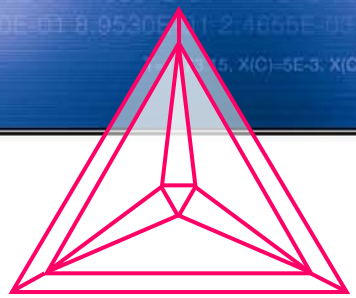


Thermo-Calc Software

CALCULATING THERMODYNAMIC PROPERTIES

Introduction to Thermo-Calc & DICTRA: Ingot Metallurgy Forum – April 20, 2010

Paul Mason

Thermo-Calc Software Inc

http://www.thermocalc.com
E-mail: paul@thermocalc.com

Phone: 724-731-0074
Fax: 724-731-0078

Outline

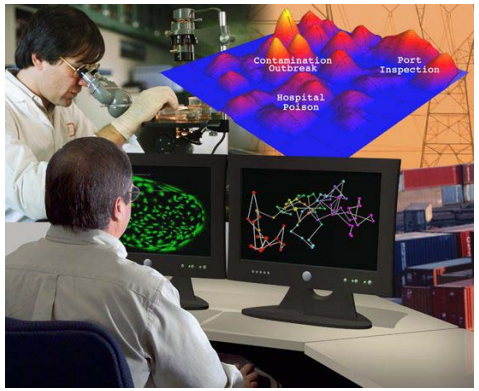
- Introduction to Thermo-Calc and DICTRA
- Examples related to ingot metallurgy:
  - Peak shifting of phosphorous during solidification
  - Homogenizing a Ni-based superalloy
- Questions

Outline

- **Introduction to Thermo-Calc and DICTRA**
- Examples related to ingot metallurgy:
  - Peak shifting of phosphorous during solidification
  - Homogenizing a Ni-based superalloy
- Questions

Benefits of modeling and simulation

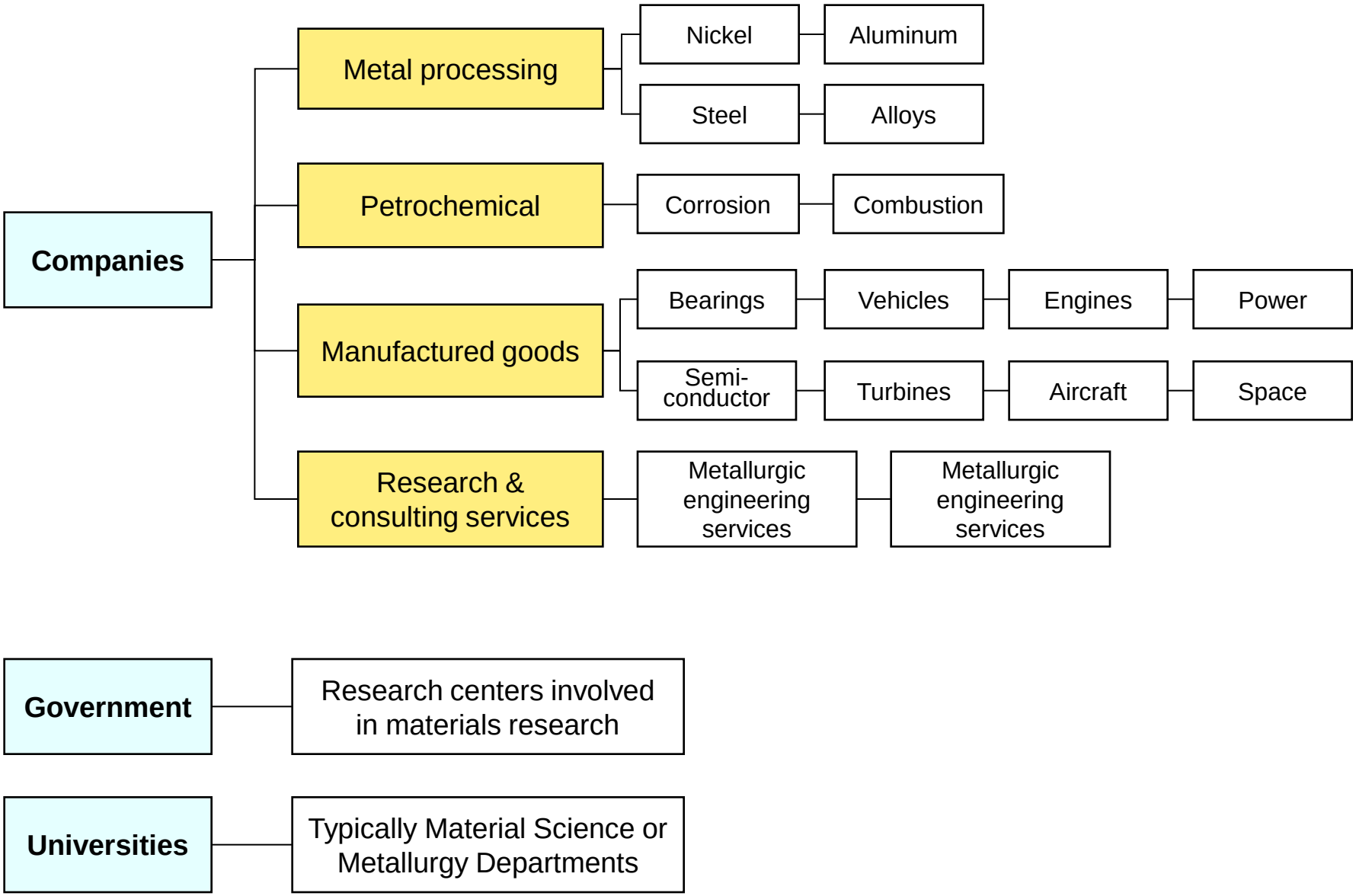
Thermo-Calc Software



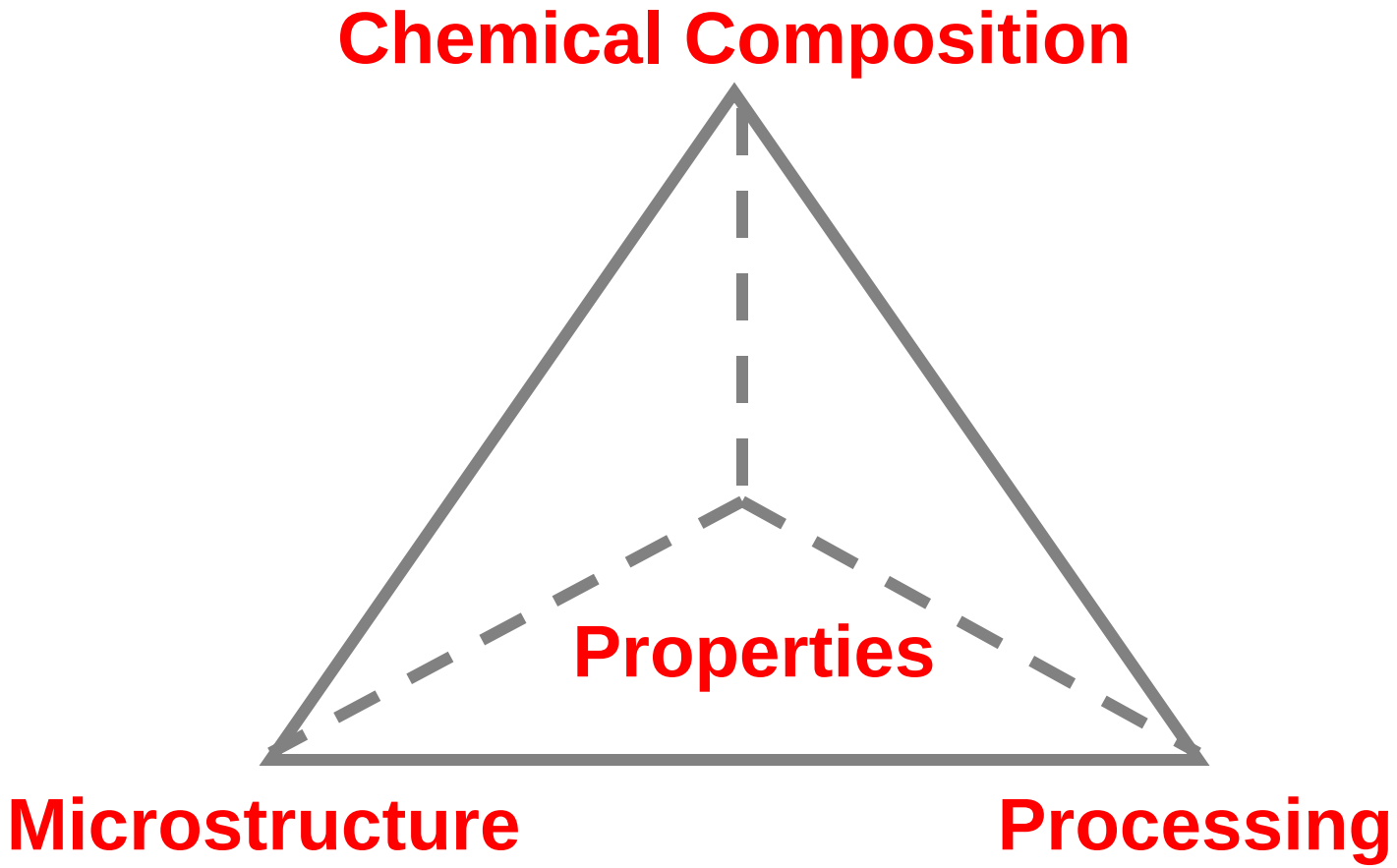
- ROI of $3-$9 for every $1 invested (source IDC White paper on Modeling and Simulation: The Return on Investment in Materials Science, July 2004) sponsored by Accelrys Inc
- Accelerated development and implementation of new materials into plant and products.
- Better understanding of the material (stronger patents, understanding tail effects of compositional variation that can be difficult to determine experimentally)
- Innovative – can make calculations for a wider range of composition space than you would normally based on incremental development methods => lead to breakthrough ideas.
- Does not replace the need for experiment and testing, but compliments it by better targeting of experiments.
- Utilizes real world experience, coupled with scientific understanding and prediction to reduce trial and error and minimize waste (opportunity cost, materials etc)
- Relevant experiments not always possible (e.g. canister material for nuclear waste storage).

Thermo-Calc Software Customer Segments

Thermo-Calc Software



Paradigm of Materials Science and Engineering



Computational thermodynamics

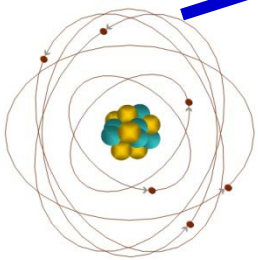
Thermo-Calc Software

- Computational Thermodynamics is an interdisciplinary science as thermodynamics is involved in many applied sciences. It makes use of computer software and assessed thermodynamic databases to perform realistic calculations of thermodynamic properties of multicomponent system.

- The development of consistent databases where each phase is described separately using models based on physical principles and parameters assessed from experimental data is a key feature of this technique.

From Atoms to Microstructure

Thermo-Calc Software



Interfacial energy & Volume & Elastic constants

Thermodynamics: Gibbs energy

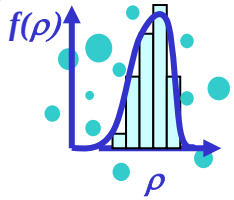
Phase Field Method

Langer-Schwartz

CALPHAD

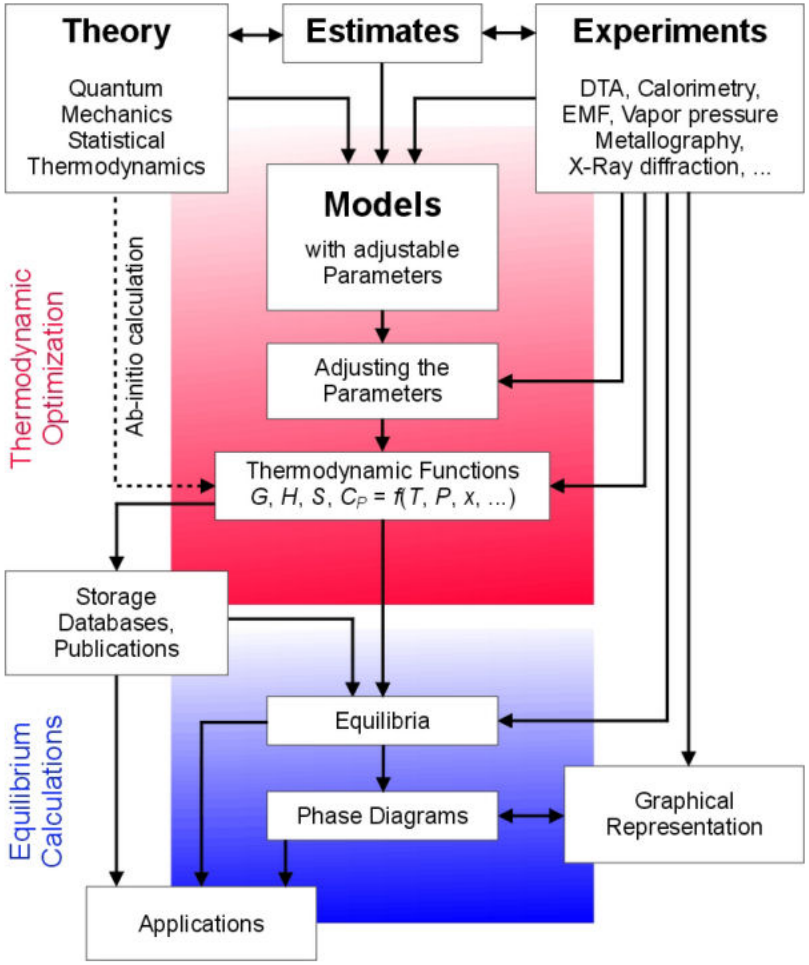
First Principles Calculation

Diffusion: Mobility



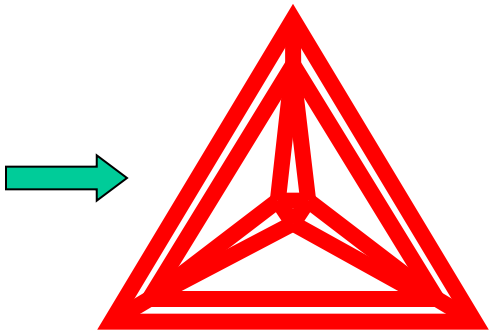
Mission: to predict microstructure evolution and materials properties.

The CALPHAD method

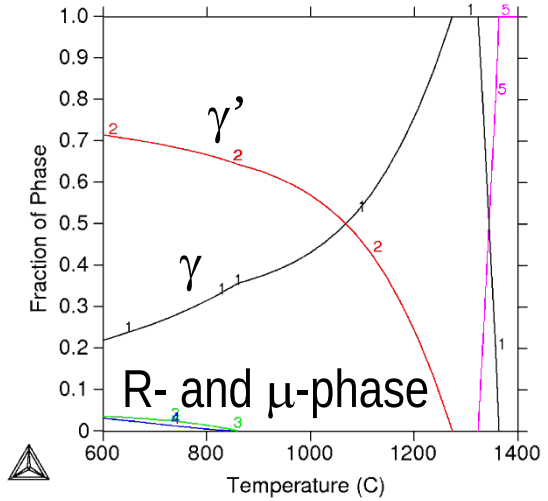


Underlying basis of Thermo-Calc

Thermodynamic Database



Thermo-Calc



Description of Gibbs free energy for the individual phases

$$G_m^{\phi}\left(T, P, x_i^{\phi}\right)$$

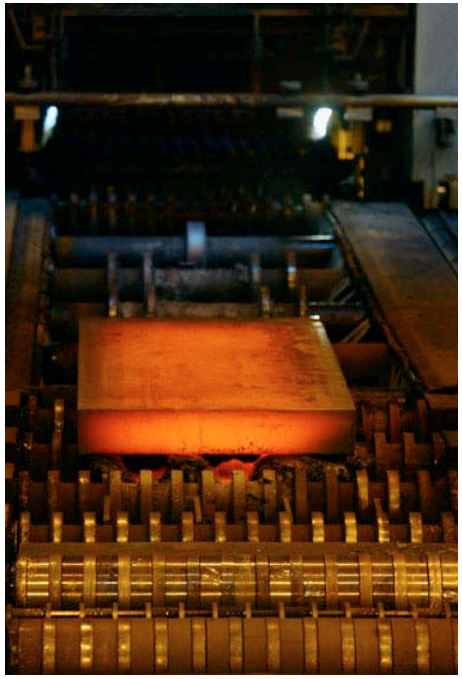
Minimization of the total Gibbs free energy under given conditions.

$$G = \sum_{\phi} N^{\phi} G_m^{\phi}\left(T, P, x_i^{\phi}\right)$$

$$\frac{\partial G}{\partial x_i^{\phi}} = 0$$

Functionality of Thermo-Calc

- Calculating stable and meta-stable heterogeneous phase equilibrium
- Amount and composition of phases
- Transformation temperatures, e.g. liquidus and solidus temperature
- Predicting driving forces for phase transformations
- Phase diagrams (binary, ternary, isothermal, isoplethal, etc.)
- Molar volume, density and thermal expansion
- Scheil-Gulliver (non-equilibrium) solidification simulations
- Thermochemical data such as;
  - enthalpies
  - heat capacity,
  - activities, etc.
- Thermodynamic properties of chemical reactions
- **And much, much more….**



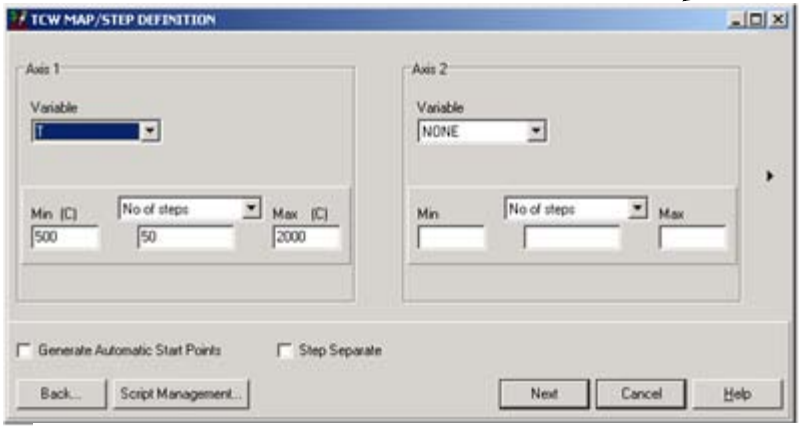
- Designing and optimization of alloys
- Design and optimization of processes

4 Steps to making a calculation

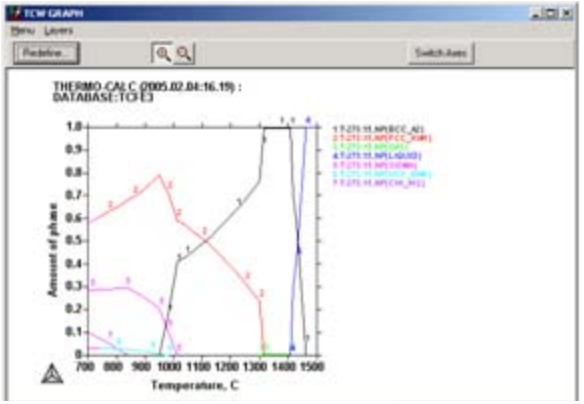
Thermo-Calc Software

1. Define your system
TCW Material

2. Set your input conditions
TCW Conditions



3. Set calculation variables.
TCW Map/Step Definition



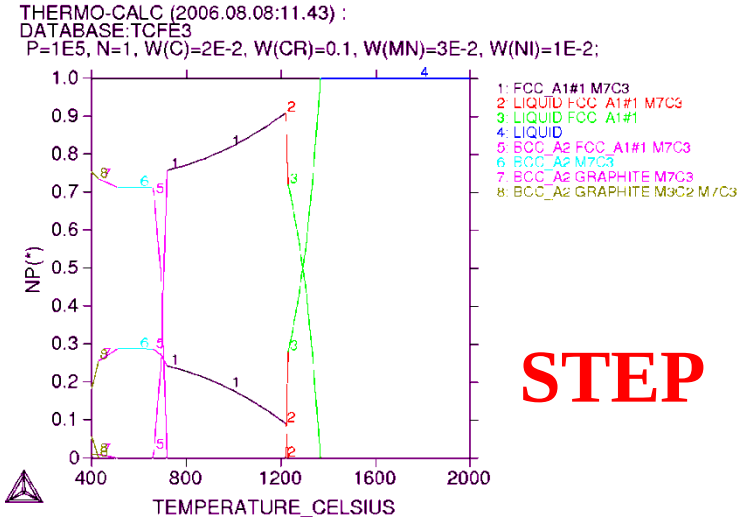
4. Plot your output
TCW Diagram Definition

4 main types of calculation

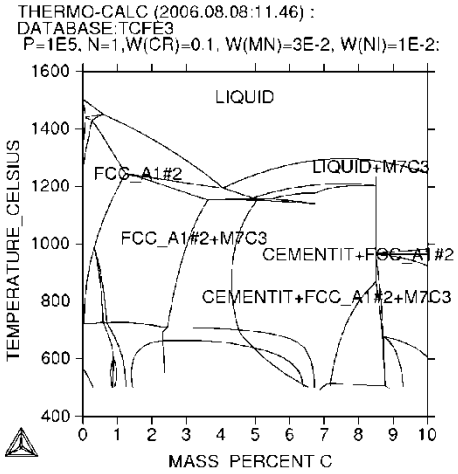
Thermo-Calc Software

```
Output from POLY-3
Tue Aug 08 2006 11:41:39

Database: TCFE3

Conditions:
T=1000, P=1E5, N=1, W(C)=2E-2, W(CR)=0.1, W(MN)=3E-2, W(NI)=1E-2
DEGREES OF FREEDOM 0

Temperature 1000K (727C, 1340F), Pressure 1.000000E+05
Number of moles of components 1.00000E+00, Mass 5.16905E+01
Total Gibbs energy -4.42393E+04, Enthalpy 2.56582E+04, Volume 5.22429E-06

Component        Moles          W-Fraction     Activity       Potential      Ref.State

C                8.6072E-02     2.0000E-02     8.9724E-02     -2.0046E+04    SER
CR               9.9412E-02     1.0000E-01     4.4290E-04     -6.4206E+04    SER
FE               7.7748E-01     8.4000E-01     6.0347E-03     -4.2489E+04    SER
MN               2.8227E-02     3.0000E-02     4.6517E-05     -8.2943E+04    SER
NI               8.8074E-03     1.0000E-02     3.3158E-05     -8.5758E+04    SER


FCC_A1#1         STATUS ENTERED            Driving force  0.0000E+00
Number of moles 7.5868E-01, Mass 4.1735E+01
Mass fractions:
FE 9.44835E-01   CR 1.41596E-02   C  3.93605E-03
MN 2.47653E-02   NI 1.23038E-02

FCC_A1#2         STATUS ENTERED            Driving force  0.0000E+00
Number of moles 0.0000E+00, Mass 0.0000E+00
Mass fractions:
FE 9.44835E-01   CR 1.41596E-02   C  3.93605E-03
MN 2.47653E-02   NI 1.23038E-02

M7C3#1  STATUS ENTERED            Driving force  0.0000E+00
Number of moles 2.4132E-01, Mass 9.9559E+00
Mass fractions:
CR 4.59839E-01   C  8.73393E-02   NI 3.42660E-04
FE 4.00536E-01   MN 5.19435E-02
```

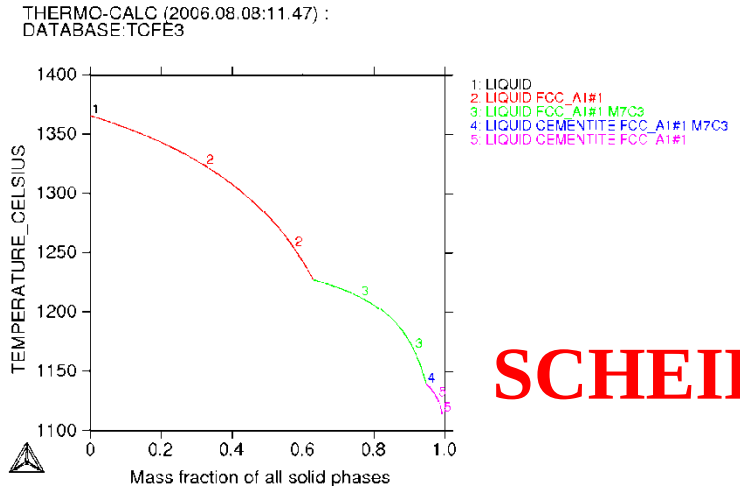
Single Pt Eqm



STEP



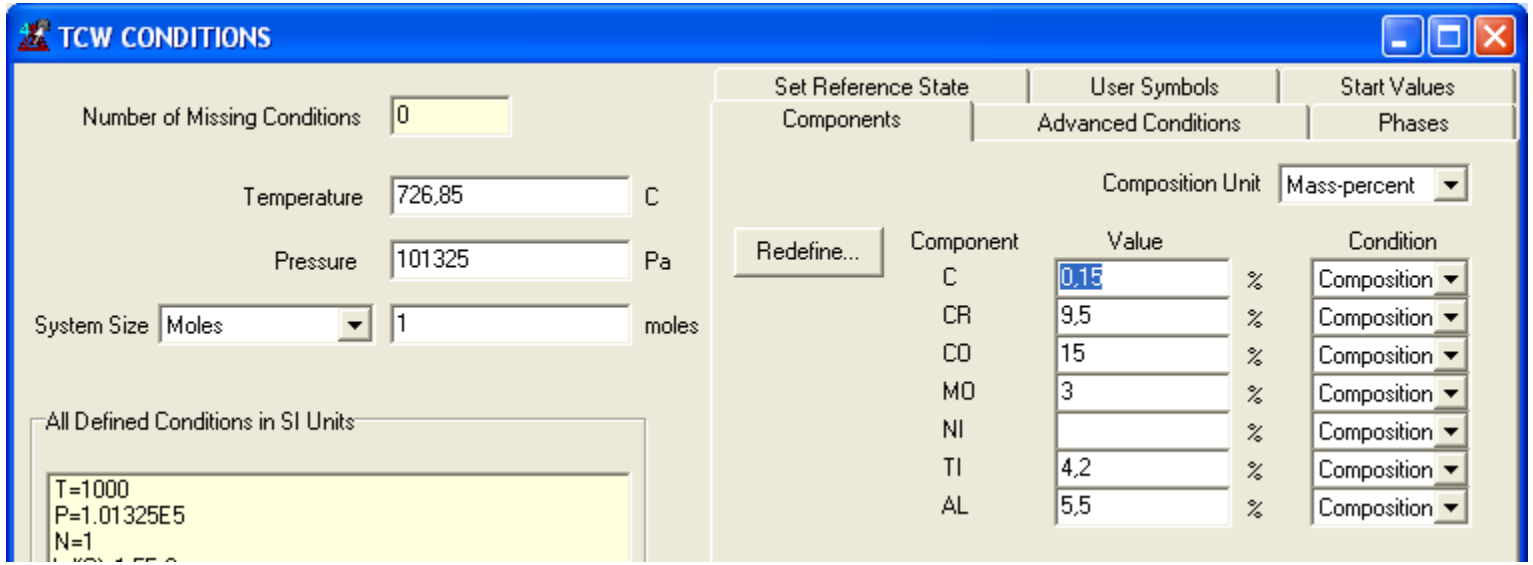
MAP



SCHEIL

Single point eqm calculation (i)

Thermo-Calc Software

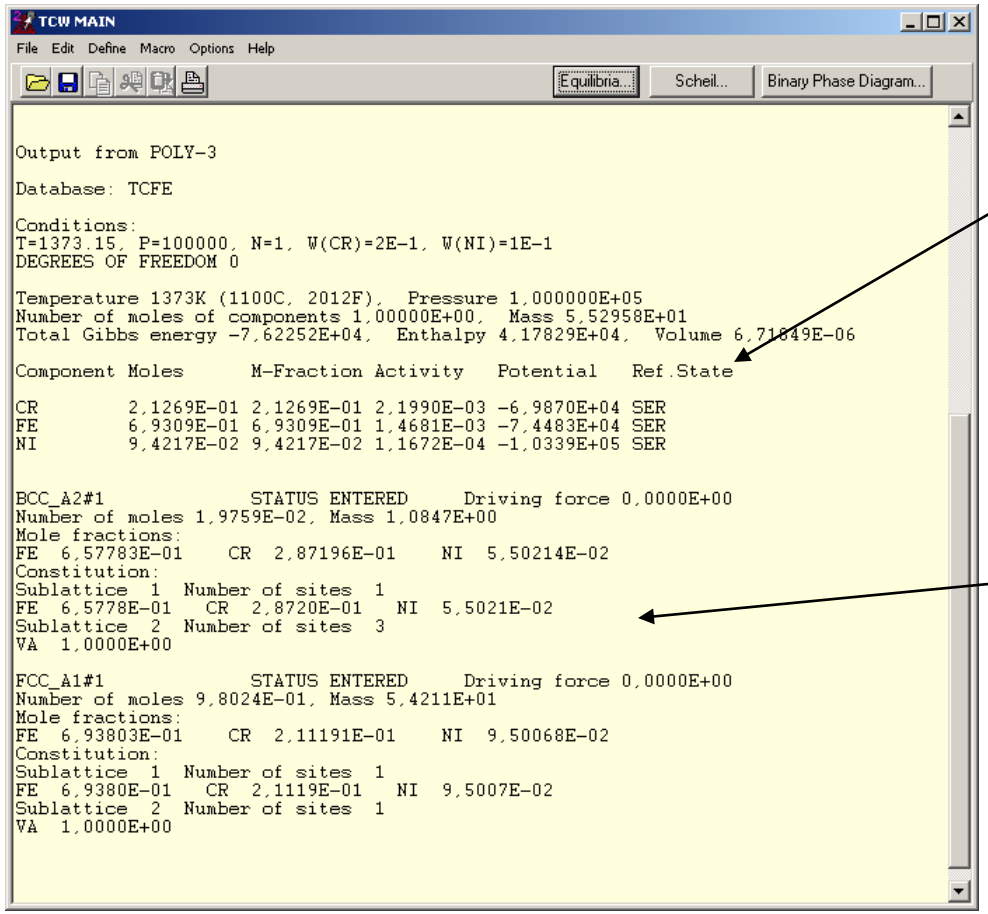


In Thermo-Calc it's possible to set many different conditions!

E.g. Composition, Temperature, Pressure, Chemical potential, Activity, Amount of phase, Enthalpy, and much more.

Single point eqm calculation (ii)

Thermo-Calc Software



Thermodynamic Properties:

Gibbs Energy

Enthalpy

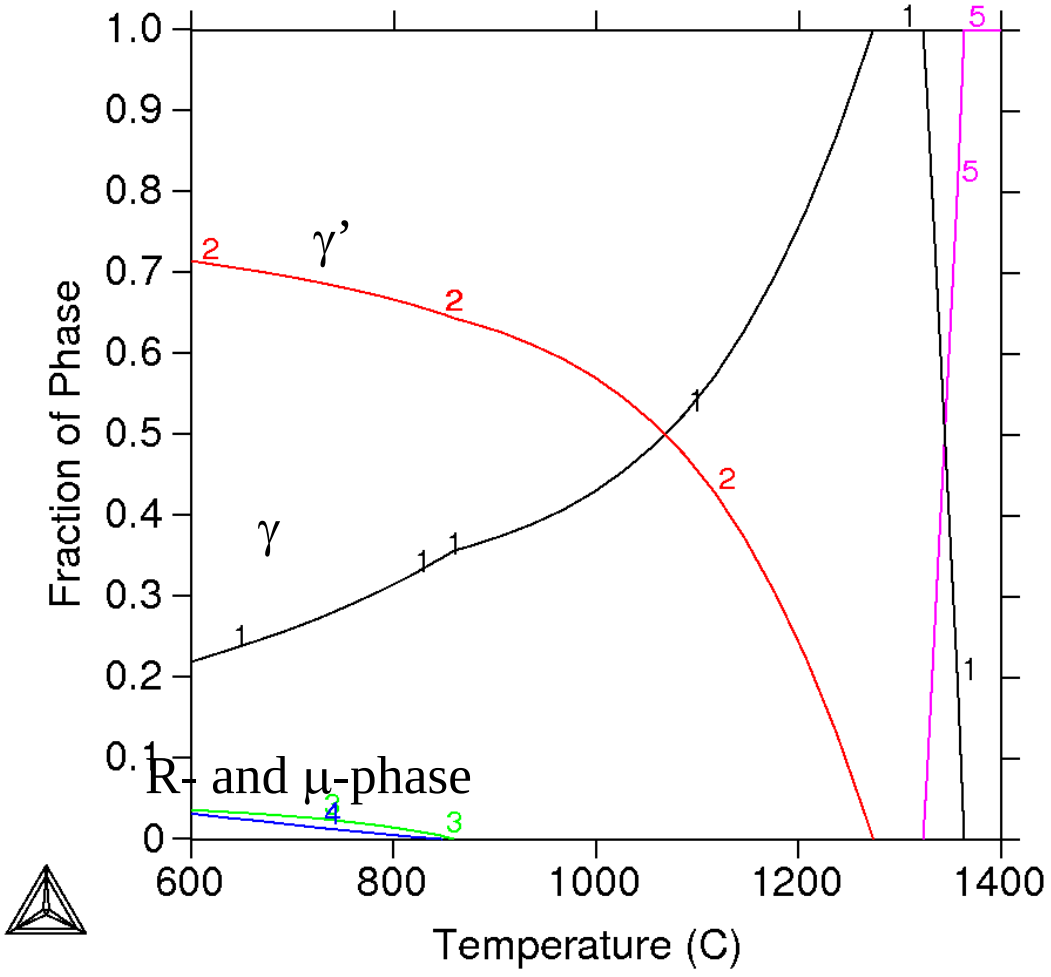
Activities

Phases:

Equilibrium amounts

Equilibrium compositions

Step Calculation (i)

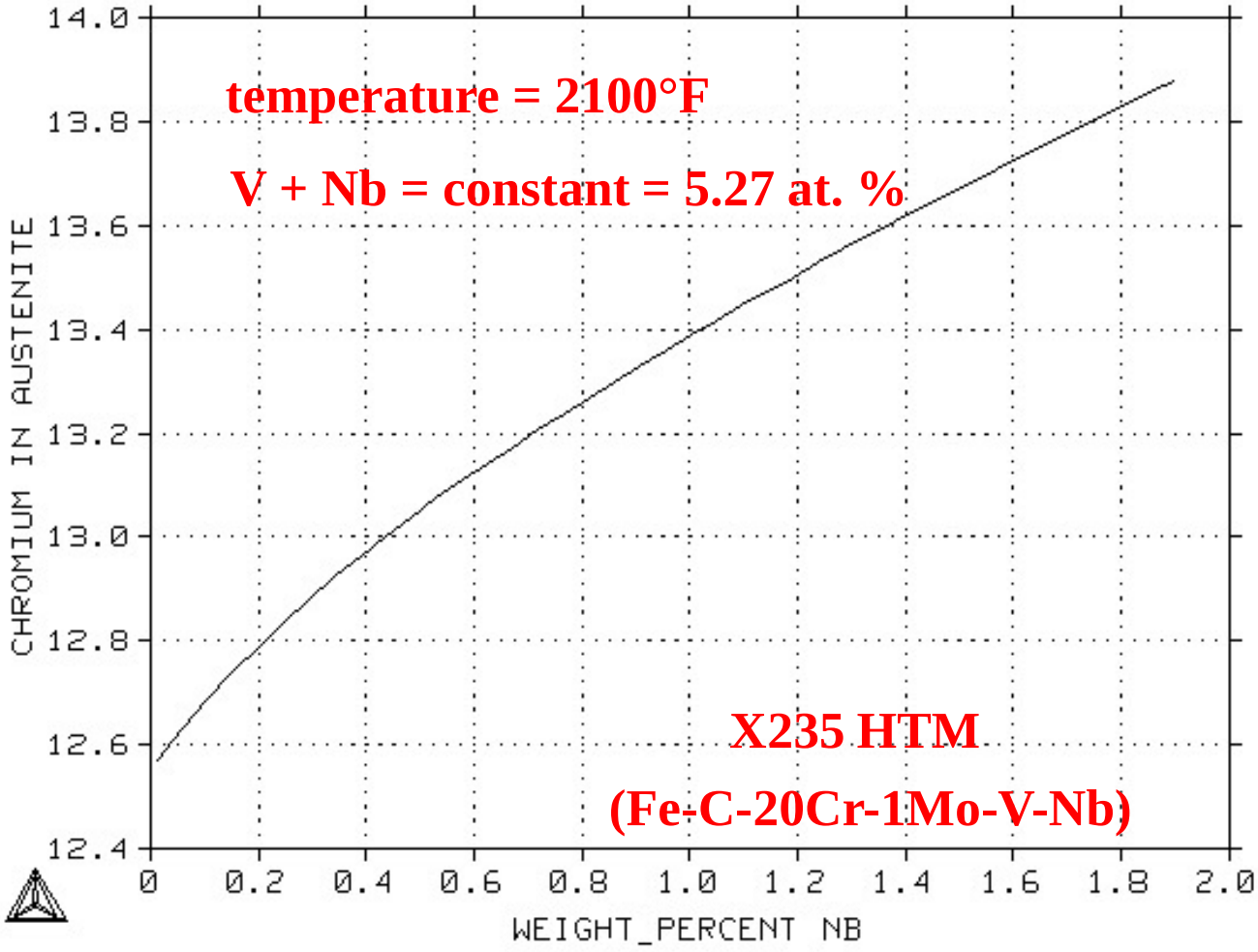


Plotting e.g.

- Chemical potentials
- Activities
- Phase compositions
- Phase fractions
- Thermodynamic quantities, such as e.g. G, H, S etc,
- Derivatives, e.g. Cp =dH/dT
- Driving forces
- Density, thermal expansion etc.
- User functions
- .....
- …

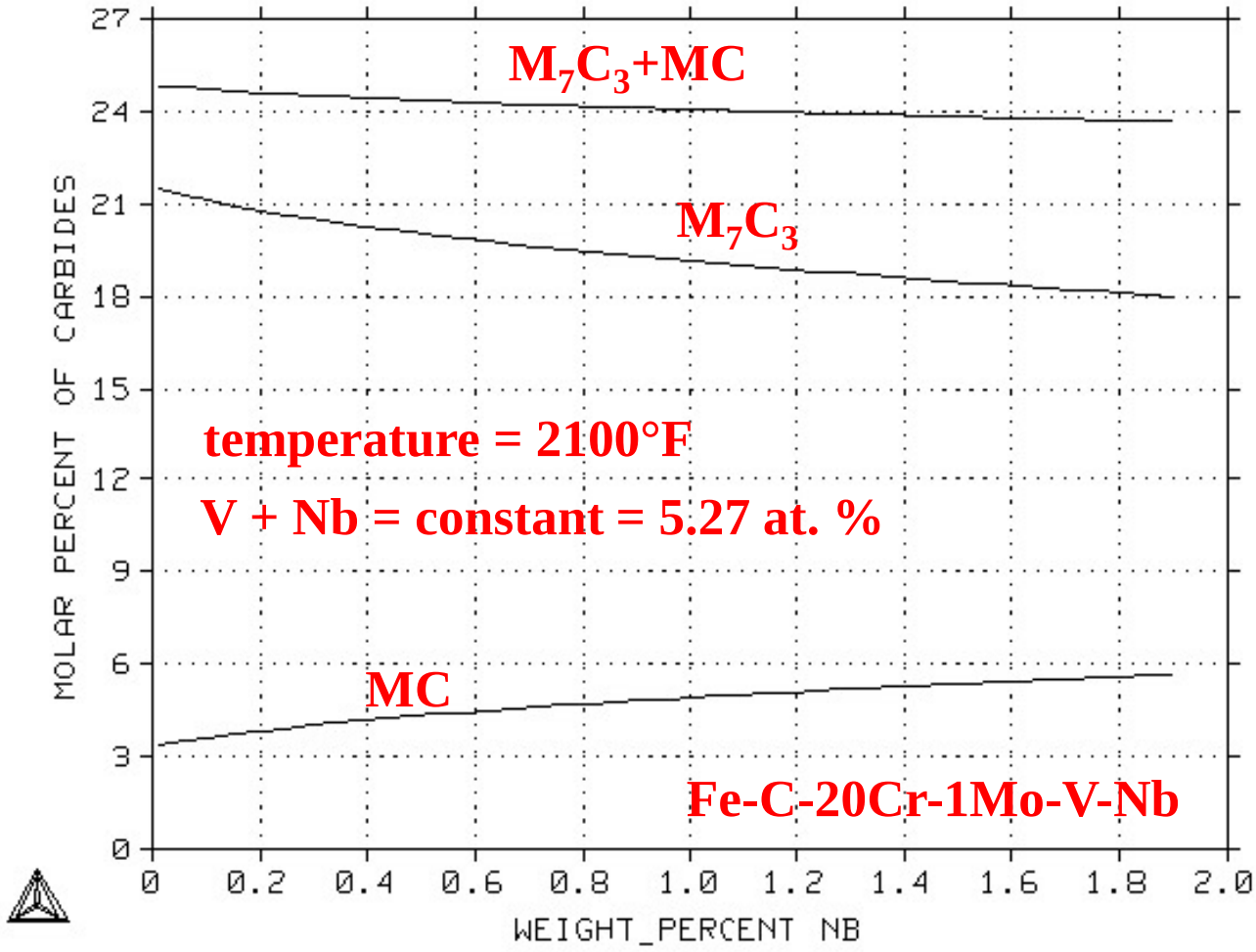
Step Calculation (ii)

Example provided by Alojz Kajinic, Crucible Research (ATI Powder).
Effect of substituting Nb for V



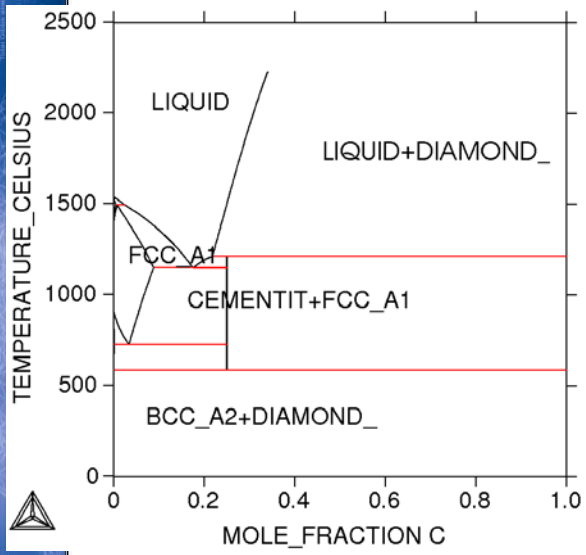
Step calculation (iii)

Example: Influence on carbide stability when replacing V with Nb

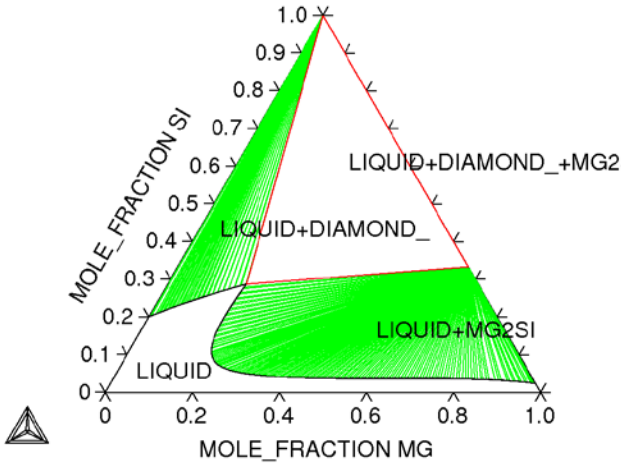


Map calculations

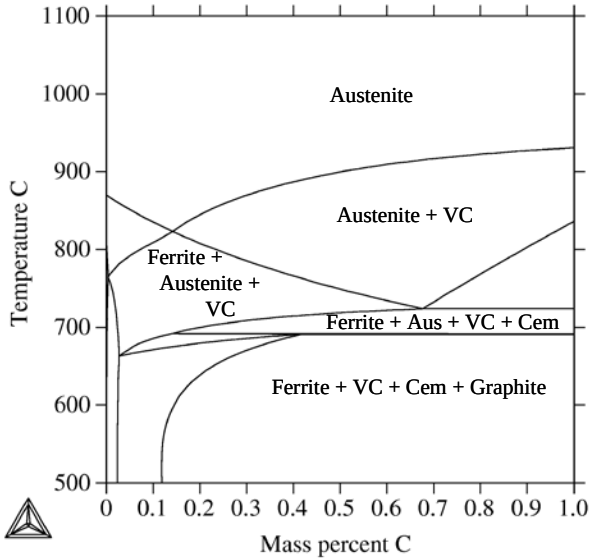
Thermo-Calc Software



Fe-C metastable binary

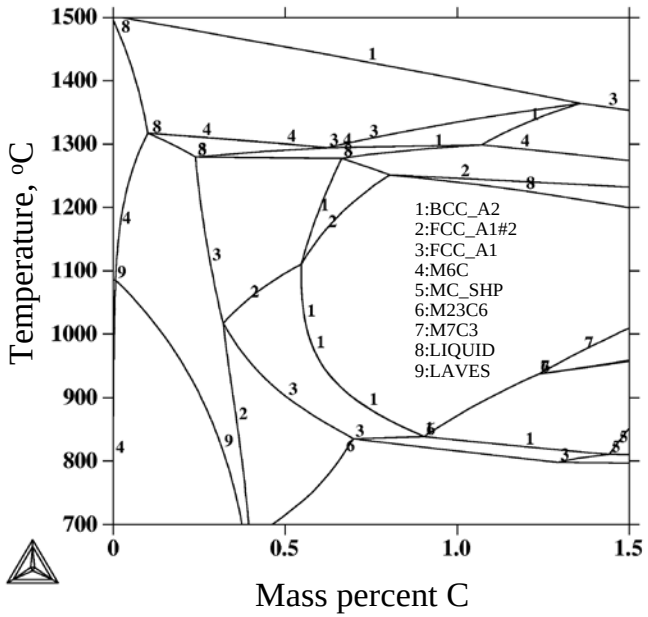


Al-Mg-Si ternary at 700 deg. C



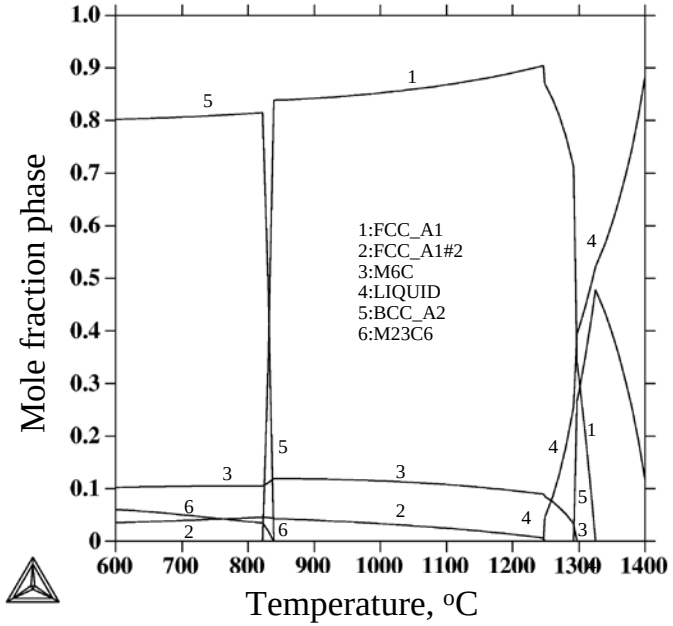
Fe-1.5Mn-0.3Si-0.1V-C HSLA Steel

Differences of map vs step



Phase diagram for a M42 high speed steel.

The lines represent where a phase appears or disappears, numbers show on which side of the line that phase is present. The alloy is Fe-4Cr-5Mo-8W-2V-0.3Mn-0.3Si-C(wt%).



Property diagram for a M42 high speed steel.

Shows how the fractions of the phases in the system vary with temperature. The alloy is Fe-4Cr- 5Mo-8W-2V-0.3Mn-0.3Si-0.9C.

Scheil calculations (i)

Equilibrium methods (lever-rule)
Solute diffusion is rapid, i.e. complete solute back diffusion → uniform composition in both solids and liquid

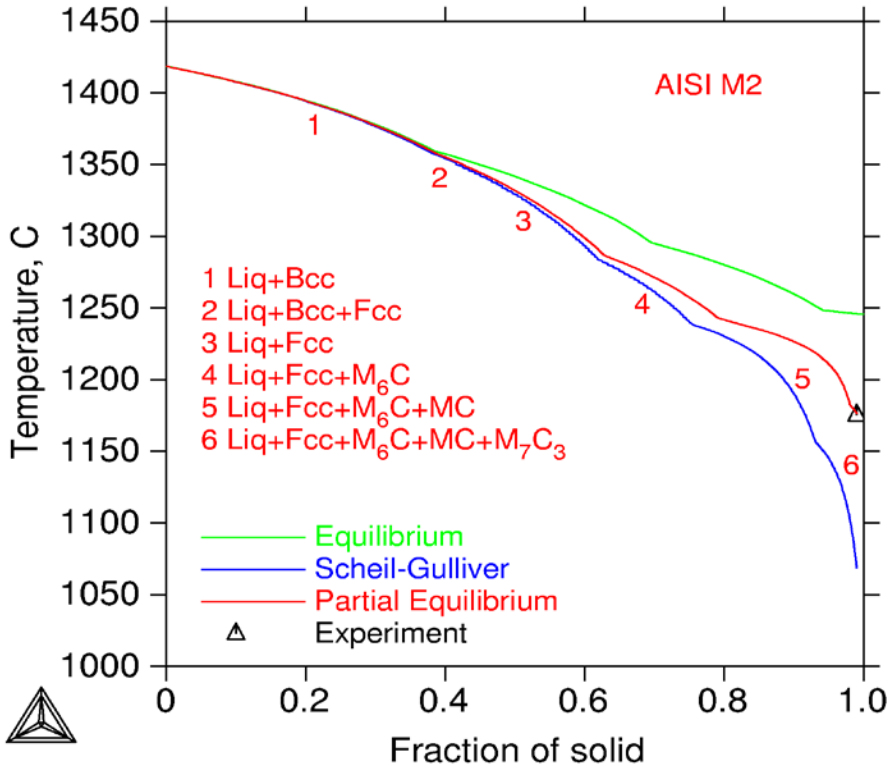
Non equilibrium methods (SCHEIL)
Negligible diffusion in solids, i.e. no solute back diffusion → solids retain same composition through solidification

Partial equilibrium methods (SCHEILC)
Complete interstitial but negligible substitutional solute back diffusion

Moving phase boundary methods (DICTRA)
Full integration of thermodynamics and kinetics

Scheil Calculations (ii)

Example: Solidification simulation showing fraction solid curve



Element	Mass%
Fe	Bal.
C	0.88
Si	0.3
Mn	0.32
Cr	3.9
Ni	0.36
Mo	4.9
Cu	0.1
Co	0.3
W	6.1
V	1.9

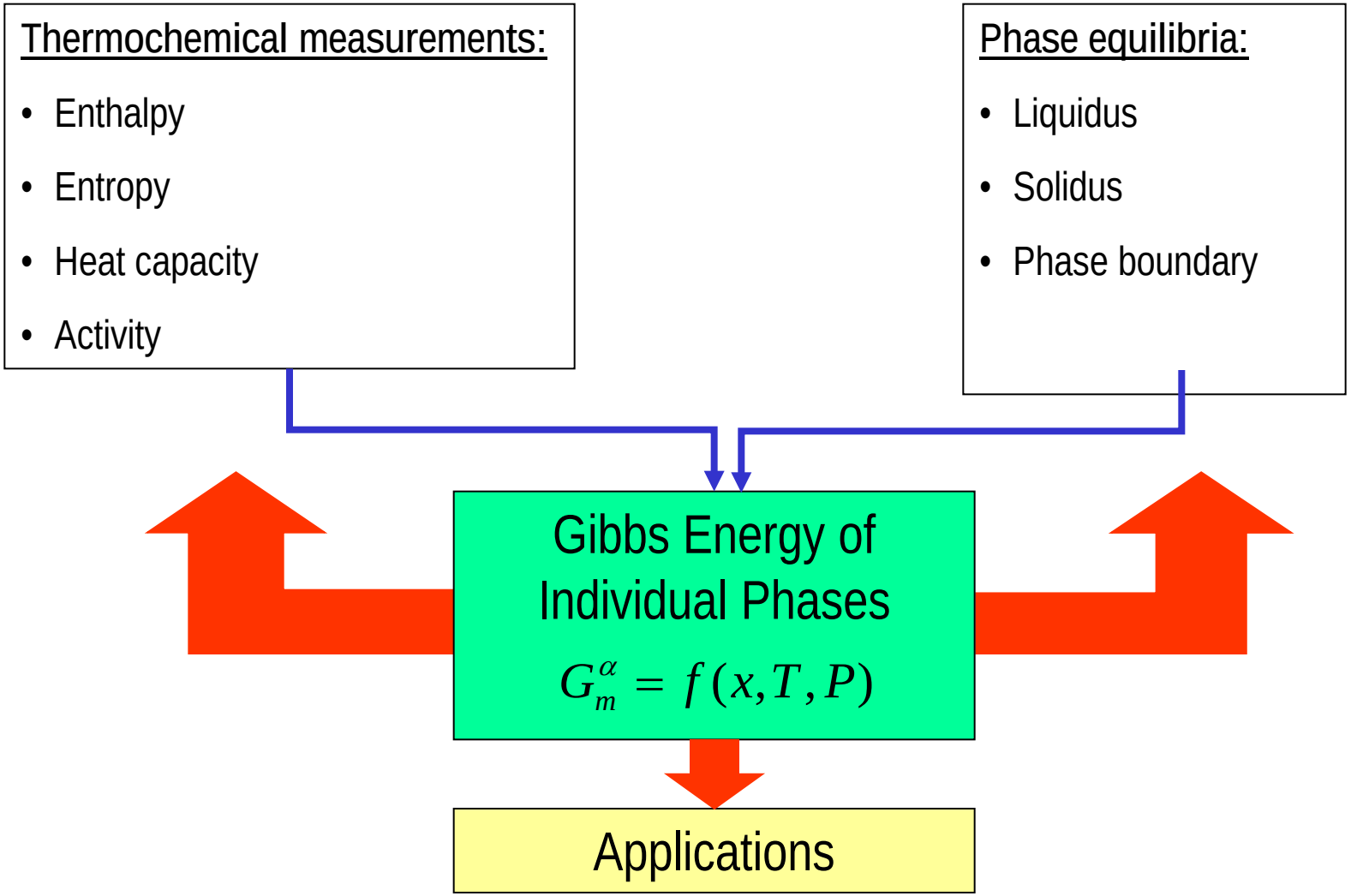
Q. Chen & B. Sundman, Materials Transactions, 43(3)551(2002).

Thermodynamic databases

A wide range of thermodynamic databases are available for:

- Steels and Fe-alloys
- Nickel-base superalloys
- Aluminium/Titanium/Magnesium-base alloys
- Gases, pure inorganic/organic substances, & general alloys
- Slag, metallic liquids, and molten salts
- Ceramic systems, and hard materials
- Semiconductors, and solder alloys
- Noble metal alloys
- Materials processing, process metallurgical & environmental aspects
- Aqueous solutions, materials corrosion & hydrometallurgical systems
- Minerals, and geochemical/environmental processes
- Nuclear materials, and nuclear fuel/waste processing

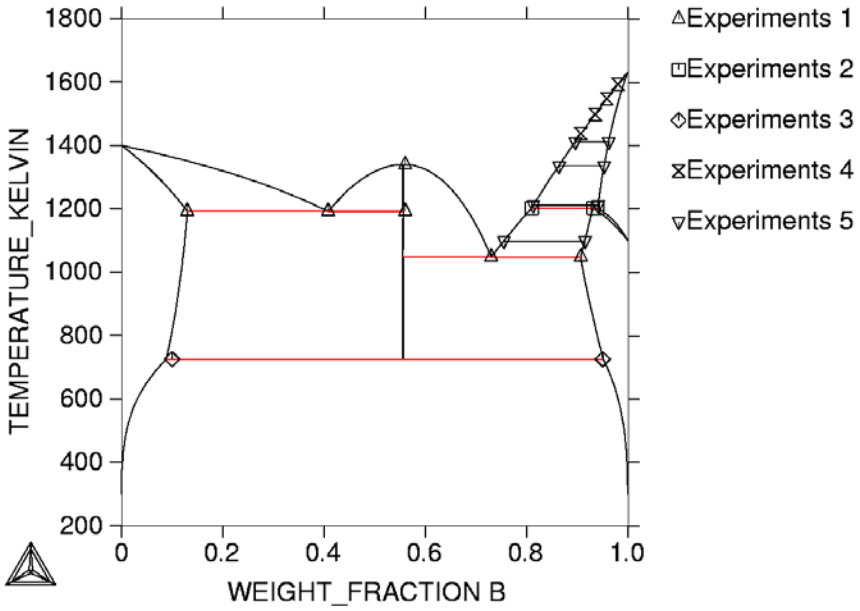
Database development (i)

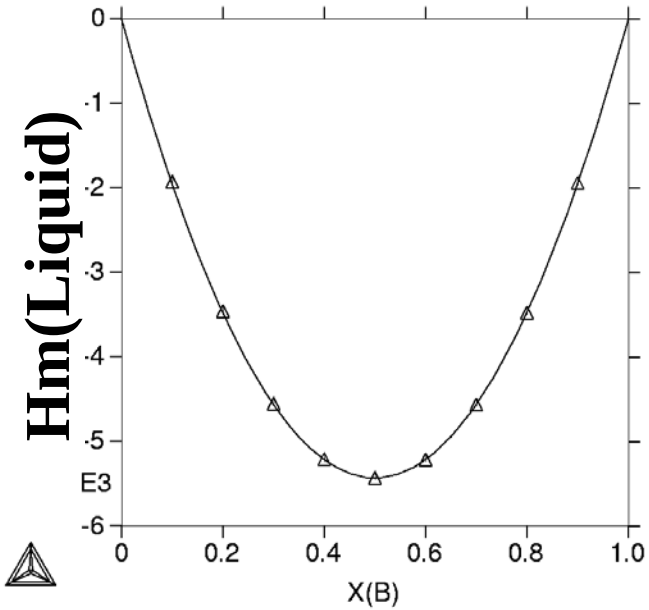


Database development (ii)

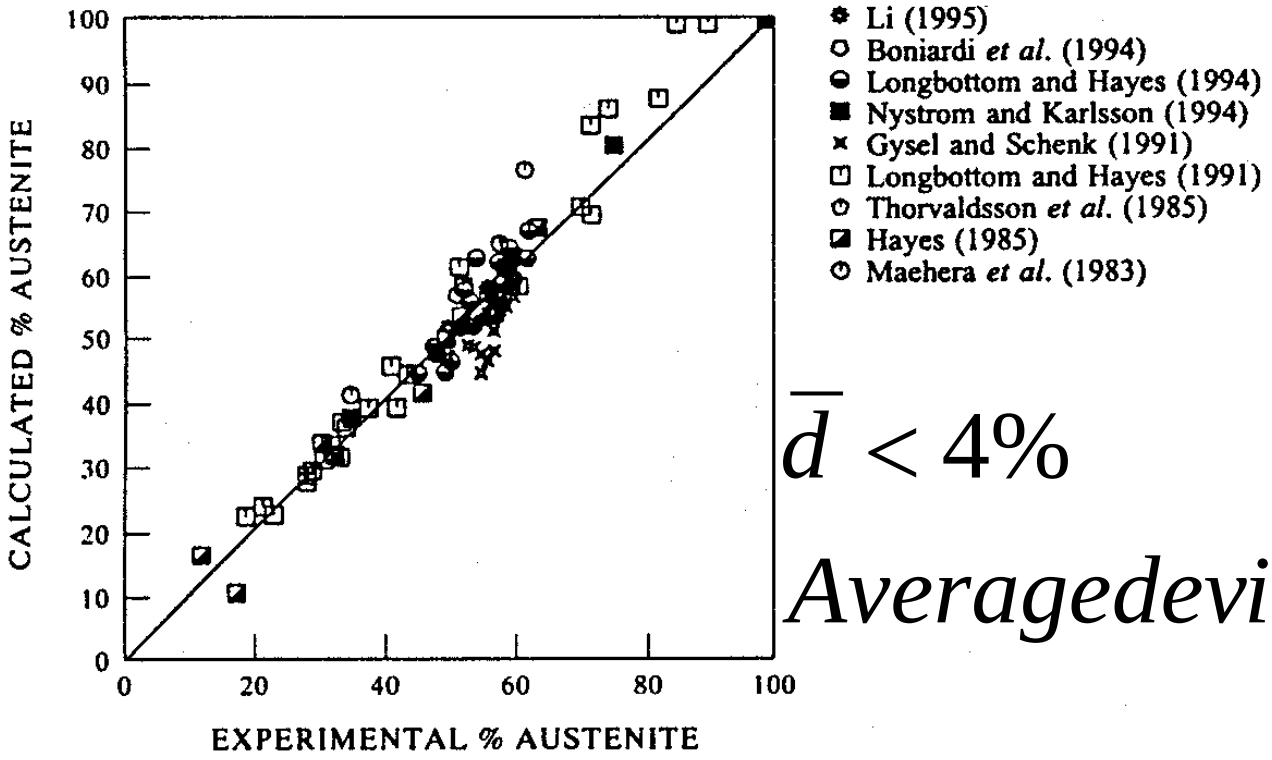
Thermo-Calc Software

- Normally collected from the literature
- Reliable data is selected and critically assessed
- Both phase diagram data or thermodynamic data ($\Delta H, C_p$...) can be used





Database development (iii)



$\overline{d} < 4\%$

Averagedeviation

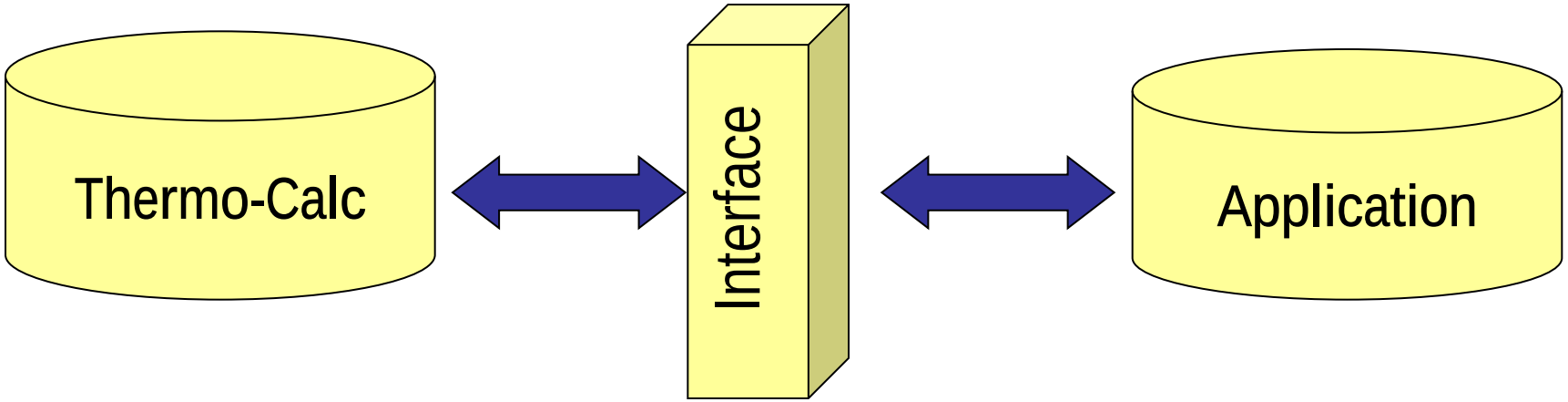
Figure 10.40 Comparison between calculated and experimentally observed % of austenite in duplex stainless steels. (Data from Longbottom and Hayes (1991) represent dual phase steels.).

From: Saunders & Miedownik: "Calphad -a comprehensive review"

Thermo-Calc programming interfaces

Application program interface

A prescribed set of subroutines, functions or classes by which a programmer writing an application program can make requests to Thermo-Calc.



Examples:

- Prediction of mechanical properties of hot rolled steels (SSAB)
- PrecipiCalc (QuesTek Innovations)
- Microstructure modelling – Phase Field Method (ACCESS e.V.)
  - Peritectic solidification in steels
  - Precipitation of γ'
  - α/β transformation in Ti64

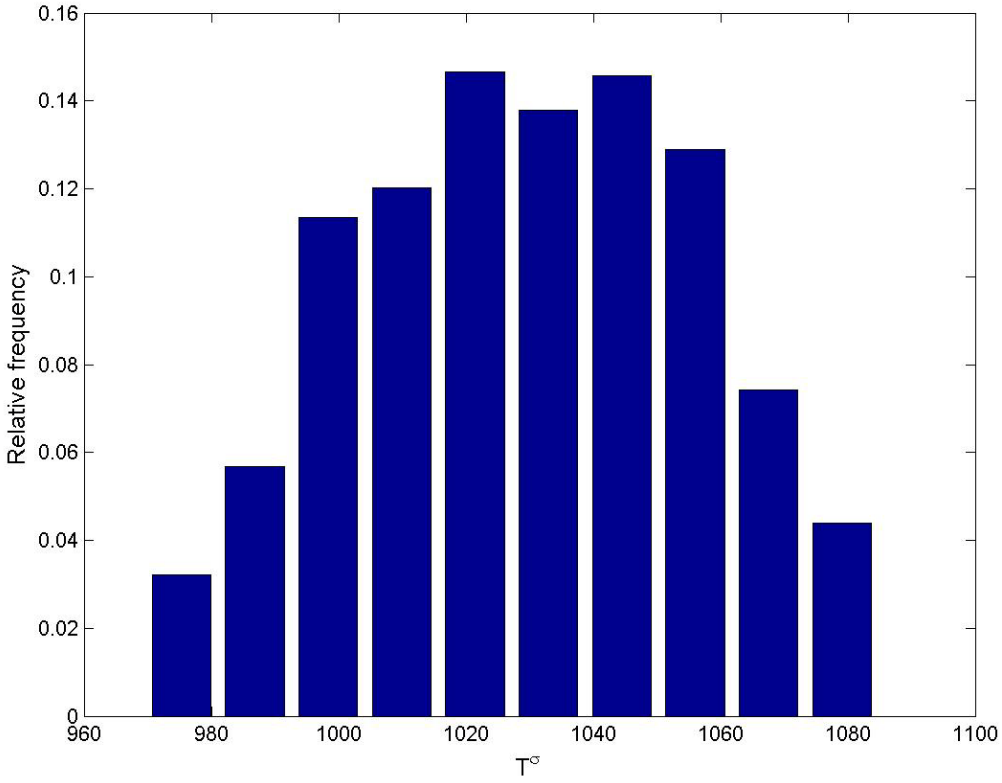
Calculation of tendency to form sigma phase: SAF 2507

Nominal composition:

Fe – 25% Cr – 7% Ni – 4% Mo – 0.27% N – 0.02% C

Predict the temperature when sigma-phase becomes stable within some composition variation:

Fe	Base
Cr	23 – 27%
Ni	6 – 8%
Mo	3 – 5%
N	0.25 – 0.29%
C	0 – 0.03%



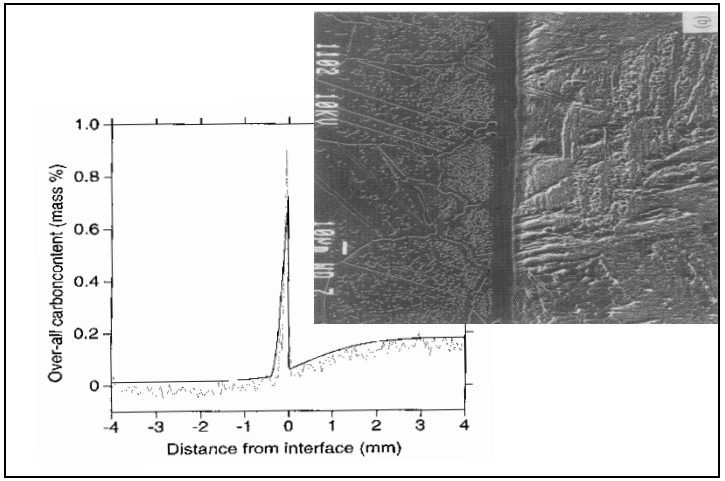
DICTRA (i)

A general software package for simulation of DIffusion Controlled TRAnsformations in multi component alloys.

The result of more than 20 years and 60 man-years R&D at:

- Royal Institute of Technology (KTH) in Stockholm, Sweden
- Max-Planck Institute für Eisenforschung in Düsseldorf, Germany

Example: Interdiffusion in compound

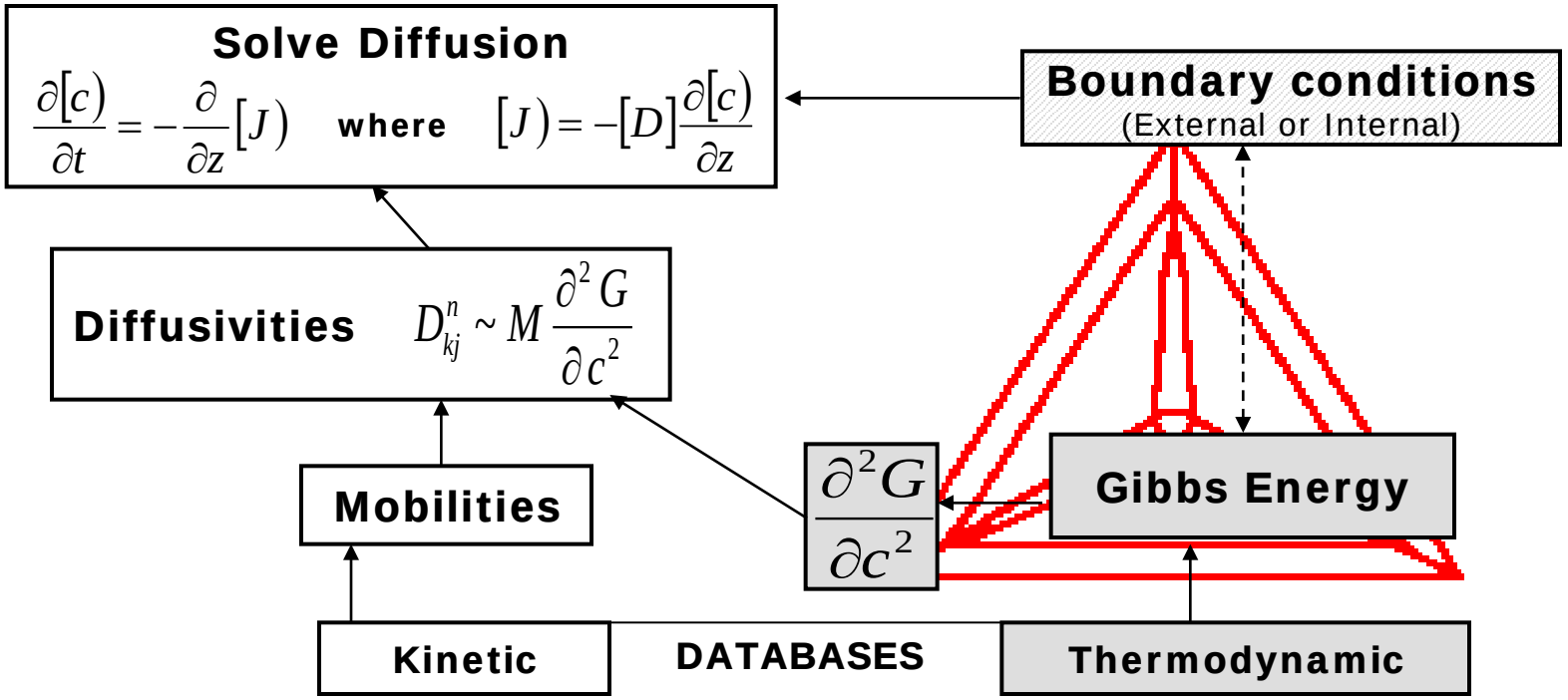


Emphasis has been placed on linking fundamental methods to critically assessed thermodynamic and kinetic data, allowing simulations and predictions to be performed with realistic conditions on alloys of practical importance.

Helander et al., ISIJ Int. 37(1997), pp. 1139-45

DICTRA (ii)

All simulations depend on assessed kinetic and thermodynamic data which are supplied in databases.



A numerical finite difference scheme is used for solving a system of coupled parabolic partial differential equations.

Mobility databases

Mobility databases available for use with DICTRA:

- MOBFE1- Steels and Fe-alloys
(compatible with TCFE6)

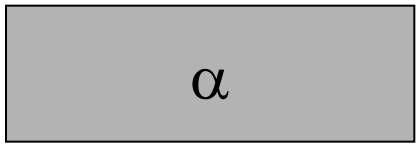
- MOB2 - Steels and Fe-alloys
(compatible with TCFE5, SSOL4)

- MOBNI1 - Nickel-base superalloys
(compatible with Thermotech Ni-data Ver 8)

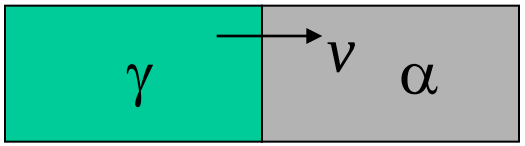
- MOBAl1 – Aluminium
(Compatible with Thermotech Al-data Ver 7)

Types of DICTRA calculations

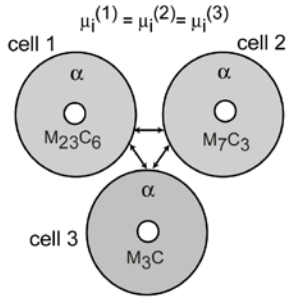
Single phase



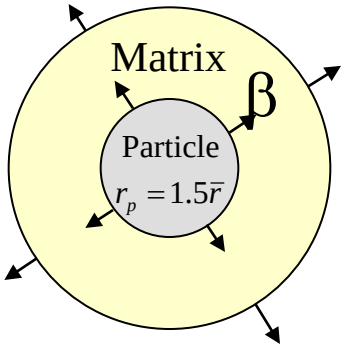
Moving boundary



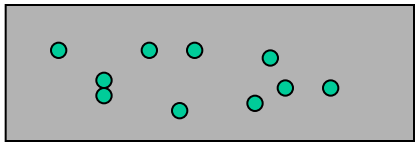
Cell



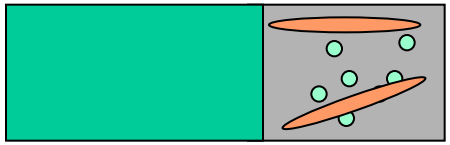
Coarsening



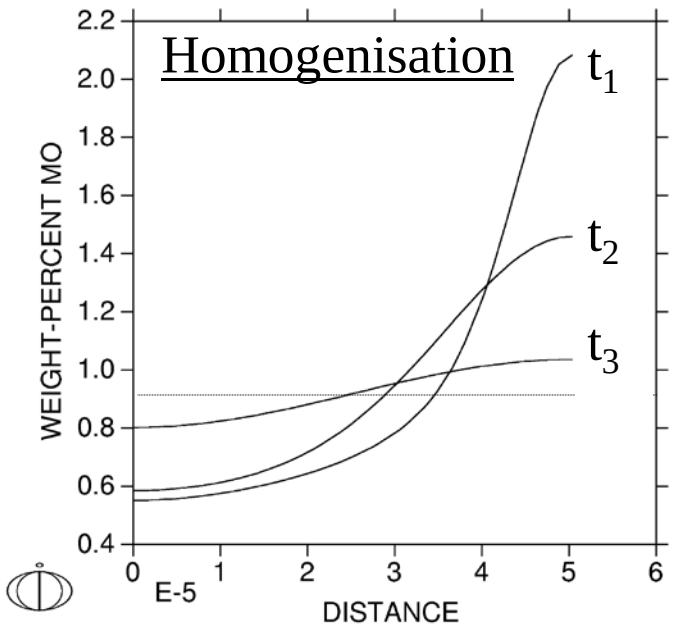
Disperse system

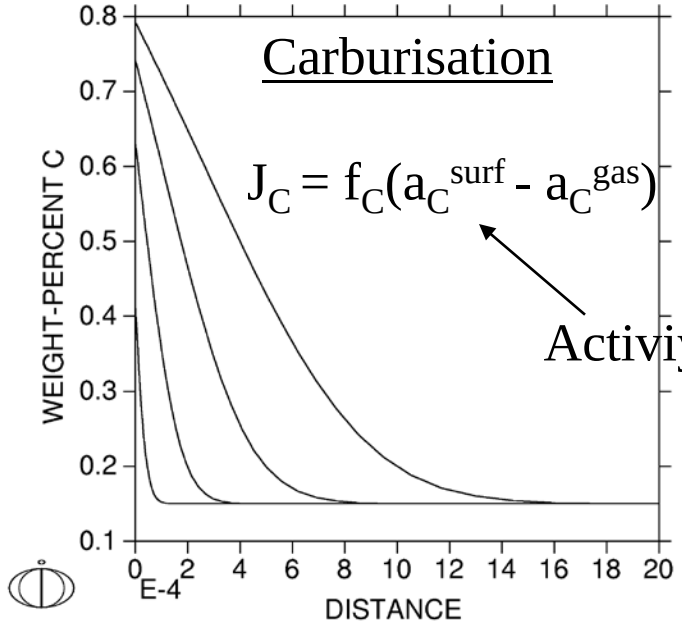


Homogenization



Straight-forward non-complex simulations, usually on homogenisation or carburisation treatments





Boundary conditions can be specified as functions of time, temperature and pressure.

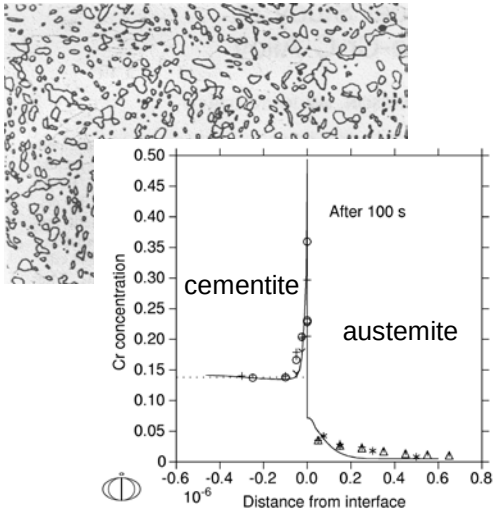
Different functions may be used in different time intervals.

Diffusion with moving interfaces

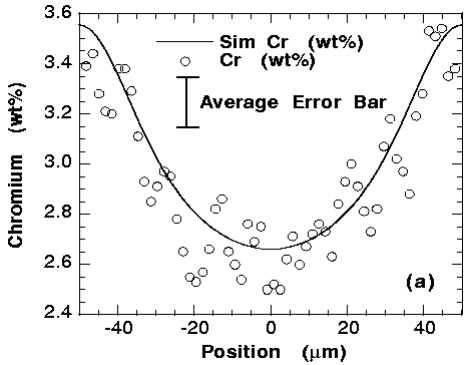
Thermo-Calc Software

- γ to α transformations in steel
- Growth or dissolution of carbides
- Microsegregation during solidification
- Nitriding of steels
- Nitrocarburising of steels
- s-phase precipitation in stainless steels
- Transient Liquid-Phase bonding of alloys
- Sintering of cemented carbides
- *and much more …*

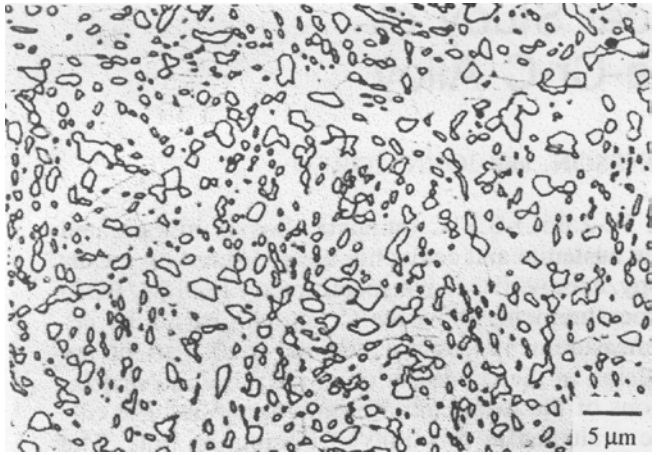
Carbide dissolution

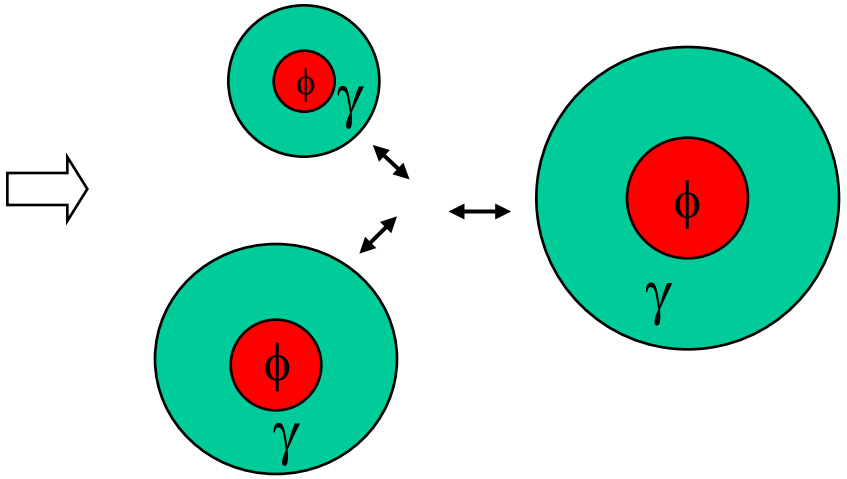


Microsegregation during solidification



Cell calculations





- Growth or dissolution of particle distributions
- Competing growth or dissolution
- Interdiffusion across an immobile interface

Conditions for cell boundaries:

✓ Equal diffusion potentials Φ_i for the elements

$$\Phi_i = \mu_i - \mu_n$$ for subst. elements

$$\Phi_i = \mu_i$$ for interstitial elements

✓ Flux balances to conserve the mass of the elements

$$\frac{J_i^{cell\#1}}{n^{cell\#1}} = \frac{J_i^{cell\#2}}{n^{cell\#2}}$$ n, cell distribution factors

Coarsening or Oswald ripening

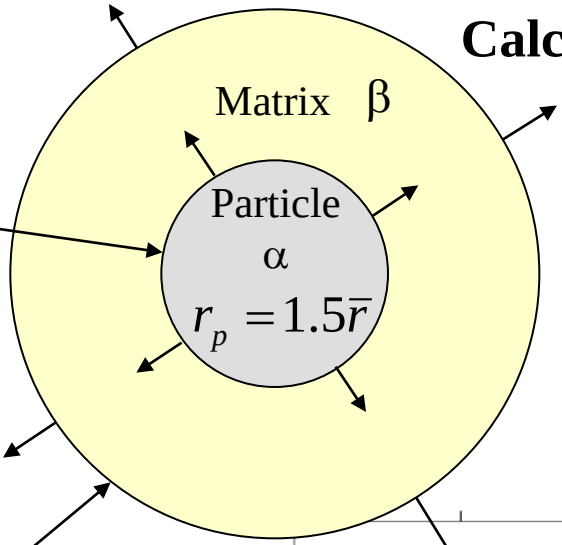
Thermo-Calc Software

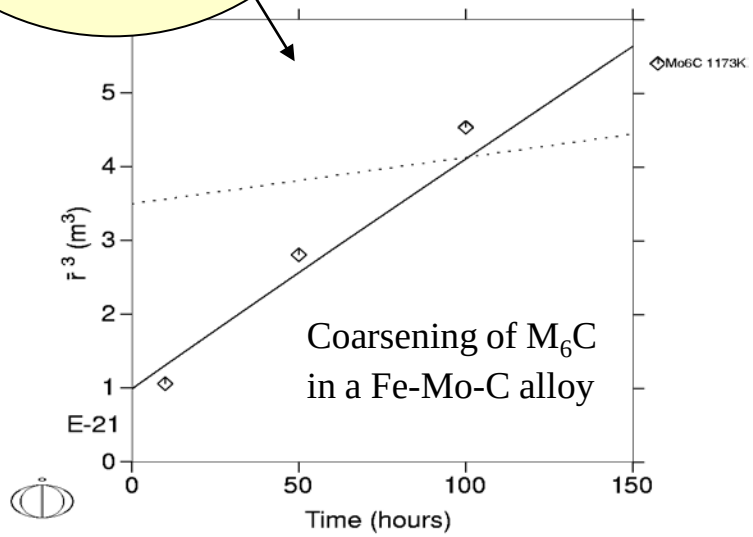
Moving phase interface with α and β in local equilibrium.

$\frac{2\sigma V_m}{r_p}$ Interfacial energy contribution added to the α phase.

Equilibrium as defined by the average composition in the system.

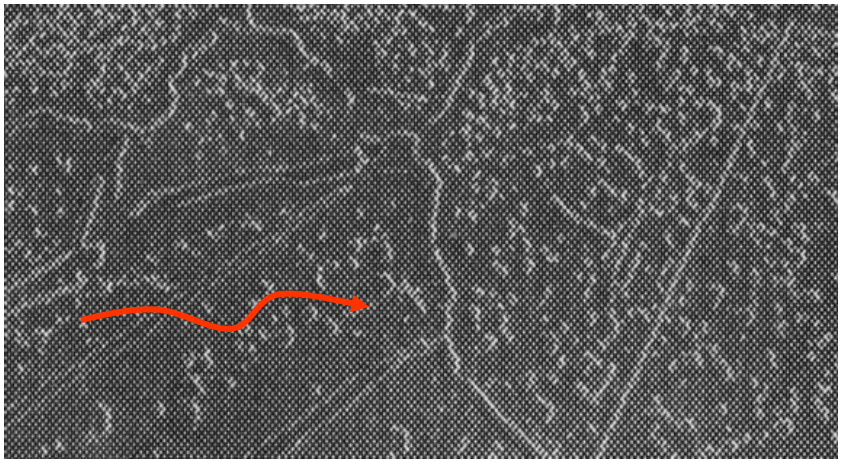
$\frac{2\sigma V_m}{\bar{r}}$ Interfacial energy contribution added to the α phase.

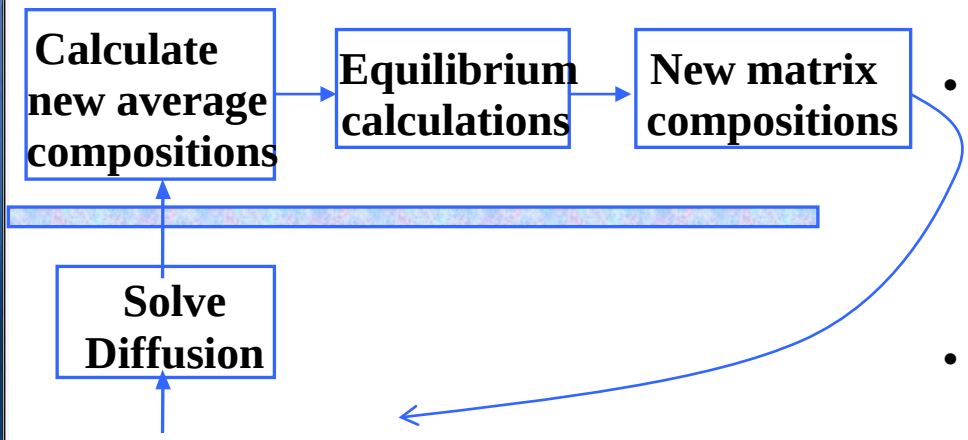




Assumptions:

- Diffusion takes place in the matrix phase only.
- Equilibrium holds locally in each node.



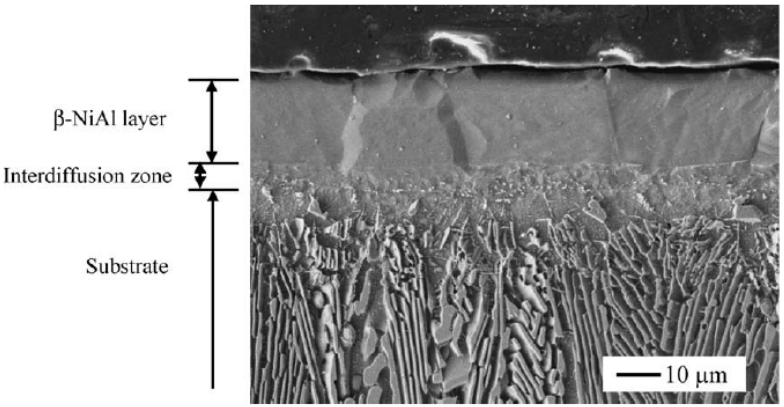


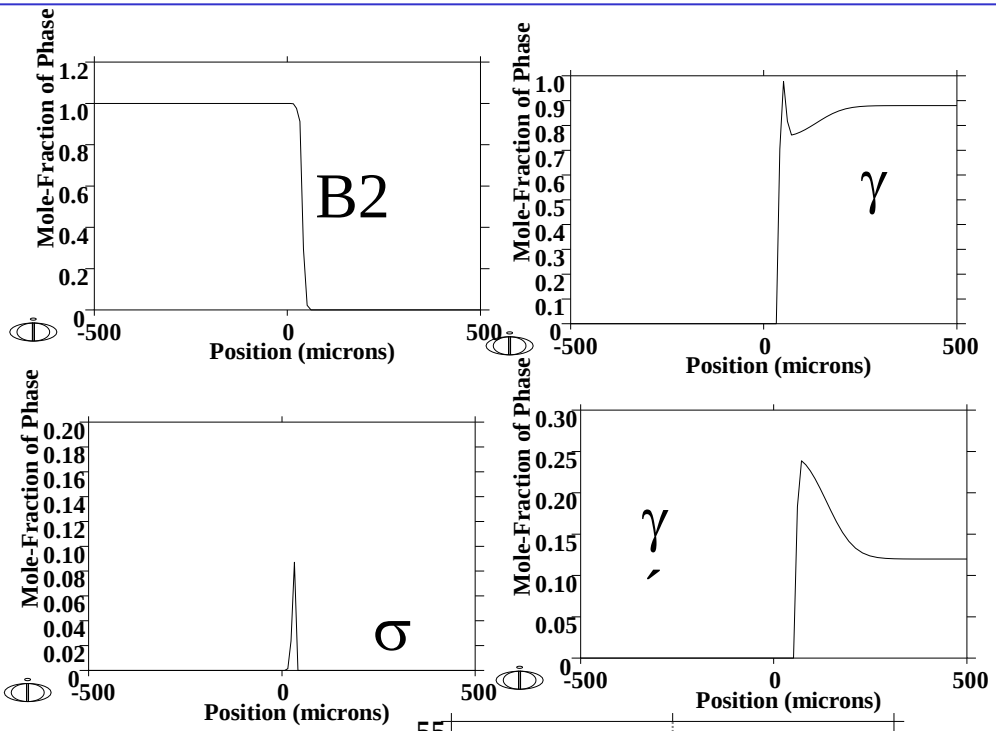
- Carburisation of high-temperature alloys
- Interdiffusion in composite materials
  - coating/substrate systems
  - weldments between steels
  - joints of dissimilar steels
- Gradient sintering of cemented carbide work-tool pices

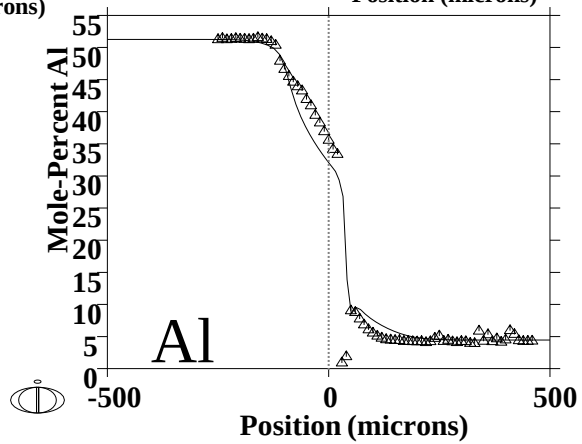
Homogenization model

Thermo-Calc Software

Coating degradation due to interdiffusion





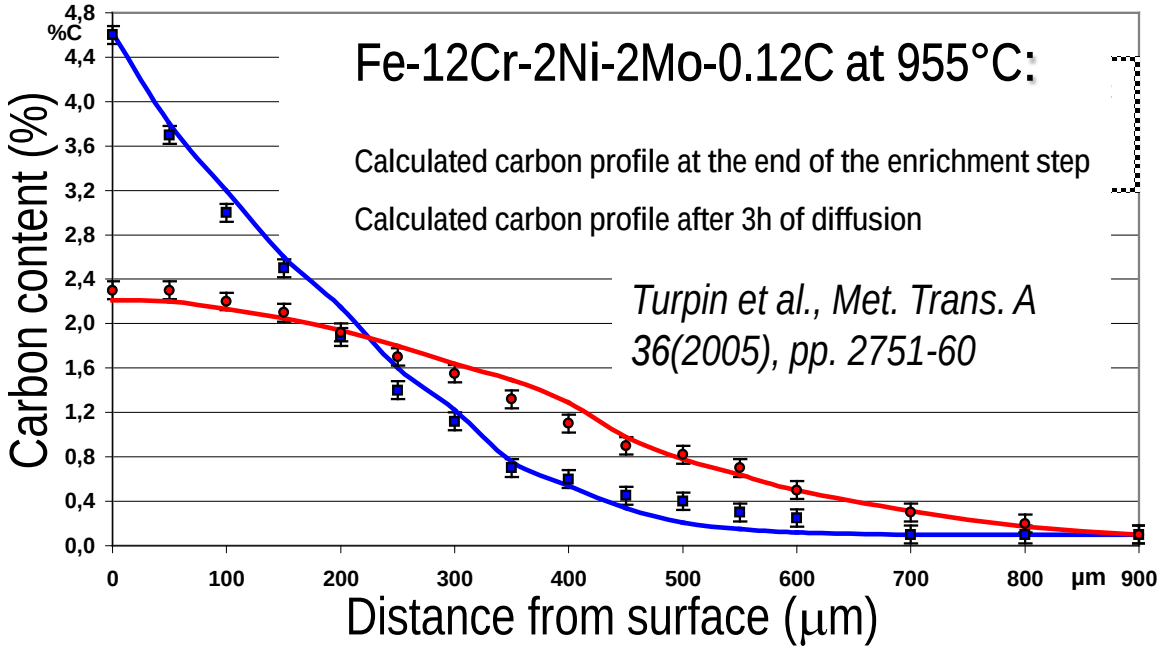


- Complex problem involving solving multicomponent diffusion problem in multiphase region.
  Coating – Ordered BCC_B2, Substrate – Ordered FCC_L12
  Interdiffusion zone – Can form phases like mu and sigma
- Need for multicomponent kinetic data in β-NiAl, γ and γ'

Industrial type applications

Thermo-Calc Software

Example: Simulation of carbon evolution in high alloyed steels by Aubert & Duval, France.



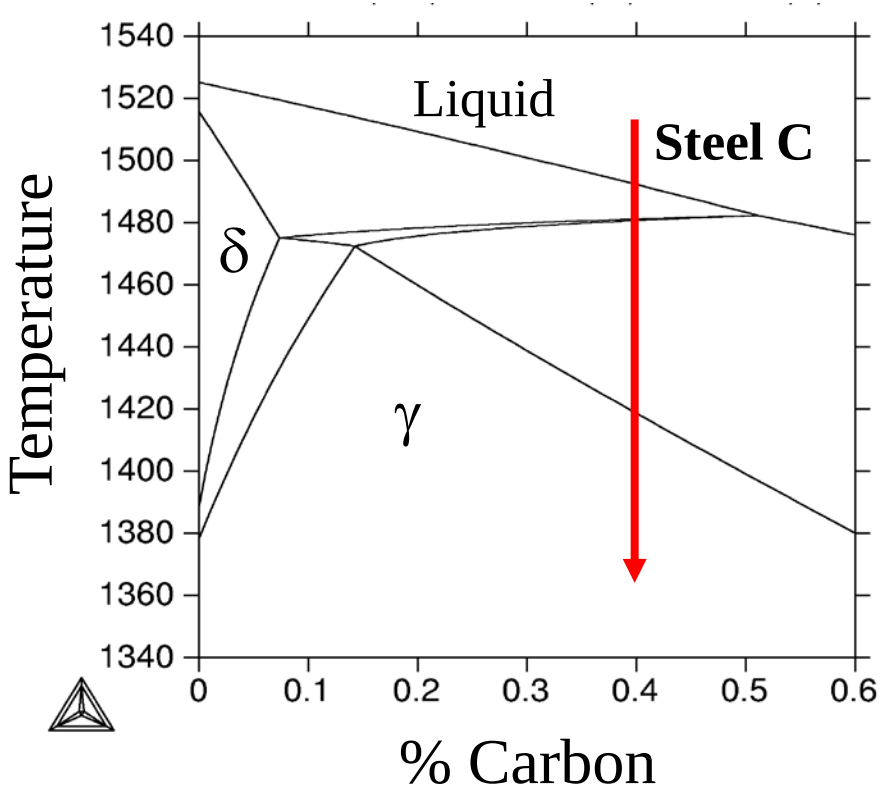
Outline

- Introduction to Thermo-Calc and DICTRA
- **Examples related to ingot metallurgy**:
  - **Peak shifting of phosphorous during solidification**
  - Homogenizing a Ni-based superalloy
- Questions

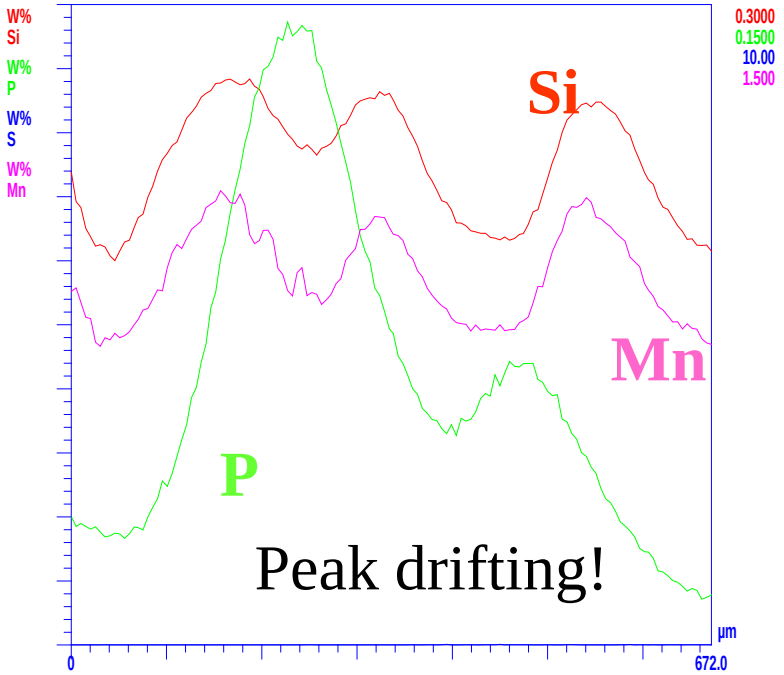
Observed micro-segregation in Steel C

Steel C:

Fe - 0.8% Mn – 0.7%Si – 0.03%P – 0.4% C

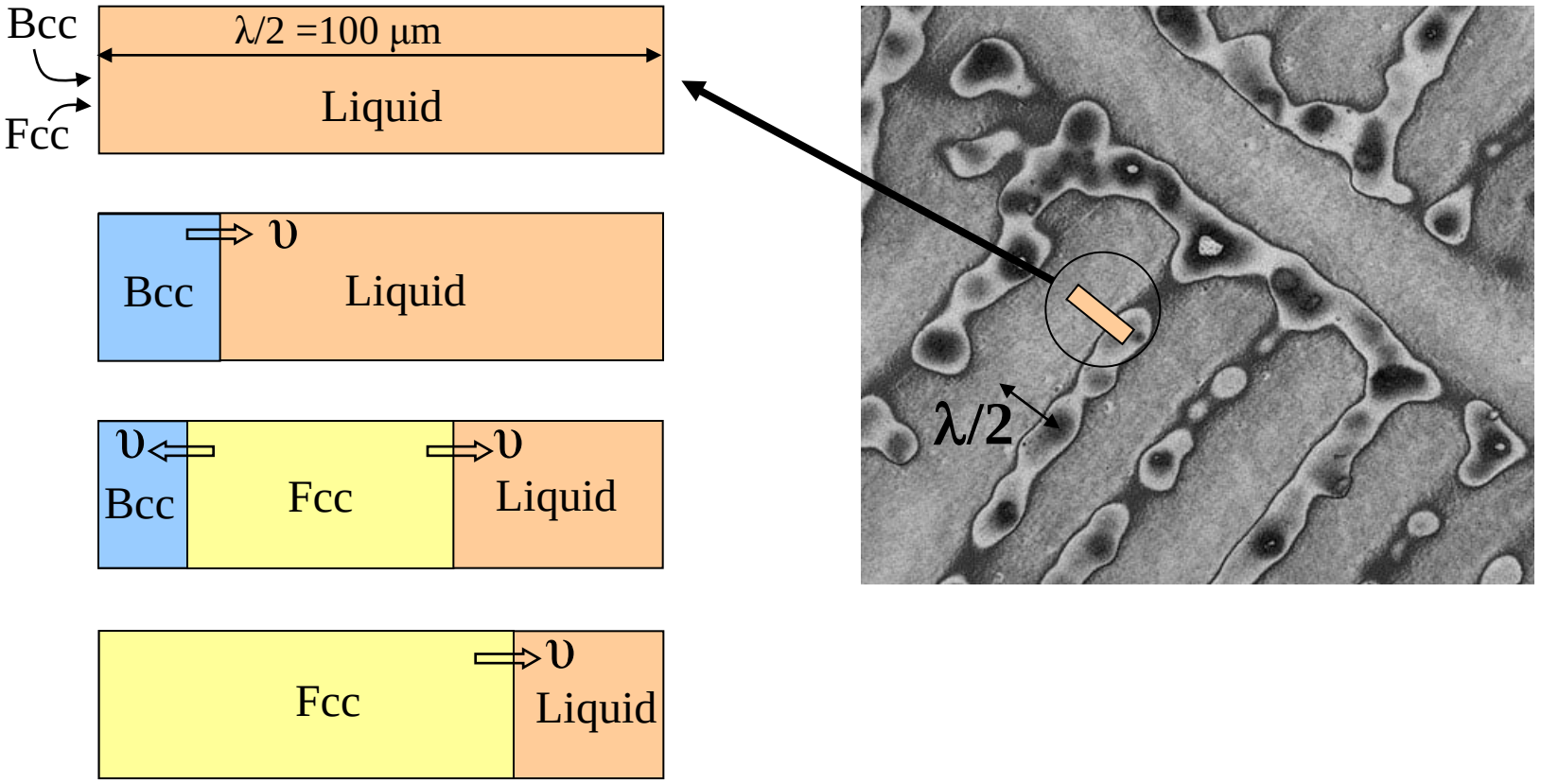


Line-scans across the dendrite arms (performed by Corus-UK)

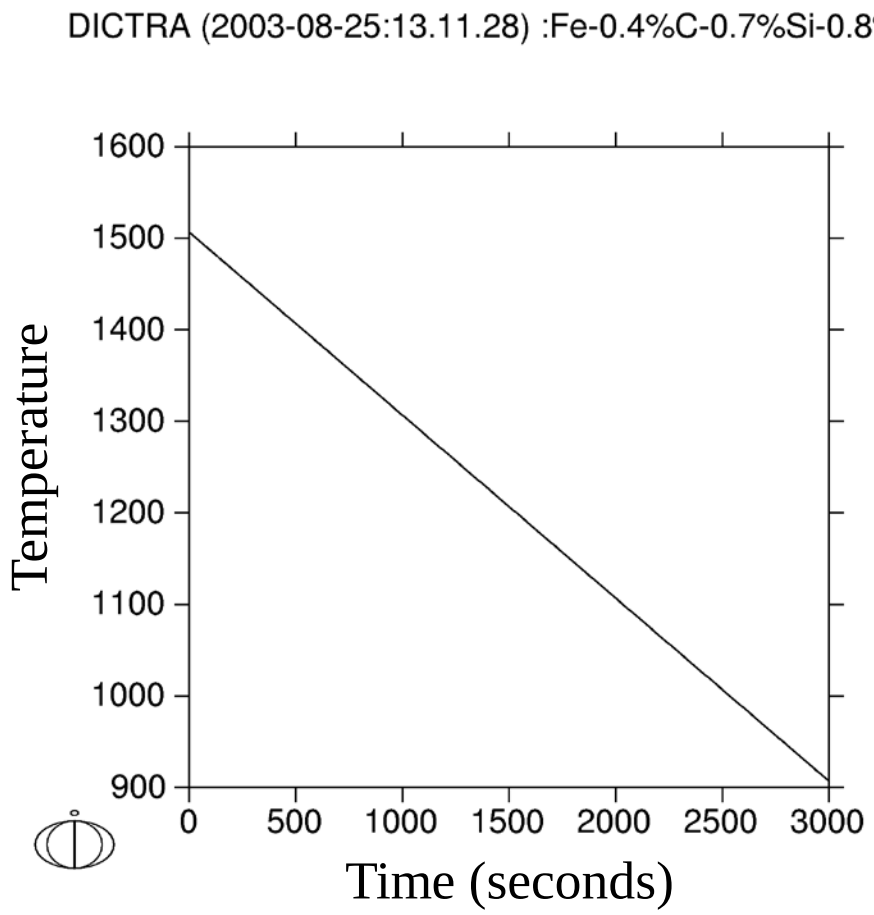


Question: Why does the P peak drift away from the Mn and Si peaks?

Analysis using DICTRA



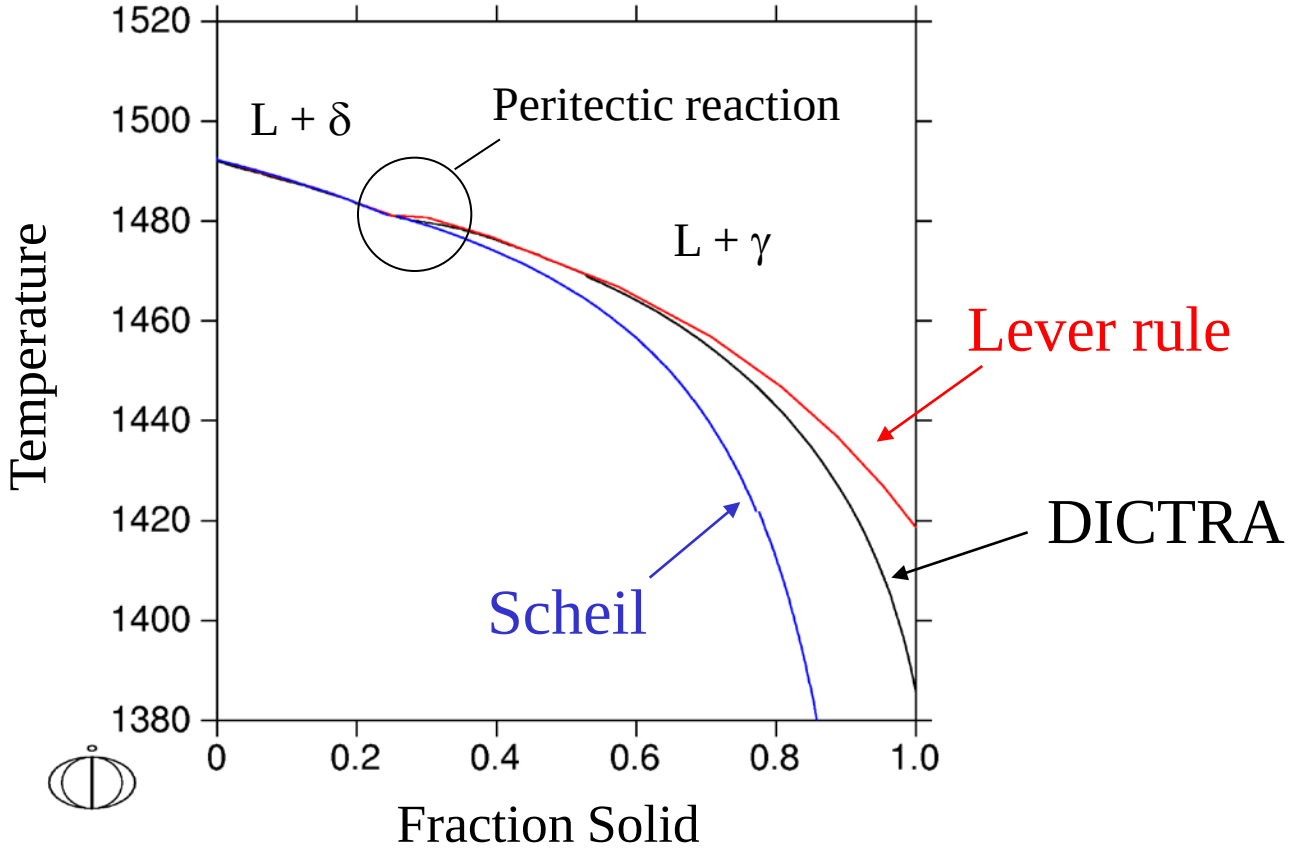
- Secondary dendrite arm spacing assumed to be 200 μm.



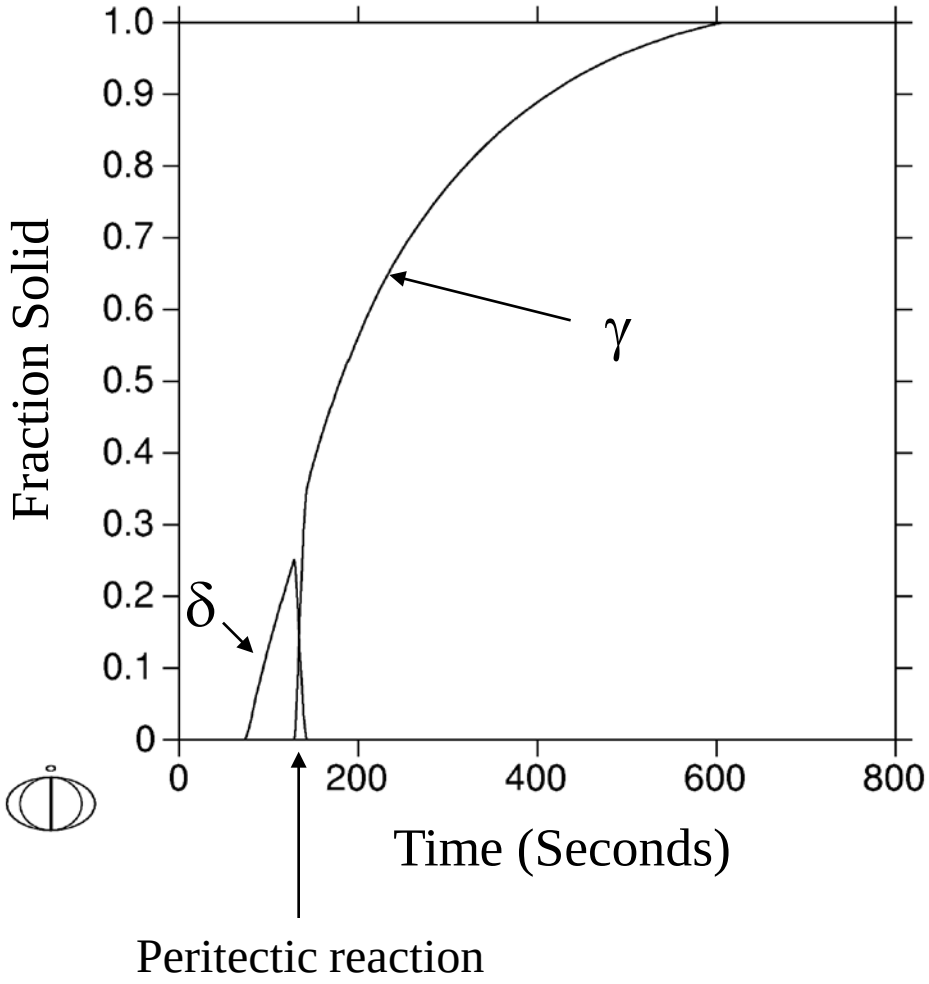
Cooling rate assumed to be 0.2 ºC/s

- More advanced cooling functions may of course also be imposed.
- Also possible to instead define a condition on the rate of latent heat removal from the system.

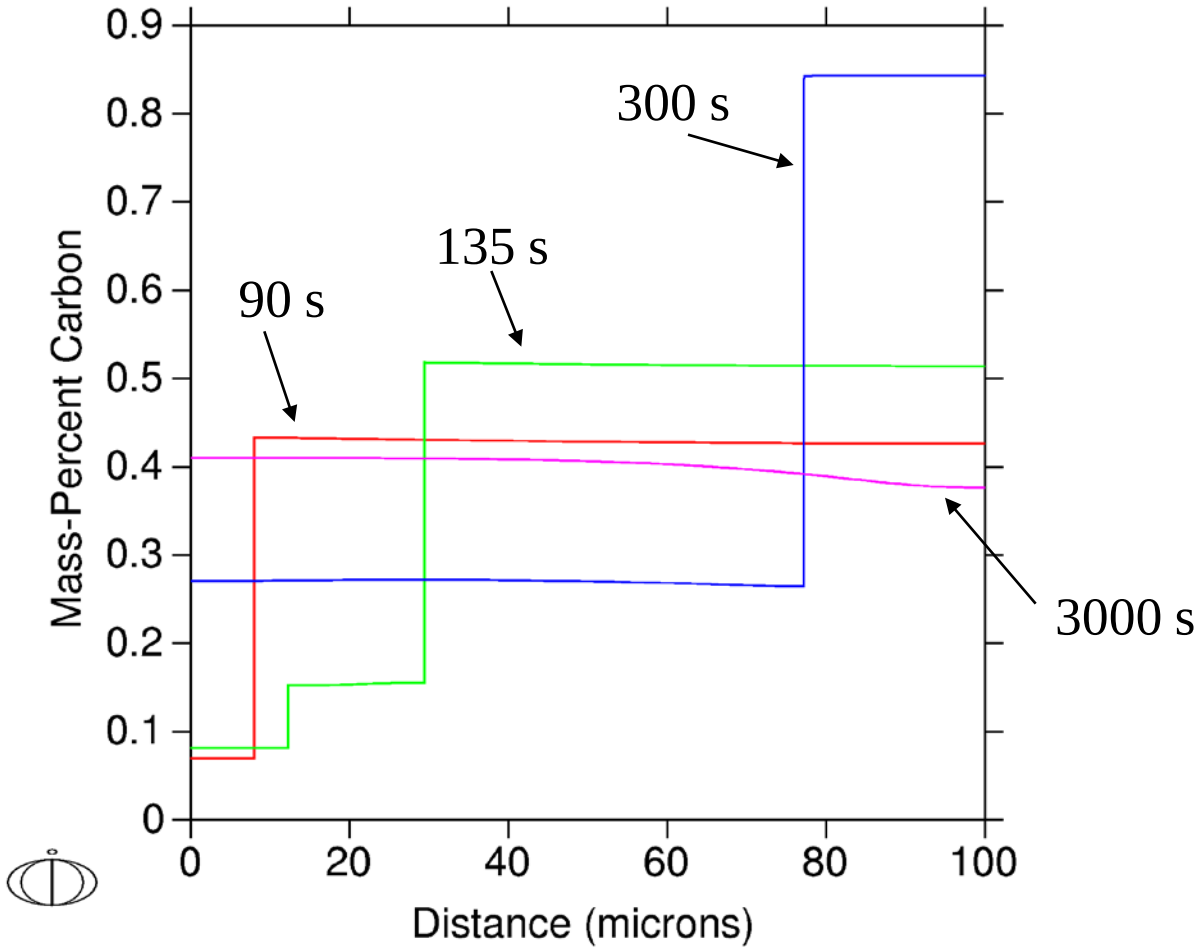
Solidification range



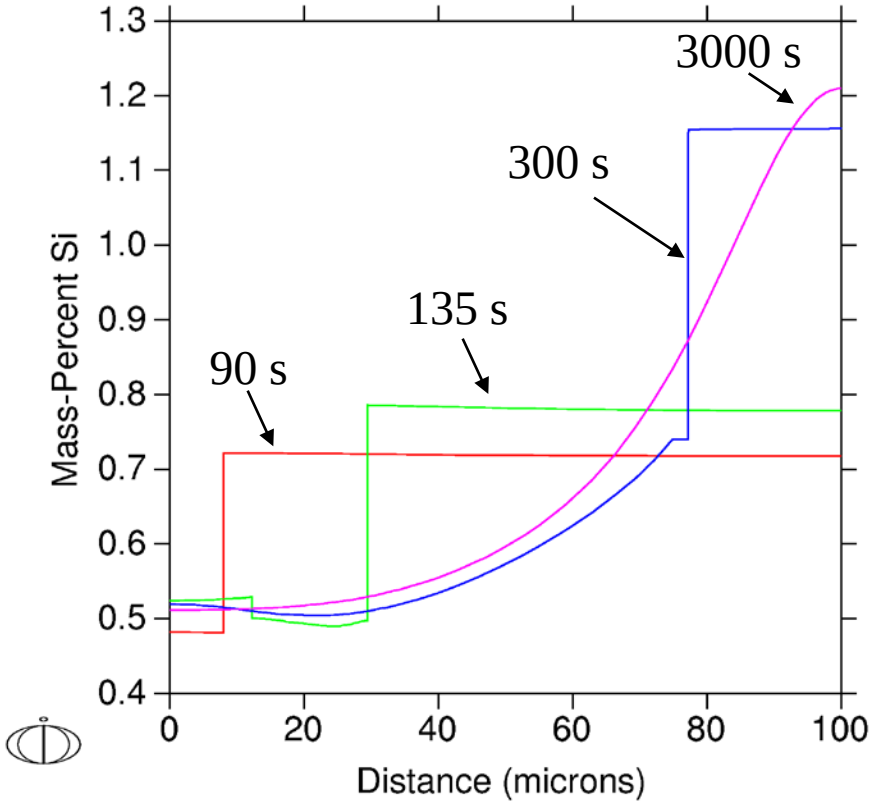
Fraction of solid phases

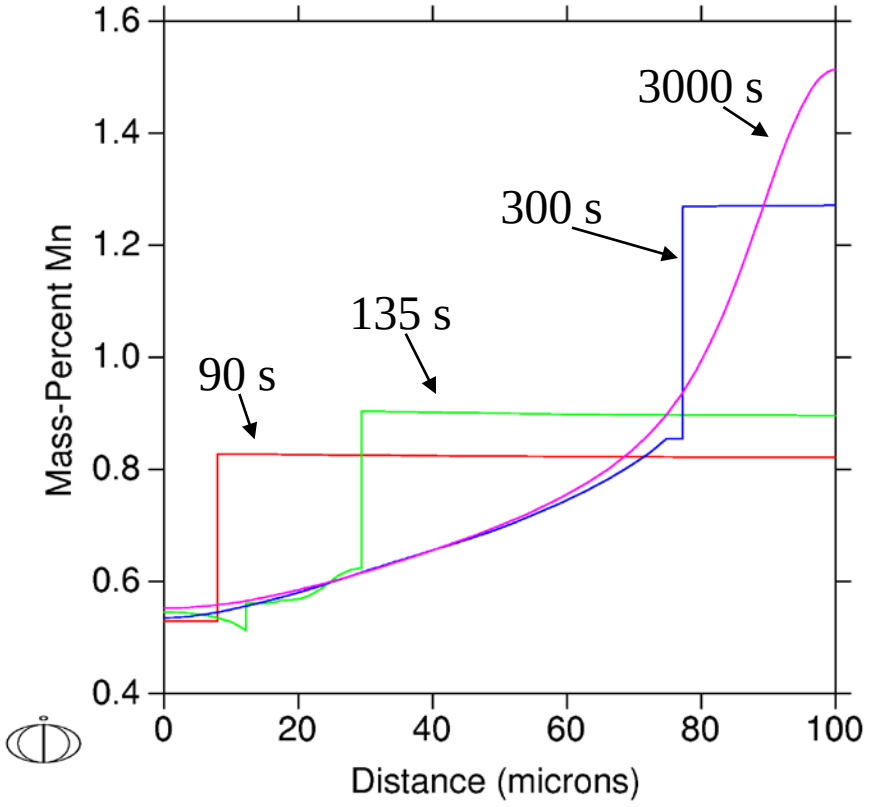


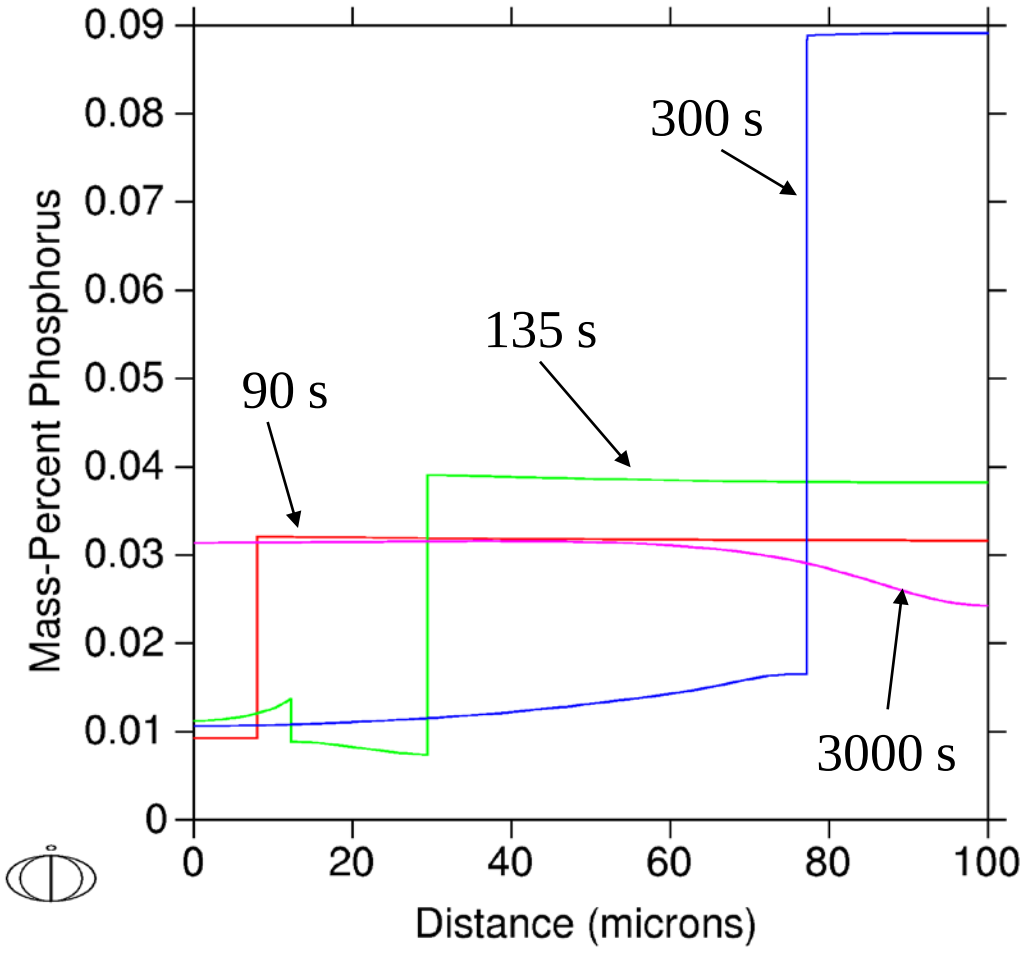
Carbon profiles during solidification



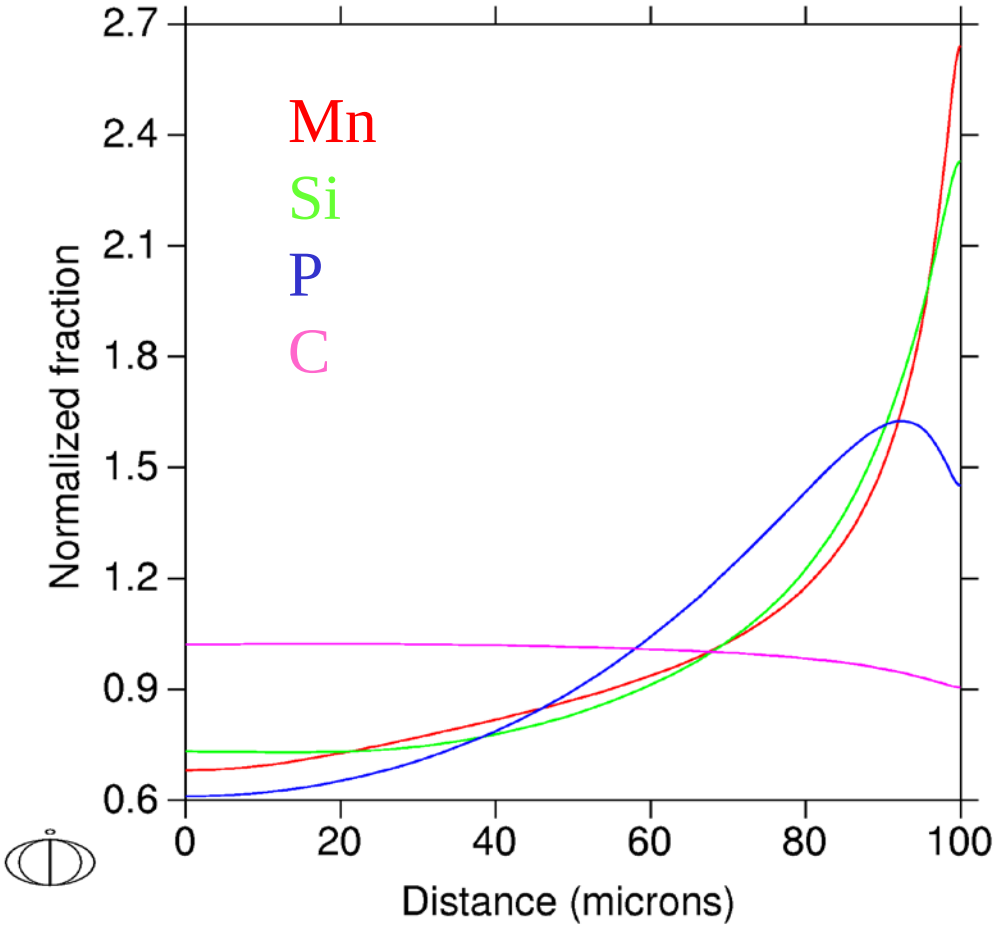
Silicon and Manganese





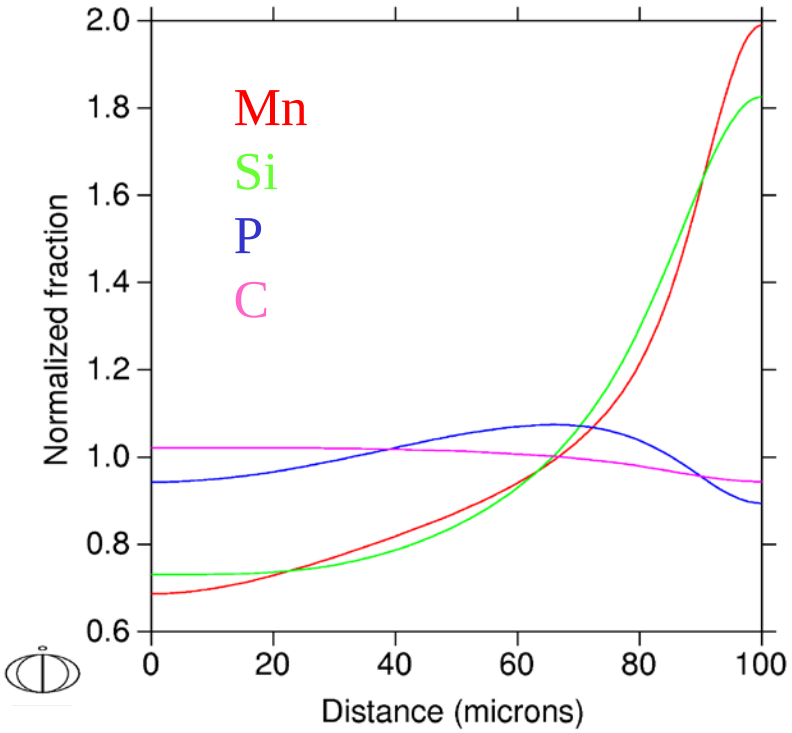

0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Mass-Percent Phosphorus
0
20
40
60
80
100
Distance (microns)
300 s
135 s
90 s
3000 s

Segregation profiles after 610 s
(when the last melt disappears)

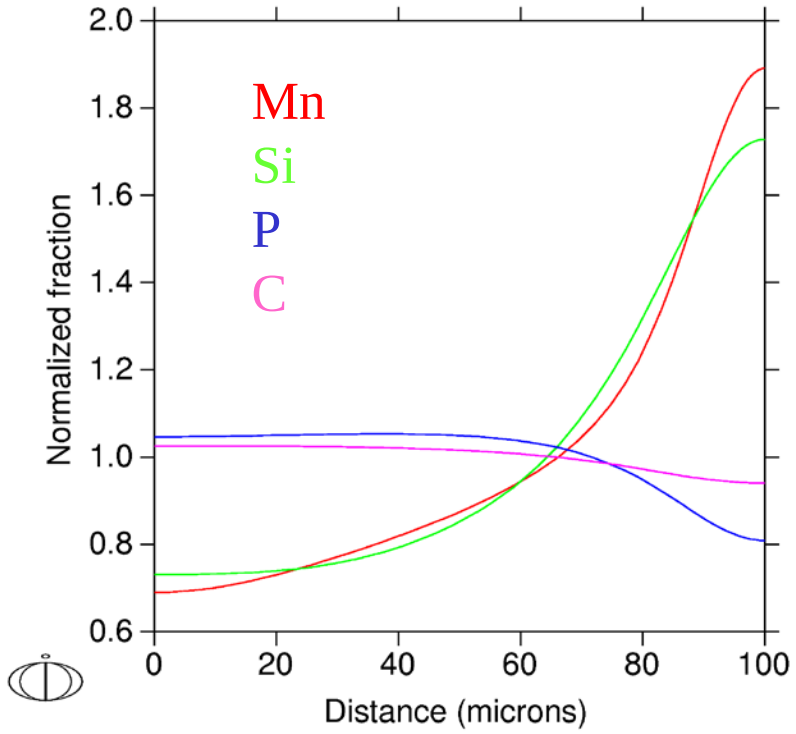


Segregation profiles after 1000 and 3000 s

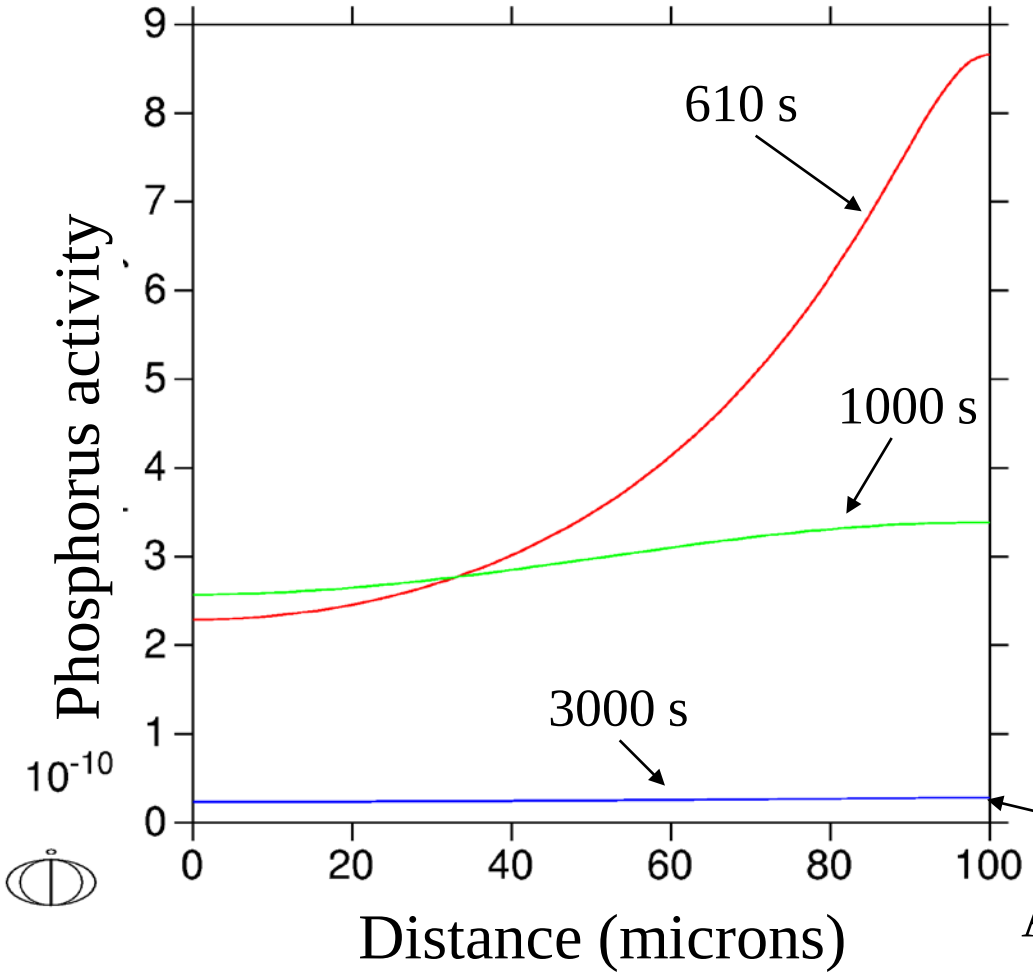
after 1000 s



after 3000 s



The solution



- ✓ Mn and Si increase the phosphorus activity.
- ✓ Phosphorus diffusion much faster compared to Mn and Si diffusion.

At the late stage further phosphorus redistribution is controlled by slow Mn and Si diffusion.

Outline

- Introduction to Thermo-Calc and DICTRA
- **Examples related to ingot metallurgy**:
  - Peak shifting of phosphorous during solidification
  - **Homogenizing a Ni-based superalloy**
- Questions

Homogenizing a Ni based superalloy

Homogenizing a Nickel based superalloy: Thermodynamic and kinetic simulation and experimental results.

Paul D Jablonski and Christopher J Cowen (NETL, Albany, OR)

Met. Trans. B. Vol 40B, April 2009 (pp 182-186)

Table I. Target and Measured Chemistry (in Weight Percent) of the Nimonic 105 Alloy Cast for This Study

Nimonic 105	C	Cr	Mo	Co	Al	Ti	Mn	Si	B
Target	0.15	14.85	5	20	4.7	1.1	0.5	0.5	0.05
Measured	0.16	14.61	5.02	20.04	4.43	1.1	0.51	0.51	0.05

Homogenizing a Ni based superalloy

Thermodynamic data from the Thermotech Ni-data database
Mobility data from the MOBNi1 database.

Scheil calculation used to predict the fraction solid curve and incipient melting temp - 1142°C.

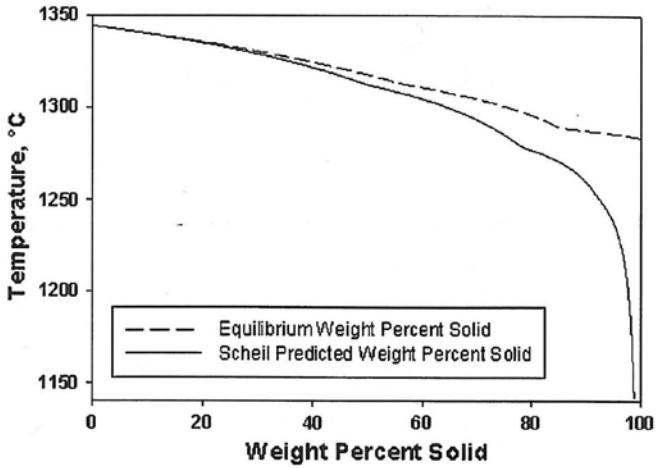


Fig. 1—Equilibrium and Scheil predicted solidification ranges for the Nimonic 105 alloy.

and extent of chemical microsegregation - amounts of each alloying element in the FCC (γ) phase

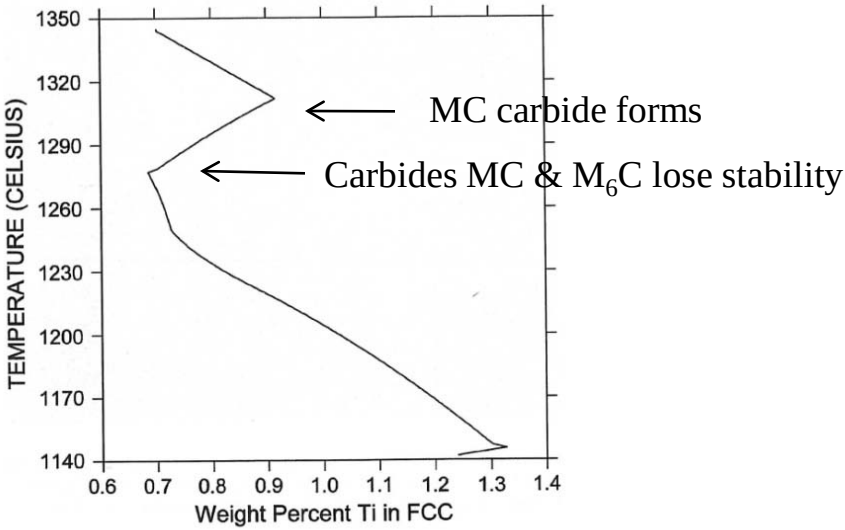


Fig. 2—Calculated amount of Ti in the fcc phase as a function of temperature.

Homogenizing a Ni based superalloy

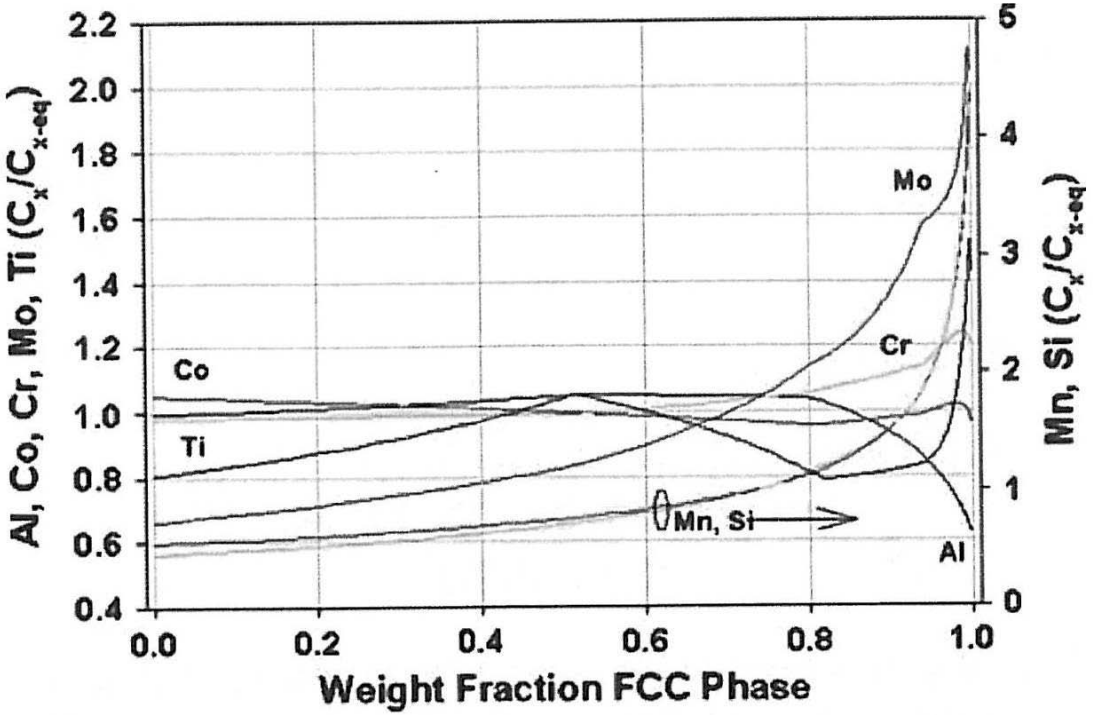


Fig. 3—Normalized Scheil predicted segregation across a dendrite (from center to edge).

Homogenizing a Ni based superalloy

Thermo-Calc Software

DICTRA simulations performed to simulate homogenization.
Assumptions: Diffusion distance of 50 μm based on approx one half of the maximum secondary dendrite arm spacing. Weight fraction of FCC scaled to this distance and read into DICTRA along with the chemistry profiles across the FCC dendrites from the Scheil simulations.

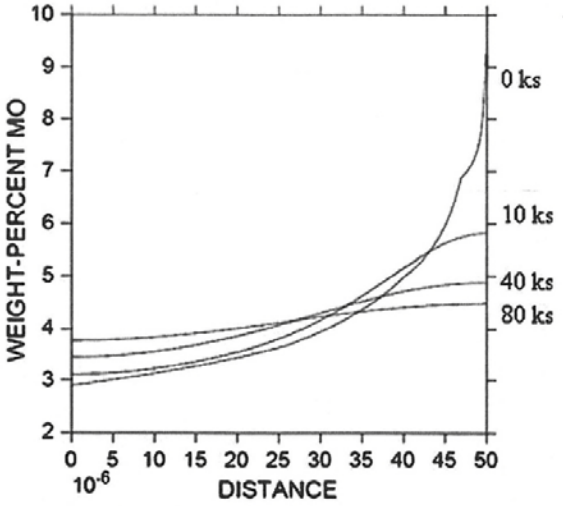


Fig. 4—Weight percent Mo as a function of distance (*m*) across a dendrite (from center to edge) for the following time sequences at 1100 °C: 0, 10, 40, and 80 ks.

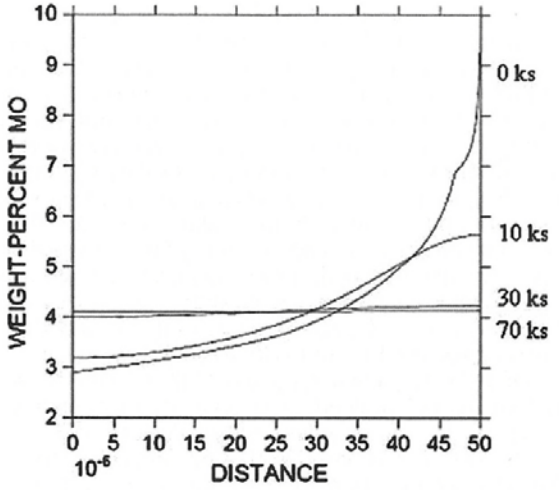


Fig. 5—Weight percent Mo as a function of distance (*m*) across a dendrite (from center to edge) for the following time sequences at 1100 °C: 0 and 10 ks; and 1100 °C/10 ks + 1200 °C/30 and 70 ks.

First heat treatment simulated at 1100°C (below incipient melting temp). But incipient melting temp changes with chemical profile. In second case calculated a new incipient melting temp after 10,000 secs of 1275°C. Significant improvement of the alloy homogeneity was predicted even after only 8.33 hrs (30,000 secs) @1200°C after the initial 10,000 secs @ 1100°C.

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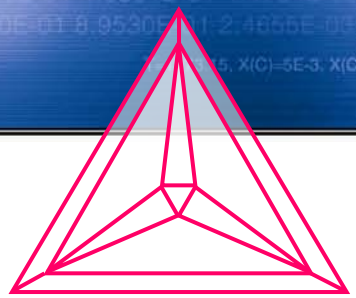

Thermo-Calc Software

CALCULATING THERMODYNAMIC PROPERTIES

Thank you!

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