tsai & Yeh (2014) ❖ Zhang (2008) ❖ Guo (2011)

Solid solution vs intermetallics

- ❑ **Intermetallics**
  - o Compounds between metals
  - o Brittle? Detrimental?
  - o Stoichiometric or very limited homogeneity?
- ❑ **Intermetallics >> solutions**
- ❑ **Depending structures**
- ❑ **Ordering and disordering**

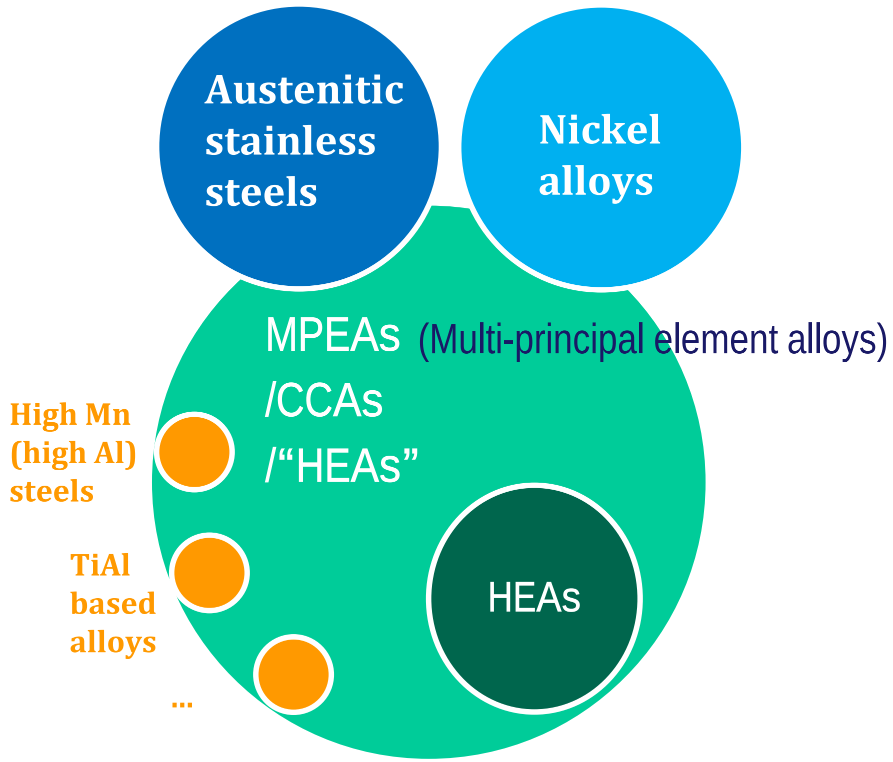






MPEAs and HEAs

SSS: Simple solid solution
IMs: intermetallics and the solutions based on them



Methods for reliable materials design

Avoid oversimplification, by considering

- specific systems
- specific structures
- specific compositions
- various intermetallics
- solutions bases on intermetallics

being capable of predicting/calculating

- 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
- ...

Calphad+++

Crystallography

Ab-initio calculations
(electron configuration)

Phase equilibria

Assessments

Advanced phase model
Model parameters

Modeling

Gibbs energy descriptions

Thermodynamic databases

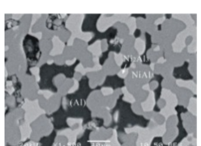
Database development

Calculation

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

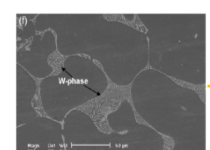
Phase equilibria
All sorts of phase diagrams

Solidification simulation



equilibrium

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



as-cast

Calphad: Thermodynamics & kinetics

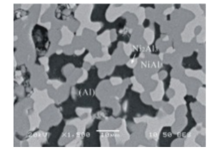
Thermo-Calc Software

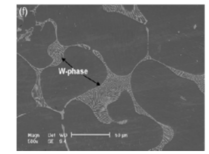
Thermodynamic Database

Thermo-Calc

Equilibrium calculation
Solidification simulation

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



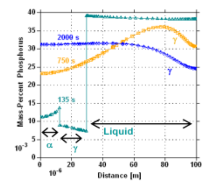


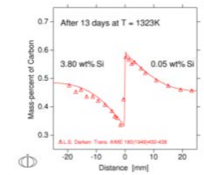
+

Mobility Database

Diffusion module (DICTRA)

Diffusion-controlled phase transformations





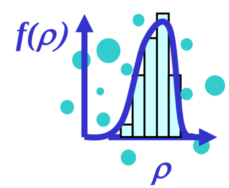
+

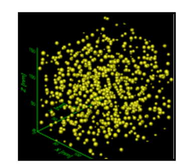
Property Database

Precipitation module (TC-PRISMA)

Nucleation, growth, coarsening

Multi-particle precipitation kinetics





Interfacial energy
Volume

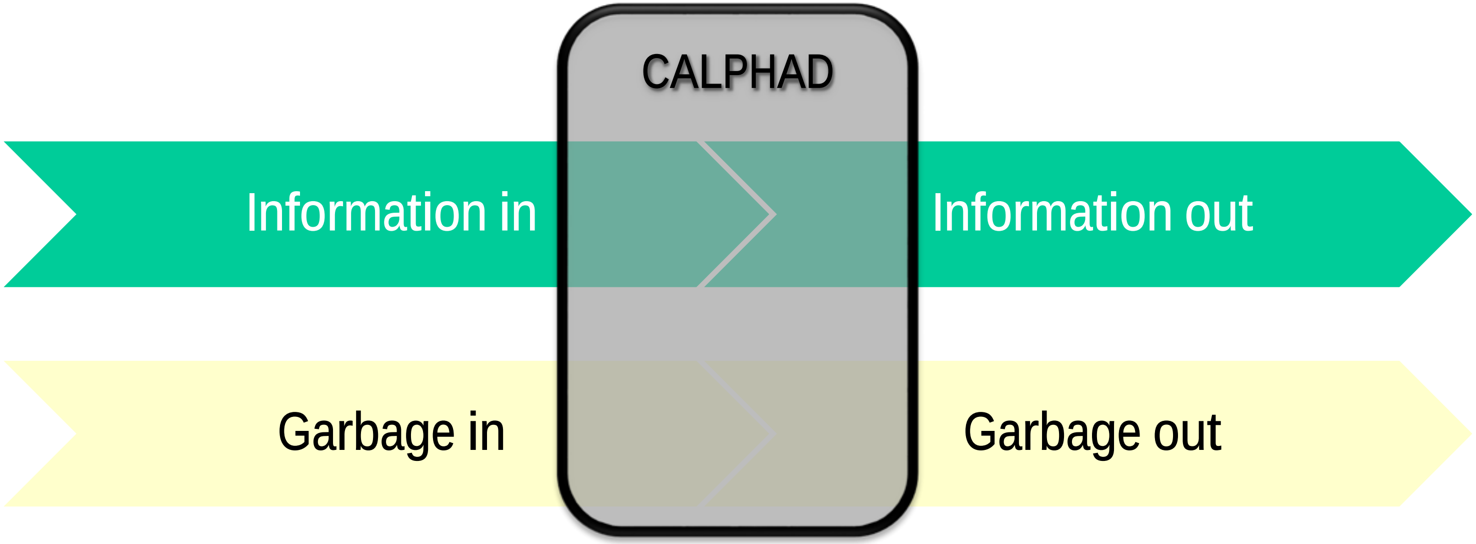
Elastic constants
Viscosity
...

Ultimate goal: microstructure evolution and materials proerties

Quality is the key to reliable predictions

Thermo-Calc Software

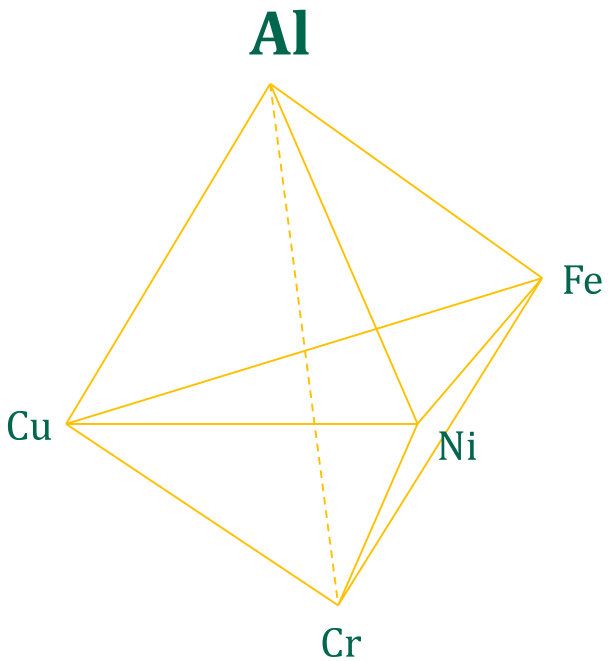
- Reliability of a calculation depends on the quality of the database.
- Each database has its blind zone. Be aware of where you are.



Challenge 1

- **Large numbers of binary and ternary systems to be assessed**

- **Quinary system**
  - 10 binaries + **10** ternaries
  - 4 Al-binaries + 6 Al-ternaries
- **15 element framework**
  - 105 binaries + **455** ternaries
  - 14 Al-binaries + 91 Al-ternaries
- **25 element framework**
  - 300 binaries + **2300** ternaries

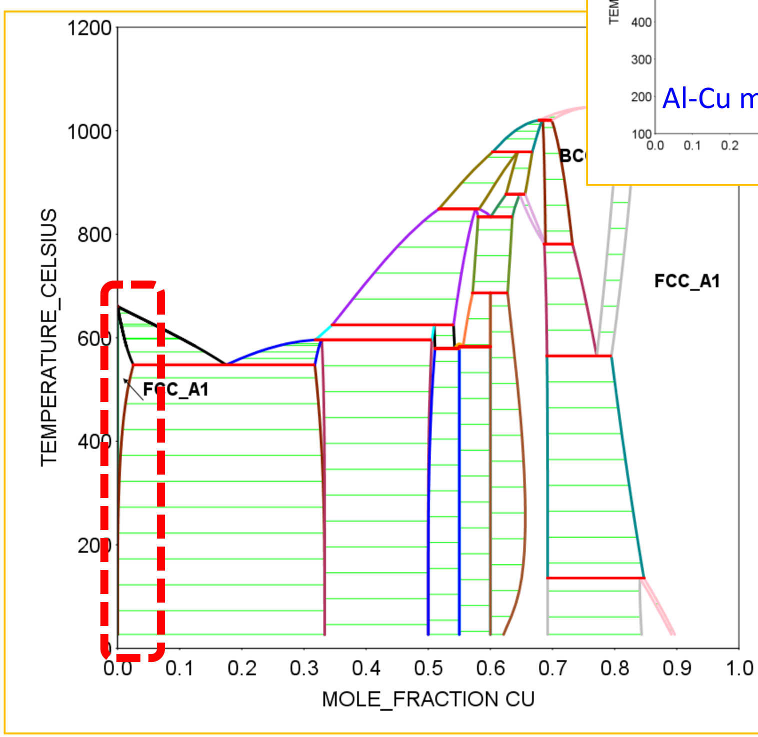


- **Our strategies**
  - Starting with a relatively small (but decent) framework
  - Starting with the hottest systems
  - A long-term project

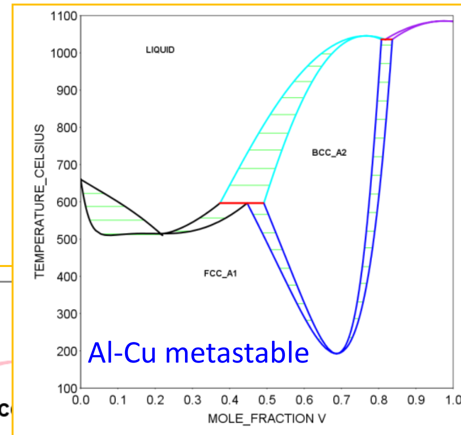
Challenge 2

- **Descriptions of individual systems and phases valid over a wide range**
  - Extrapolation to metastable regions

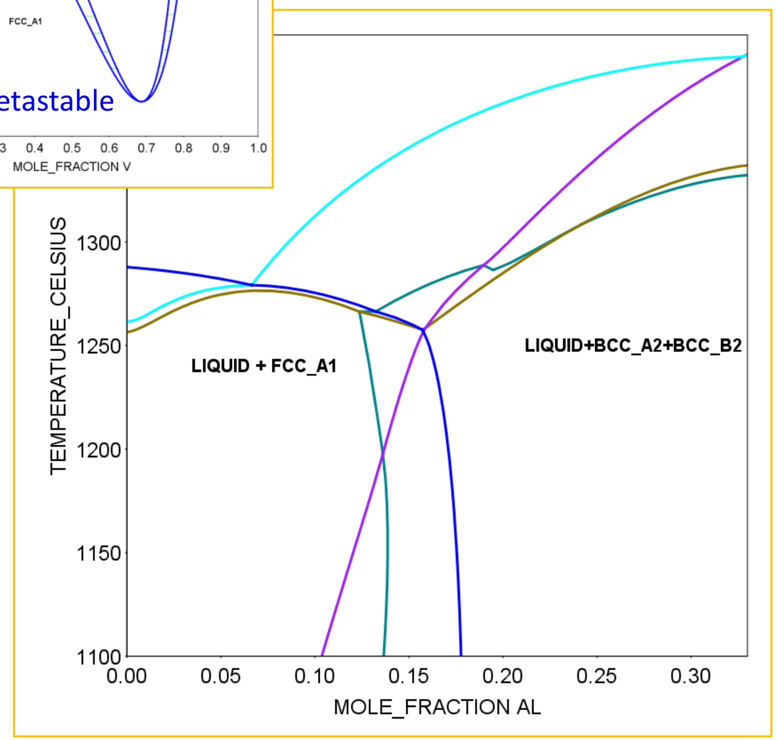
$$G_m^{ex} = \sum_i \sum_j x_i x_j \sum_{n=0}^{m} \left[L_{i,j}^{(n)} (x_i - x_j)^n \right] + \sum_i \sum_j \sum_k x_i x_j x_k L_{i,j,k}$$



Al-Cu stable



Al-Cu metastable



CoCrCuFeNi-Al

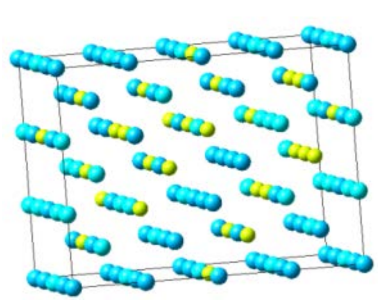
Challenge 2: Recipes

HT DFT calculations

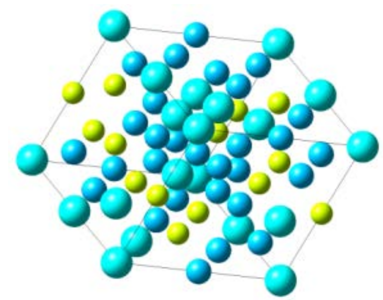
- ❑ **Binary solid solutions**
  - o SQSs (Special quasirandom structures)
  - o CPA (Coherent potential approximation)
- ❑ **Ternary solid solutions**
  - o SSOSs **(a small set of ordered structures)**

Supercells → SQSs → SSOSs

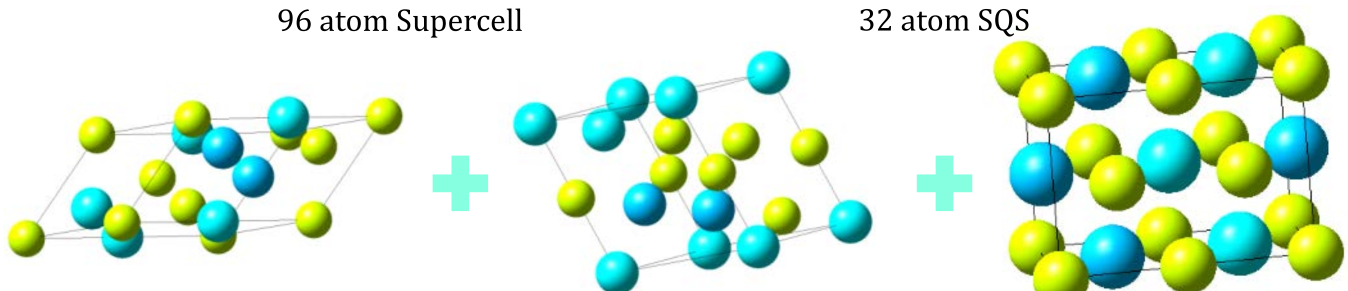
- ▪Higher efficiency
- ▪Similar accuracy



96 atom Supercell



32 atom SQS



SSOSs Ti_2AlV

❖ Jiang (2016)

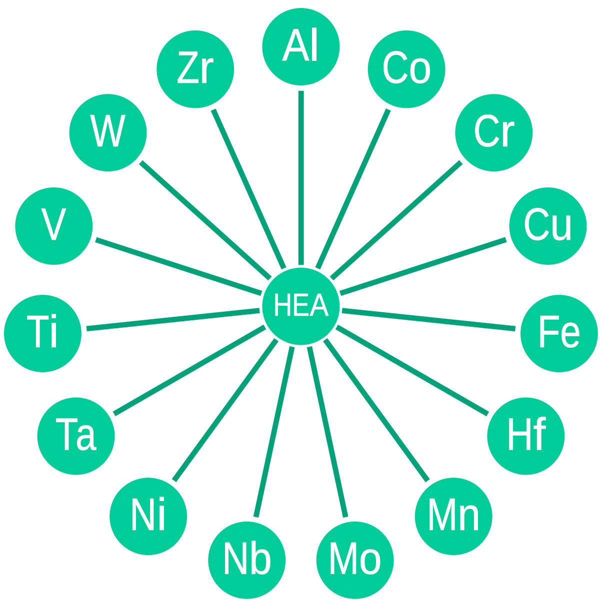
TCHEA1: Overview

- for HEAs and other types of MPEAs
- 15 element framework
- ALL binaries assessed
- 104 ternaries assessed
- 96 ternaries tentatively assessed
- ALL solid phases in assessed systems

Raymundo Arroyave

(Texas A & M University)

- 216 HEAs
- 70 % on target

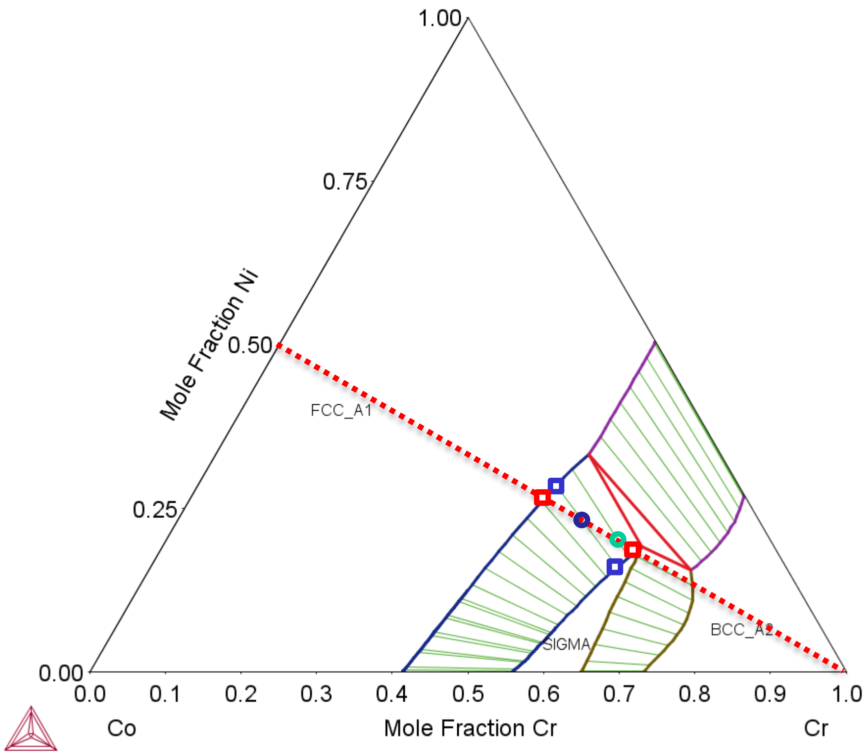


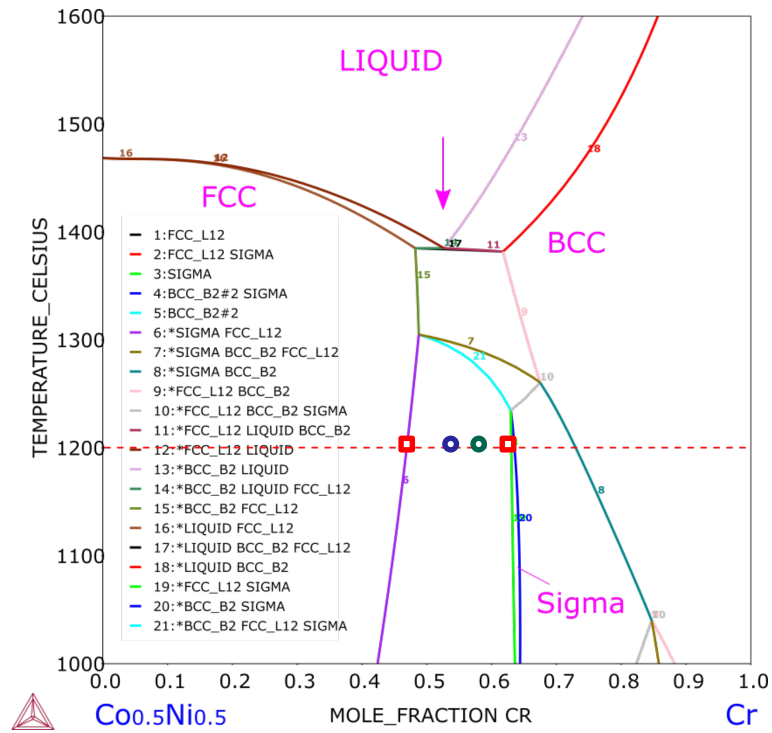
Highlight

- Phases 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)

To bridge the knowledge gap

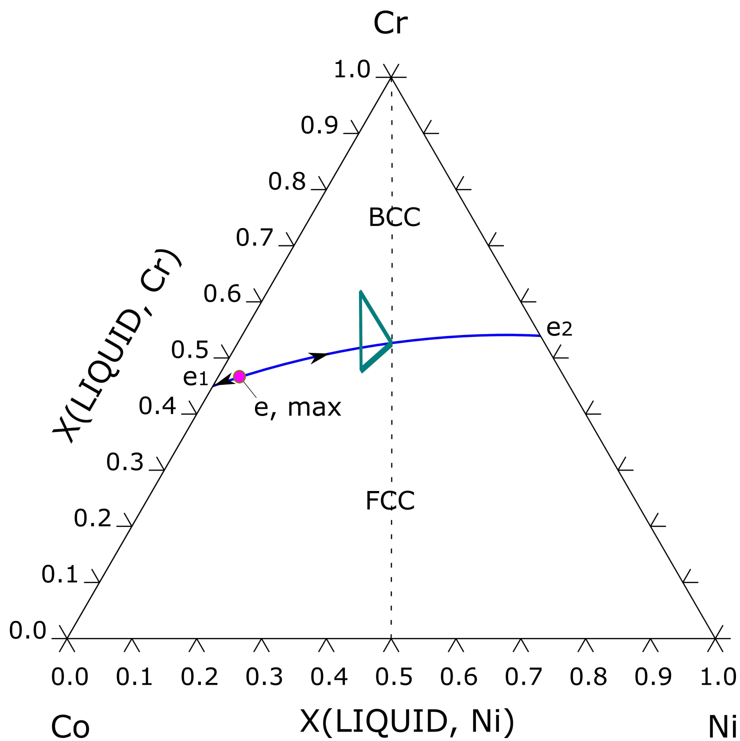
- Different backgrounds, knowledges, interests, languages
- "Pseudo-binary" cannot be arbitrarily constructed
- Vertical sections
- Tie-lines

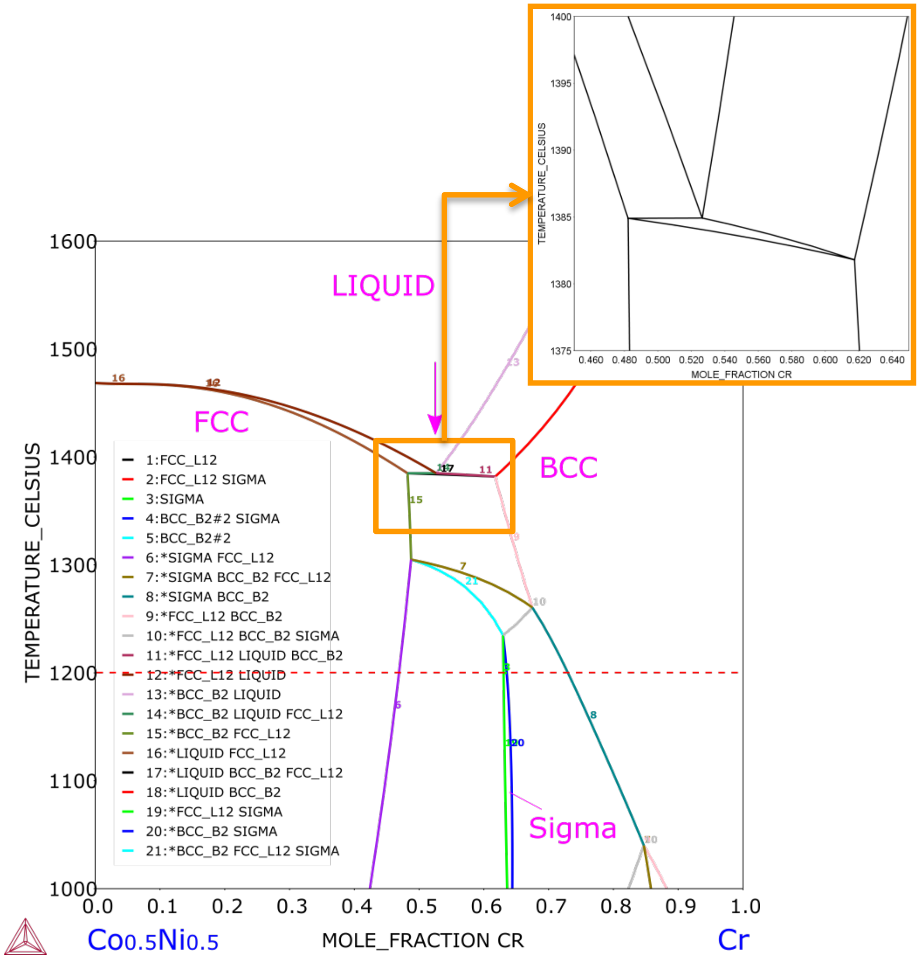




To bridge the knowledge gap

- "Pseudo-binary" cannot be arbitrarily constructed
- Solidification path





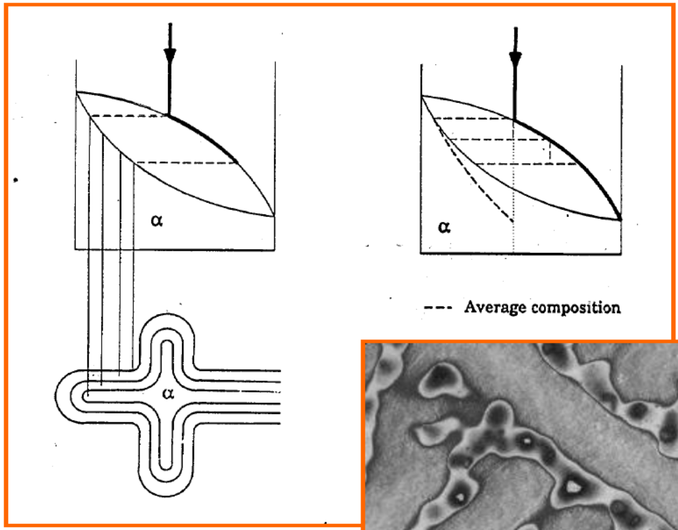
To bridge the knowledge gap

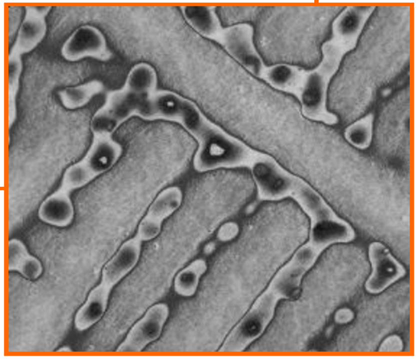
Thermo-Calc Software

❑ Solidification simulations

- Most alloys start with casting
- Understanding and predicting
  - o Finally solidified microstructures
  - o Solidification process
    - Phase formation sequence
    - Phase reactions
    - Transformation temperatures

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





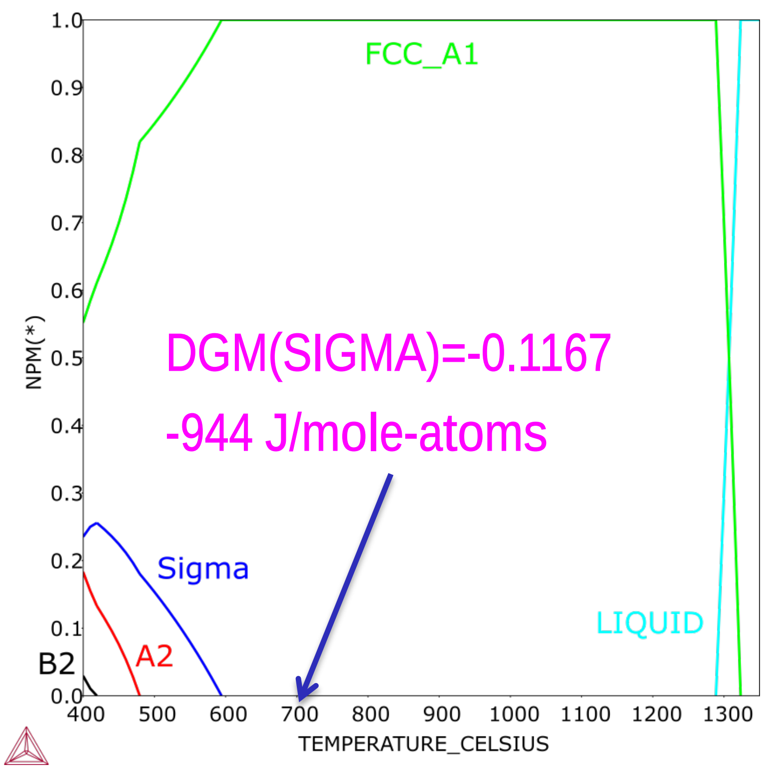
- Using TCHEA and Thermo-Calc
  - o Equilibrium calculation
  - o Scheil (non-equilibrium) calculation
  - o Check both of them

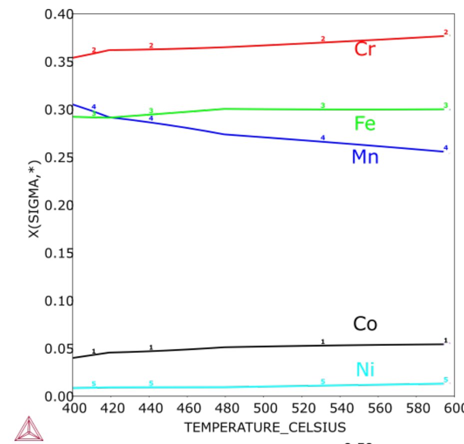
Co-Cr-Fe-Mn-Ni

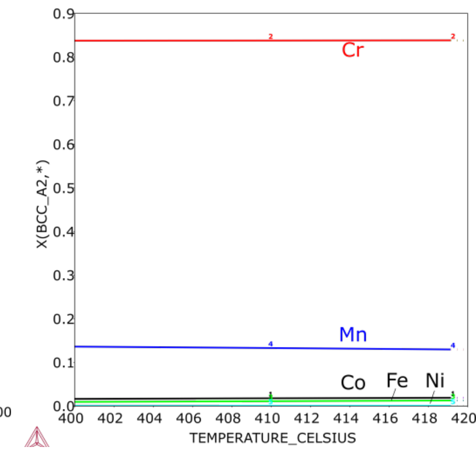
- [2004Can] spinning casting, only FCC
- [2016Ott

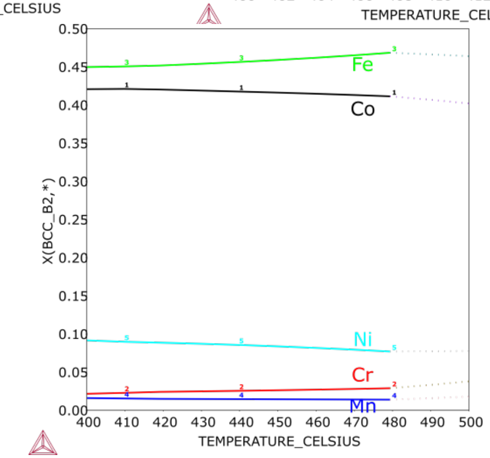
900 °C, 500 d	fcc		
700 °C, 500 d	fcc	Cr-rich sigma	
500 °C, 500 d	Mn & Ni-rich $L1_0$	Cr-rich A2	Fe & Co-rich B2

- Easo George, ICHEM2016



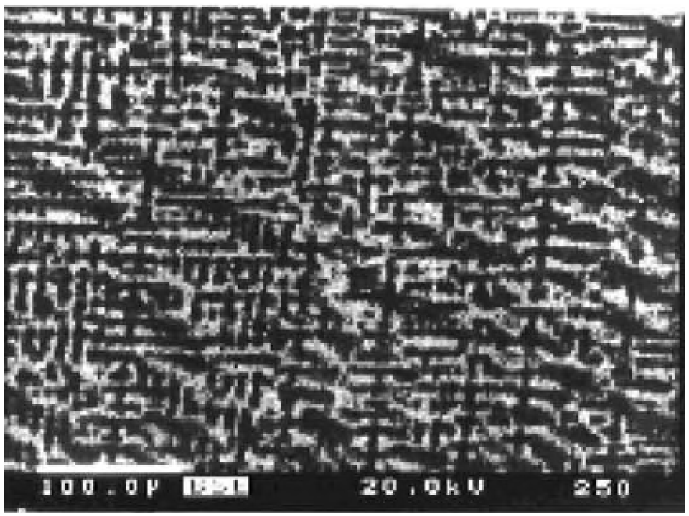


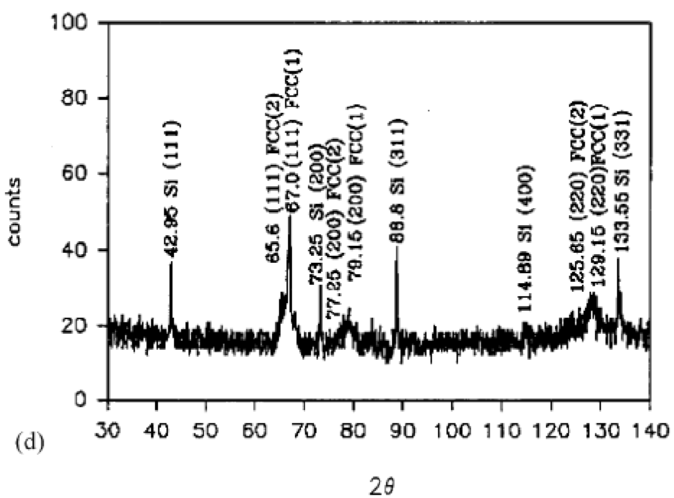


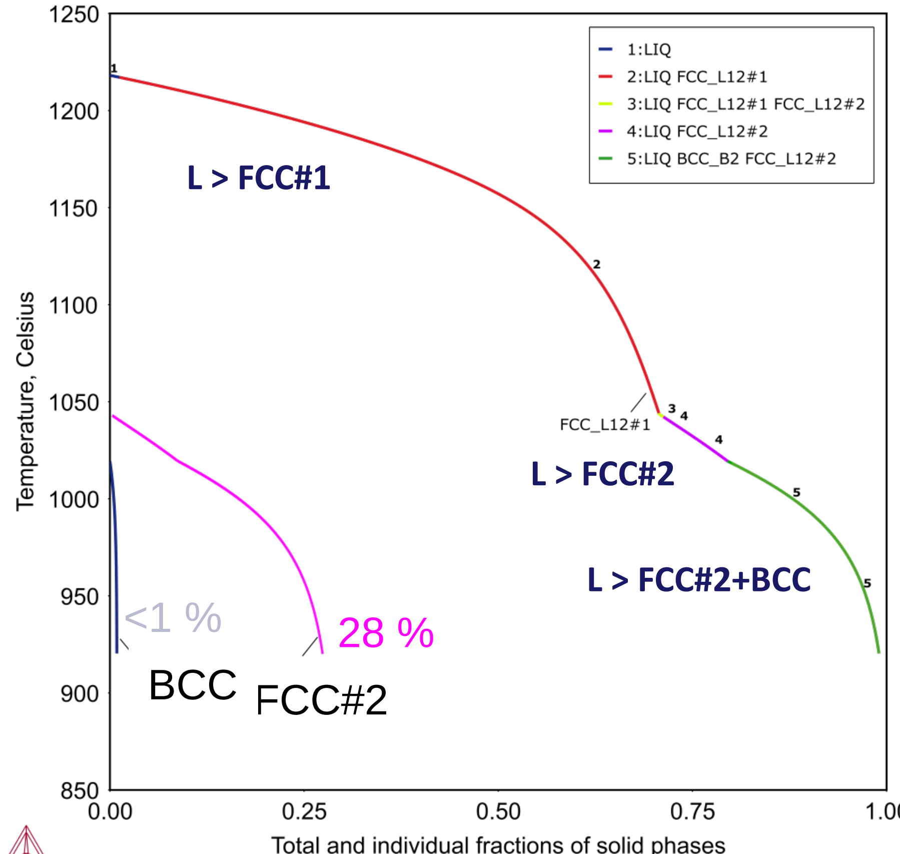


Co-Cr-Fe-Mn-Ni-Cu

- [2004Can] spinning, FCC dendrites, interdendritic segregation, no 2nd phase
- Cu-poor FCC#1; Cu-Mn-Ni rich FCC#2; Cr-rich BCC
- BCC undetected by XRD: too little or suspended by the rapid cooling







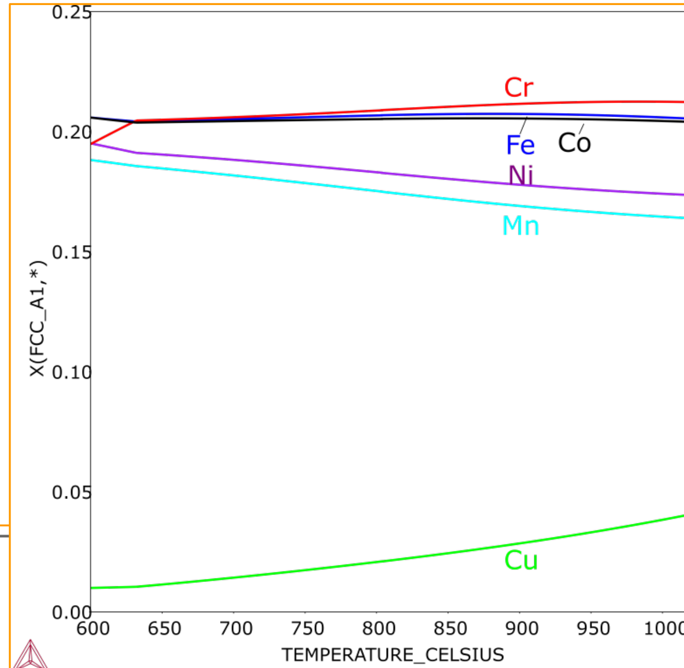
Scheil calculation

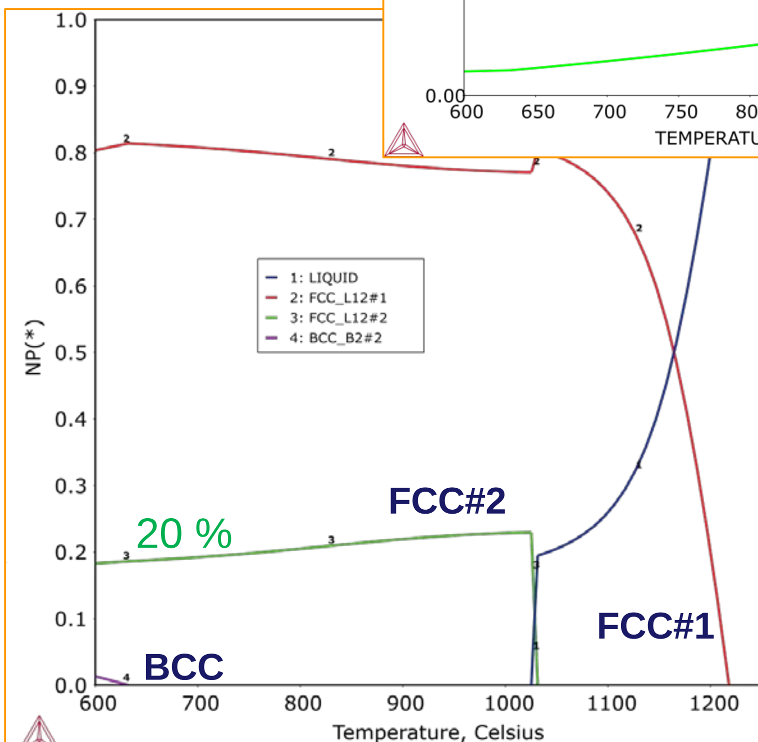
Co-Cr-Fe-Mn-Ni-Cu

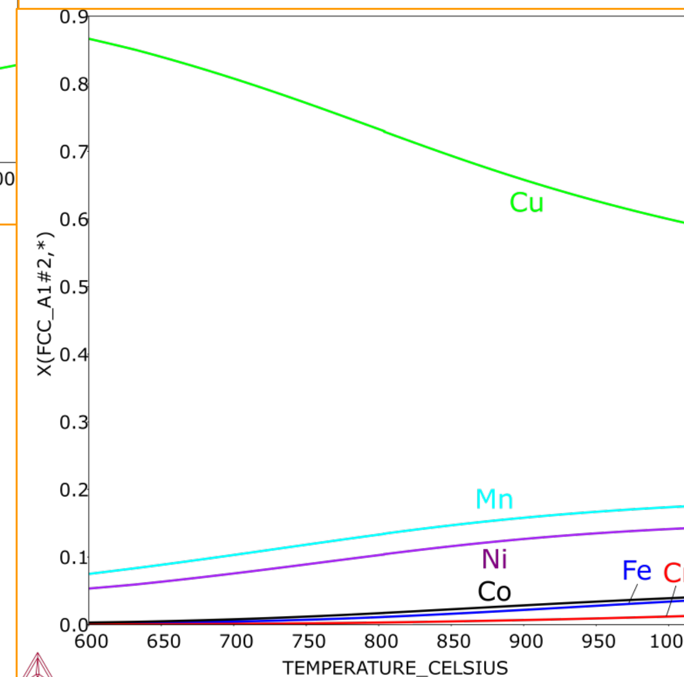
Equilibrium calculation

A smaller amount of FCC#2

A peritectic reaction was predicted

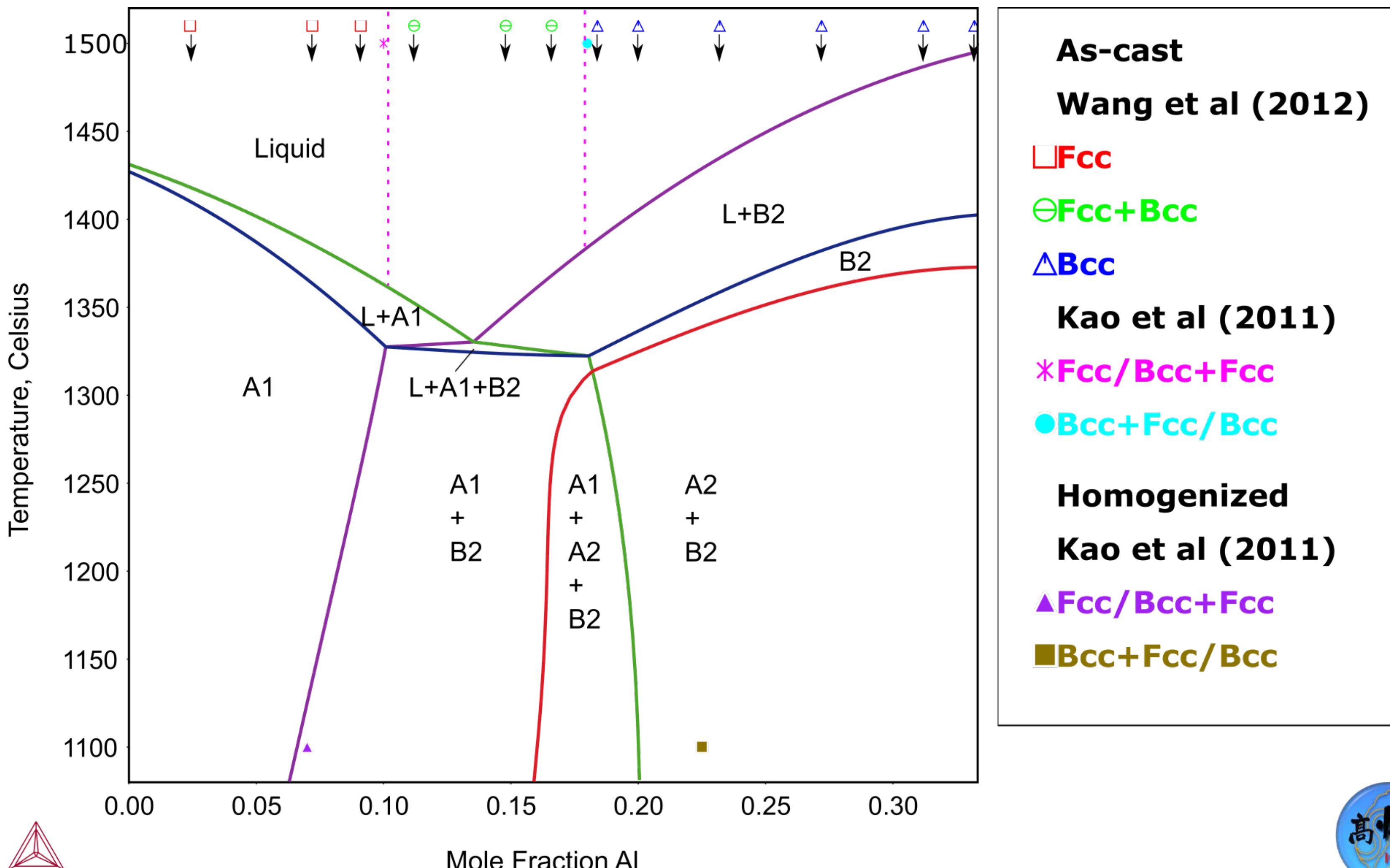






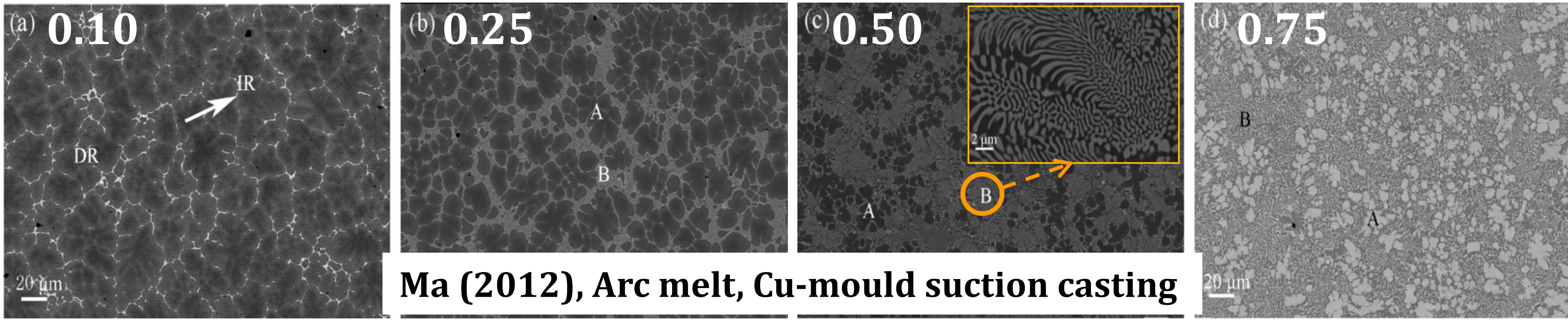
CoCrFeNi-Al

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

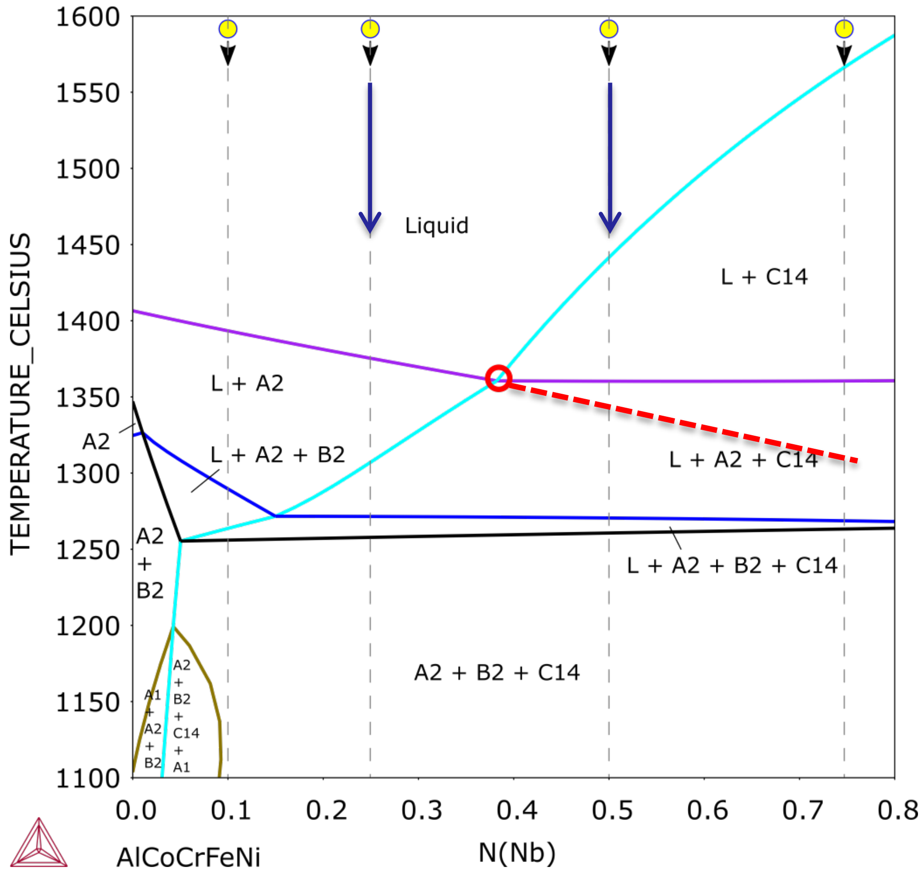


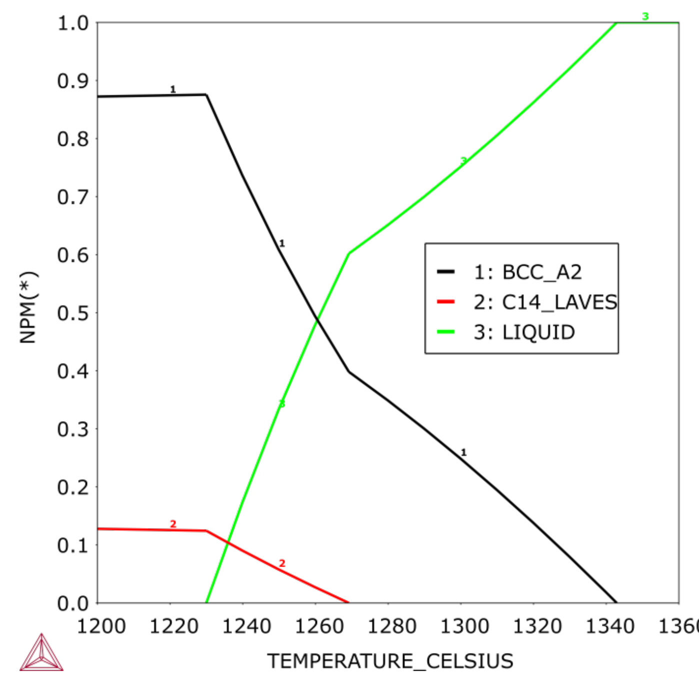
AlCoCrFeNi-Nb

Thermo-Calc Software



Ma (2012), Arc melt, Cu-mould suction casting





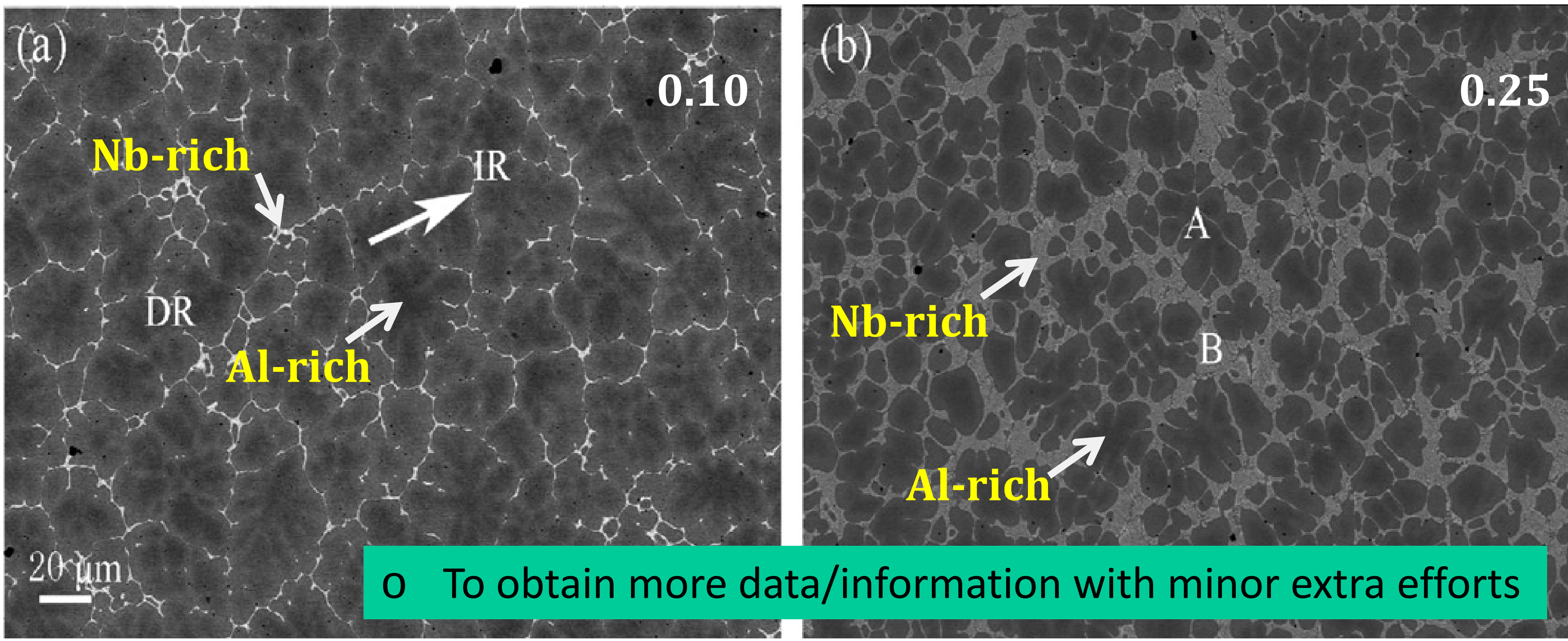
Phases, amounts, trans. T

AlCoCrFeNi-Nb

- Phases, amount, transition T, **Phase compositions**

Ma (2012), Arc melt, Cu-mould suction casting

Alloys	Regions	Al	Co	Cr	Fe	Nb	Ni
$AlCoCrFeNb_{0.1}Ni$	DR	35.84	15.96	9.29	10.45	3.41	25.05
	ID	12.17	17.20	17.23	17.38	27.65	8.36
$AlCoCrFeNb_{0.25}Ni$	A	27.22	17.35	15.94	16.35	2.72	20.41
	B	12.20	20.05	22.23	20.30	10.70	14.51



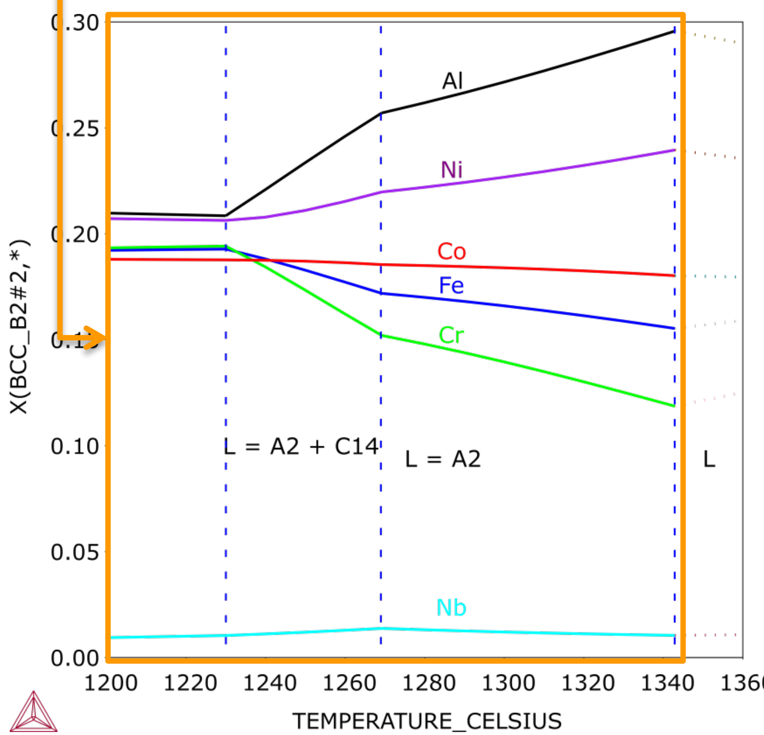
o To obtain more data/information with minor extra efforts

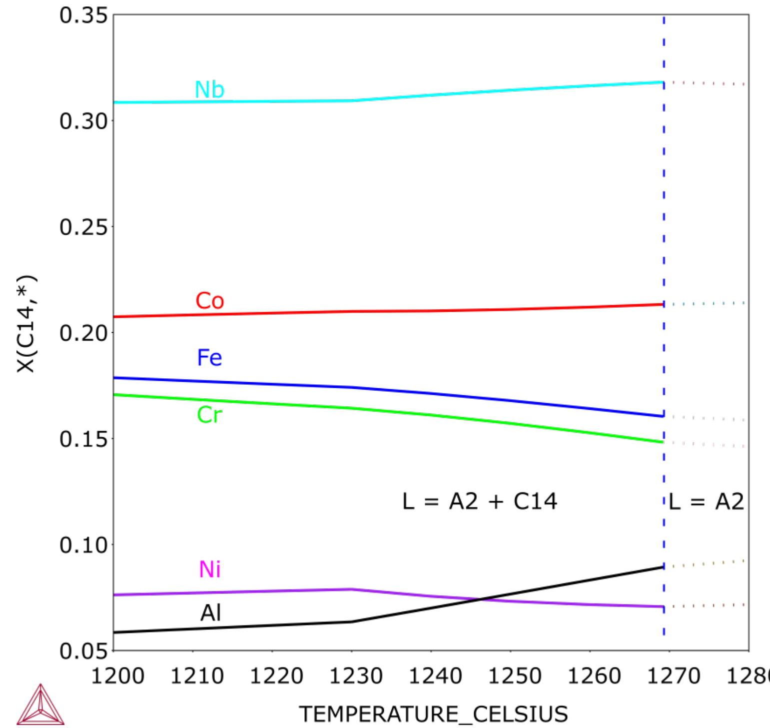
The contrasts indicate a composition microsegration, which was not experimentally examined, but can be analyzed with calculations.

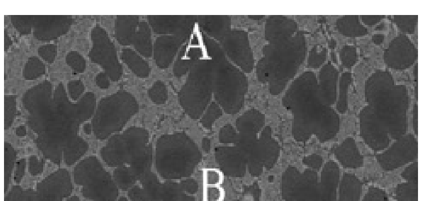
AlCoCrFeNi-Nb

- Phases, amount, transition T, Phase compositions, **Micro-segregation**

Alloys	Regions	Al	Co	Cr	Fe	Nb	Ni
$AlCoCrFeNb_{0.25}Ni$	A	27.22	17.35	15.94	16.35	2.72	20.41
	B	12.20	20.05	22.23	20.30	10.70	14.51





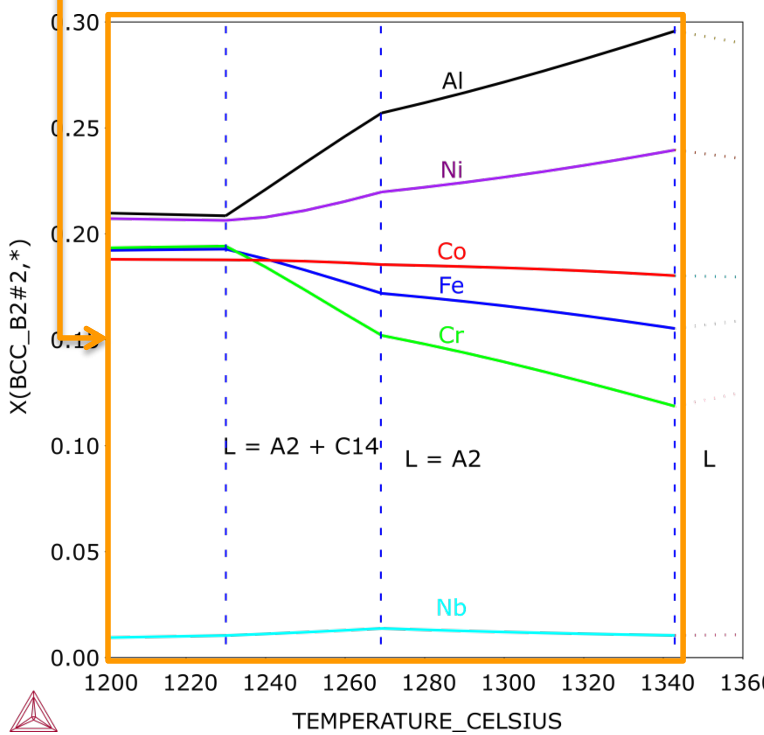


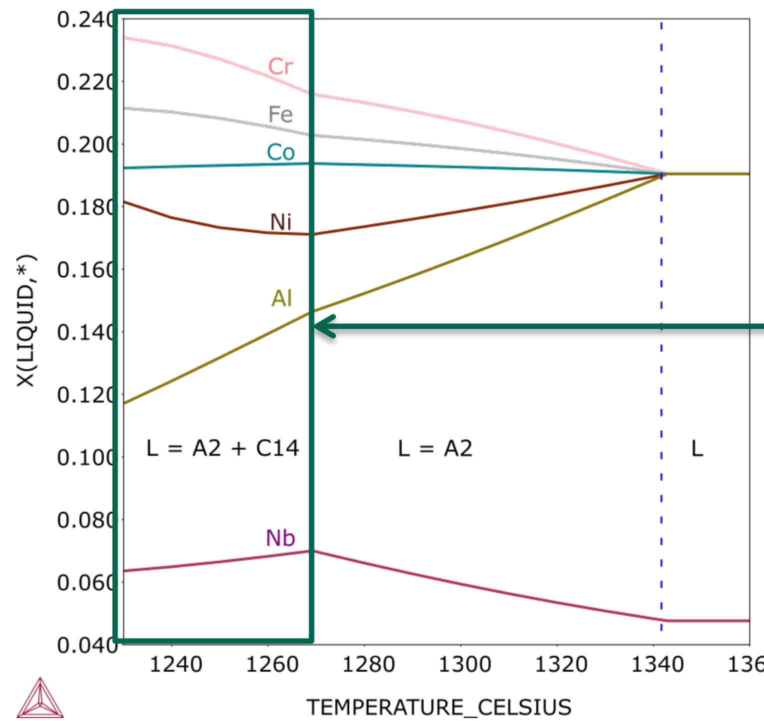
Region B is a mixture, instead of a single phase of C14!

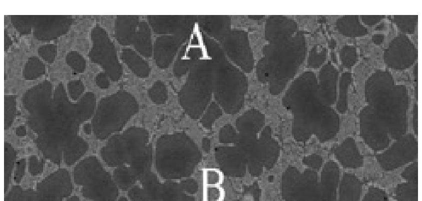
AlCoCrFeNi-Nb

- Phases, amount, transition T, Phase compositions, **Micro-segregation**

Alloys	Regions	Al	Co	Cr	Fe	Nb	Ni
AlCoCrFeNb$_{0.25}$Ni	A	27.22	17.35	15.94	16.35	2.72	20.41
	B	12.20	20.05	22.23	20.30	10.70	14.5



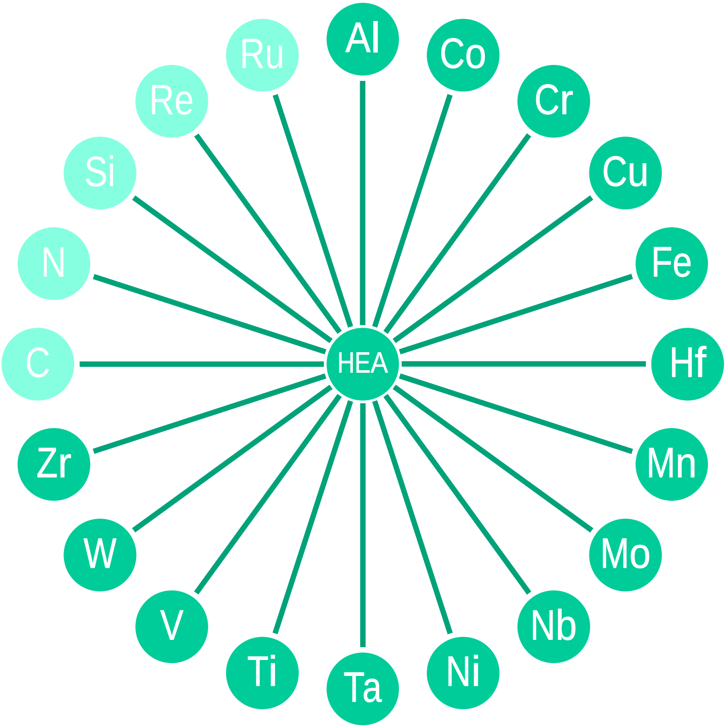




- Make full use of the experimental data
- Make appropriate interpretations

TCHEA(n)

- A long-term project for continuous development
- Next version TCHEA2
  - +C, +N, +Si, +Re, +Ru
  - Updates of important systems
  - + new systems
  - Updates based on validations



- + Cooperation
- + What you are most interested in

Summary

- **New challenges to the development of HEA databases**
  - Reliable descriptions for wide compositional ranges
  - Number of assessed systems
- **Reliability of calculation results depends on**
  - Quality of the database
  - How the calculations are performed
  - How the results are interpreted
  - Knowledge gaps to bridge
- **TCHEA is specially tailored for HEAs/MPEAs**
  - The materials design
  - The process analysis

References

[2004Can] B. Cantor, et al., Mat. Sci. Eng. A 375-377 (2004) 213-218.

[2004Yeh1] J.W. Yeh, et al., Adv. Eng. Mater., 6 (2004) 299-303.

[2004Yeh2] J.W. Yeh, et al., Metall. Mater. Trans. A, 35 (2004) 2533-2536.

[2005Ton1] C.J. Tong, et al., Metall. Mater. Trans. A, 36A (2005) 881-893.

[2005Ton2] C. Tong, et al., Metall. Mater. Trans. A 36 (2005) 1263-1271.

[2006Yeh] J.W. Yeh, Ann Chim-Sci Mat. 31 (2006) 633–648.

[2008Zha] Y. Zhang, Y.J. Zhou, et al. Adv. Eng. Mater. 10 (2008) 534–538.

[2010Zhu] J.M. Zhu, H.F. Zhang, et al. J. Alloy. Compd. 497 (2010) 52-56.

[2011Guo] S. Guo, C.T. Liu, Prog. Nat. Sci.: Mater. Intl. 21(6) (2011) 433-446.

[2011Kao] Y.F. Kao, et al. J Alloy Compd, 509 (2011) 1607-1614.

[2012Ma] S.G. Ma, Y. Zhang, Mater Sci Eng A 532 (2012) 480-486.

[2012Wan] W.R. Wang, et al., Intermetallics, 26 (2012) 44-51.

[2013Ott] F. Otto, et al., Acta mater. 61 (2013) 2628-2638.

[2013Wan] S. Wang, Entropy, 15 (2013) 5536-5548.

[2014Tsa] M. Tsai, J. Yeh, Mater. Res. Lett., 2 (2014) 107-123.

[2015Mir] D.B. Miracle, Mater. Sci. Technol. 31(10) (2015) 1142-1147.

[2015Sen] O.N. Senkov, et al., Nature, 6 (2015) 6529:1-17.

[2016Mir] D.B. Miracle, O.N. Senkov, Acta Mater (2016) 1-64.

[2016Jia] Chao Jiang, Blas P. Uberuaga, Phys. Rev. Lett. 116 (2016) 105501.