Modeling of oxide growth

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1) Materials Science and Engineering

2) Thermo-Calc Software AB

Acknowledgements:

Samuel Hallström, Reza Naragi, Lars Höglund, Torbjörn Jonsson, John Morral

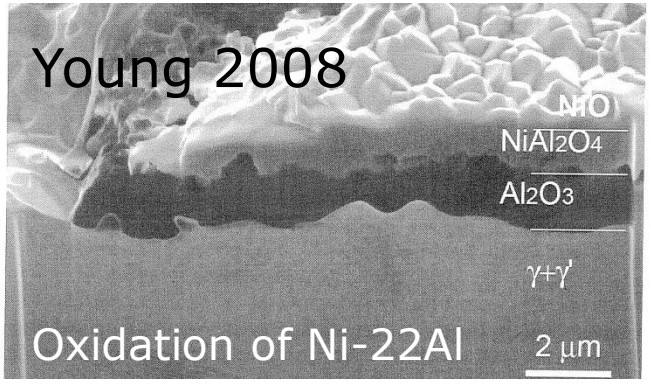
Aim of modelling

Understand and predict oxidation in metallic alloys (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



What we need to model oxidation:

Methods

- Thermodynamic calculations
- Diffusion simulations (DICTRA)

Data

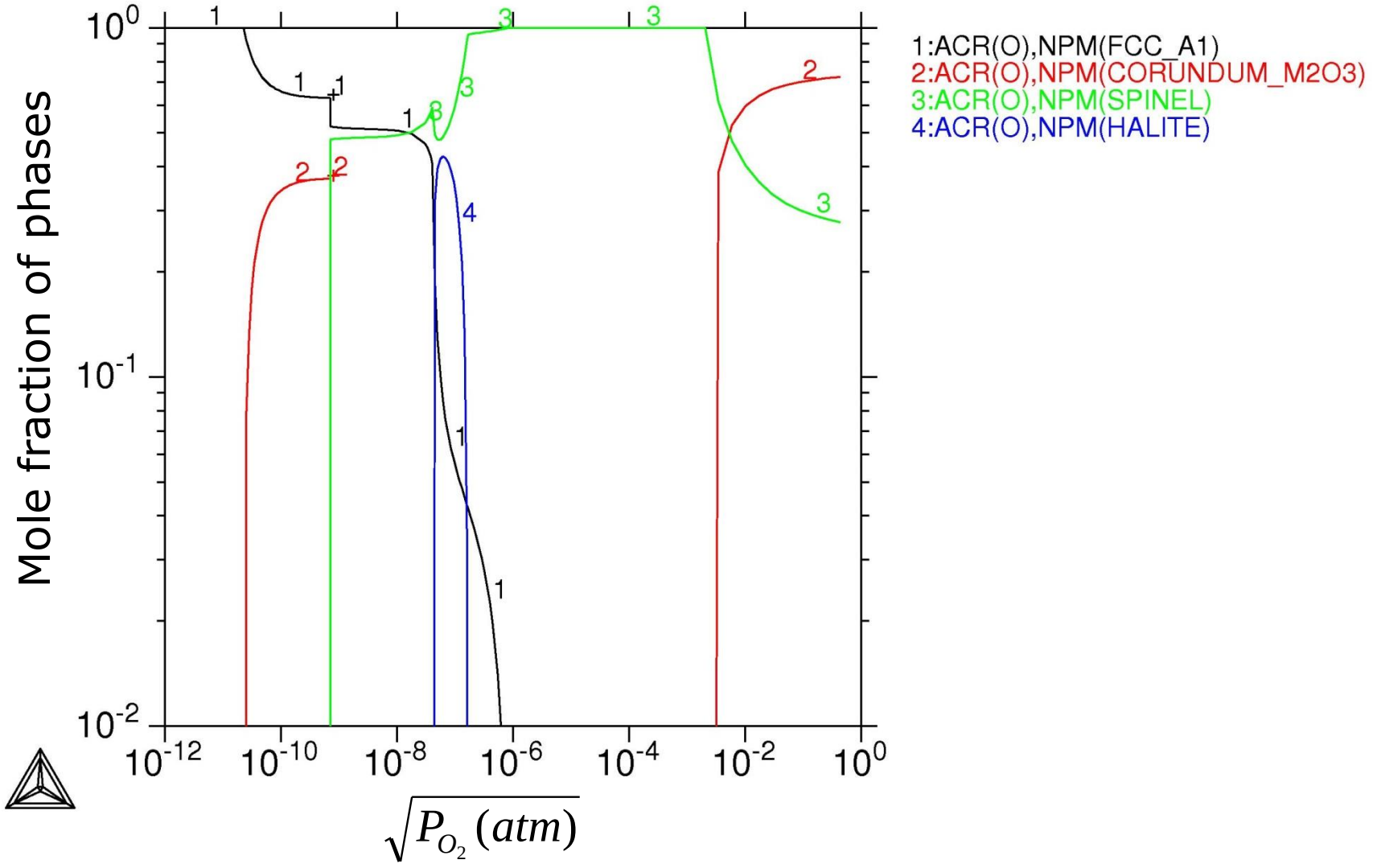
- Thermodynamics
- Kinetics
- Parameters that characterize a given material (grain sizes etc)

Thermodynamic considerations

- Oxidation of pure metals give oxide layers (except for very early stages) – Gibbs phase rule
- Oxidation of alloys may give oxide layers and/or internal oxidation.
- In Ni-base alloys or steels Cr and Al form much more stable oxides than Ni or Fe.

Equilibrium calculations

Fe-18Cr-8-Ni at 1000 °C (TCFE6)



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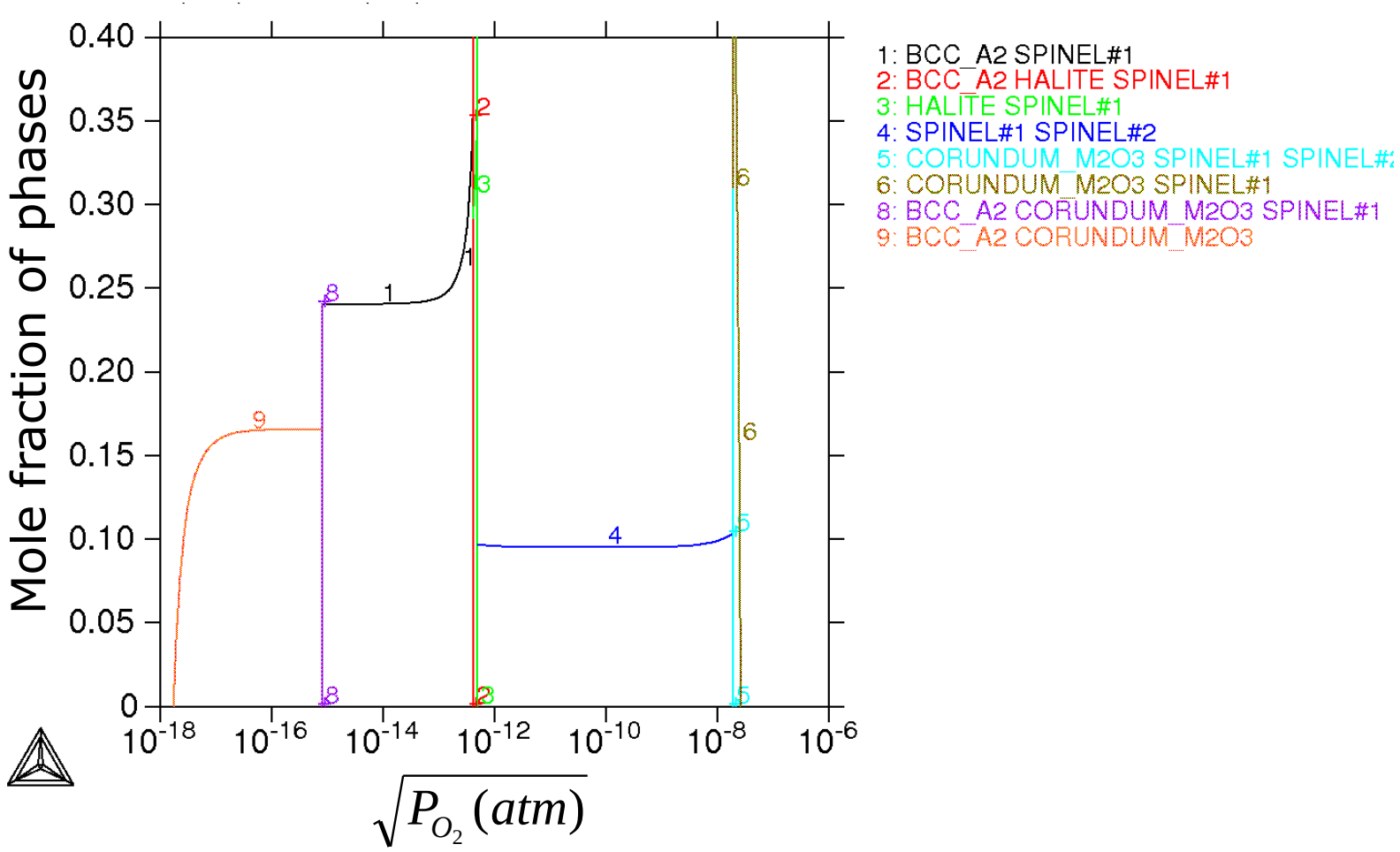
Fe-12 mass % Cr at 600 °C



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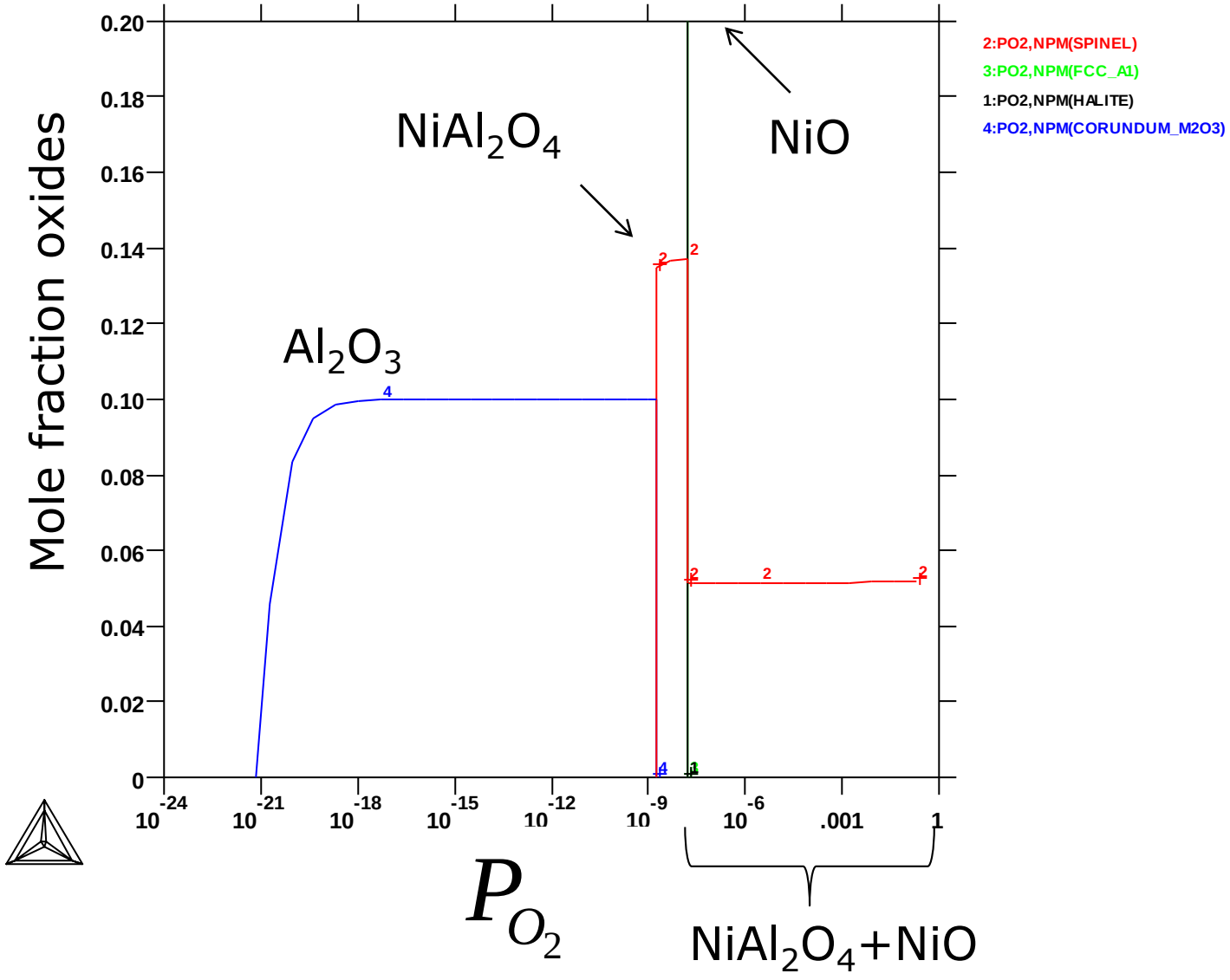
Ni-2 mass% Al at 1200 °C (TCFE7)



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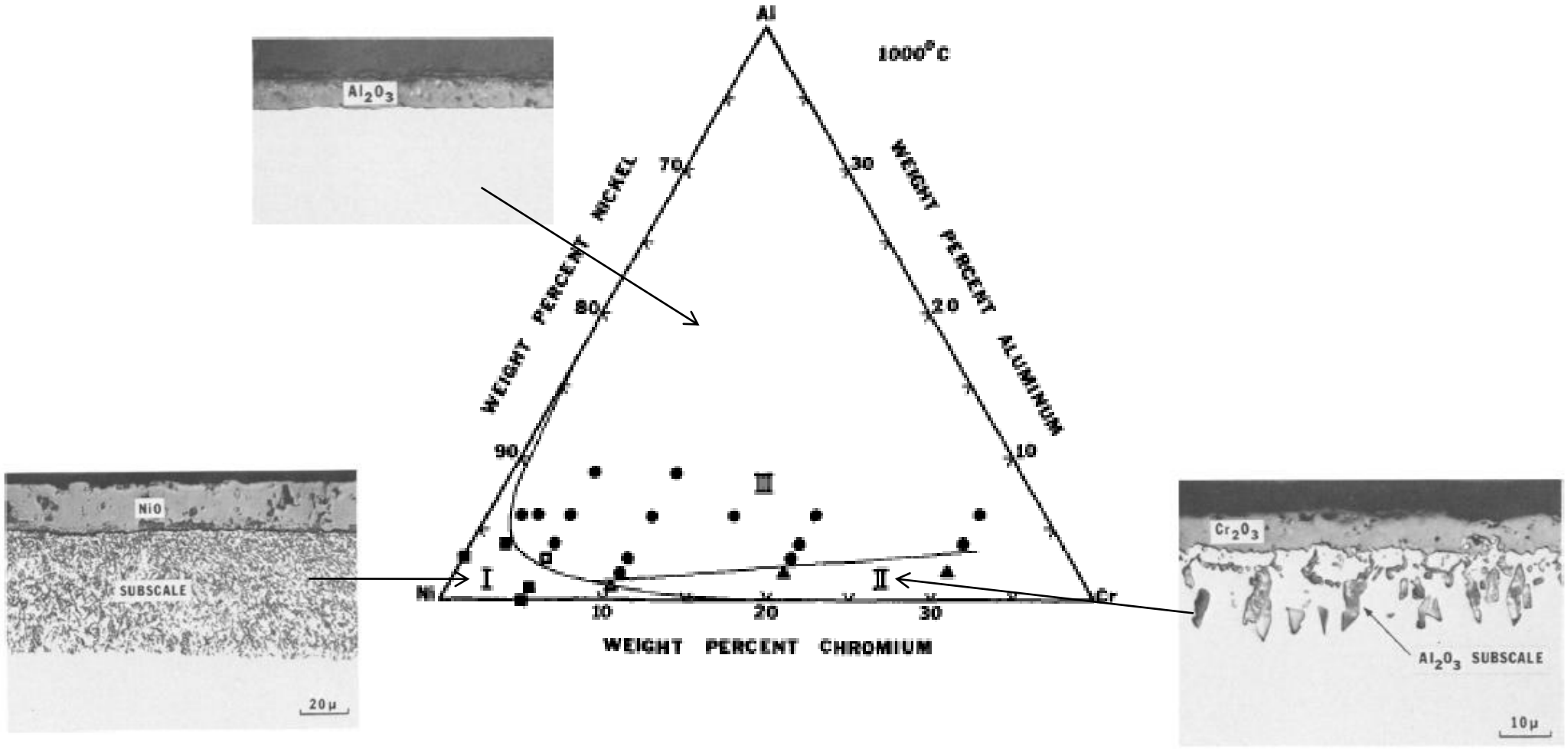
Giggins and Pettit (1971)



Thermodynamic lesson:

If:

- the oxygen activity monotonically decreases from surface to bulk

and

- the alloy composition does not change,

→ the sequence of phases may be predicted from a straightforward thermodynamic calculation which is in reasonable agreement with observations.

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The interdiffusion genome

- Systematic work to build up highly processed databases combined with appropriate models to predict thermodynamics, phase quilibria and kinetics of engineering materials.
  - Steels, Ni-base super alloys, light alloys etc
  - Disordered and ordered phases
  - Carbides, nitrides, oxides
- Based on fluxes expressed with thermodynamic driving forces :

$$J = -L\nabla\mu = -L\frac{\partial\mu}{\partial c}\nabla c = -D\nabla c$$

$$D = L\frac{\partial\mu}{\partial c}$$

L matrix contains diffusional mobilities.

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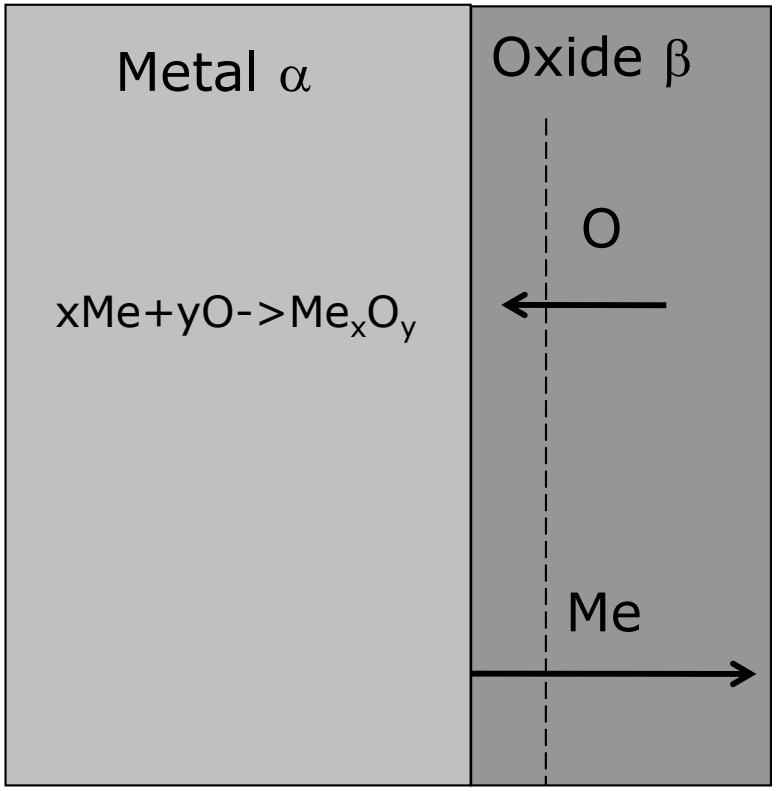
Defect based models of diffusion in oxides

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.

Inward and outward growth of oxides scales



Atmosphere with O_2

- Oxygen diffusion in the oxide layer gives inward growth
- Metal diffusion in the oxide layer gives outward growth

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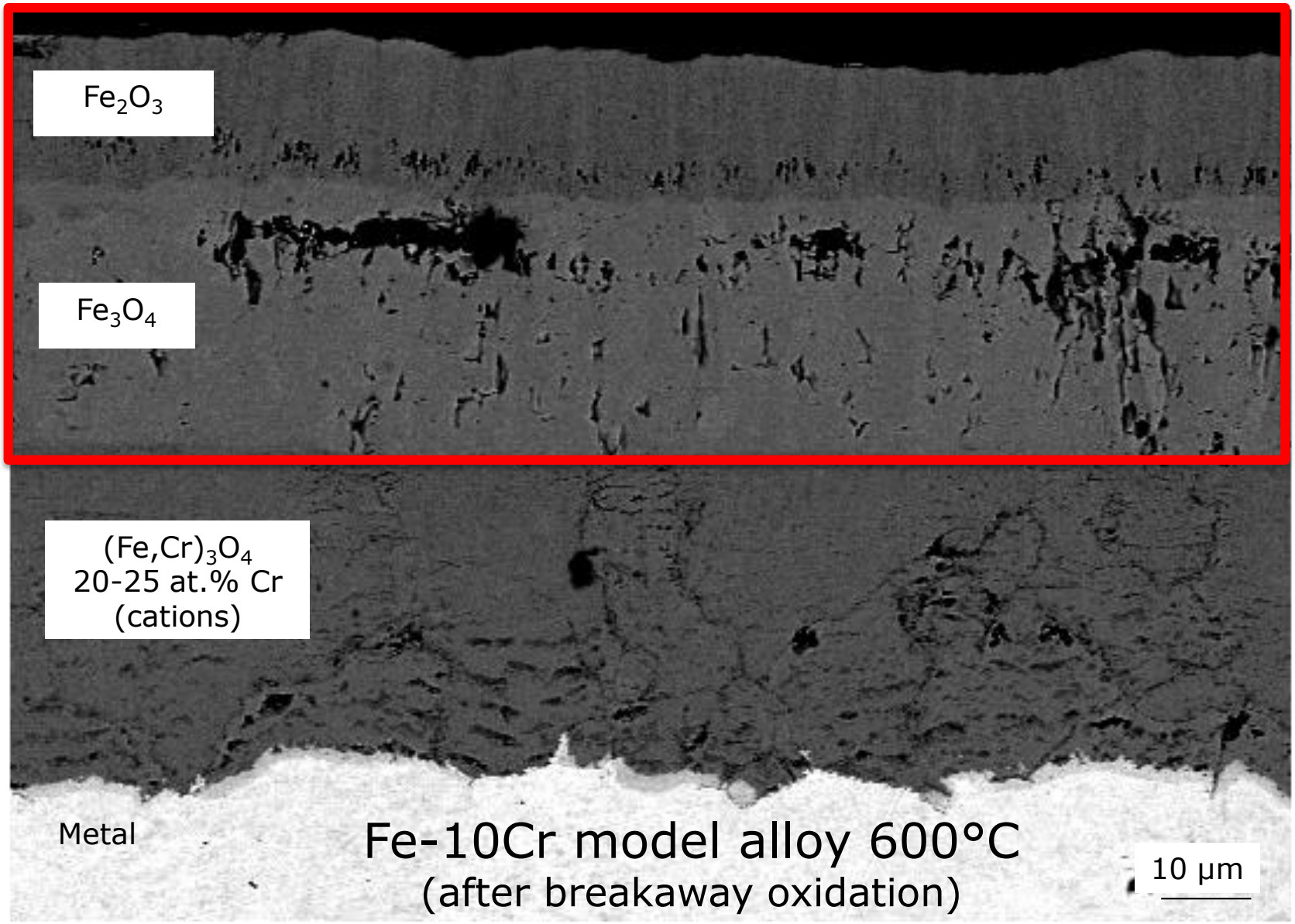
Internal oxidation

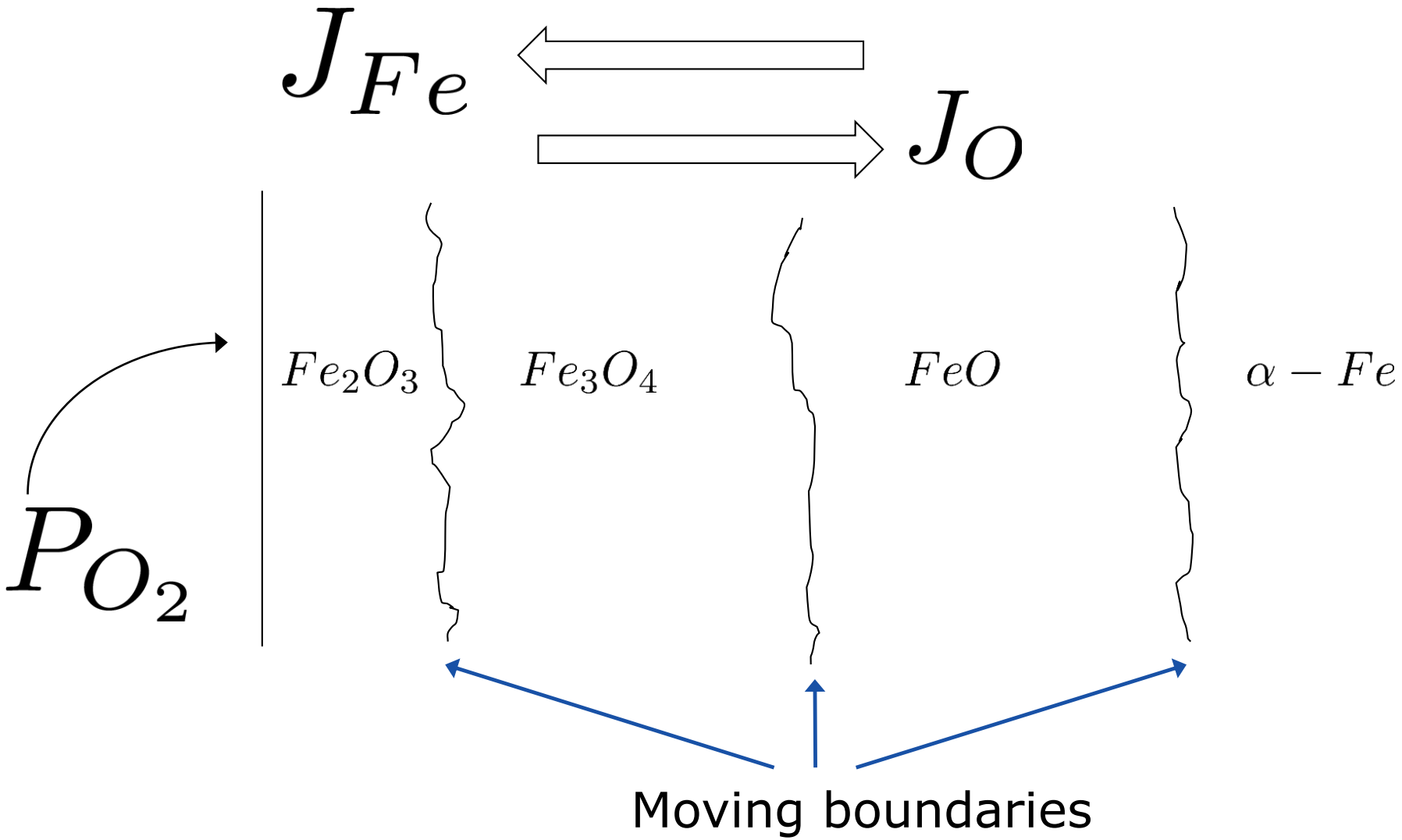
Internal oxidation needs oxygen diffusion into the metal, i.e. oxygen diffusion through an oxide scale and through the metallic bulk are both important.

Importance of iron oxide

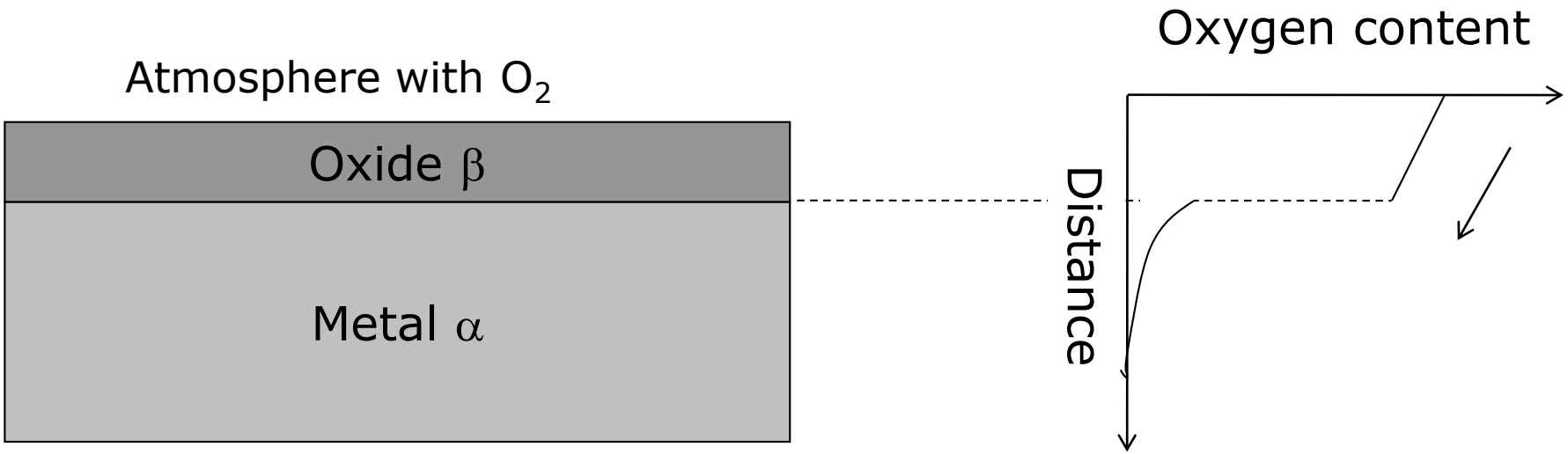
Pujilaksono, B. et al *Oxidation of Binary FeCr Alloys (Fe–2.25Cr, Fe–10Cr, Fe–18Cr and Fe–25Cr) in O2 and in O2 + H2O Environment at 600 °C.* Oxidation of Metals, 2011. **75**(3): p. 183-207.



Simulation setup



How fast do the layers grow?



Flux balances in sharp-interface modelling!

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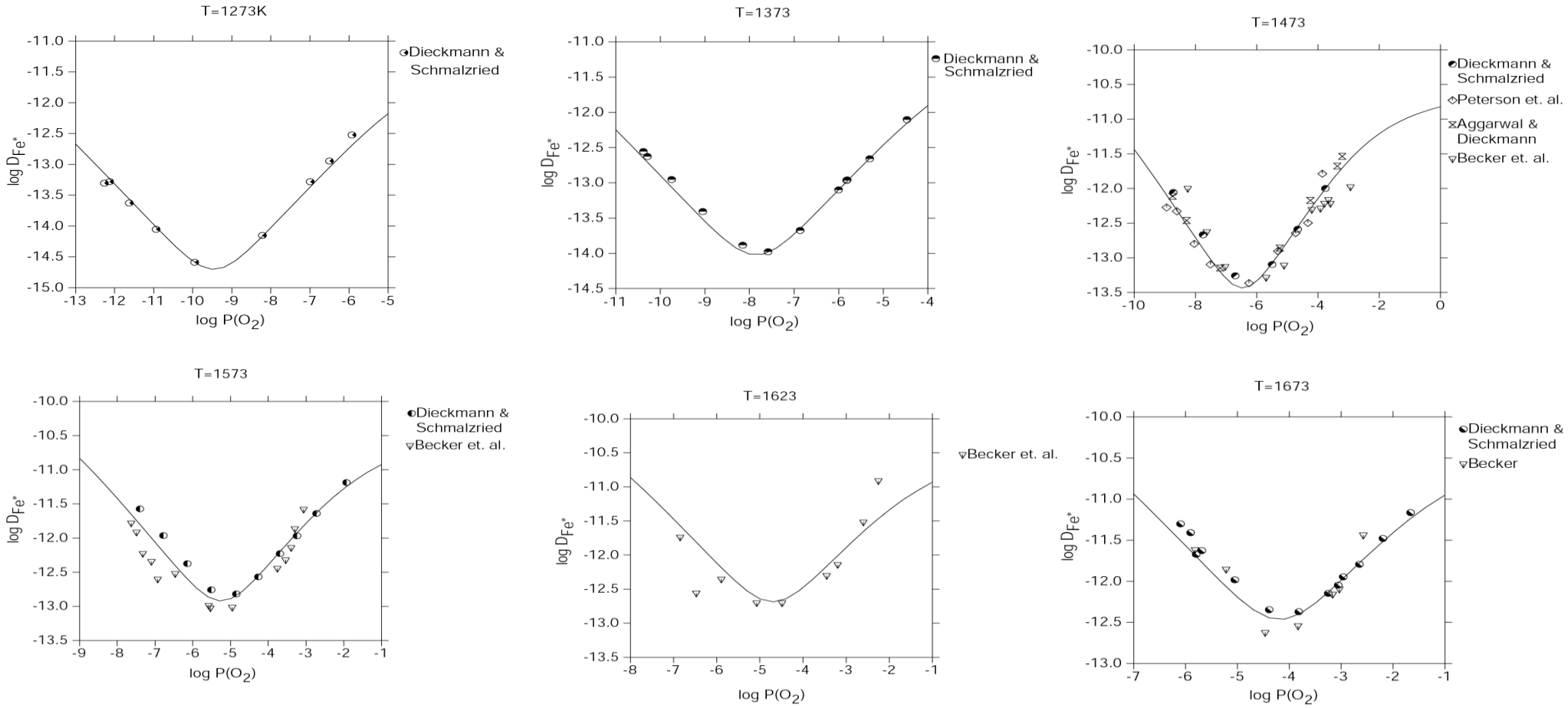
Example of recent work

- 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)



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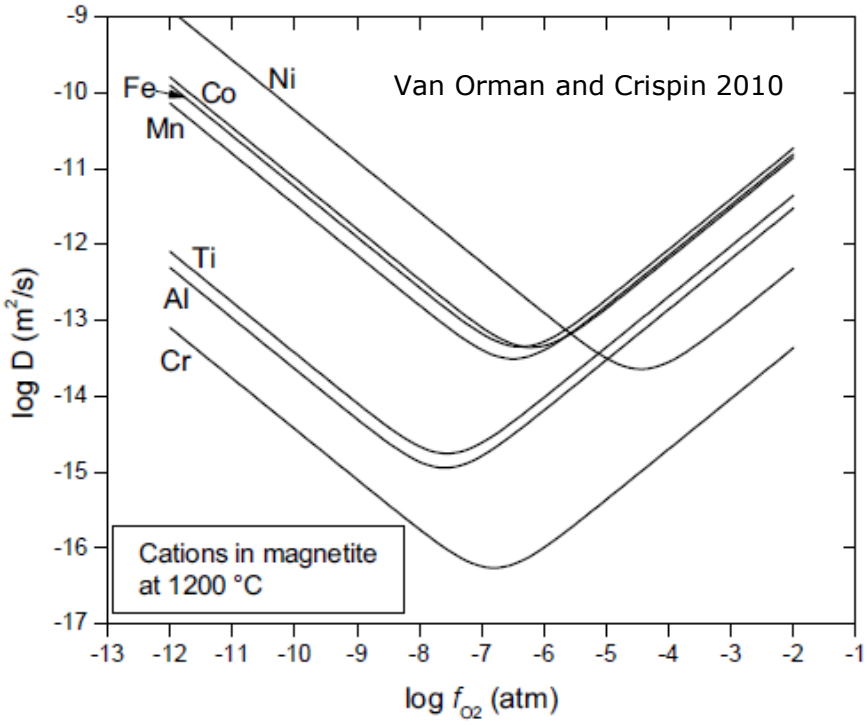
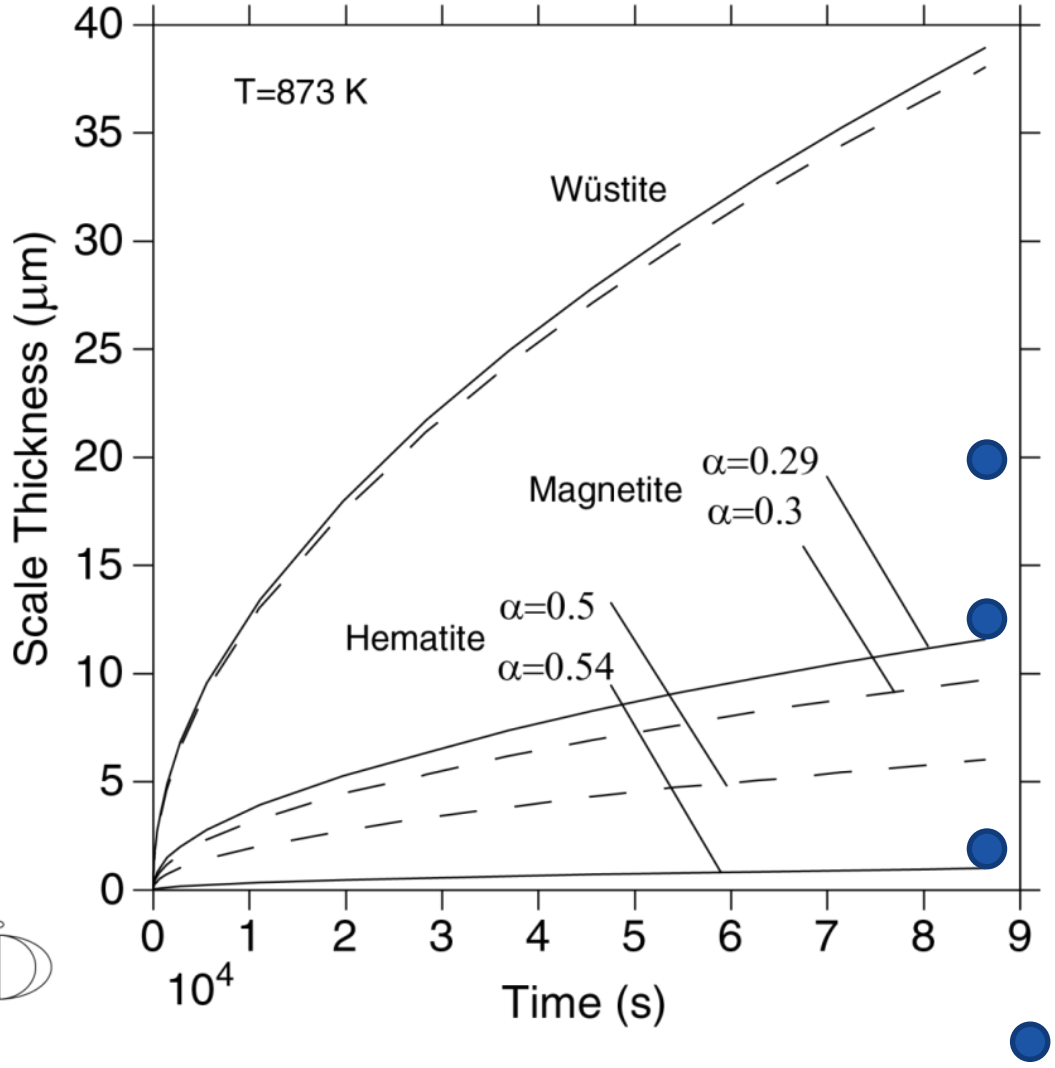
Alloy elements in spinel (lattice fixed frame of reference)



Cr content of inward growing spinel will inherit Cr content of alloy.

Simulation of oxidation of Iron with moving boundaries



873 K, dry oxygen, 24 h

A-type grain boundary diffusion:

$$M^{eff} = \left(1 - f^{gb}\right) M^{bulk} + f^{gb} M^{gb}$$

$$f^{gb} = \delta / d$$

$$\delta \sim 0.5\,\mathrm{nm}$$

$$d^{mag} \sim 3\,\mu\mathrm{m}$$

$$d^{hem} \sim 0.1\,\mu\mathrm{m}$$

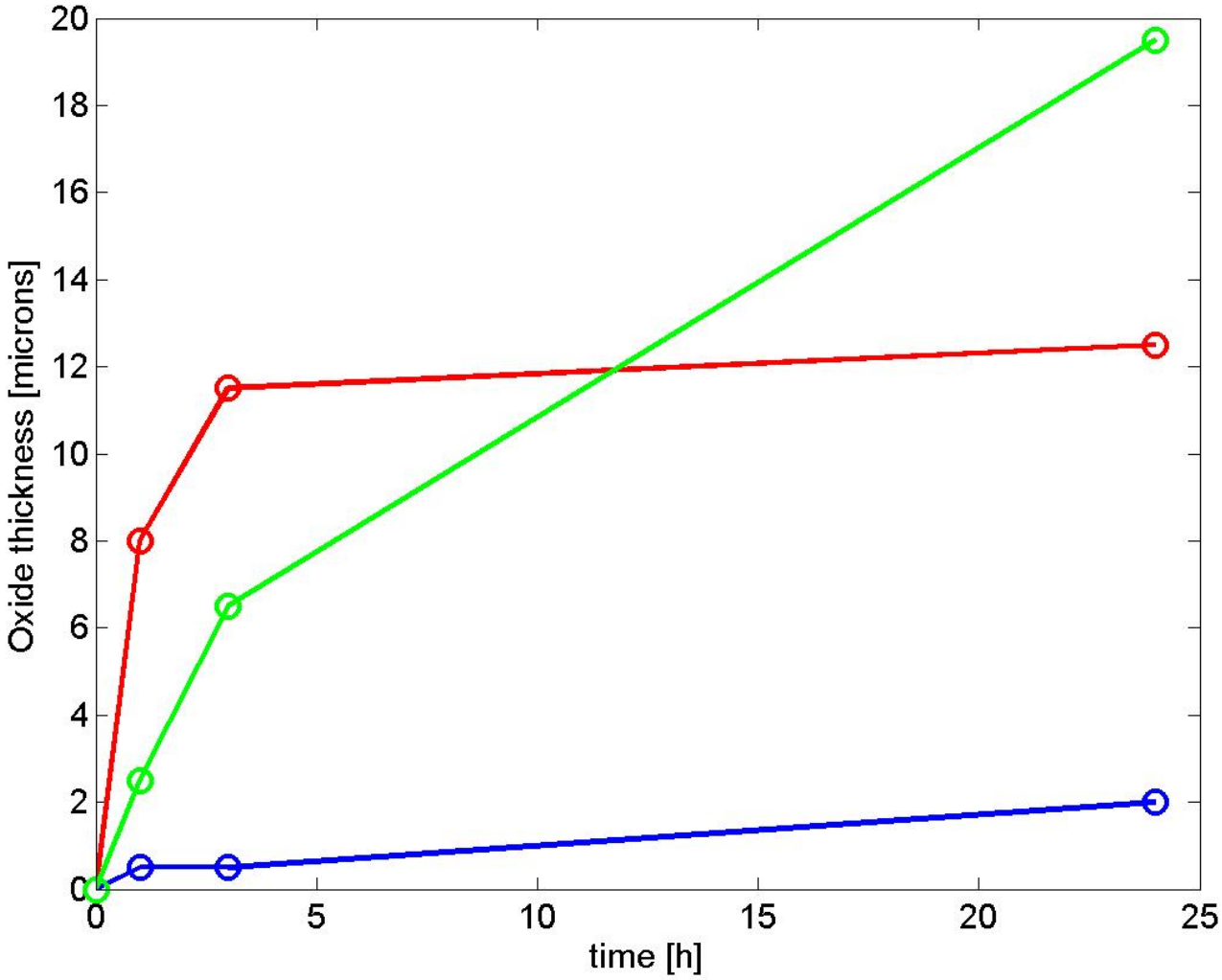
$$M^{bulk} = M_0^{bulk} \exp\left(\frac{-Q^{bulk}}{RT}\right)$$

$$M^{gb} = M_0^{bulk} \exp\left(\frac{-\alpha Q^{bulk}}{RT}\right)$$

Simulations performed by Naraghi

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

Experimental oxide thickness, 600°C, dry O_2



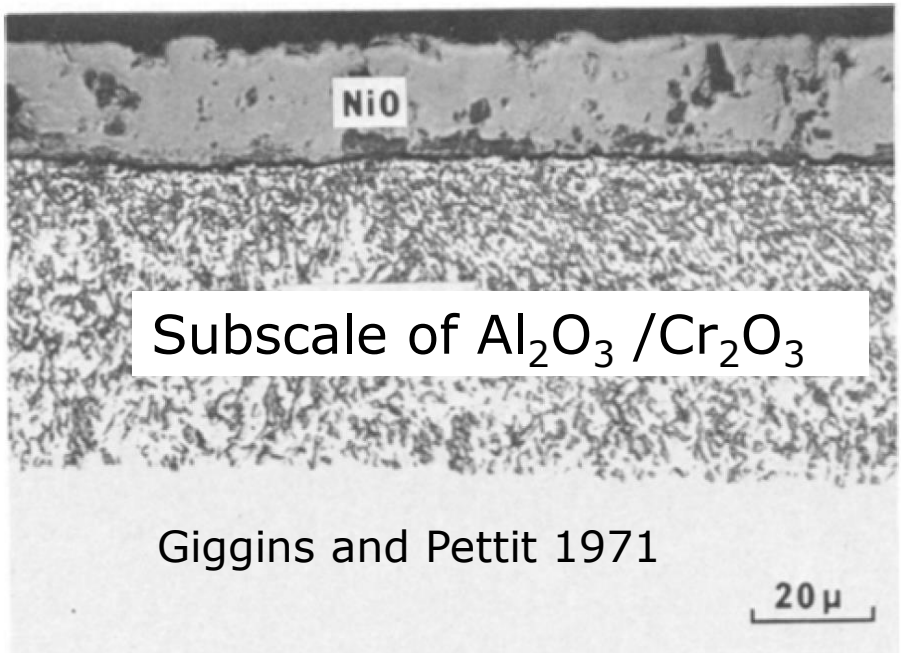
Wustite

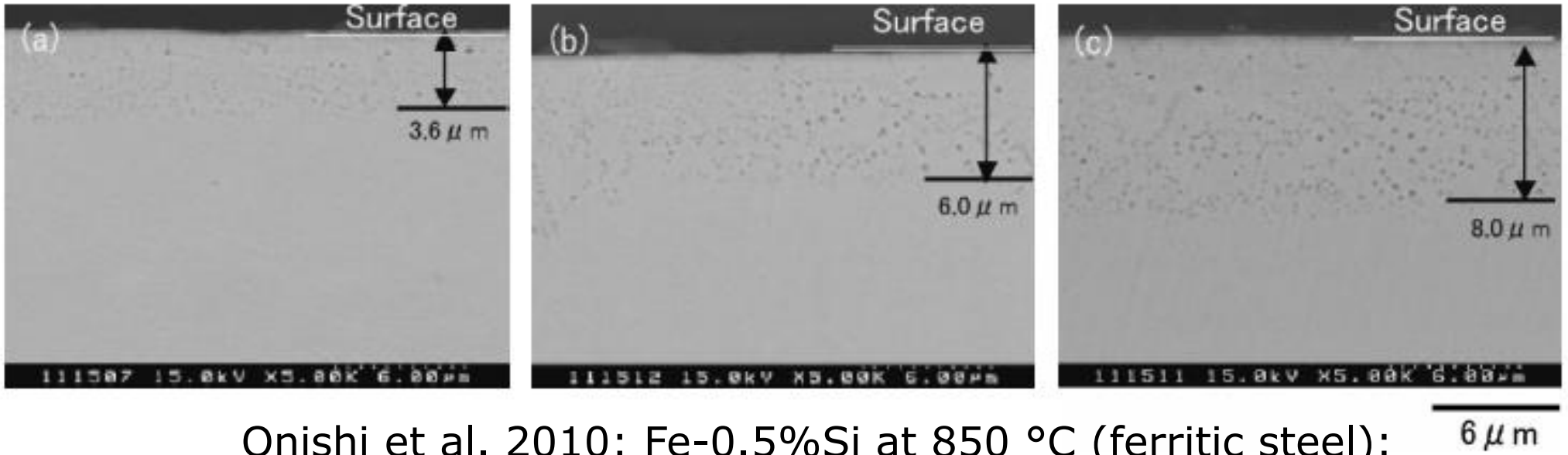
Magnetite

Hematite

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

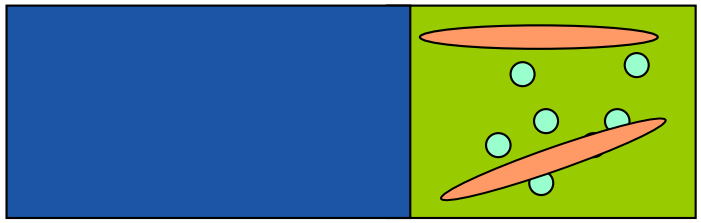
Internal oxidation





Onishi et al. 2010: Fe-0.5%Si at 850 °C (ferritic steel):

The Dictra homogenization model

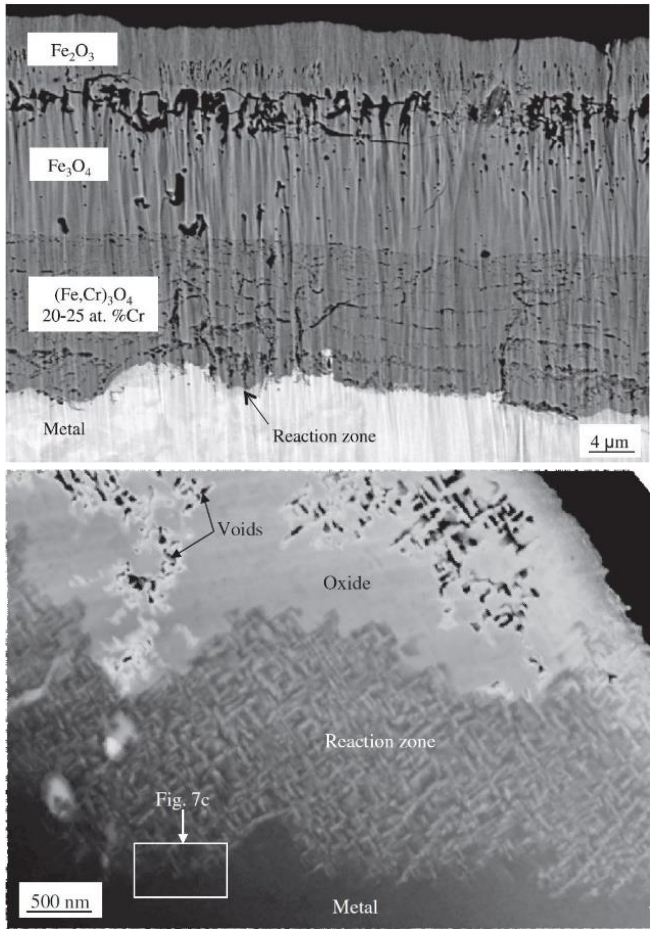


- A model for multiphase simulations
- Not necessary to predefine phase region sequence

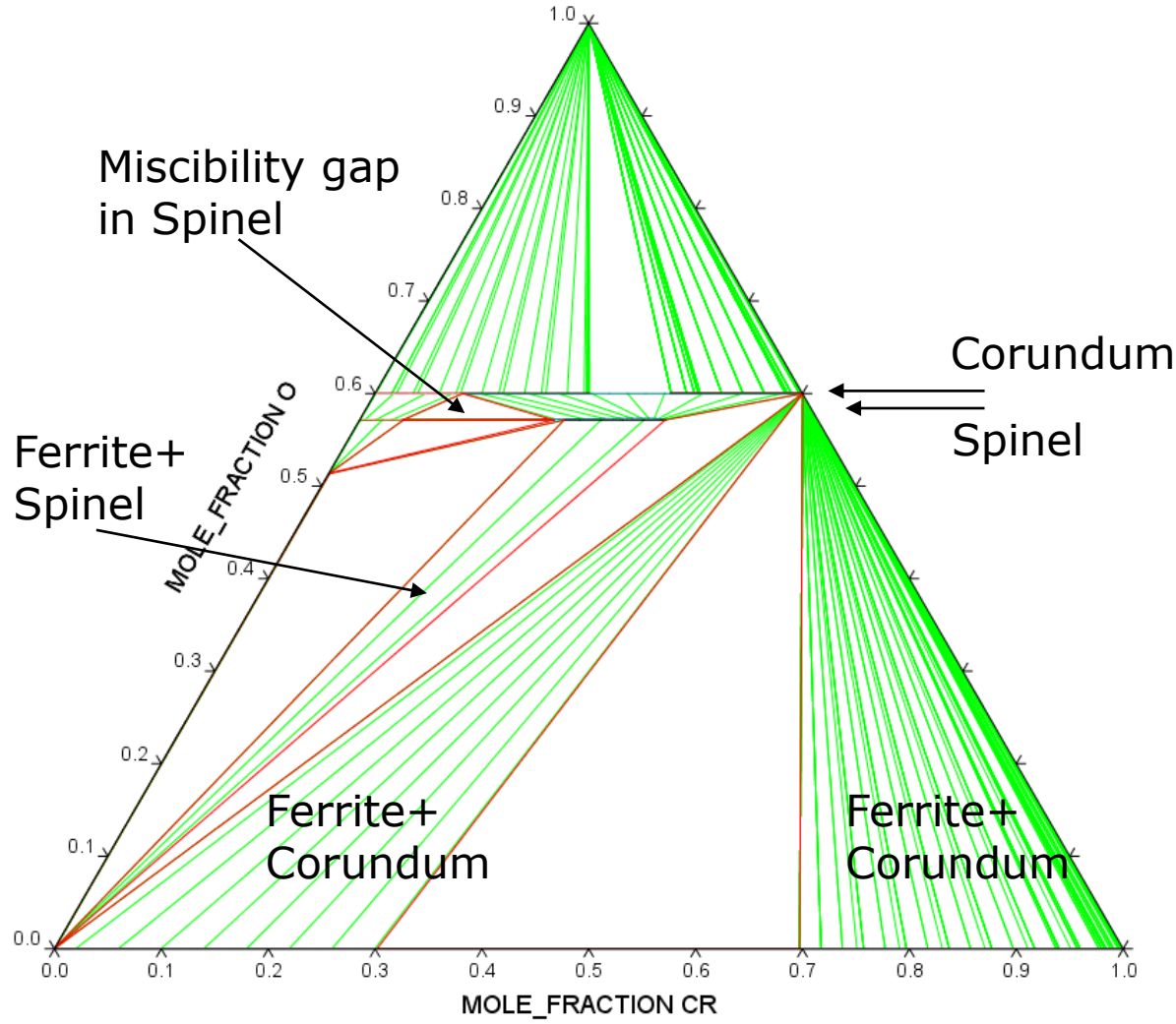
Larsson, Engström, Acta Mat 54(2006)2431
Larsson, Höglund, Calphad 33(2009)495

Why use the homogenization model?

Oxidation of Fe-10Cr at 600°C (micrographs after 24 h)



Jonsson et al, Corrosion Science 75(2013)326



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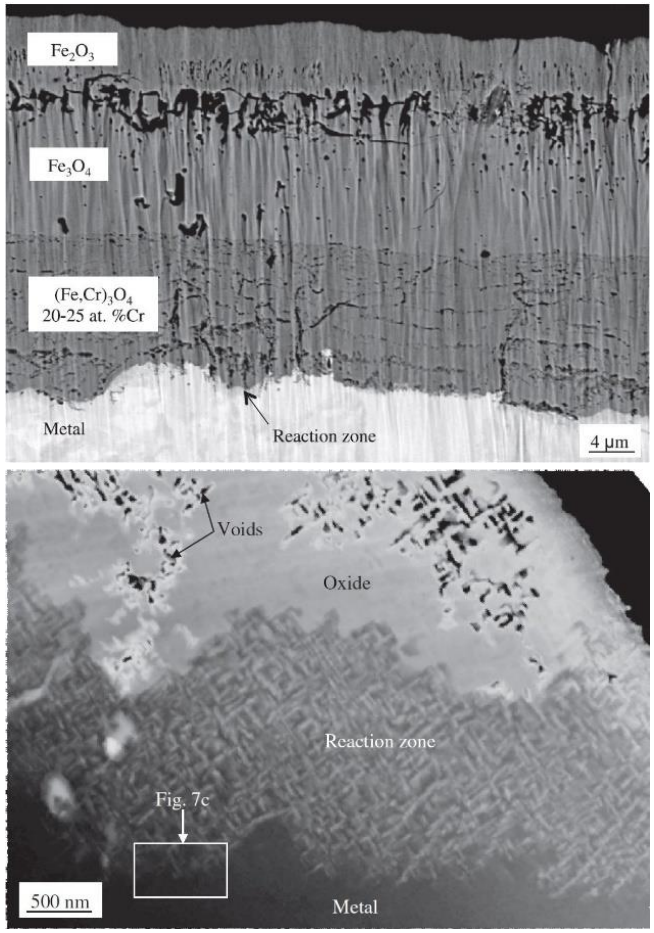

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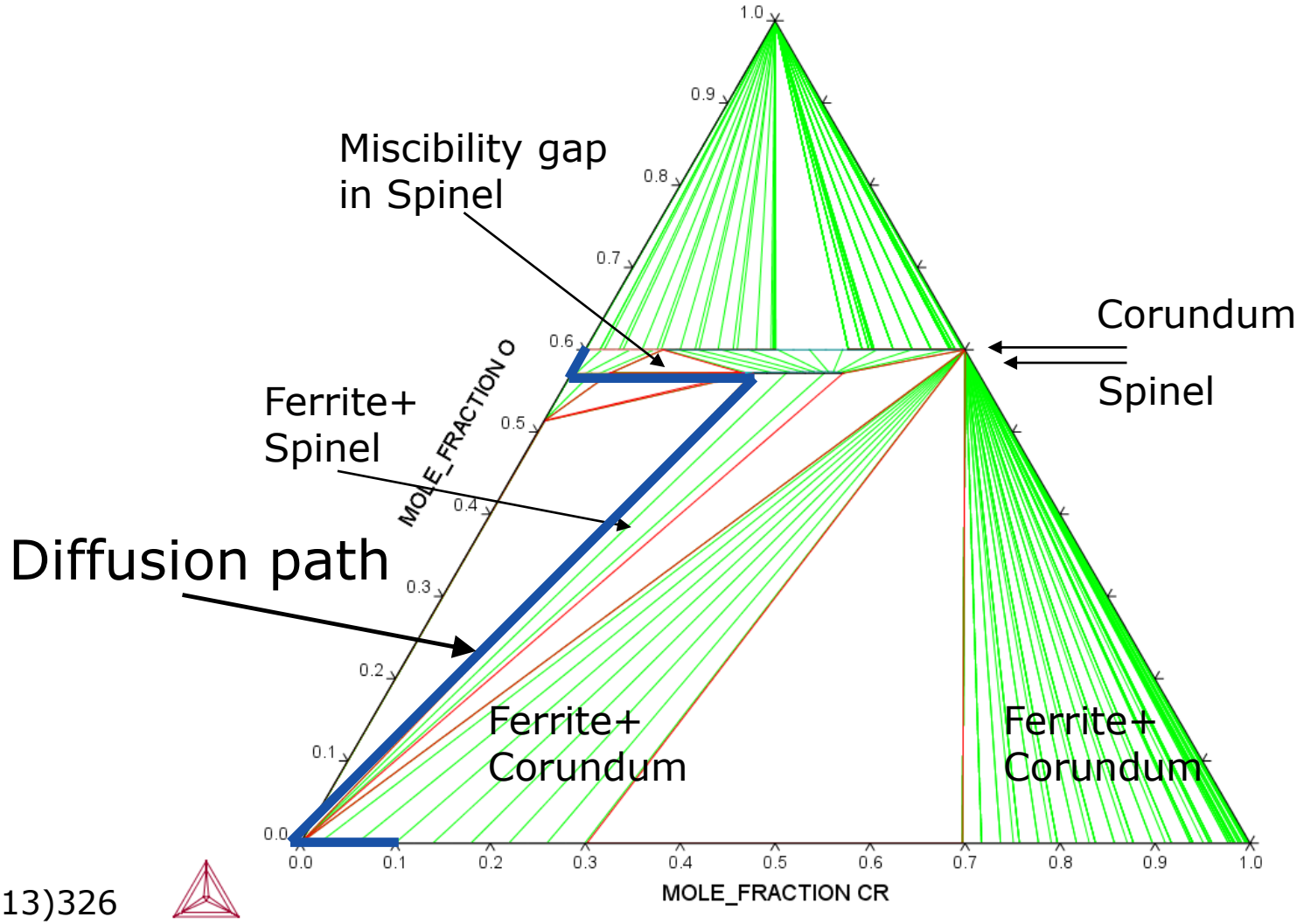
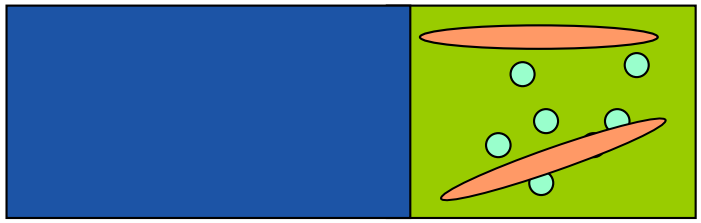


The Dictra homogenization model



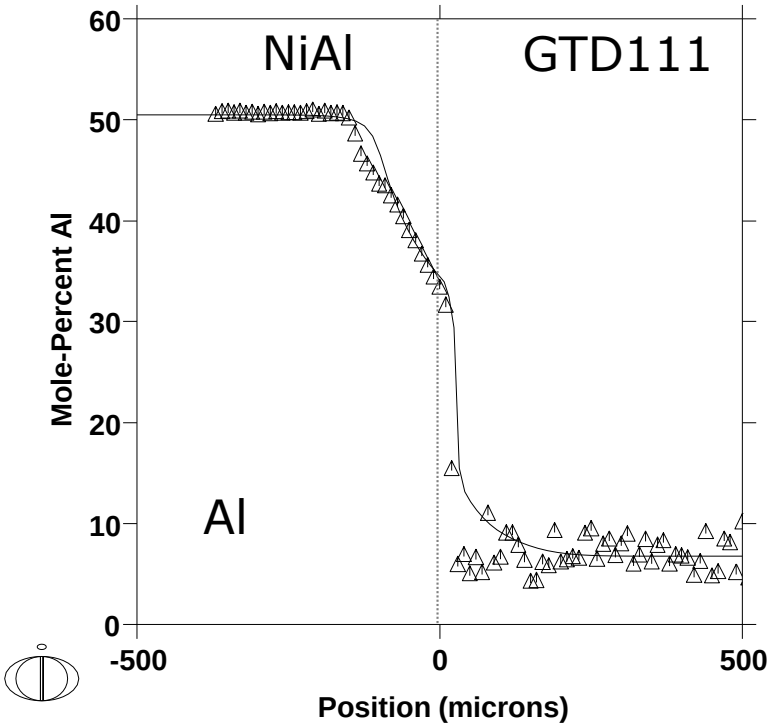
- No explicitly introduced phase interfaces
- No front tracking
- Assume full local equilibration
  - Local overall composition → local phase fractions,
    local phase compositions, etc.

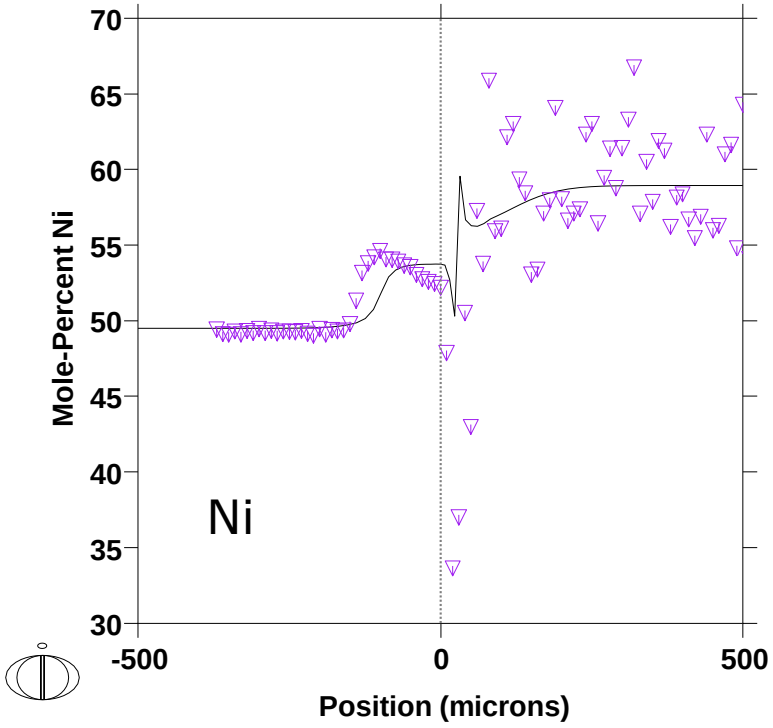
Larsson, Engström, Acta Mat 54(2006)2431
Larsson, Höglund, Calphad 33(2009)495

Example: NiAl coating on superalloy GTD111

	Ni	Al	C	Co	Cr	Mo	Ta	Ti	W
NiAl-Coating	Bal	50.5	-	-	-	-	-	-	-
GTD111	Bal	6.9	0.48	9.5	16.6	0.97	0.89	6.24	0.97

Temp.
1050°C
Time 96h

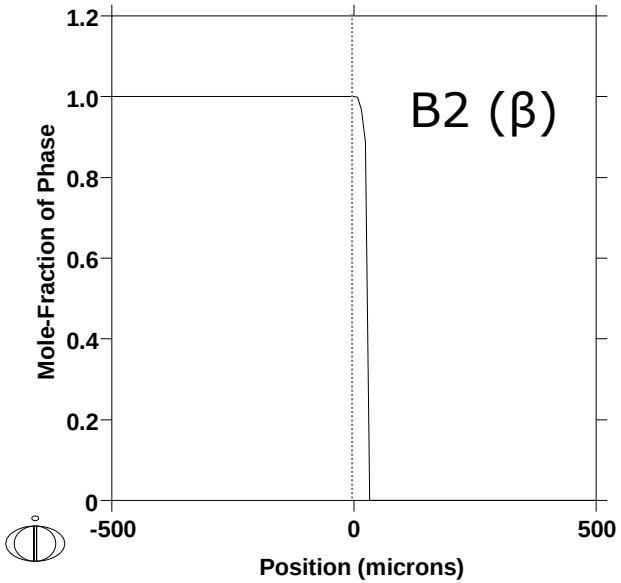




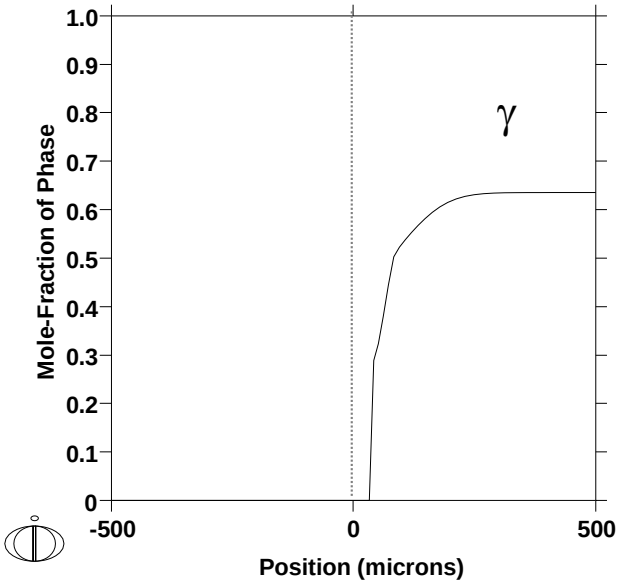
Symbols are experimental data from Perez, Patterson and Sohn,
J Phase Equilibria and Diffusion **27**(2006)659

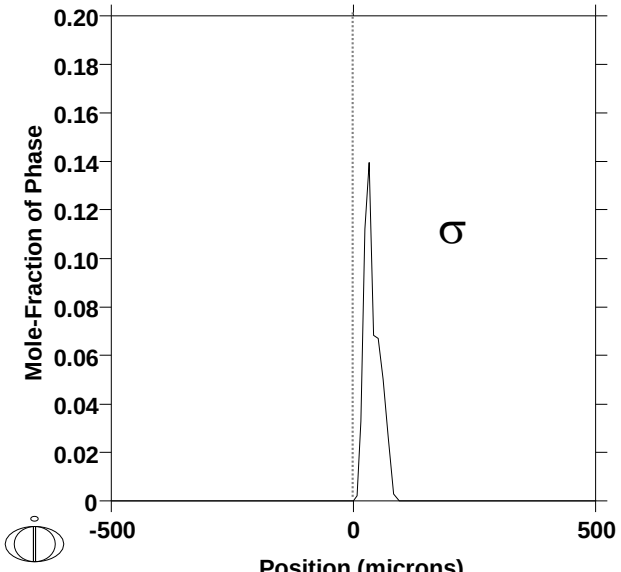
Engström et al. Adv Mater Research 278(2011)198

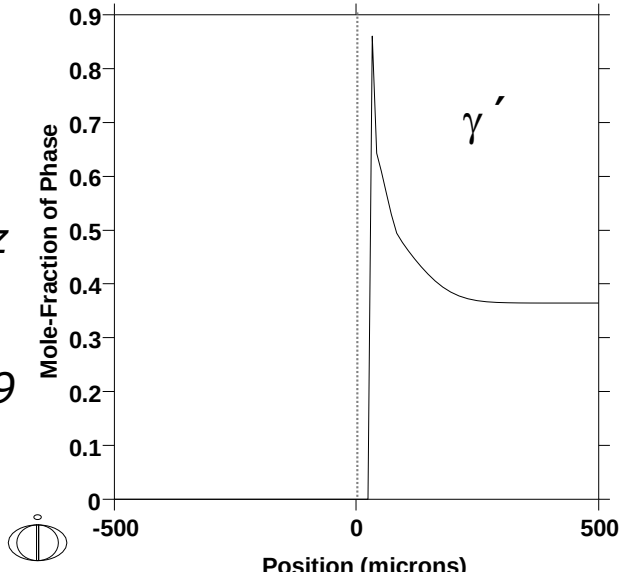
Example: NiAl coating on superalloy GTD111



Micrograph from Perez et al
*J Phase Equilibria and Diffusion **27**(2006)659*







Engström et al. Adv Mater Research 278(2011)198

Modifications of the Homogenization model for oxidation simulations

- Use of assessed molar volumes
- Solve diffusion problem in the lattice-fixed frame of reference
- Numerically challenging problem – numerous fixes introduced to increase stability

Simulation of oxidation of iron at 600°C using the homogenization model

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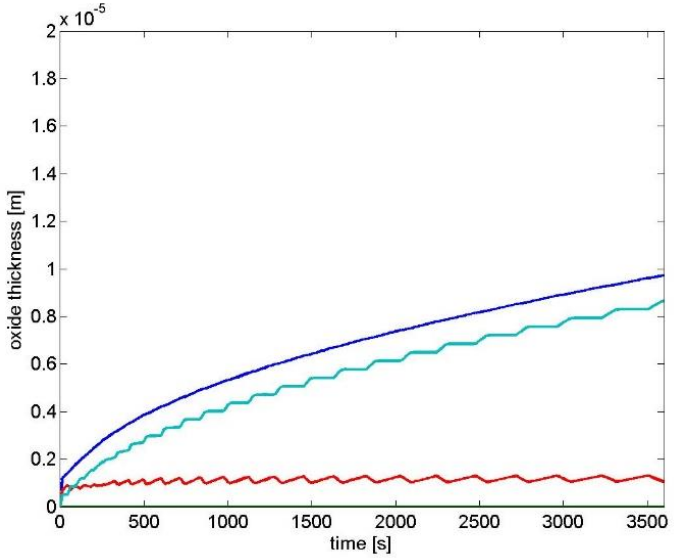
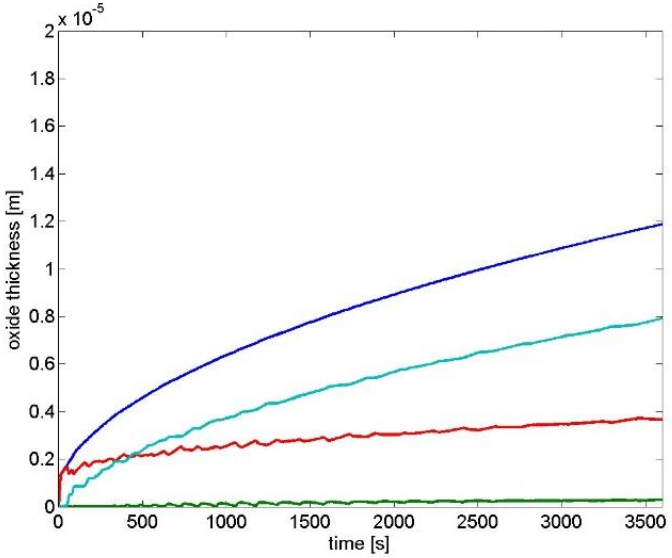
Total (Exp. 11 μm)
Wustite (Exp. 2.5 μm)
Magnetite (Exp. 8 μm)
Hematite (Exp. 0.5 μm)

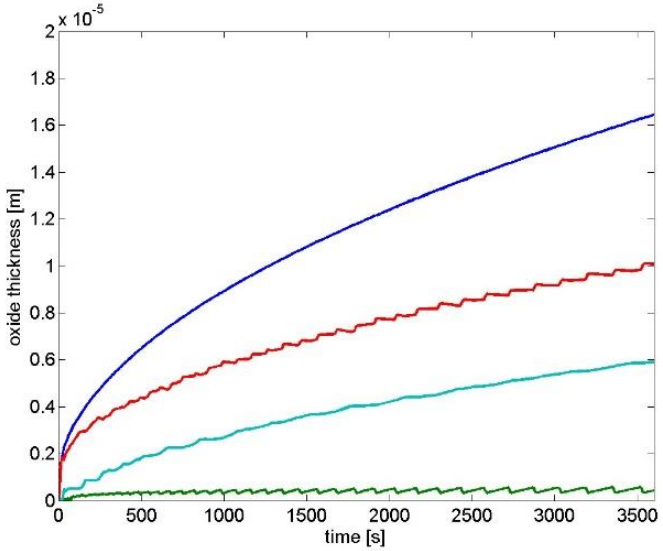
$$M^{eff} = \left(1 - f^{gb}\right) M^{bulk} + f^{gb} M^{gb}$$
$$f^{gb} = \delta / d$$
$$\delta \sim 0.5\,\mathrm{nm}$$
$$d^{mag} \sim 2\,\mu\mathrm{m}$$
$$M^{bulk} = M_0^{bulk} \exp\left(\frac{-Q^{bulk}}{RT}\right)$$
$$M^{gb} = M_0^{bulk} \exp\left(\frac{-\alpha Q^{bulk}}{RT}\right)$$



No GB contr



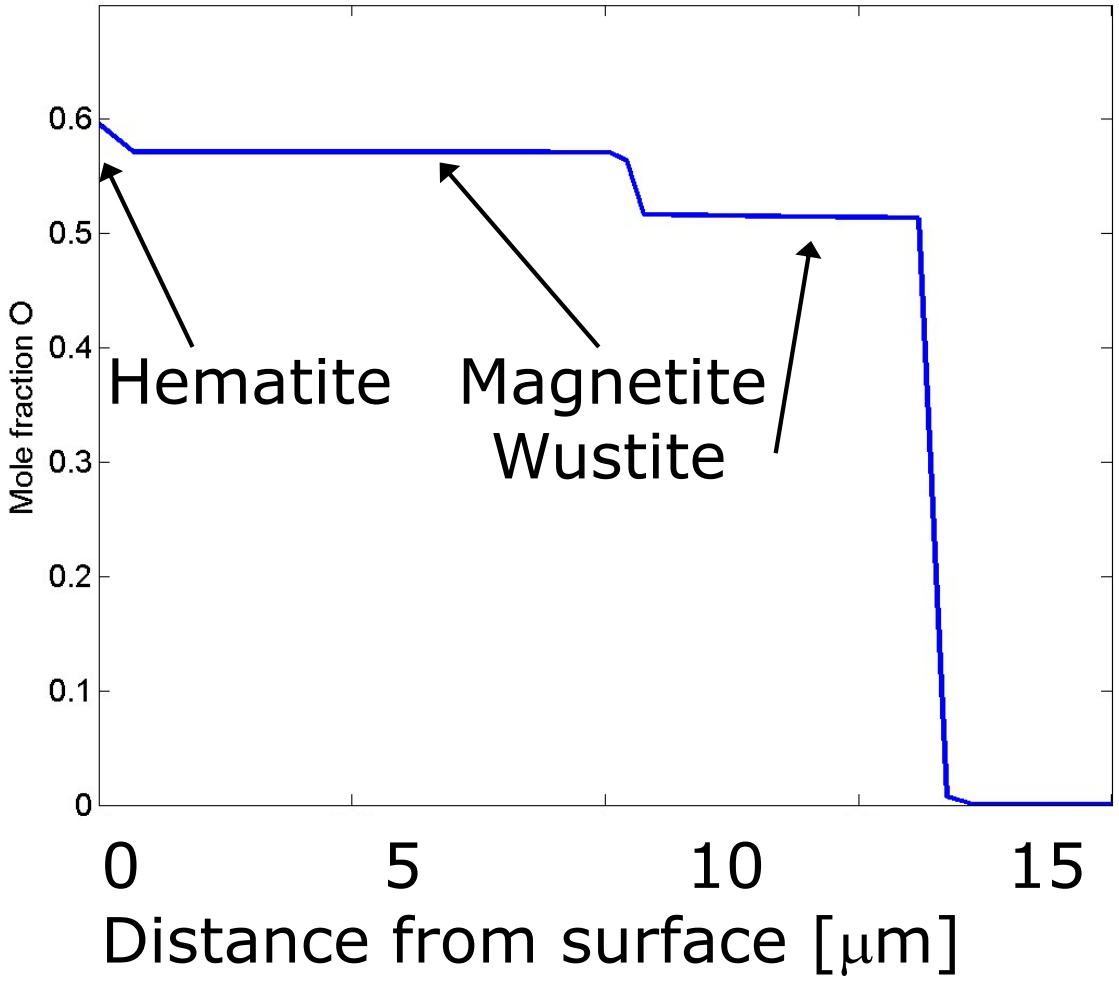
$\alpha^{mag} \sim 0.5$



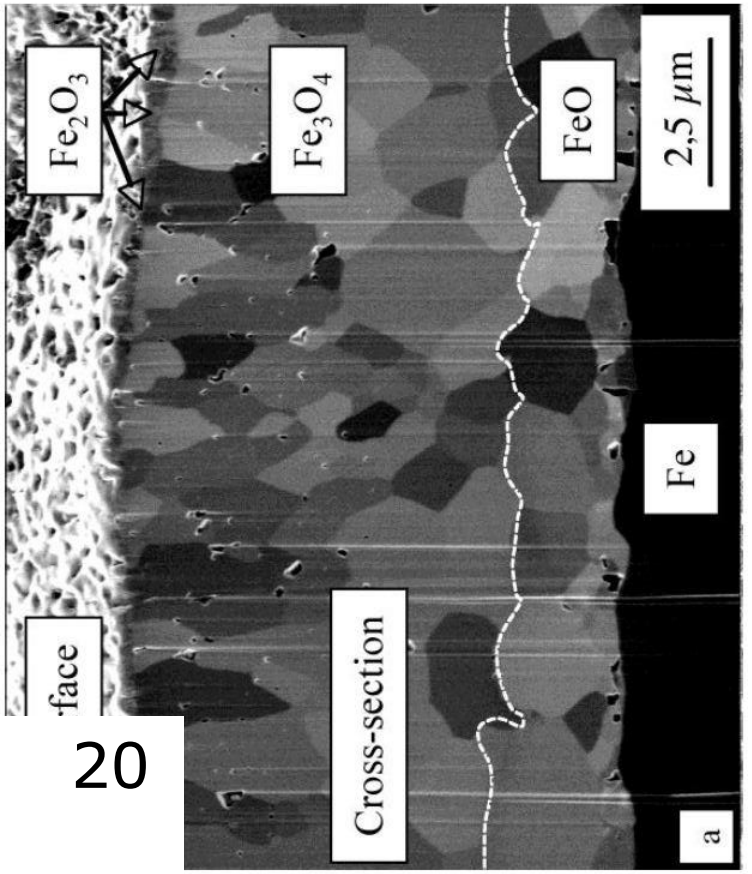
$\alpha^{mag} \sim 0.4$

Simulation of oxidation of iron using the homogenization model

600°C, 1 h
Total thickness 11 μm



$$\alpha^{mag} \sim 0.4$$



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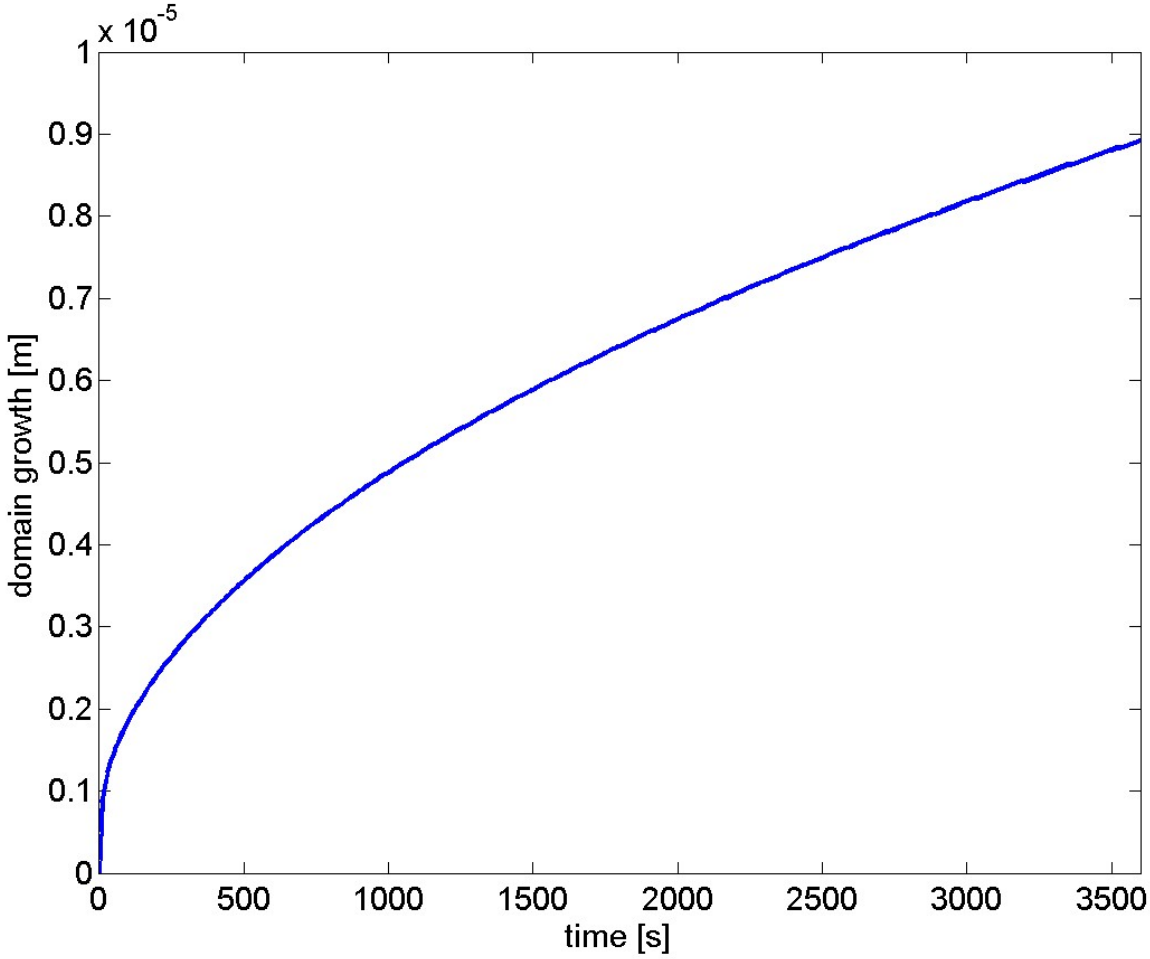
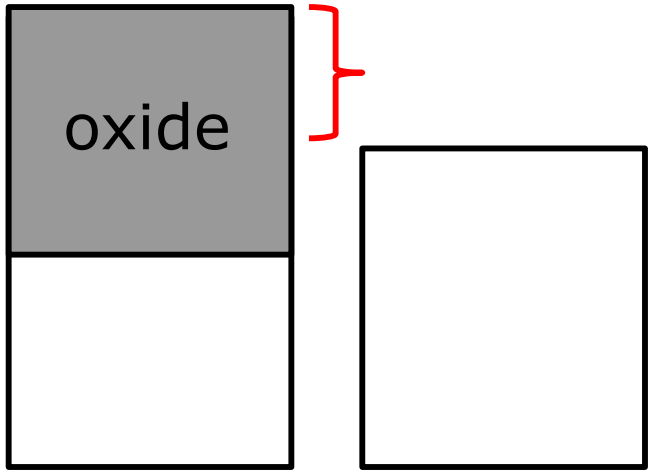
Simulation of oxidation of iron using the homogenization model



Thickening/domain growth during oxidation



Kirkendall effect - porosity

Oxygen is substitutional, divergence of oxygen flux gives Kirkendall effect:

$$\frac{v}{V_m} = -J = -J'_{O^{-2}} / x_{O^{-2}} \qquad V_m = \text{molar volume/mole of atoms}$$

Rate of density ($\rho = 1/V_m$) change:

$$\frac{1}{V_m{}^2}\dot{V}_m = \mathbf{div}(J)$$

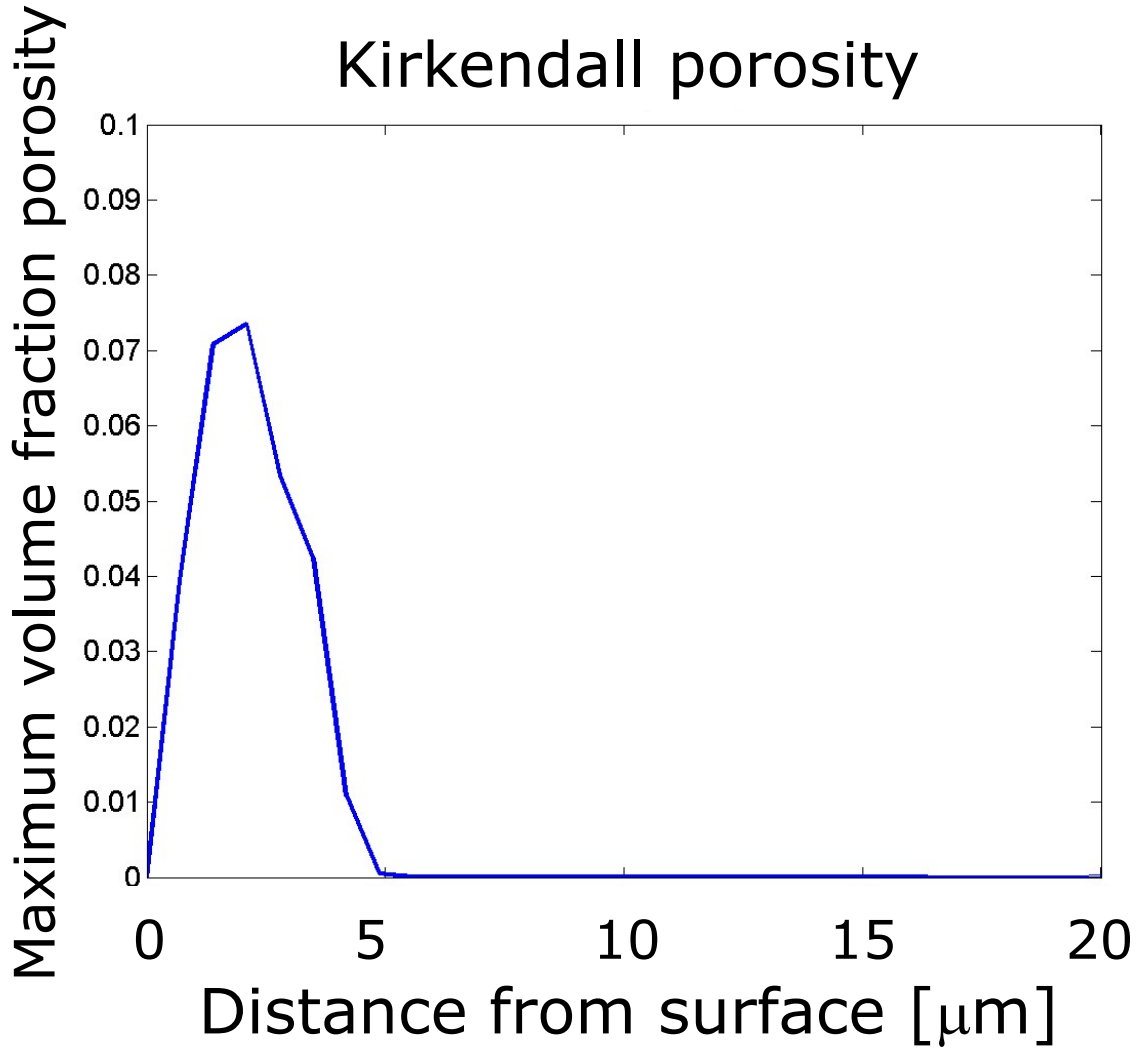
No porosity $\Rightarrow$ Strain rate:

$$\dot{\varepsilon}_{11} + \dot{\varepsilon}_{22} + \dot{\varepsilon}_{33} = \frac{1}{V_m}\dot{V}_m = V_m \mathbf{div}(J)$$

Only porosity (volume fraction f_p):

$$\frac{\dot{f}_p}{(1-f_p)^2} = -V_m \mathbf{div}(J)$$

Simulation of oxidation of iron using the homogenization model



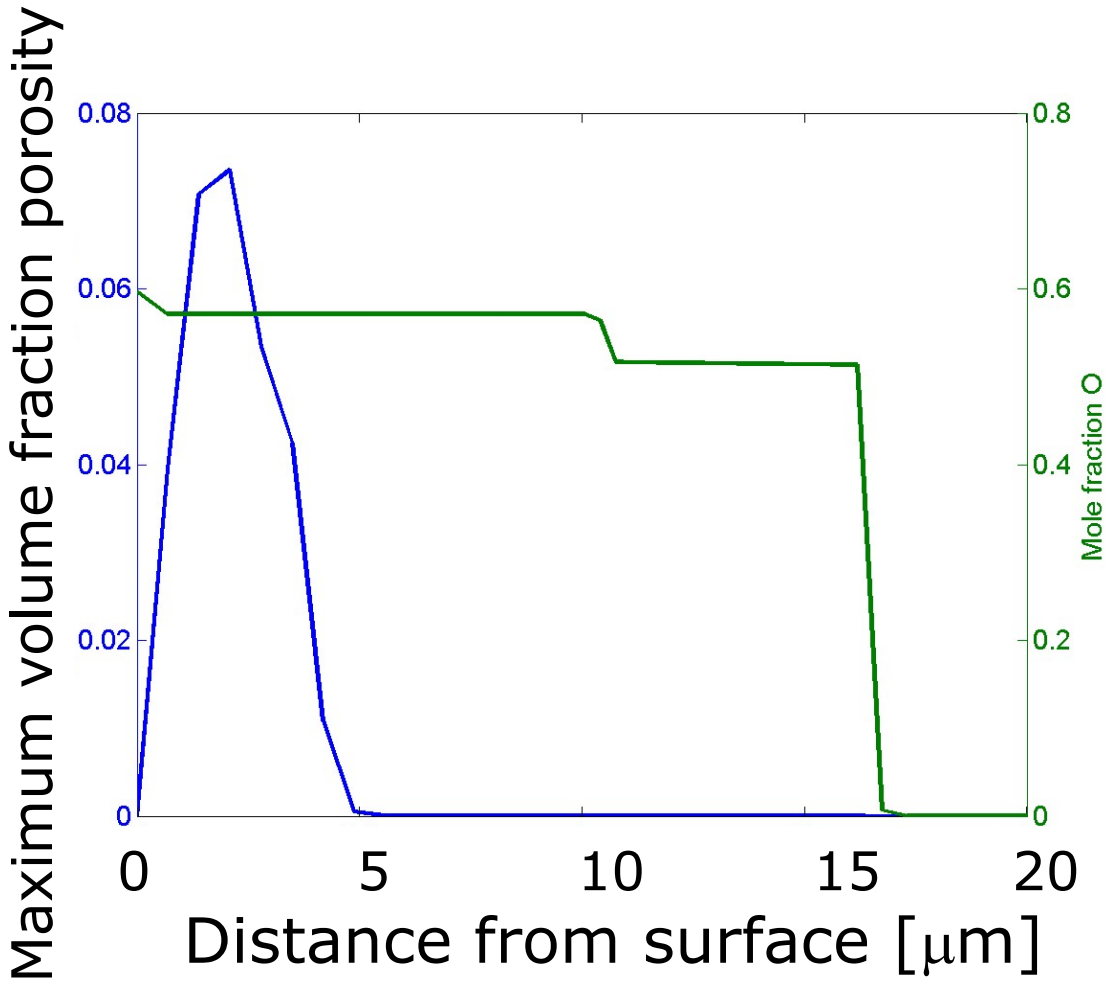
$$J_{va} = -J_O$$

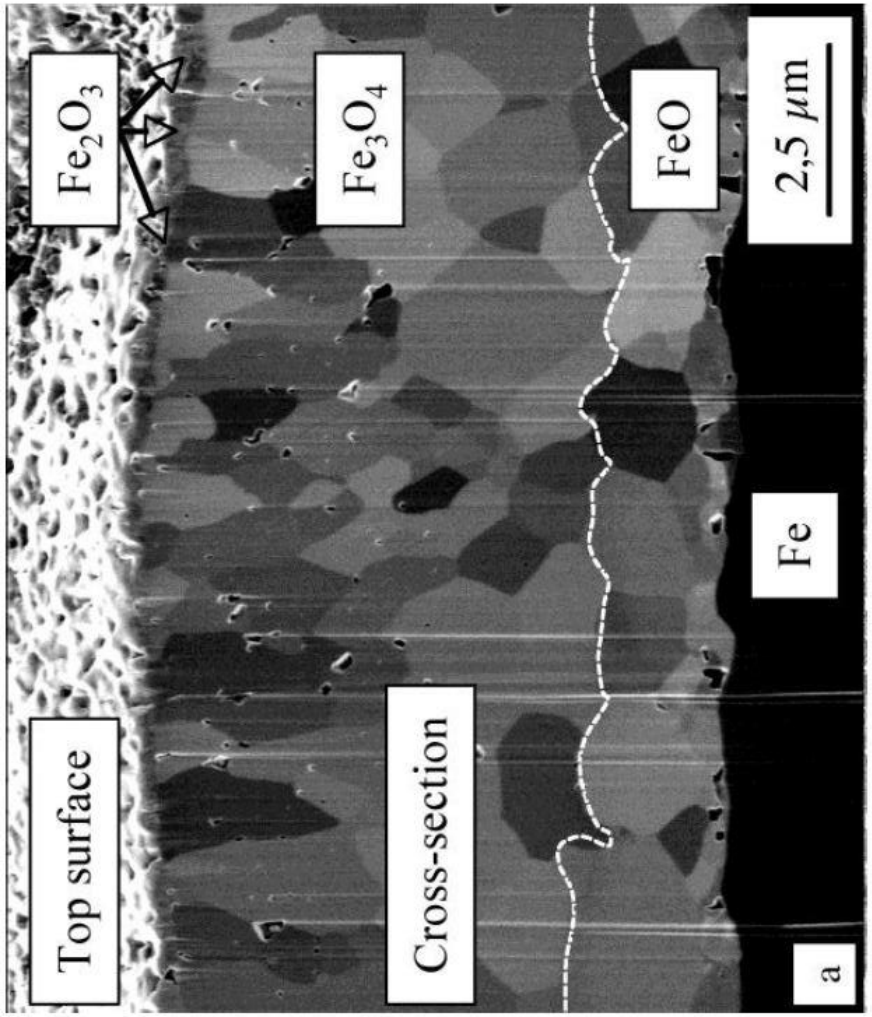
$$\frac{\partial c_{va}}{\partial t} = \frac{\partial}{\partial z}\left(-J_{va}\right) + \dot{q}_{va} \simeq 0$$

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

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

Simulation of oxidation of iron using the homogenization model





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Summary and outlook

- The diffusion genome, i.e. assessed diffusional mobilities combined with the Calphad genom may be used to predict such complex phenomena as oxidation in real alloys.
- In general Wagner's theory of internal oxidation need to be replaced by more advanced numerical simulations.
- Often numerical difficulties due to the very low oxygen content in the matrix.
- Reasonable agreement between experiment and simulation

- Next step are ternary systems, e.g. Fe-Cr-O, Fe-Al-O
- Numerous numerical implementation issues remain