Thermodynamic and Kinetic modelling - a Renaissance in materials science and engineering

John Ågren

Materials Science and Engineering

KTH (Royal Institute of Technology)

SE 100 44 Stockholm, Sweden

Acknowledgements:

Lars Höglund, Henrik Larsson, Annika Borgenstam, Martin Walbrühl,

Carrie Campbell, Roger Reed, Greg Olson

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Content

1. Introduction: 40 years ago...
2. ICME and the Materials genome
3. Materials design
4. Multiscale modeling
   1. Atomistic
   2. Mesoscale
5. Examples:
   1. Gradient formation in cemented carbides
   2. Phase-field modelling
   3. Modelling of oxidation
6. Conclusions

1. Introduction: 40 years ago...

- Not much entusiasm for thermodynamic and kinetic modelling in materials.
  - CALPHAD
    - Only applies to equilibrium and you never have equilibrium in practice
    - Most real materials are multicomponent but calculation of a ternary phase diagram was a challenge both theoretically and computationally
    - Not much collaboration: the small group of individuals active in the field each used their own model and data
  - Kinetic modelling, when used, was very simple
- Experimental caracterization based on SEM and TEM was used to study dislocations, precipitates and fracture surfaces
  - The techniques we have today were known but not much developed and were not used by materials researchers
  - Most research departments at companies and universities closed down their electron microscopy
    - The technique was difficult and expensive
    - They did not get enough out of it

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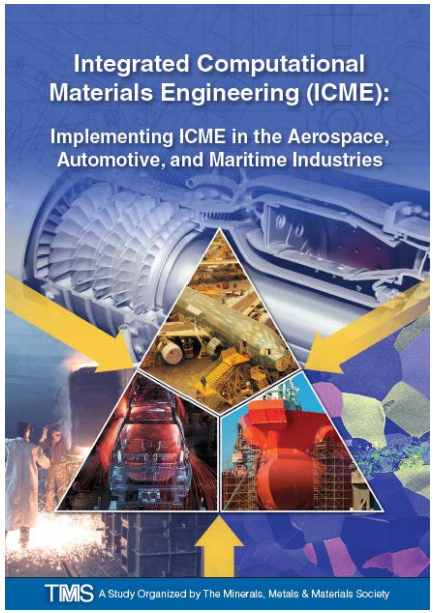
Today…

- Abundance of advanced experimental techniques to caracterize materials structure and properties.
- Abundance of advanced modelling techniques to predict materials structure and properties.
- This is reflected in research initiatives like
  - ICME (Integrated computational materials engineering)
  - MG (Materials genome)
  - 3D or 4D materials science
  - …
- Extensive industrial interest to use these methods to solve engineering problems.

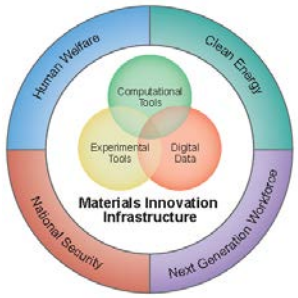
> a Renaissance in materials science and engineering

Initiatives

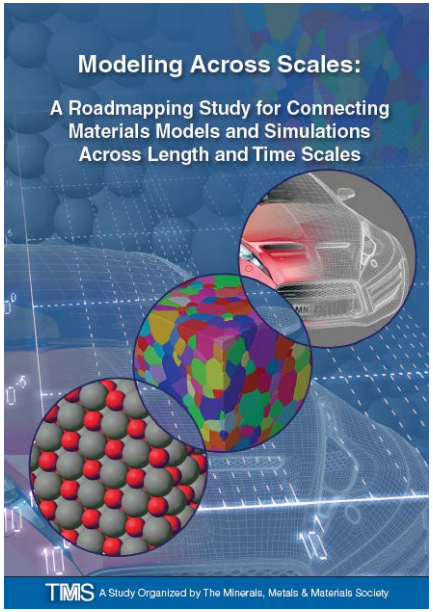


North America

- ICME
- MGI



- Northwestern University…
- Questek, Boeing, NASA, GM, NIST …



Europe

- ICMEg
- Metallurgy Europe

- KTH (Hero-m), RWTH Aachen …
- Sandvik, ABB, Thyssen, Hydro, ESA? …

The first example of materials design in industry using Computational thermodynamics (H. Widmark 1990)

- In 1983 Swedish steel producer Sandvik developed a new generation of duplex stainless steels.
  - Same price level as the conventional 18/8 steel
  - Twice the strength
  - Better corrosion resistance
  - Reduced experimental costs (2 instead of 10 years)
- Most important to have 50/50 mixture of FCC-BCC.
- Avoid TCP (e.g. sigma phase)
- Same PRE-number in both phases. PRE (Pitting Resistance Equivalent) calculated empirically from phase composition.

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2. ICME and the Materials Genome

The concept of Integrated Computational Materials Engineering (ICME) was first coined in US around 2005, as a response "... *to the industrial need to quickly develop durable components at the lowest cost. It has important potential for accelerating the development of new materials*" (Allison et al. 2006).

- Integrating;
  - Materials information from different scales of length and time
  - Personnel with different competencies
  - Product and materials performance
- Computations
  - Computational tools for covering different scales of length and time
  - Visualization
  - Representation of experimental data
- Materials Engineering
  - Directed towards materials of industrial importance

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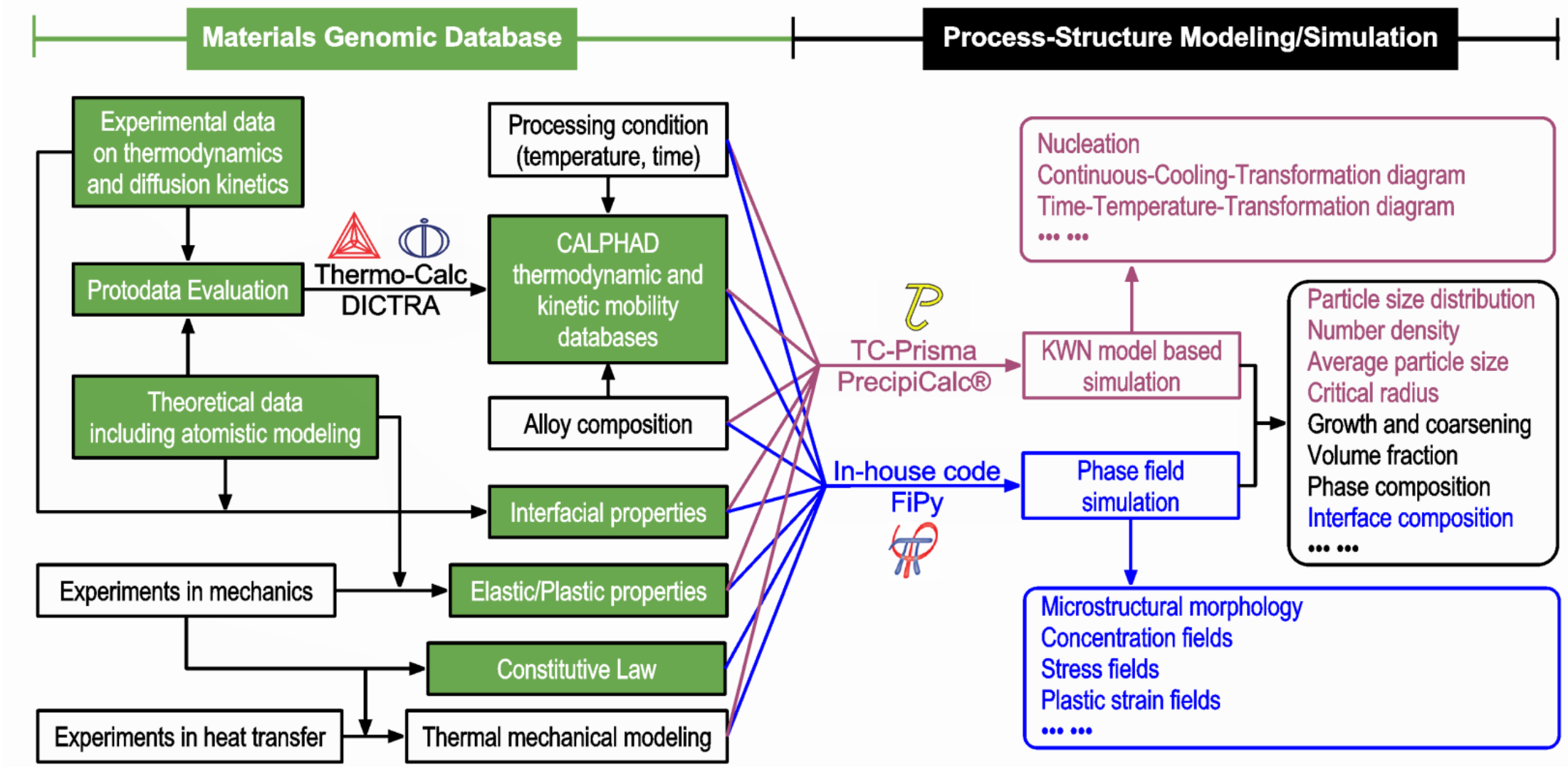
A shift in Paradigm!

Materials science is not only considered from the point of view of structure and properties, but...

is considerered as a system for accelerating the development of new materials.

Including

- Materials properties and performance
- Manufacturing and processing
- Cost analysis
- Uncertainties
- Raw materials issues (availability, health issues...)



From: W. Xiong and G.B. Olson 2015

Calphad method as a role model for materials genomic databases

- Rigorous and self consistent thermodynamic analysis
- Models to calculate Gibbs energy of each phase in a system
- Equilibrium state may be calculated for fixed composition pressure and temperature of a system
- Equilibrium state may be calculated also for other conditions
- Constrained equilibria (some order parameters frozen in)
- Stable and metastable phase diagrams
  - Projections and sections
- Driving forces for non-equilibrium states
  - Simulation of diffusion
  - Phase-field simulations

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CALPHAD is the first materials genome because it is …

- the most efficient way of integrating various pieces of information of quite different character into a coherent and useful form.
- extendable far beyond the traditional thermochemistry
- increasingly being used outside the traditional CALPHAD community

A major enabling technology in Materials science and engineering.

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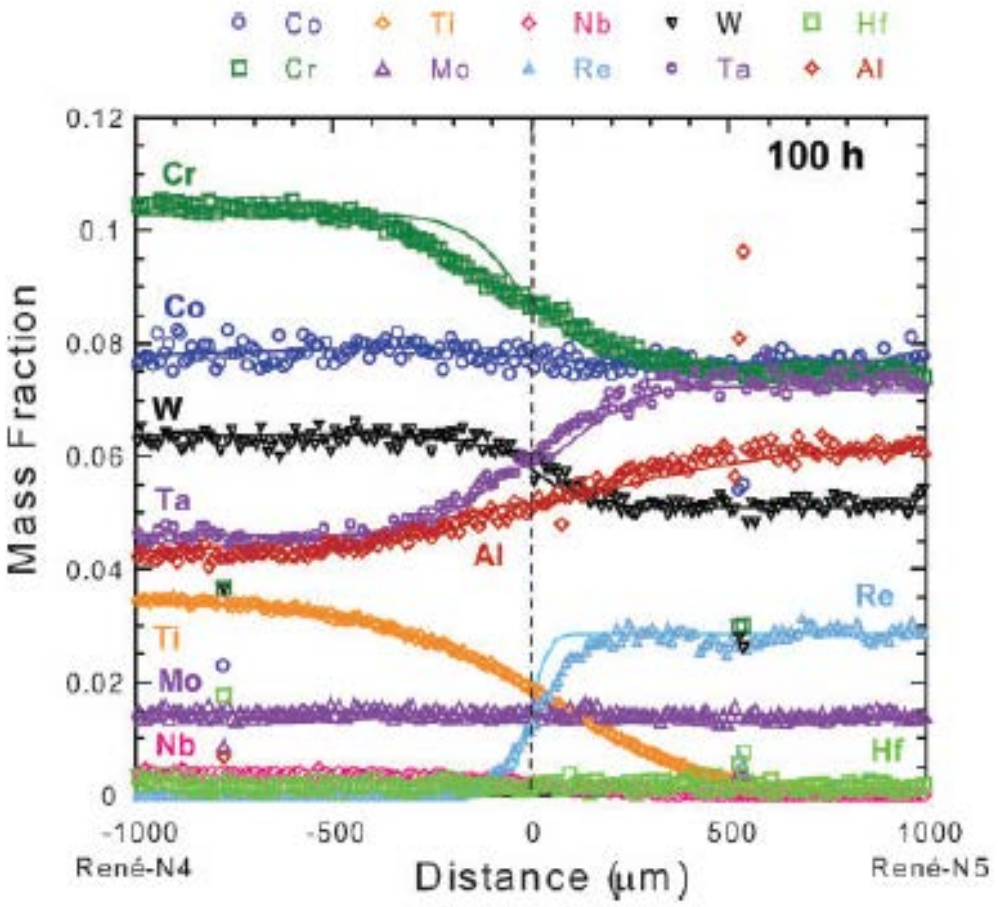
Genomic database for diffusion

- Multicomponent systems: many diffusion coefficients!
- Various type of coupling effects may make it more complicated than Fick's law.
- A CALPHAD-type of approach was suggested for information on diffusion kinetics (Andersson-Ågren 1992)
  - Allowed systematic representatation of the kinetic behaviour of multicomponent alloy systems.
- DICTRA was developed in the 1990s for numerical solution of multicomponent diffusion problems in simple geometries.

Diffusion in Ni-base alloys: Campbell et al. 2002



Assessed mobility parameters in the fcc phase [Eq. (4)]

DICTRA notation	Mobility parameter	Parameter (J/mole)	Reference
Mobility of Al			
MQ(FCC,Al:VA;0)	$\mathcal{Q}_{Al}^{Al}$	−142,000–72.1*T	[39]
MQ(FCC,Cr:VA;0)	$\mathcal{Q}_{Al}^{Cr}$	−235,000–82*T	[39]
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Al}^{Ni}$	−284,000–59.8*T	[39]
MQ(FCC,Ti:VA;0)	$\mathcal{Q}_{Al}^{Ti}$	−284,000+–59.8*T	[14]
MQ(FCC,Al,Cr:VA;0)	${}^{0}A_{Al}^{Cr}$	335,000	[39]
MQ(FCC,Al,Ni:VA;0)	${}^{0}A_{Al}^{Ni}$	−41,300–91.2*T	[39]
MQ(FCC,Cr,Ni:VA;0)	${}^{0}A_{Al}^{Ni}$	−53,200	[39]
MQ(FCC,Al,Ti:VA;0)	${}^{0}A_{Al}^{Ti}$	335,000	[14]
MQ(FCC,Ni:Ti:VA;0)	${}^{0}A_{Al}^{Ti}$	−53,200	[14]
Mobility of Co			
MQ(FCC,Co:VA;0)	$\mathcal{Q}_{Co}^{Co}$	−286,175–76.0*T	This work
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Co}^{Ni}$	−284,169–67.6*T	This work
MQ(FCC,Co,Ni:VA;0)	${}^{0}A_{Co}^{Ni}$	+10,787–11.5*T	This work
Mobility of Cr			
MQ(FCC,Al:VA;0)	$\mathcal{Q}_{Cr}^{Al}$	−261,700–3.71*T	[39]
MQ(FCC,Co:VA;0)	$\mathcal{Q}_{Cr}^{Co}$	−246,904–110*T	This work
MQ(FCC,Cr:VA;0)	$\mathcal{Q}_{Cr}^{Cr}$	−235,000–82*T	[39]
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Cr}^{Ni}$	−287,000–64.4*T	[39]
MQ(FCC,Al,Cr:VA;0)	${}^{0}A_{Cr}^{Cr}$	487,000	[39]
MQ(FCC,Al,Ni:VA;0)	${}^{0}A_{Cr}^{Ni}$	−118,000	[39]
MQ(FCC,Cr,Ni:VA;0)	${}^{0}A_{Cr}^{Ni}$	−68,000	[39]
Mobility of Hf			
MQ(FCC,Hf:VA;0)	$\mathcal{Q}_{Ni}^{Hf}$	−235,350–123*T	This work
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Ni}^{Ni}$	−251,956–71.2*T	This work
Mobility of Mo			
MQ(FCC,Co:VA;0)	$\mathcal{Q}_{Mo}^{Co}$	−256,943–94.2*T	This work
MQ(FCC,Mo:VA;0)	$\mathcal{Q}_{Mo}^{Mo}$	−254,975–81.5*T	This work
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Mo}^{Ni}$	−267,585–79.5*T	This work
Mobility Ni			
MQ(FCC,Al:VA;0)	$\mathcal{Q}_{Ni}^{Al}$	−145,900–64.3*T	[39]
MQ(FCC,Co:VA;0)	$\mathcal{Q}_{Ni}^{Co}$	−270,348–87.3*T	This work
MQ(FCC,Cr:VA;0)	$\mathcal{Q}_{Ni}^{Cr}$	−235,000–82*T	[38]
MQ(FCC,Hf:VA;0)	$\mathcal{Q}_{Ni}^{Hf}$	−286,182–84.5*T	This work
MQ(FCC,Mo:VA;0)	$\mathcal{Q}_{Ni}^{Mo}$	−286,000–82*T	This work
MQ(FCC,Ni:VA;0)	$\mathcal{Q}_{Ni}^{Ni}$	−287,000–69.8*T	[38]
MQ(FCC,Re:VA;0)	$\mathcal{Q}_{Ni}^{Re}$	−294,401–105*T	This work
MQ(FCC,Ta:VA;0)	$\mathcal{Q}_{Ni}^{Ta}$	−443,736–96*T	This work
MQ(FCC,Ti:VA;0)	$\mathcal{Q}_{Ni}^{Ti}$	−287,000–69.8*T	This work
MQ(FCC,W:VA;0)	$\mathcal{Q}_{Ni}^{W}$	−628,250–63.5*T	This work
MQ(FCC,Al,Cr:VA;0)	${}^{0}A_{Ni}^{Cr}$	−211,000	[39]
MQ(FCC,Al,Ni:VA;0)	${}^{0}A_{Ni}^{Ni}$	−11,300+65.5*T	[39]
MQ(FCC,Al,Ti:VA;0)	${}^{0}A_{Ni}^{Ti}$	−211,000	[14]
MQ(FCC,Co,Ni:VA;0)	${}^{0}A_{Ni}^{Ni}$	7866+7.65*T	This work
MQ(FCC,Cr,Ni:VA;0)	${}^{0}A_{Ni}^{Ni}$	−81,000	[38]
MQ(FCC,Ni,Re:VA;0)	${}^{0}A_{Ni}^{Re}$	−157,409	This work
MQ(FCC,Ni,Ta:VA;0)	${}^{0}A_{Ni}^{Ta}$	−668,454	This work
MQ(FCC,Ni,Ti:VA;0)	${}^{0}A_{Ni}^{Ti}$	−81,000	[14]
MQ(FCC,Ni:W:VA;0)	${}^{0}A_{Ni}^{W}$	175,736	This work

(continued on next page)

Simple substitutional model

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Statement of a materials design problem

- What is the application?
  - Market?
  - Requirements?
- The application requires a certain performance
  - The performance is defined by a number of properties
  - Properties can be measured
  - Not always trivial to translate performance into properties
  - Cost and price important properites!
- Properties of a material can often be predicted from its composition and processing,
  - sometimes with very high precision and sometimes at least approximately.
  - Sometimes one has to rely on emprirical relations without understanding.
- But…
  - Production of the material, cost?
  - Aging – how does the performance change during usage?

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The **problem** is to design a material that fullfills the performance requirements for one or several given applications, i.e. to determine alloy composition and processing conditions for this material, i.e. the **recipe**.

Cohen's reciprocity

Engineering
(Design)

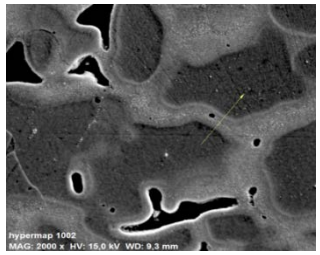
Performance

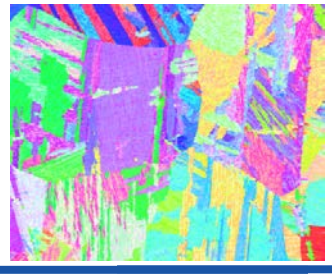
Properties

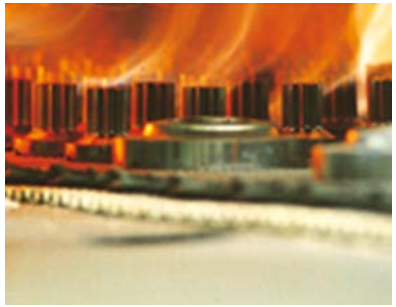
Structure

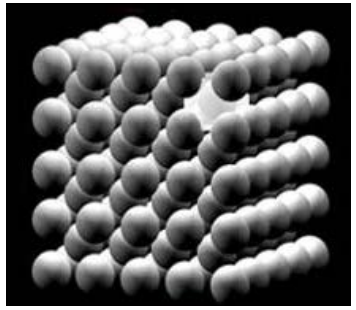
Process

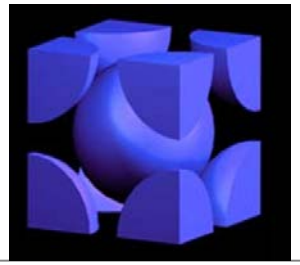
Science
(Understand)

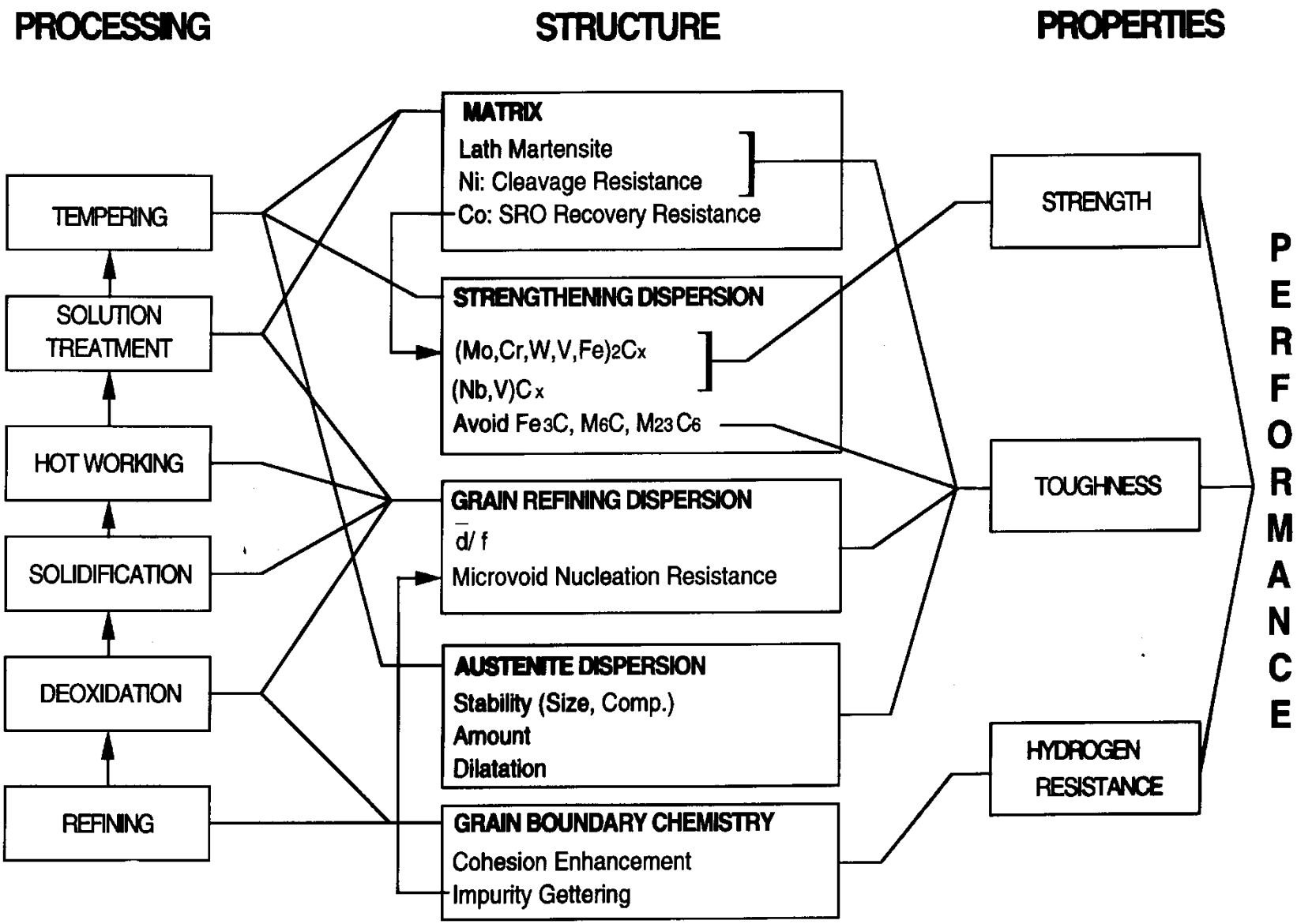




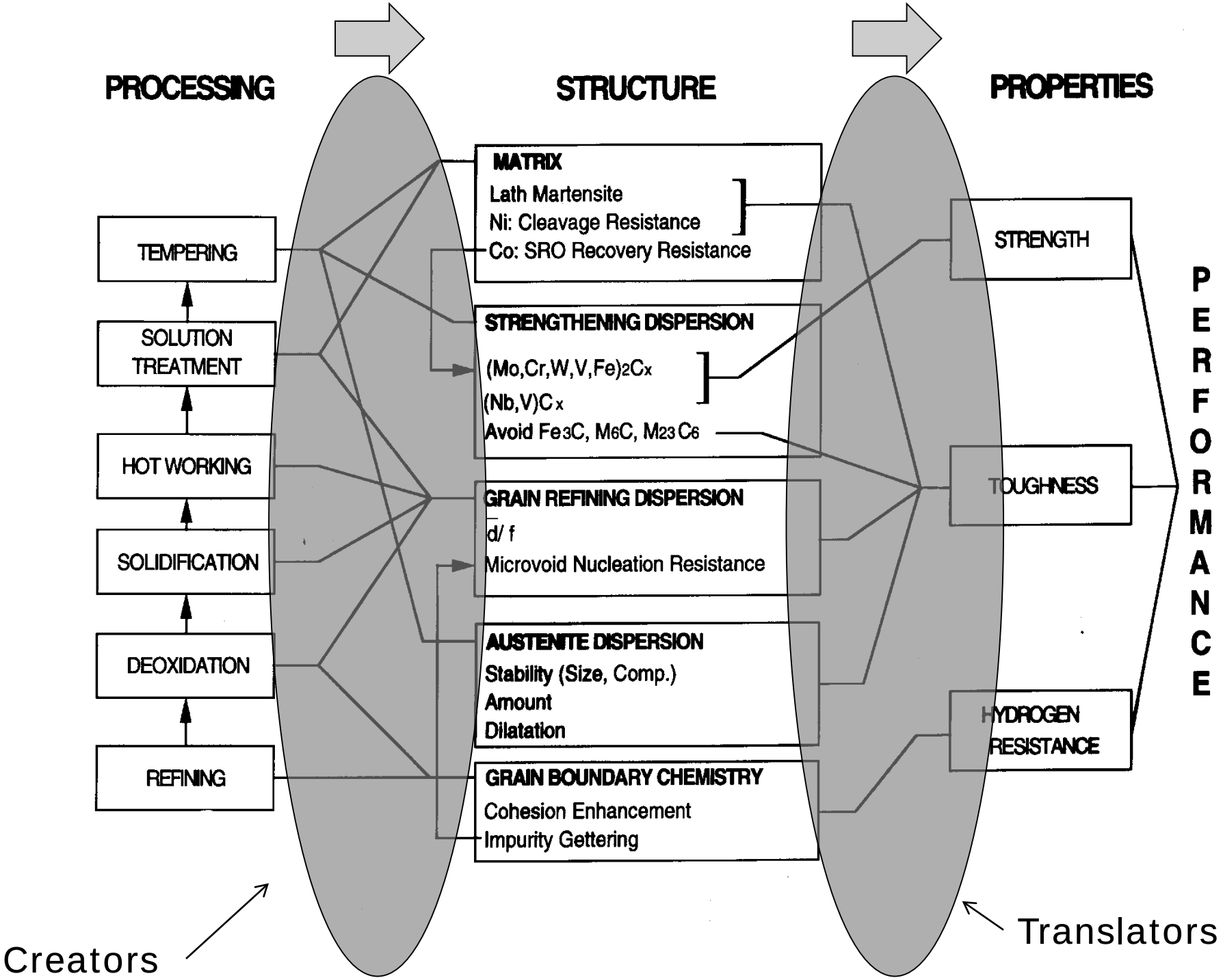








Systems view for the materials science of high-strength steels (From Olson).


PROCESSING
STRUCTURE
PROPERTIES
TEMPERING
SOLUTION TREATMENT
HOT WORKING
SOLIDIFICATION
DEOXIDATION
REFINING
MATRIX
Lath Martensite
Ni: Cleavage Resistance
Co: SRO Recovery Resistance
STRENGTHENING DISPERSION
(Mo,Cr,W,V,Fe)2Cx
(Nb,V)Cx
Avoid Fe3C, M6C, M23C6
GRAIN REFINING DISPERSION
d/ f
Microvoid Nucleation Resistance
AUSTENITE DISPERSION
Stability (Size, Comp.)
Amount
Dilatation
GRAIN BOUNDARY CHEMISTRY
Cohesion Enhancement
Impurity Gettering
STRENGTH
TOUGHNESS
HYDROGEN RESISTANCE
PERFORMANCE
Creators
Translators

We thus need a set of models

- Translator, models that predict the properties from the microstructure e.g.
  - mechanical properties like yield stress, strain hardening etc
  - wear resistance
  - oxidation resistance at elevated temperatures
  - corrosion properties, e.g. PRE-number
  - ...
- Creator, models to predict the microstructure from processing e.g.
  - dendrite arm spacing
  - micro segregation
  - grain size distributions
  - particle size distributions
  - phases and their composition
  - ...

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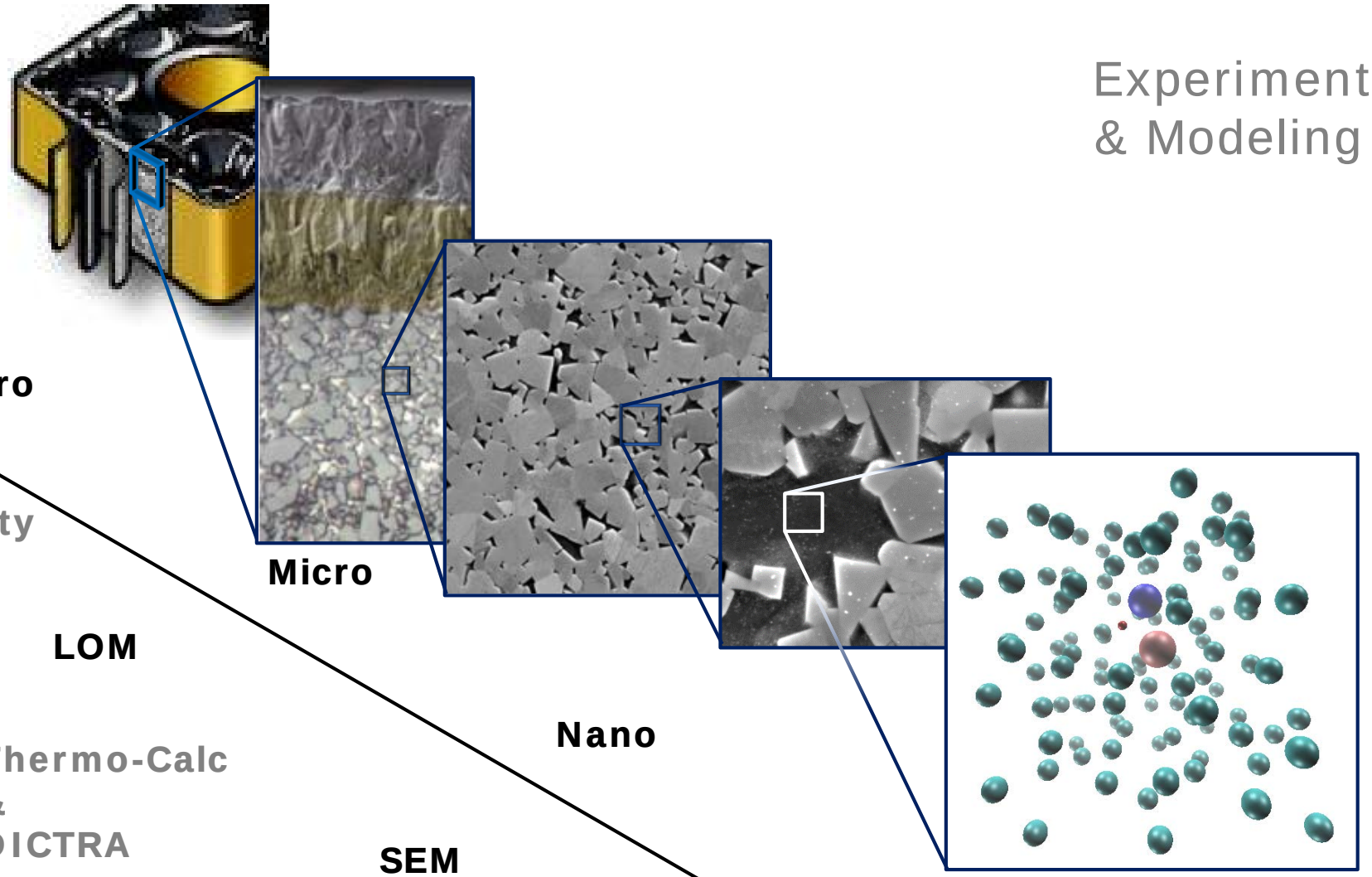
4. Multiscale modeling



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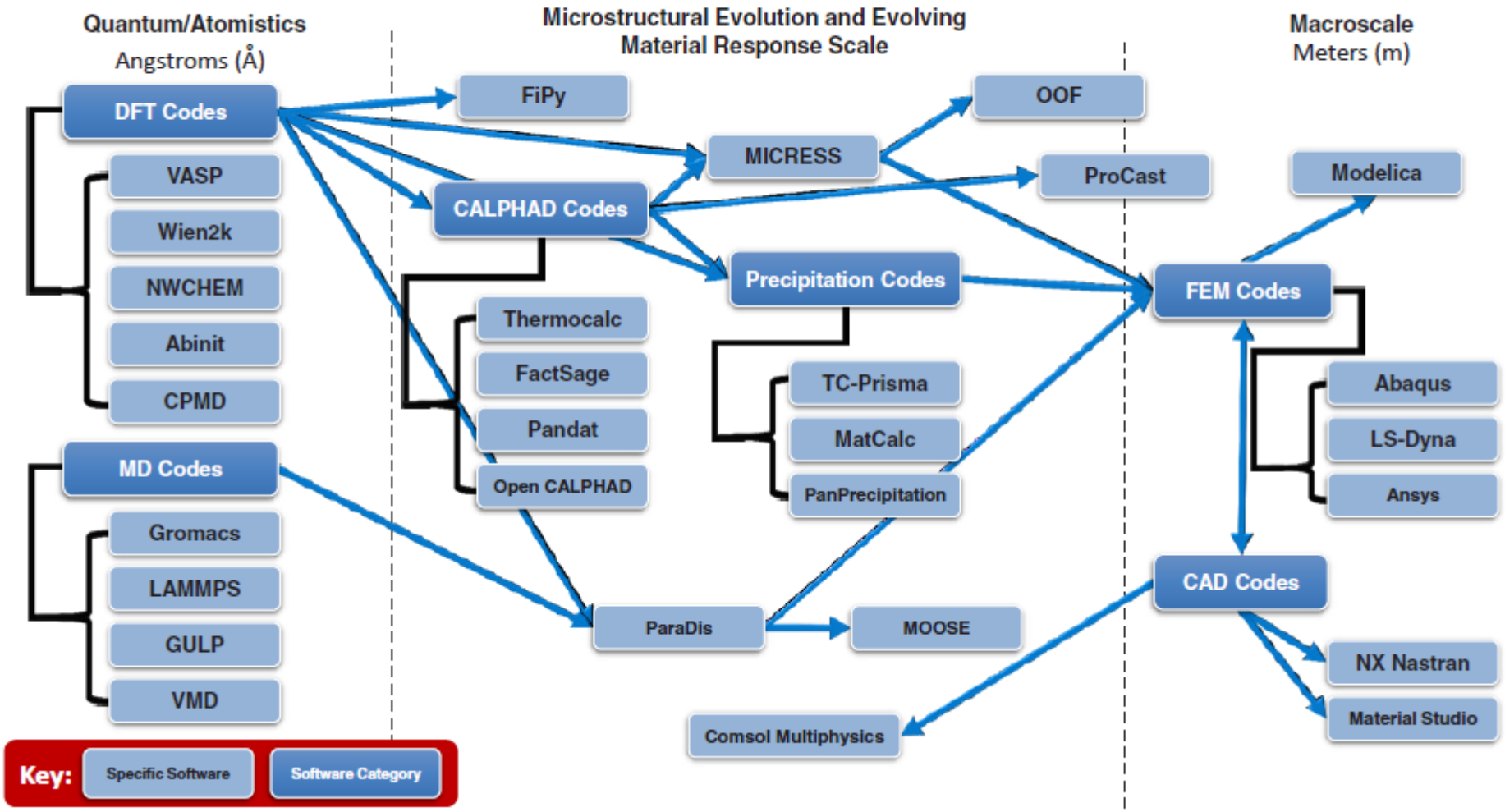
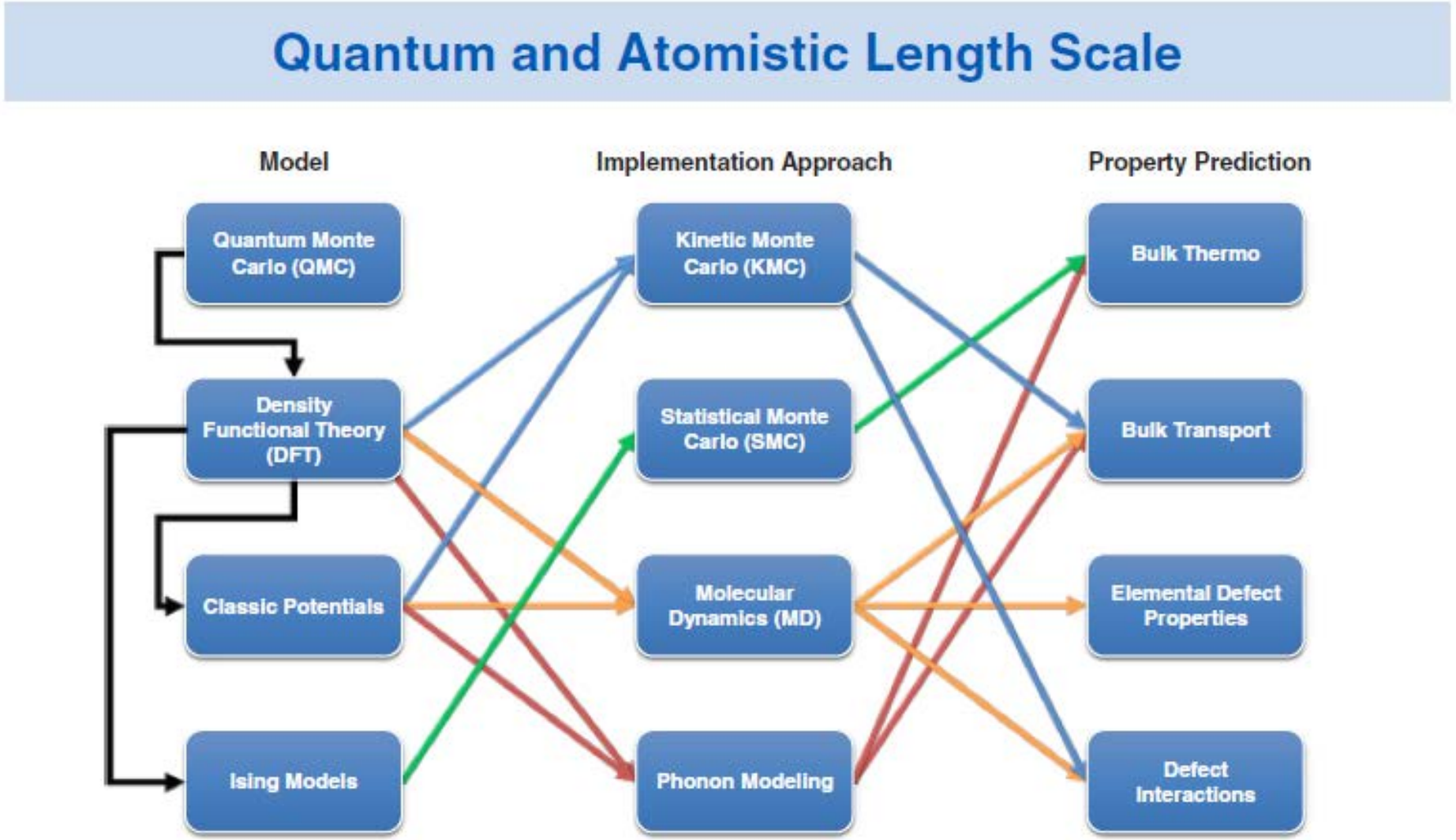
Tools in ICME

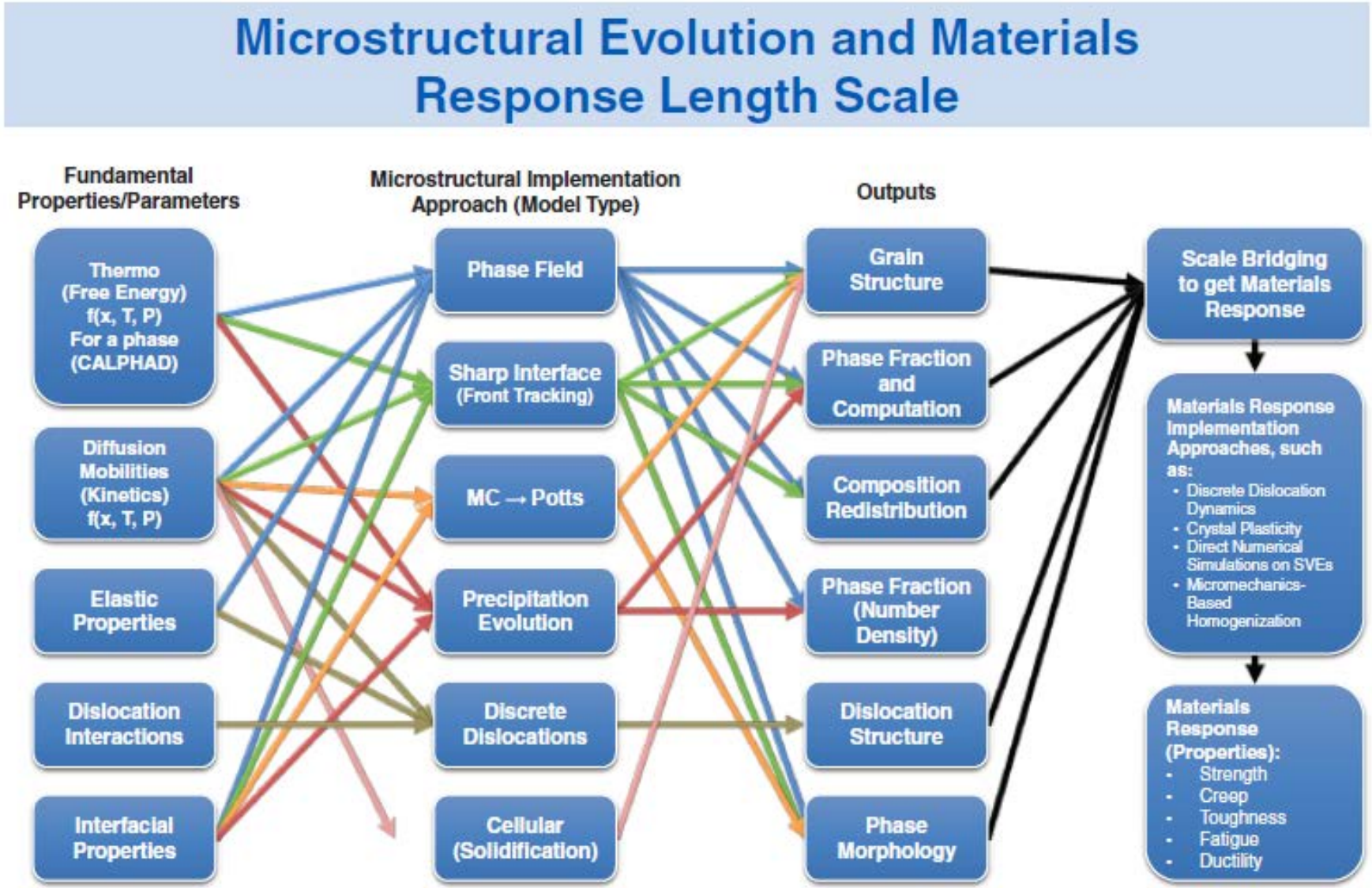
Some Common Software Input-Output Relationships



4.1 Atomistic modeling DFT & MD



4.2 Mesoscale modeling



Mesoscale modeling CALPHAD

Thermo-Calc

Thermodynamic and phase diagram calculations for multicomponent systems

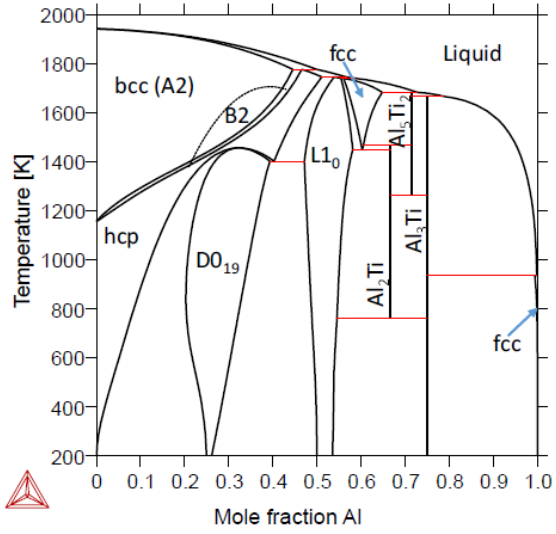
DICTRA

Simulation of DIffusion Controlled phase TRAnsformations

TC-PRISMA

Simulation of 3D multiparticle diffusive precipitation kinetics

www.thermocalc.com



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5. Examples:
5.1 Gradient formation in cemented carbides

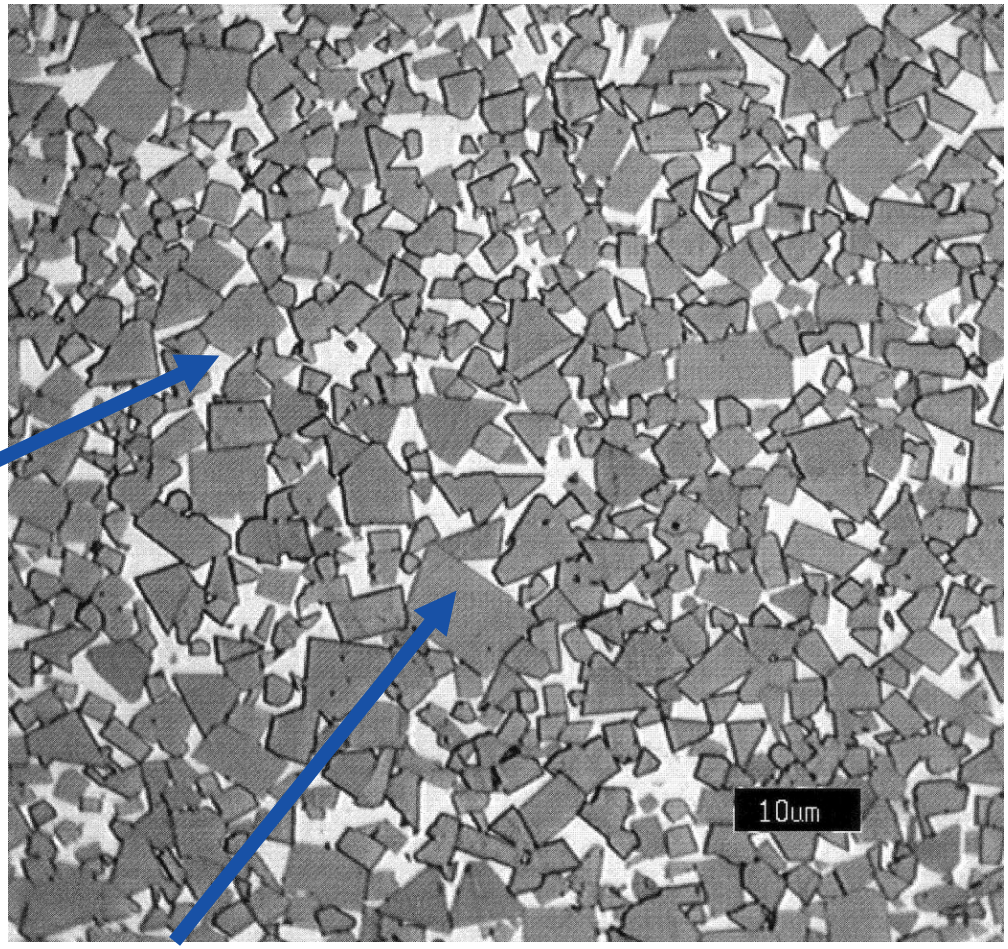
Diffusion in the liquid Co binder of cemented carbides: *Ab initio* molecular dynamics and DICTRA simulations

- Martin Walbrühl (2015)

Cemented Carbides

- Wear resistant & high in hardness
- Powder metallurgy (liquid-phase-sintering)

Binder phase: Co



Secondary hard phase:
FCC -> e.g. Ti(C,N)

WC

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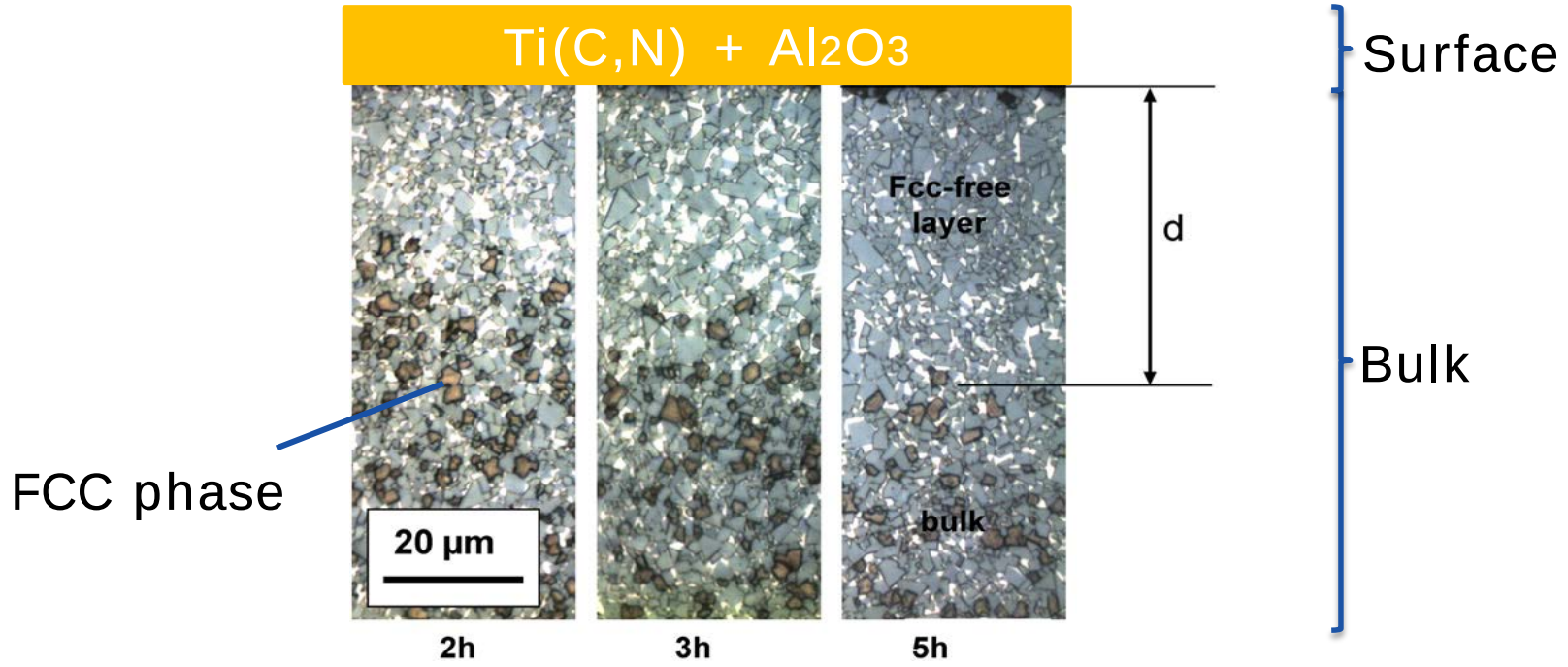
Tools are coated (architectured) and a structure gradient below the coating is beneficial!

Predicting gradient formation – diffusion in liquid binder
Diffusion is not accurately described in the liquid



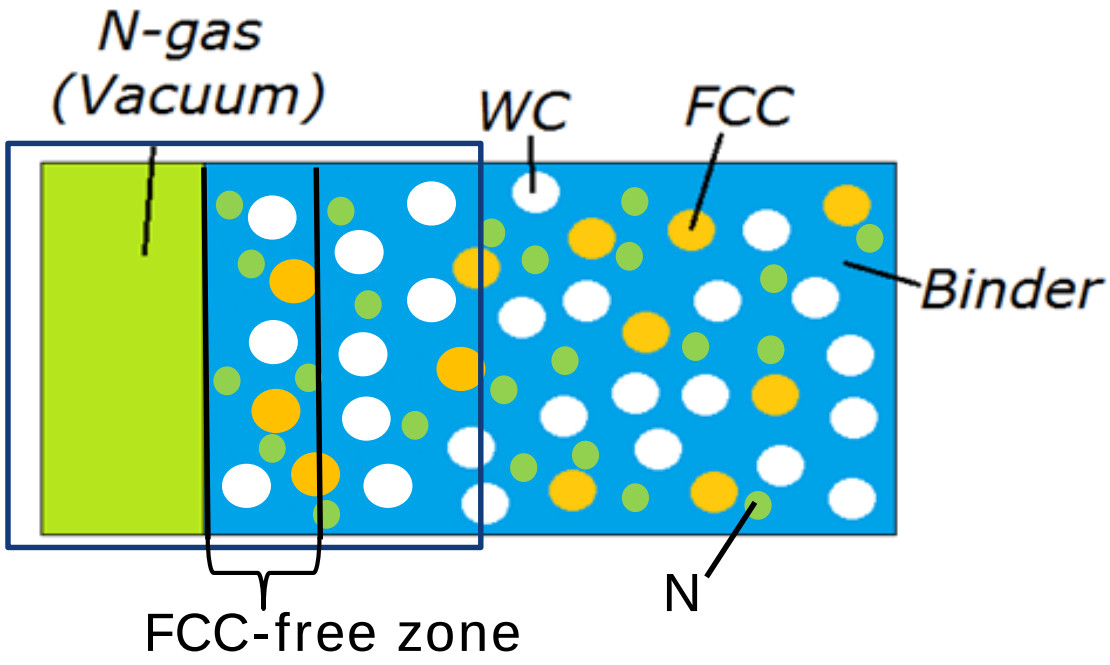
Method

- Calculate the diffusion parameters for Co, W, Ti, C & N with *Ab initio* Molecular Dynamics (AIMD)
- Simulate gradient formation with DICTRA using these parameters

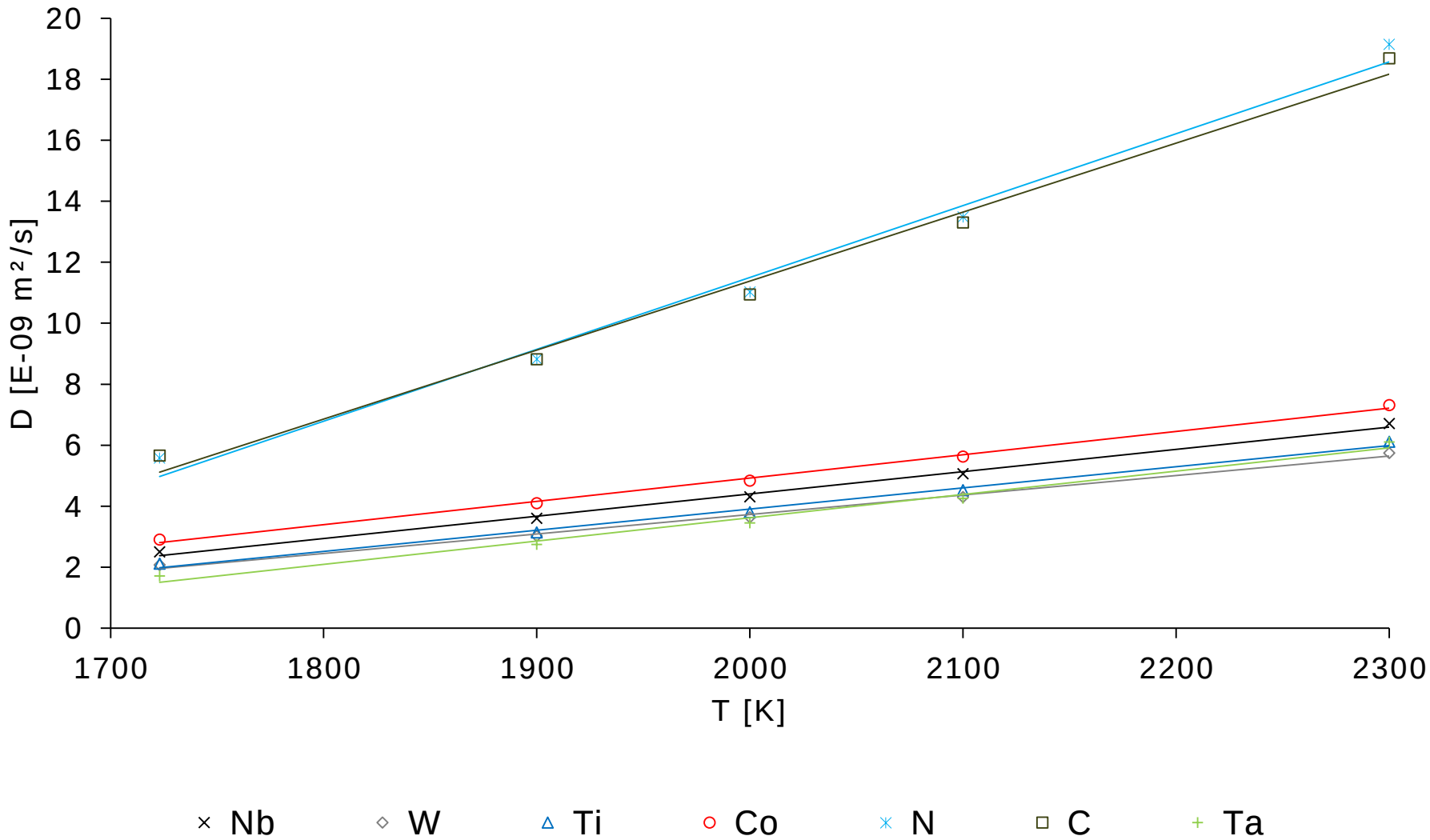
The homogenization model in DICTRA

- Two step calculation
  - Diffusion step
  - Thermodynamic equilibrium

- N activity 10^{-14}
- FCC and WC as dispersed particles

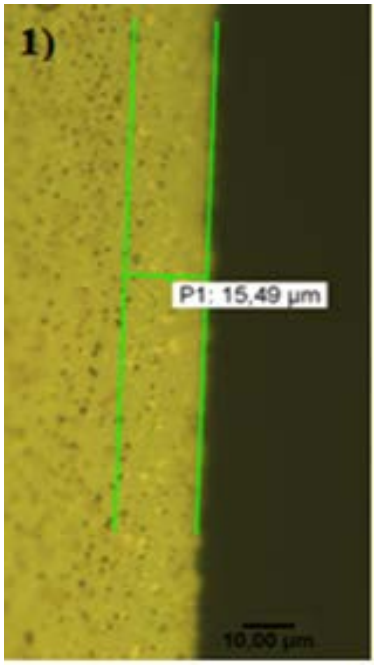


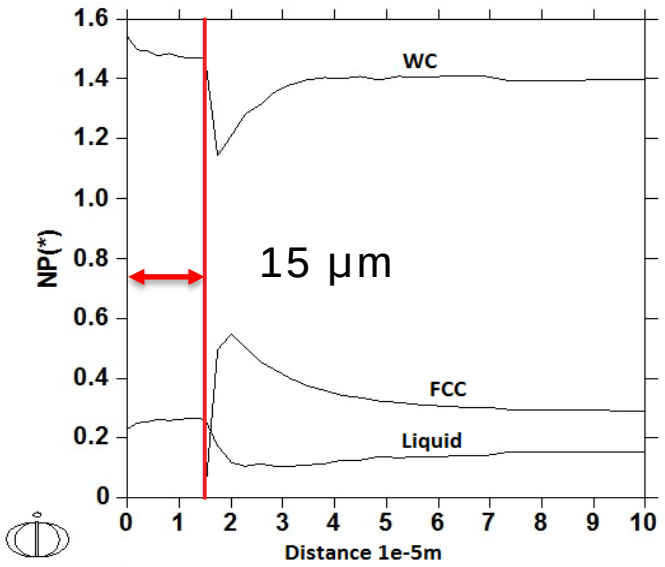
Kinetic modeling
- Mobility data by DFT

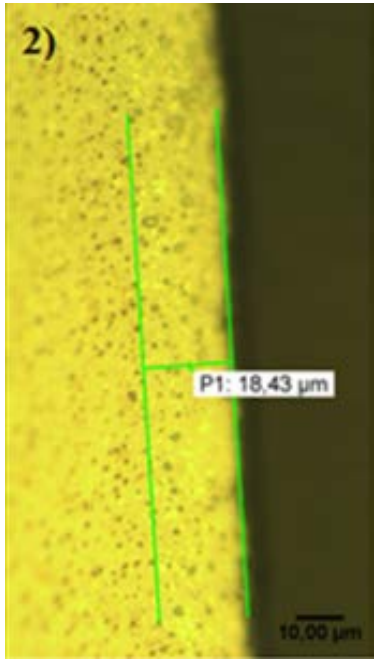


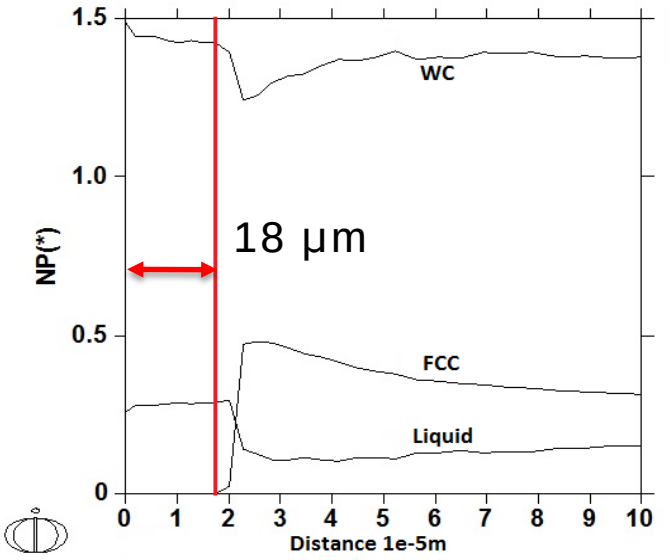
Gradients

Sintering time 1h
Sample 1 at 1673 K
Sample 2 at 1773 K







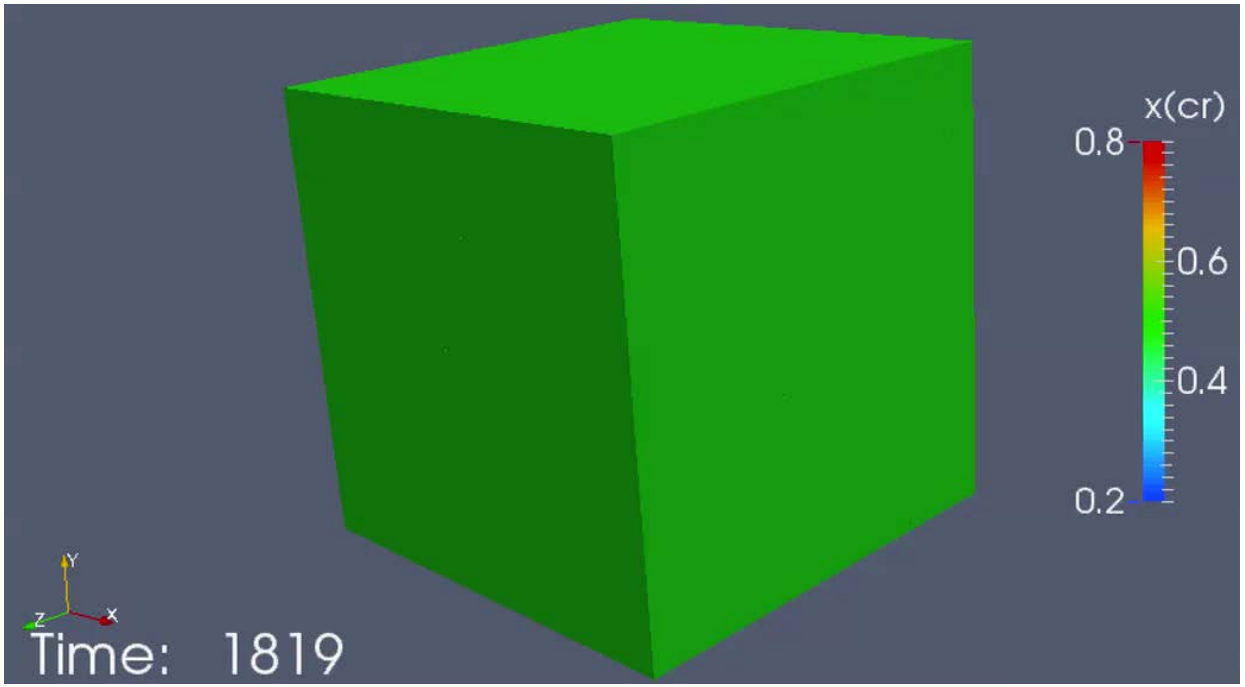


Labyrinth Factor λ

- $D_{eff} = \lambda(f) * D$
- $\lambda = f^2$

5. Examples:
5.2 Phase field

Decomposition in Fe-Cr based ferritic steels



Malik, KTH 2015
Phase field simulation on phase separation in stainless steels

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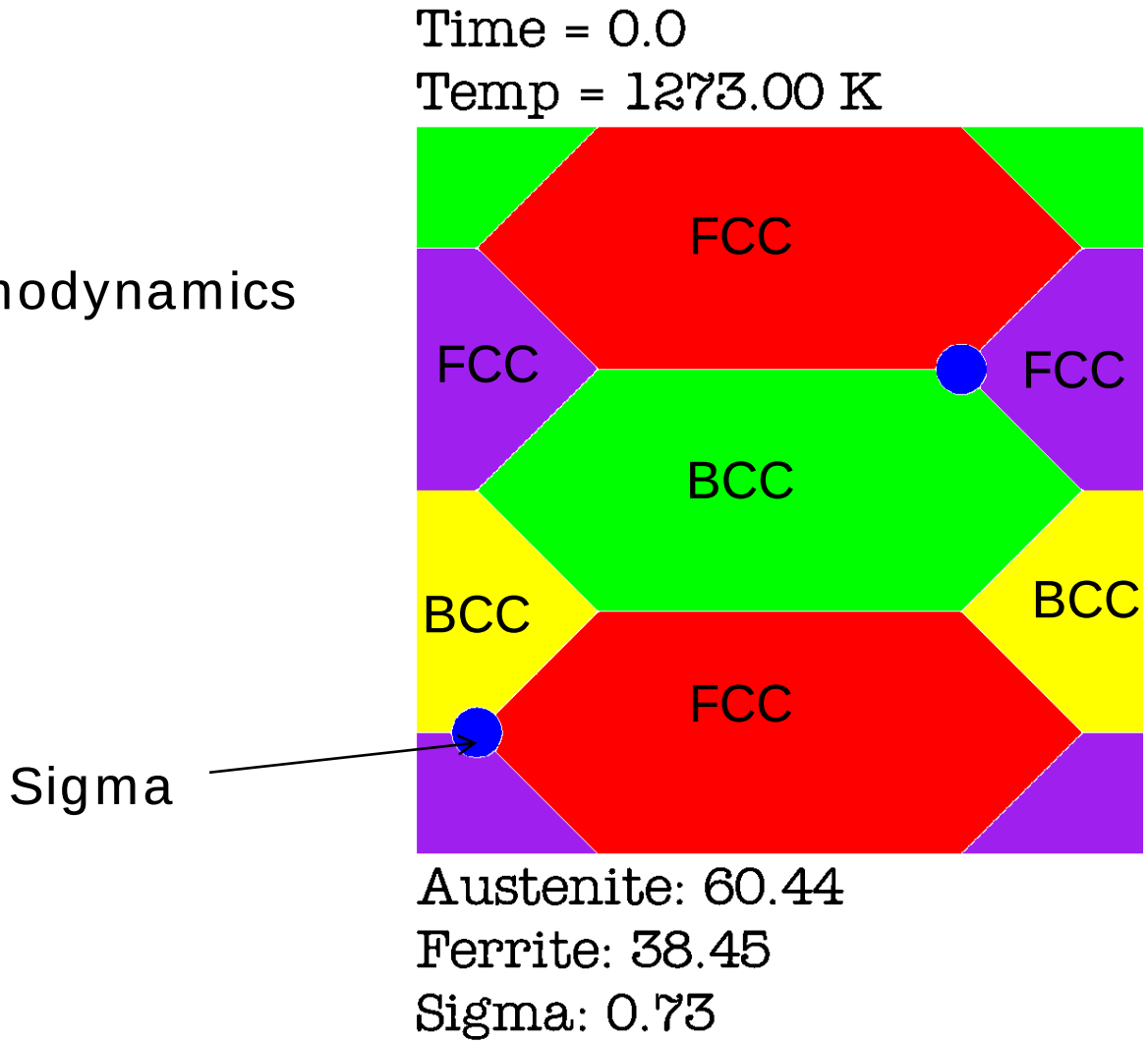
2D phase-field simulation of sigma-phase formation in duplex Stainless steel (SAF 2507)
Fe-25Cr-7Ni-4Mo with continuous cooling from 1273K to 950K

A Malik et al. 2015
(on-going work)

Full CALPHAD Thermodynamics
DICTRA Mobilities



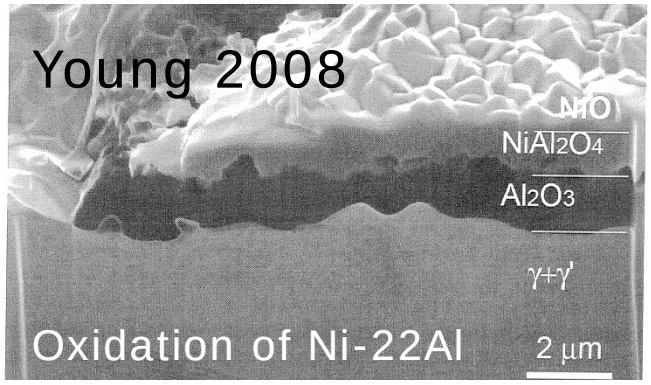
5. Examples:
5.3 Modelling of oxidation

Understand and predict oxidation (e.g. in steels, superalloy bond coates):

- Rate of oxidation
- Morphology internal/external oxidation
- What oxides form
- Porosity
- ...

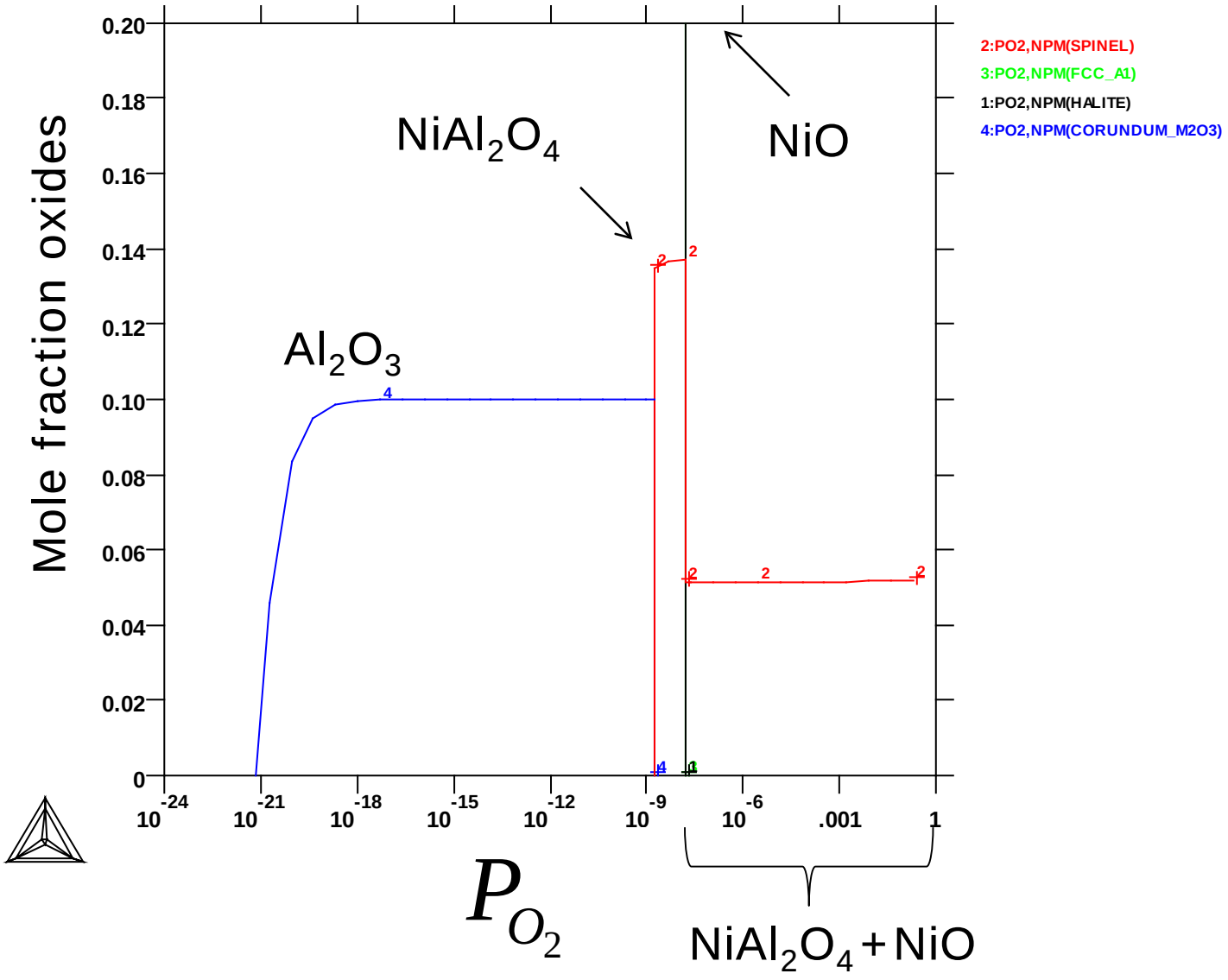
as function of

- alloy content
- external conditions

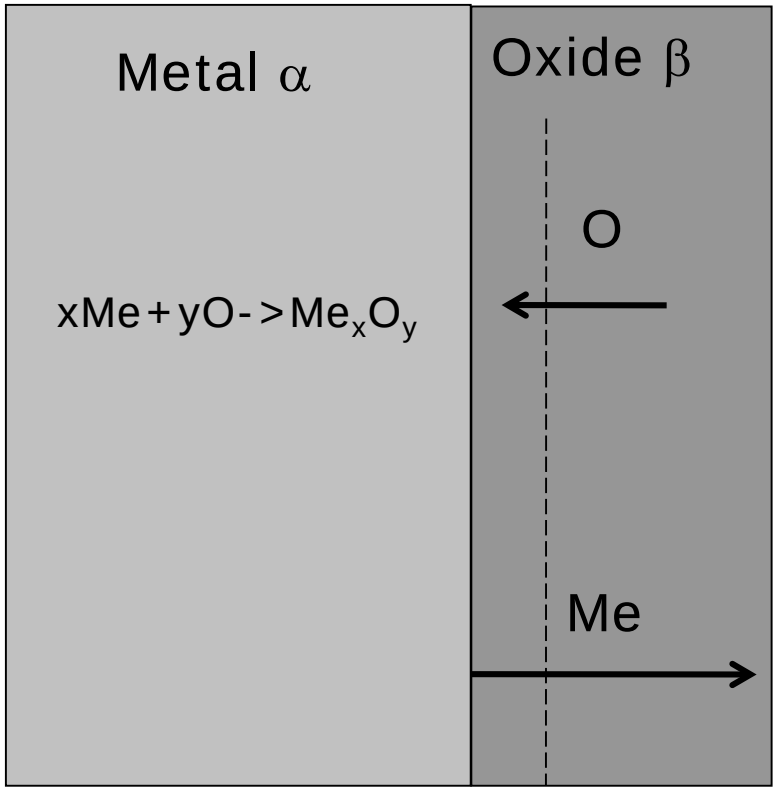


Equilibrium calculations take us quite far...

Ni-2 mass% Al at 1200 °C (TCFE7)



Growth of oxides controlled by diffusion



Atmosphere with O_2

- Oxygen diffusion in the oxide layer gives inward growth
- Metal diffusion in the oxide layer gives outward growth
- Internal oxidation needs oxygen diffusion into the metal, i.e. Oxygen diffusion through the oxide scale and the metal

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Defect based models of diffusion in oxides

Vacancy mechanism operative on different sublattices. The defect structure, the vcancy content, calculated from CALPHAD databases, and the mobility parameters are stored in mobility databases.

Generalization the Wagner model!

Account for type A grain-boundary diffusion.

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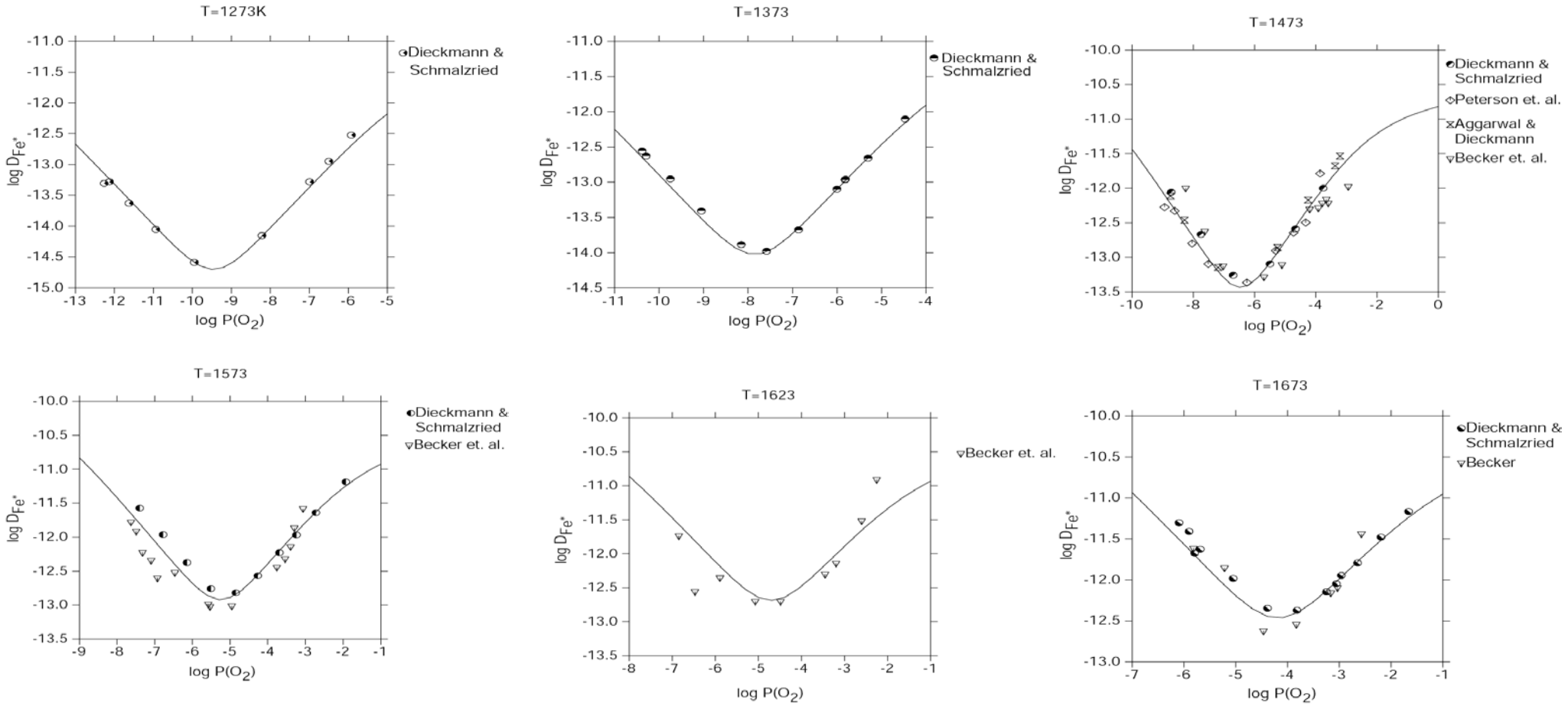
Example of recent work

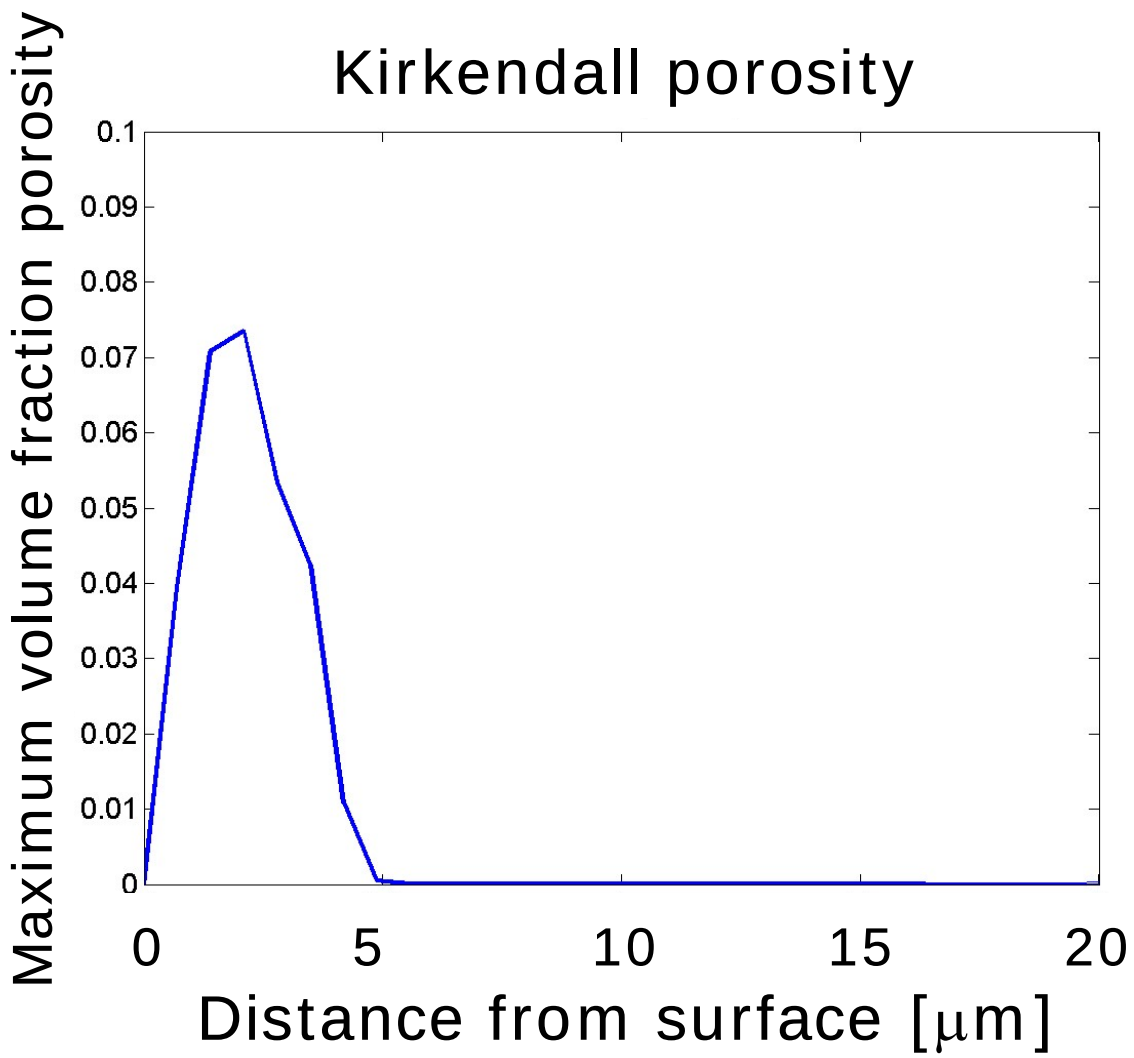
- S. Hallström et al. (2011)
  - Fe-O (Sundman thermodynamic assessment 1991) Wüstite, Magnetite, Hematite
  - Cr-O (Taylor and Dinsdale thermodynamic assessment 1990,1993)
- E. Moore et al. (2013)
  - U-O (Guéneau et al. thermodynamic assessment 2011)
- R. Naraghi et al. (on-going)
  - Fe-O, Co-O...
- H. Larsson et al. (on-going)
  - Internal oxidation of Ni-Al alloy (TCFE7 database)

Experimental data on Fe tracer diffusion in spinel - Optimization of Fe mobilities

(Hallström et al. 2011)



Simulation of oxidation of iron using the homogenization model



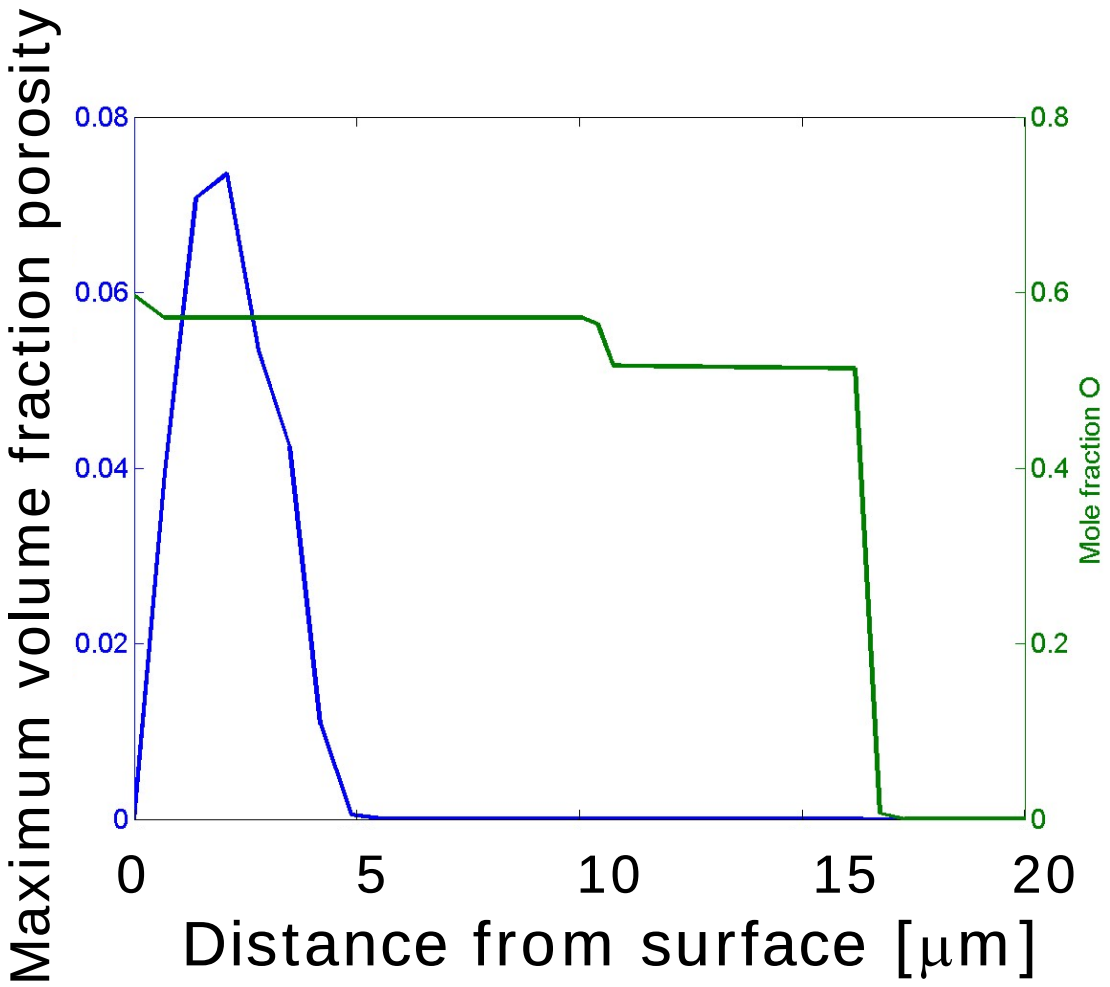
$$J_{va} = -J_O$$

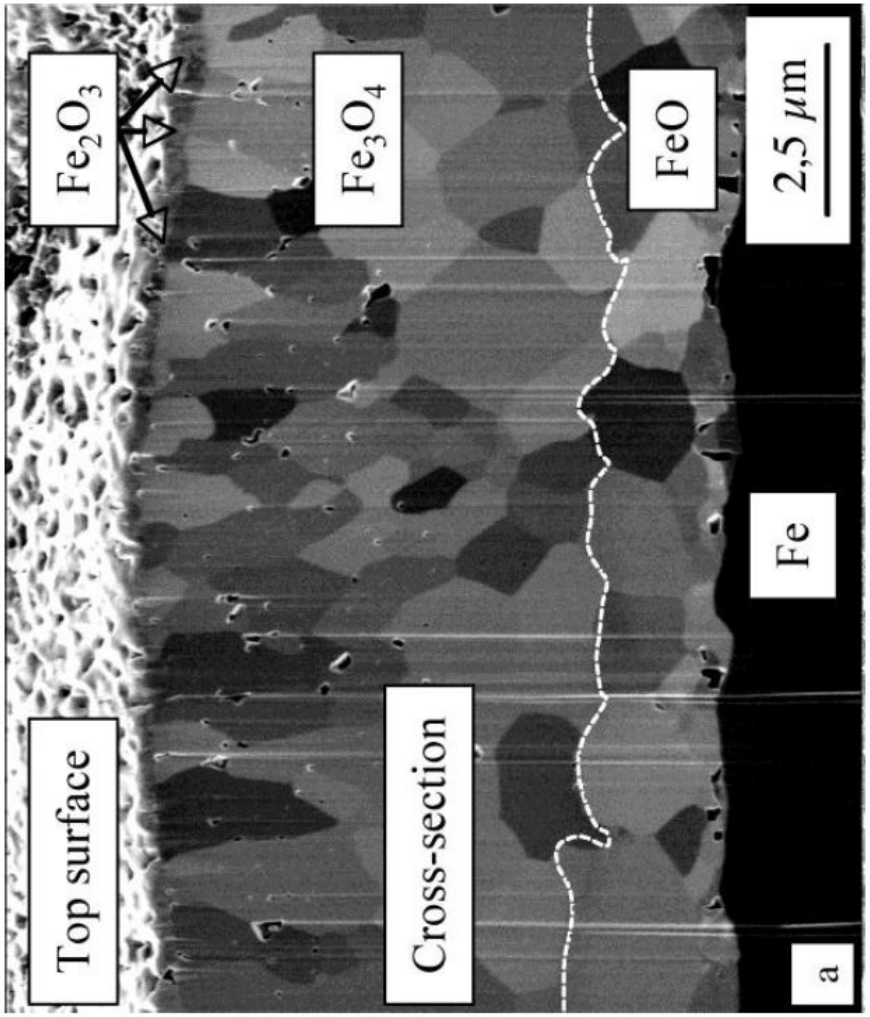
$$\frac{\partial c_{va}}{\partial t} = \frac{\partial}{\partial z}\left(-J_{va}\right) + \dot{q}_{va} \simeq 0$$

$\dot{q}_{va} < 0$ annihilation $\rightarrow$ pores

$\dot{q}_{va} > 0$ creation

Simulation of oxidation of iron using the homogenization model





Jonsson et al Mat Sci Forum 595-598(2008)1005

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6. Conclusions

- Multiscale modelling towards useful engineering tools
- Mix of increasingly advanced models
- Large scale simulations based on thermodynamic and kinetic properties of real engineering materials
- Databases
  - Experimental raw data, (Big Data)
    - High throughput experimentation
  - High quality genomic databases
    - High throughput assessment
- CALPHAD-type modelling for polymeric system?