Grain Boundary Oxidation Processes and High Temperature Corrosion

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Overview

- Theoretical Background
- Programme Description
  (Linking ChemApp with COMSOL)
- Comparison with Experimental Results
- Introducing Chemical Potentials
- Summary

Oxidation Processes

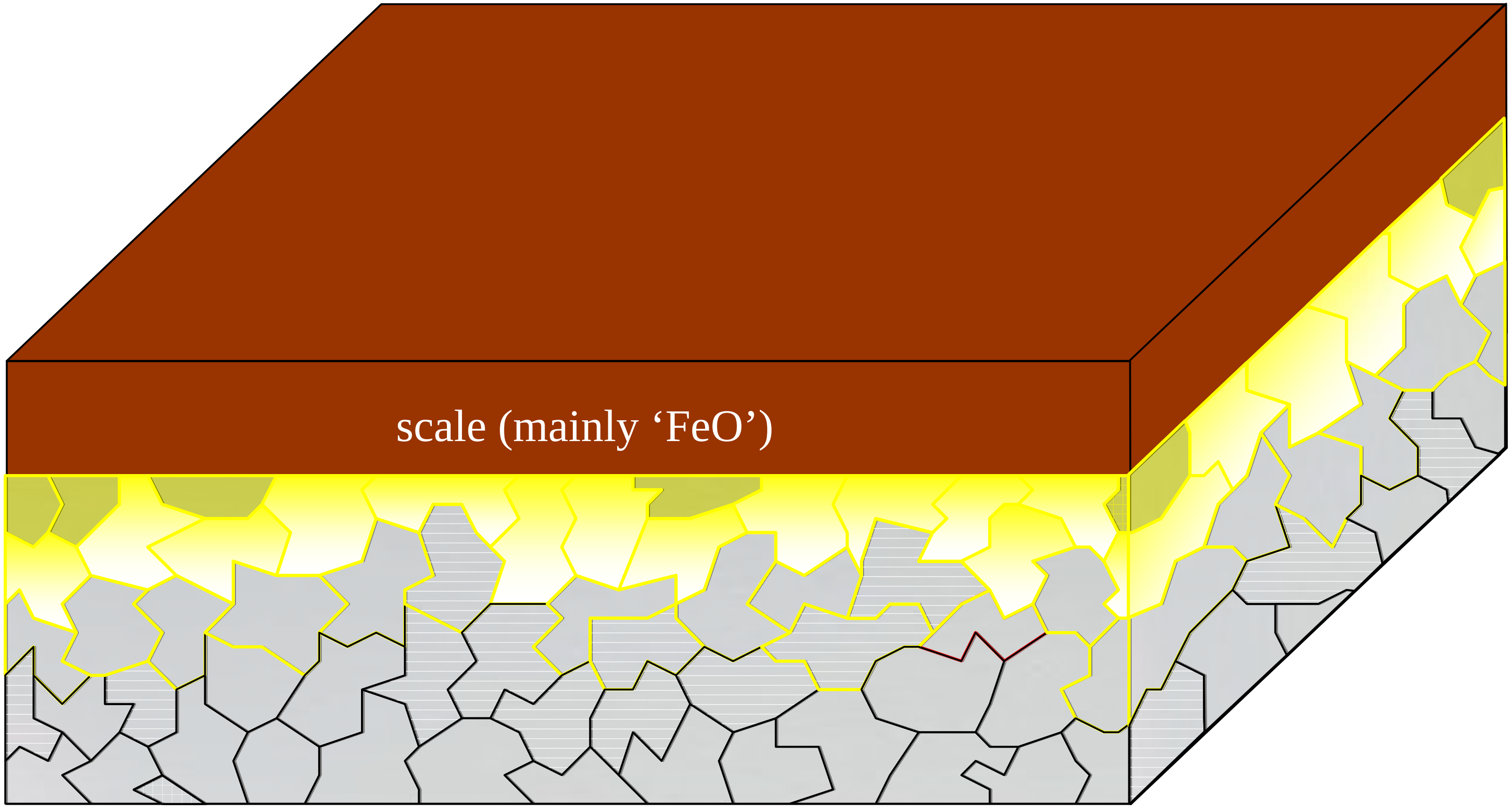


Figure: Schematic process of grain boundary oxidation in steel sheets, fabricated by the hot-rolling technique.

Oxygen Partial Pressure

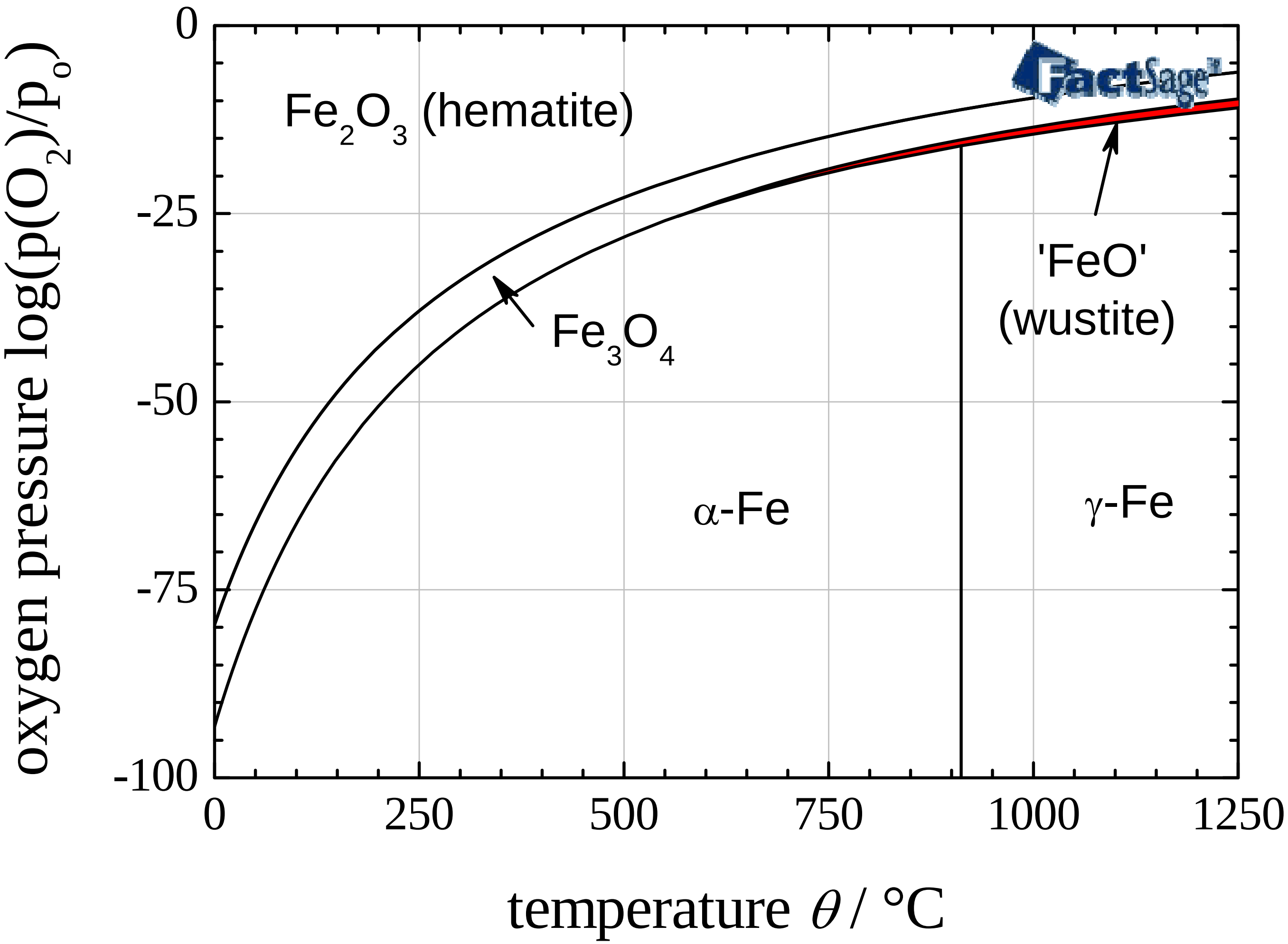


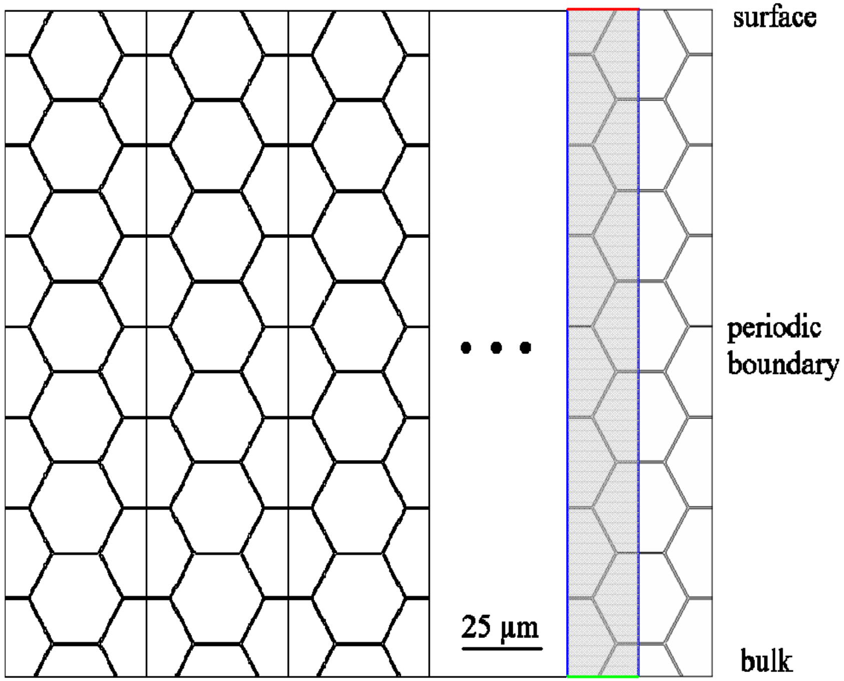
Figure: Thermodynamic stability diagram of iron and iron oxides with respect to temperature and oxygen partial pressure according to SGTE Pure Substance Data.

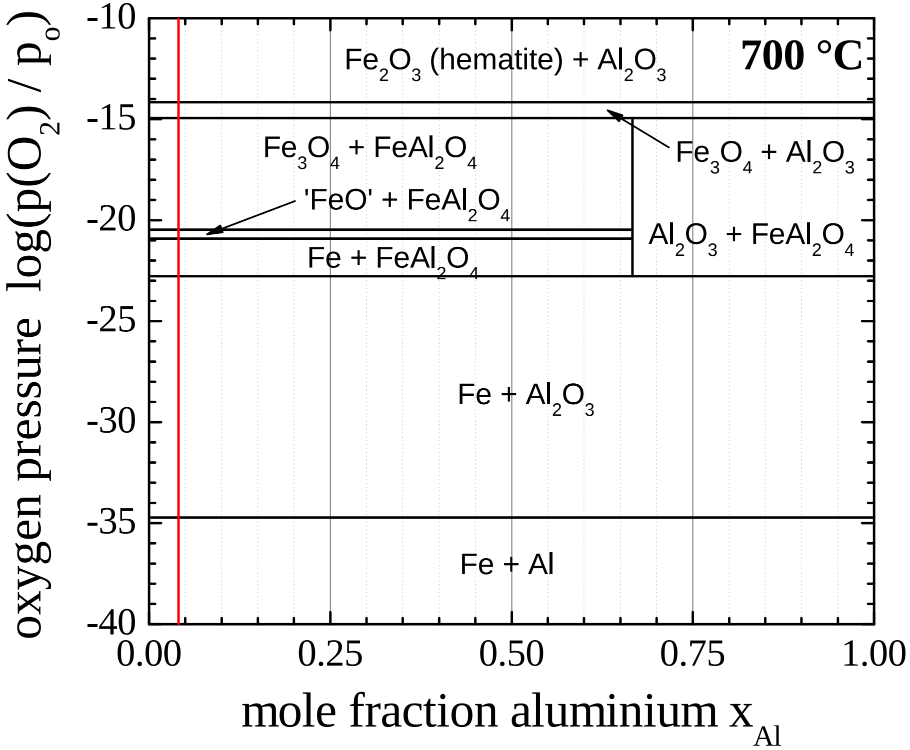
Programme Algorithm

element migration
(COMSOL Multiphysics)

$$\frac{dc_{i\,(x,t)}}{dt} = \mathrm{div}\left(D_{i\,(x,T)}.\nabla c_{i\,(x,t)}\right)$$

chemical reaction
(ChemApp)





Data Handling

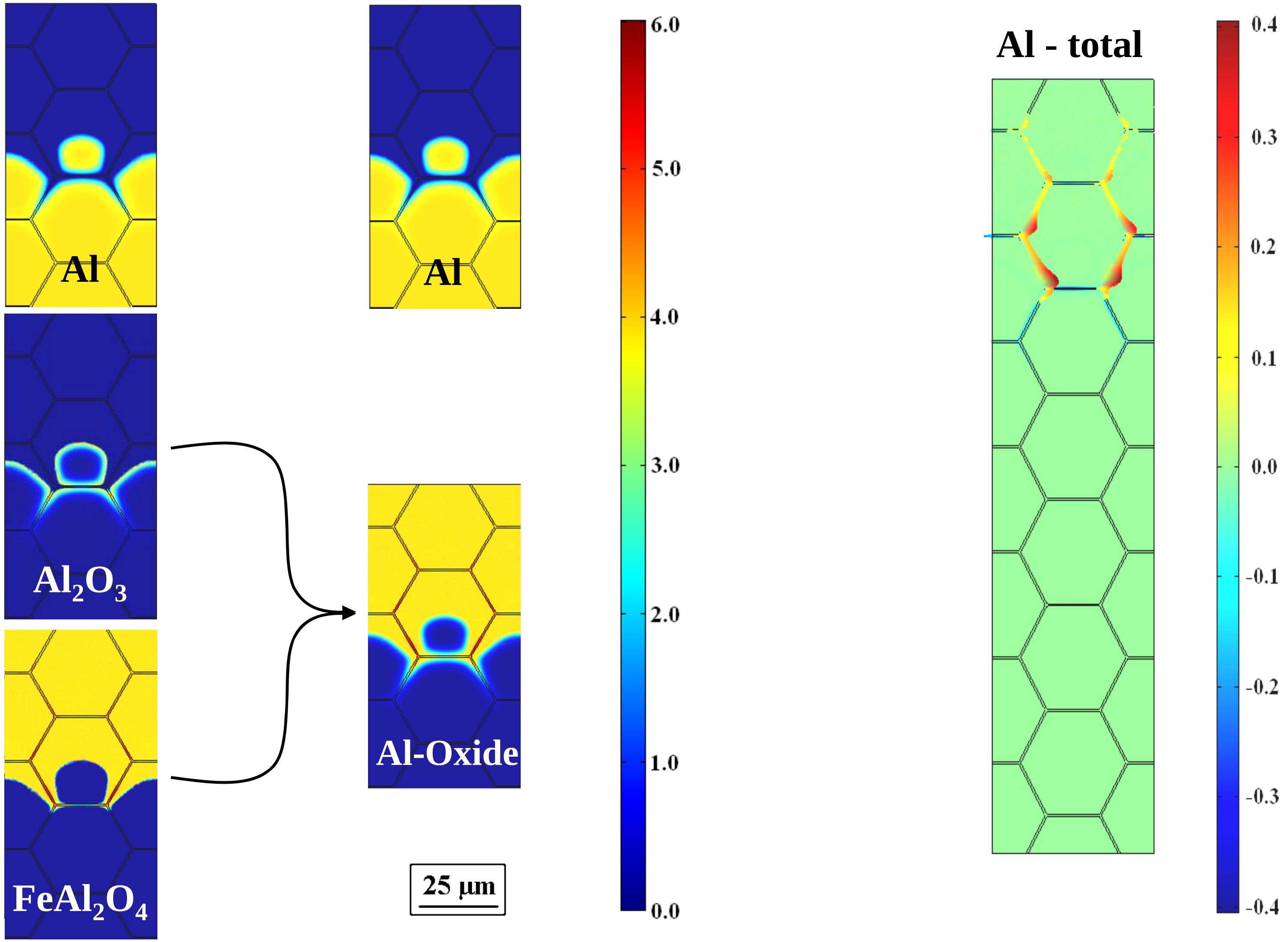
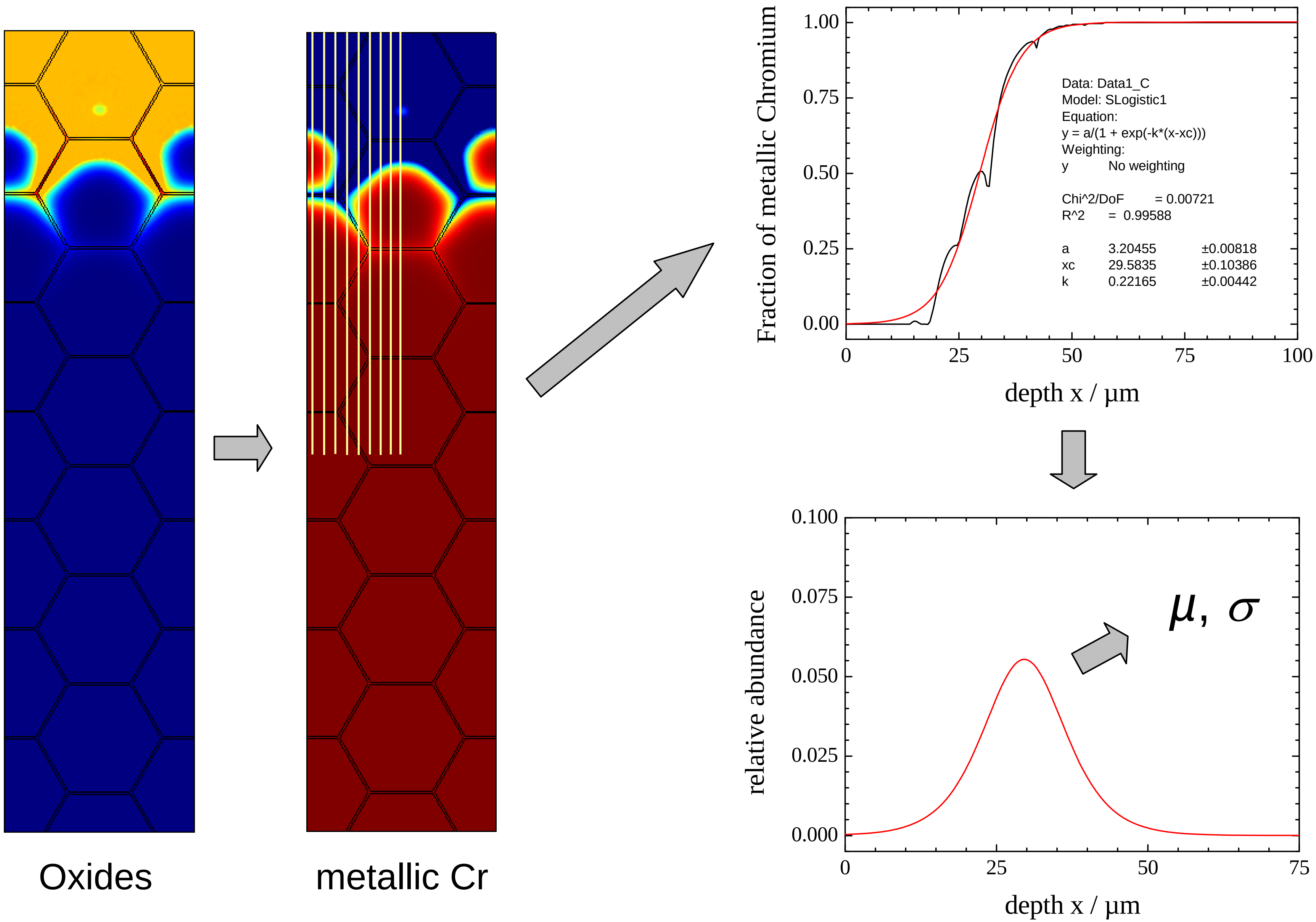


Figure: Spatial phase distributions of Fe, 2 wt-% Al (4.05 mol-% Al) after oxidation at $p(O_2) = 10^{-22}$ bar for 60 min at 700 °C.

Calculation of Oxidationdepth - Distribution



Dependencies with Grain Size

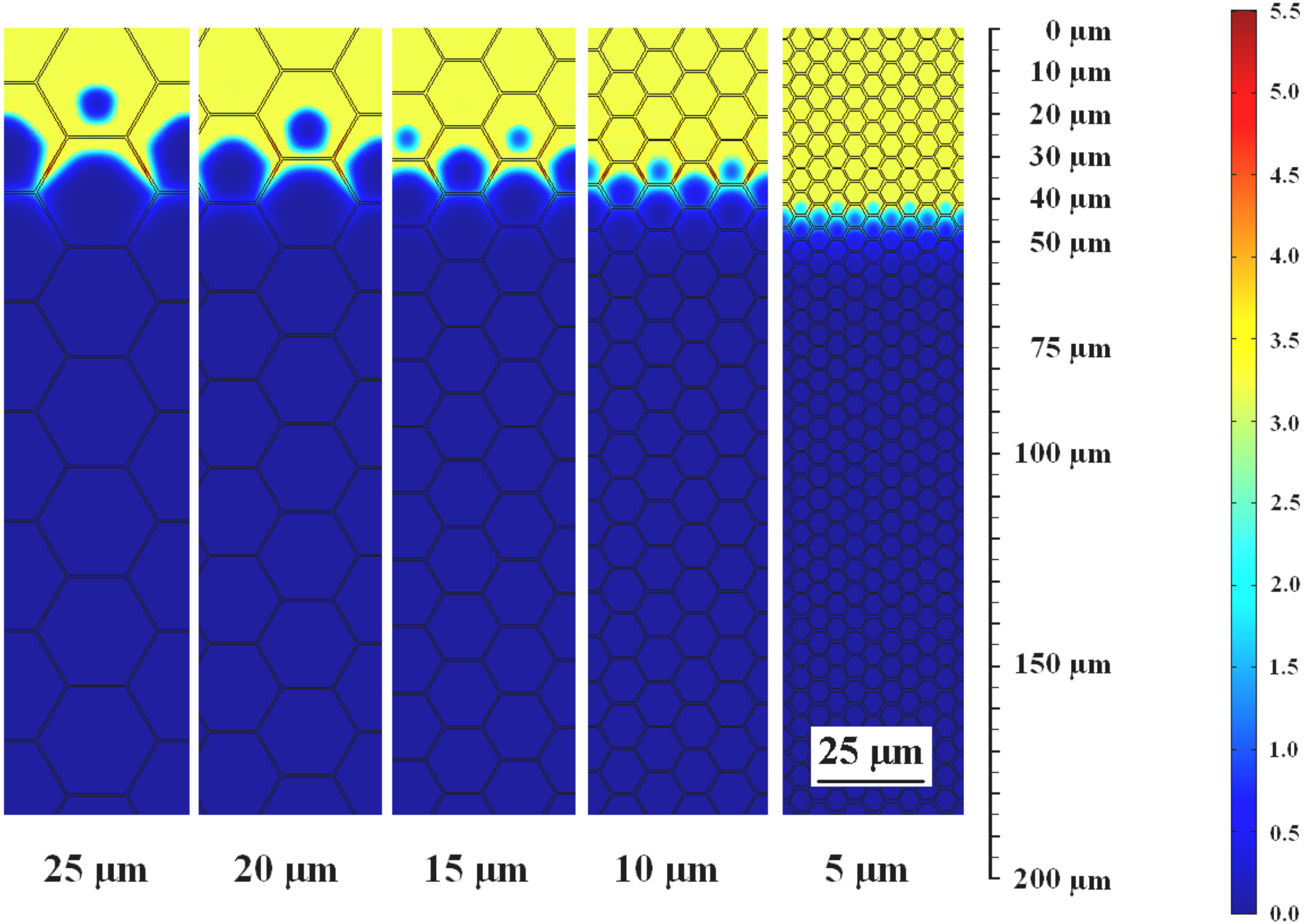


Figure: Grain size dependency of the spatial distribution of chromium oxides in Fe, 3 wt-% Cr after finished cooling procedure (d_{GB} = 500 nm).

Comparison with the Experiments

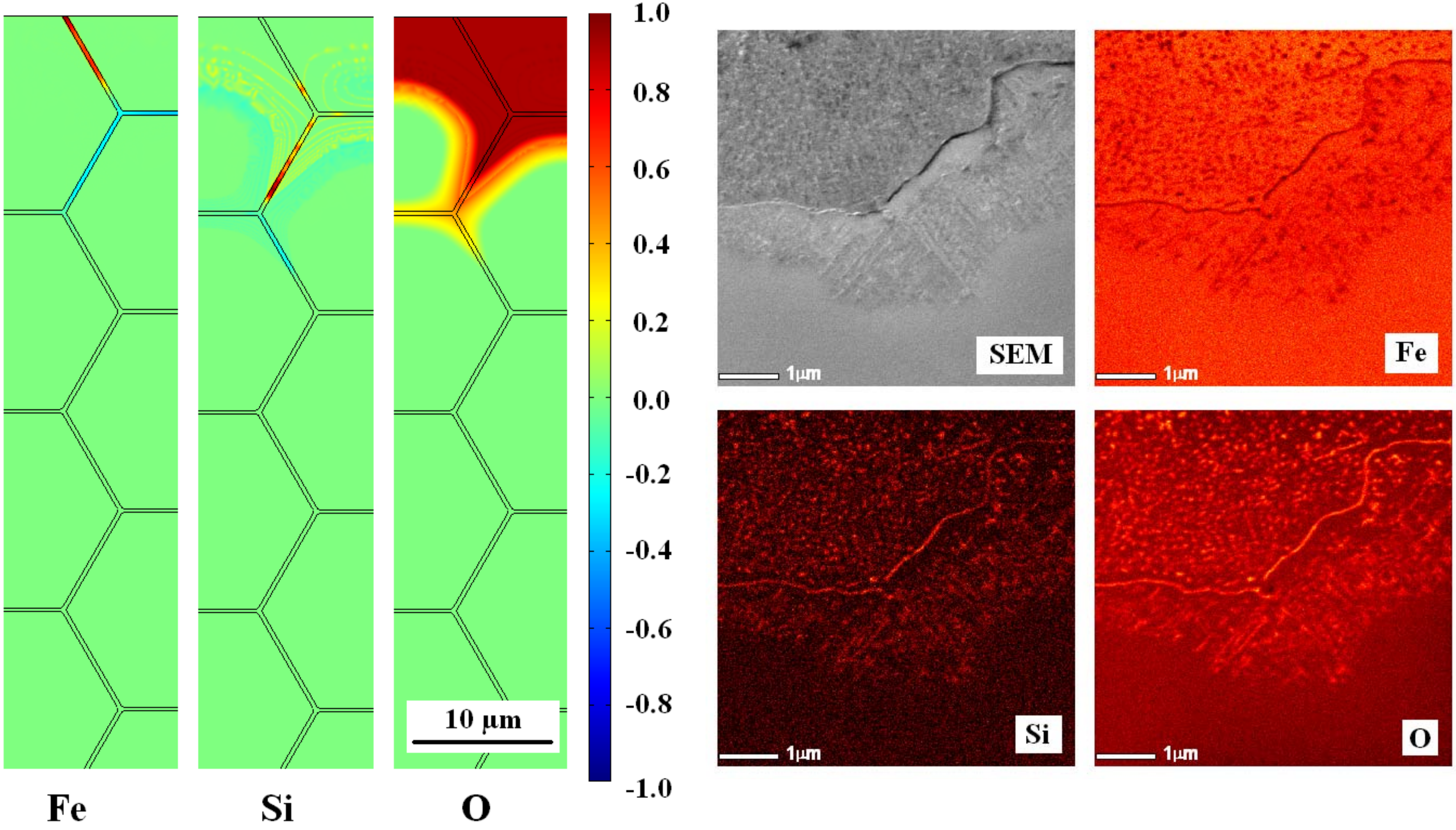


Figure: Simulation of spatial phase distributions of Fe, 1 wt-% Si (1.97 mol-% Si) after oxidation at $p(O_2) = 10^{-22}$ bar for 90 min at 650 °C (left). AES-captions (right).

Ternary Alloy Systems

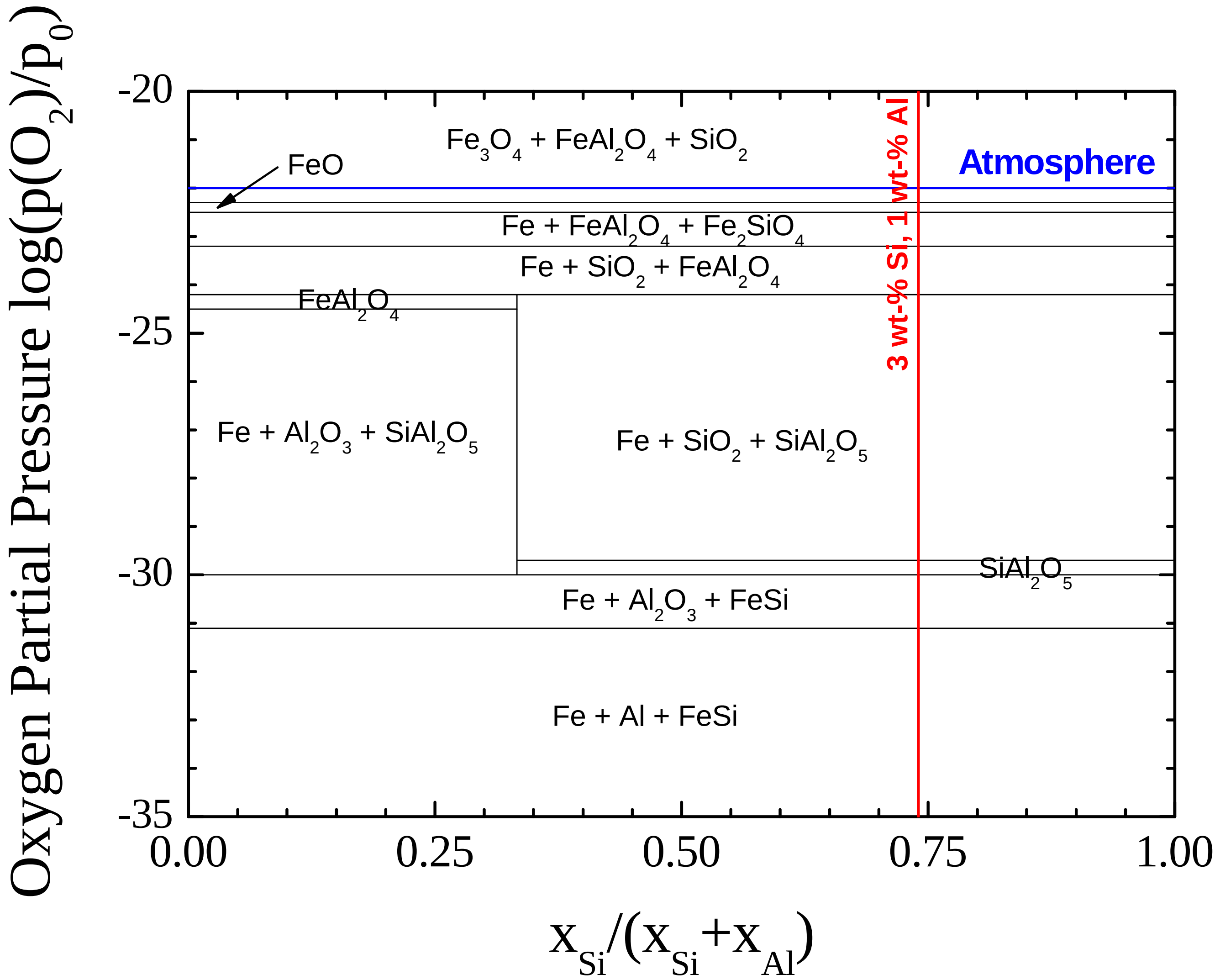


Figure: Thermodynamic stability (according to SGTE Pure Substance Data) of silicon and aluminium containing oxide phases in an iron alloy at 650 °C.

Ternary Alloy Systems

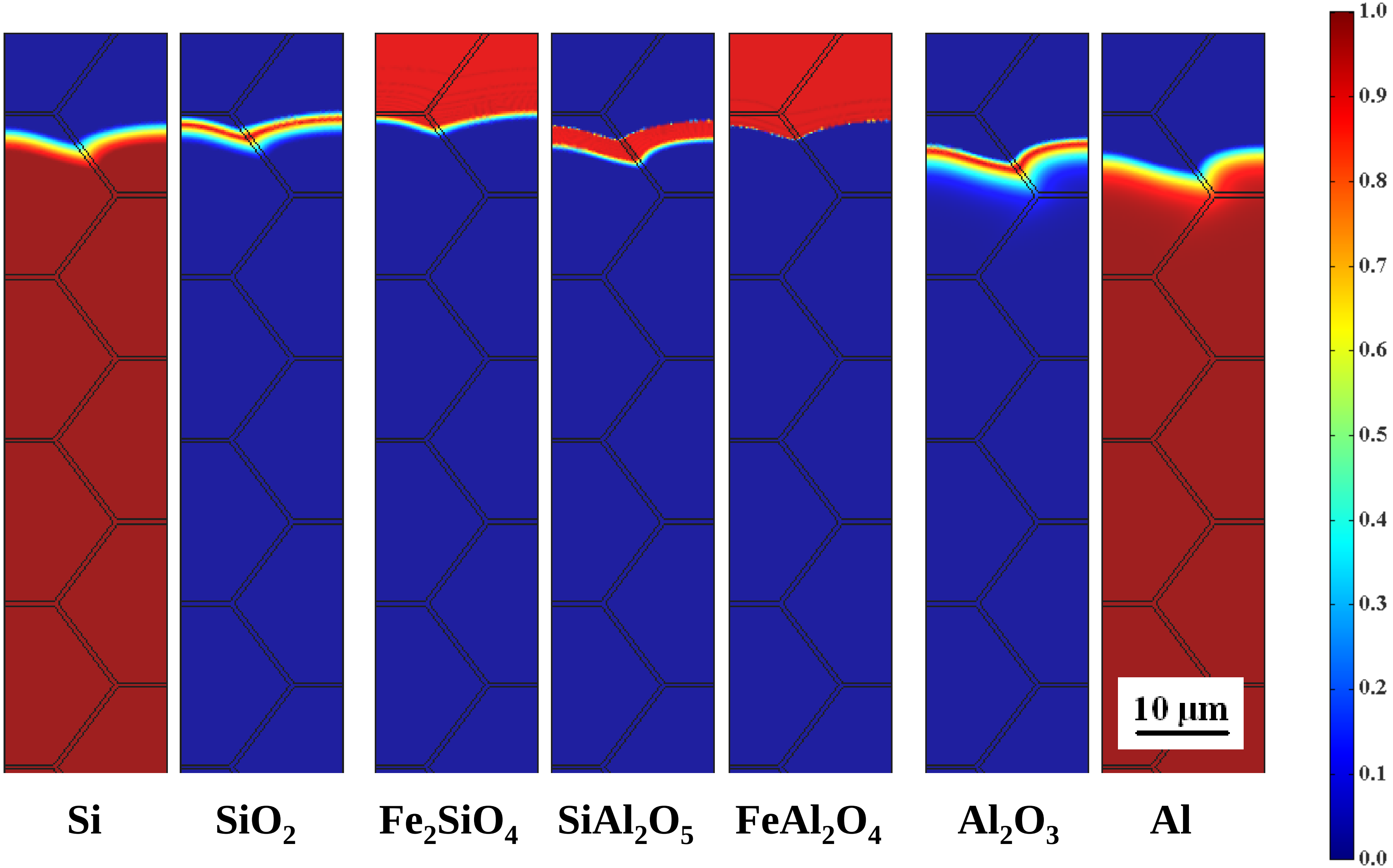


Figure: Spatial phase distributions of silicon, aluminium and their oxides in Fe, 3 wt-% Si, 1 wt-% Al after oxidation at $p(O_2) = 10^{-22}$ bar for 110 min at 650 °C.

Programme Benchmark

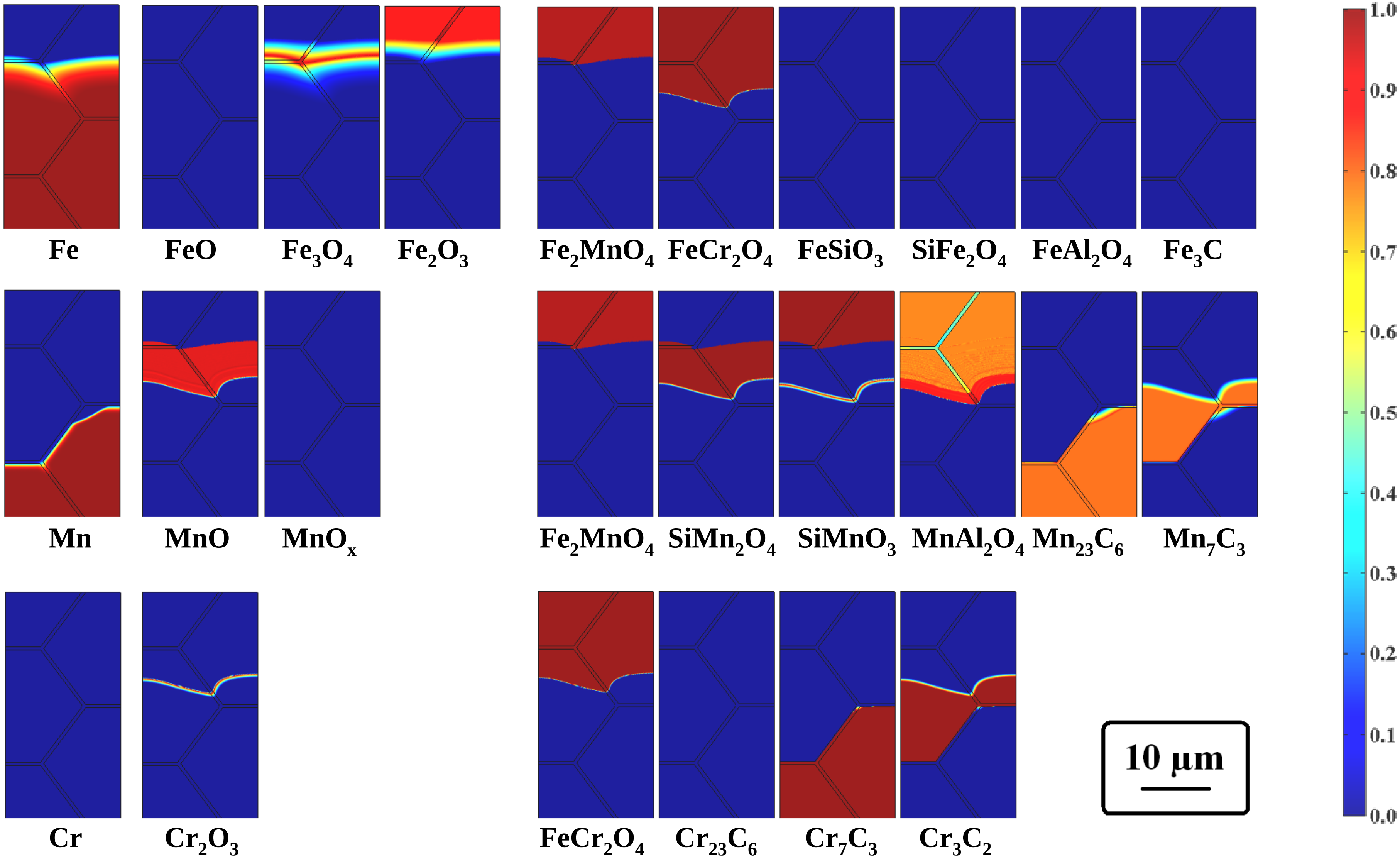


Figure: Spatial phase distributions in a real alloy after oxidation at $p(O_2) = 10^{-22}$ bar in a technical cooling programme.

Programme Benchmark

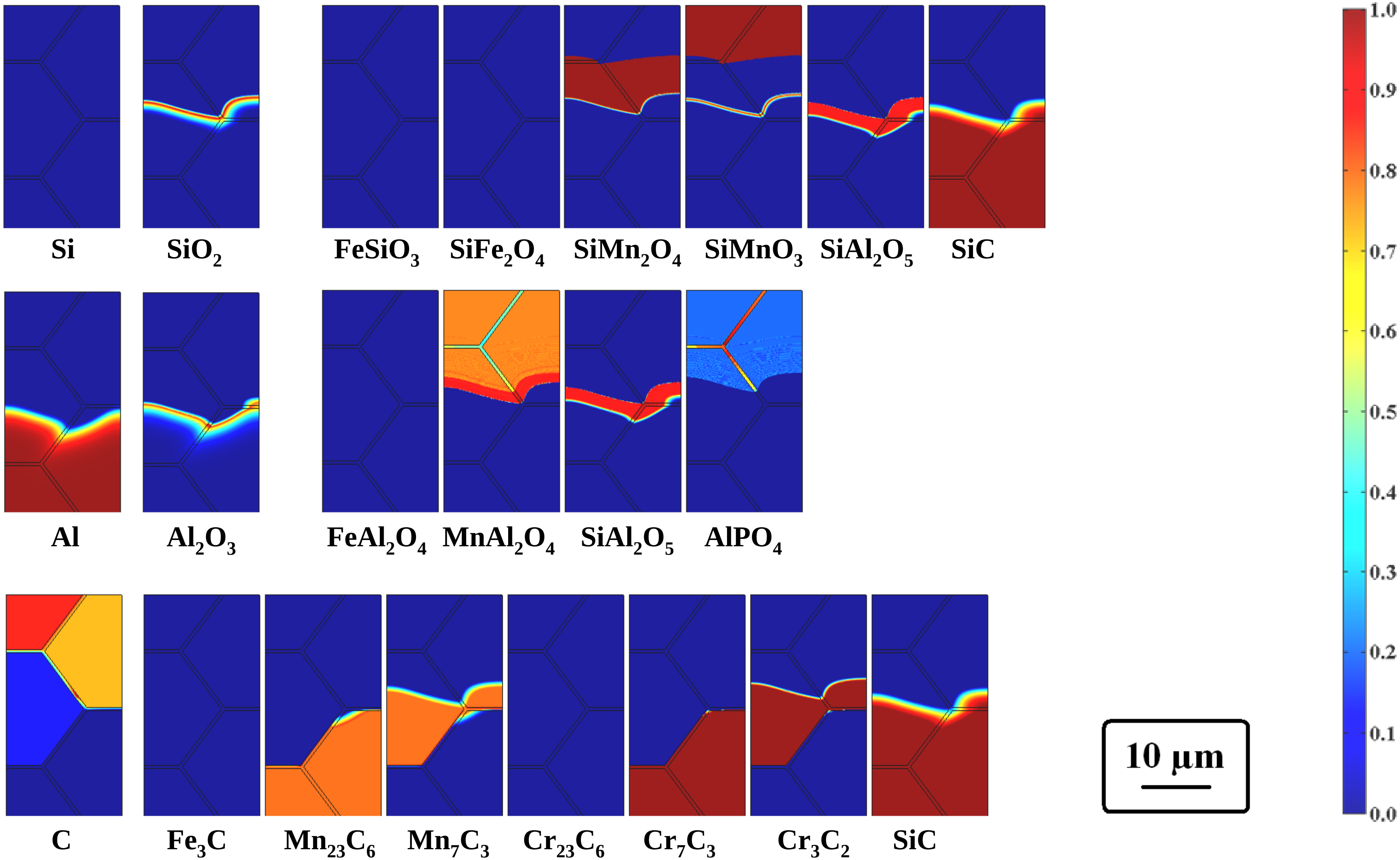


Figure: Spatial phase distributions in a real alloy after oxidation at $p(O_2) = 10^{-22}$ bar in a technical cooling programme.

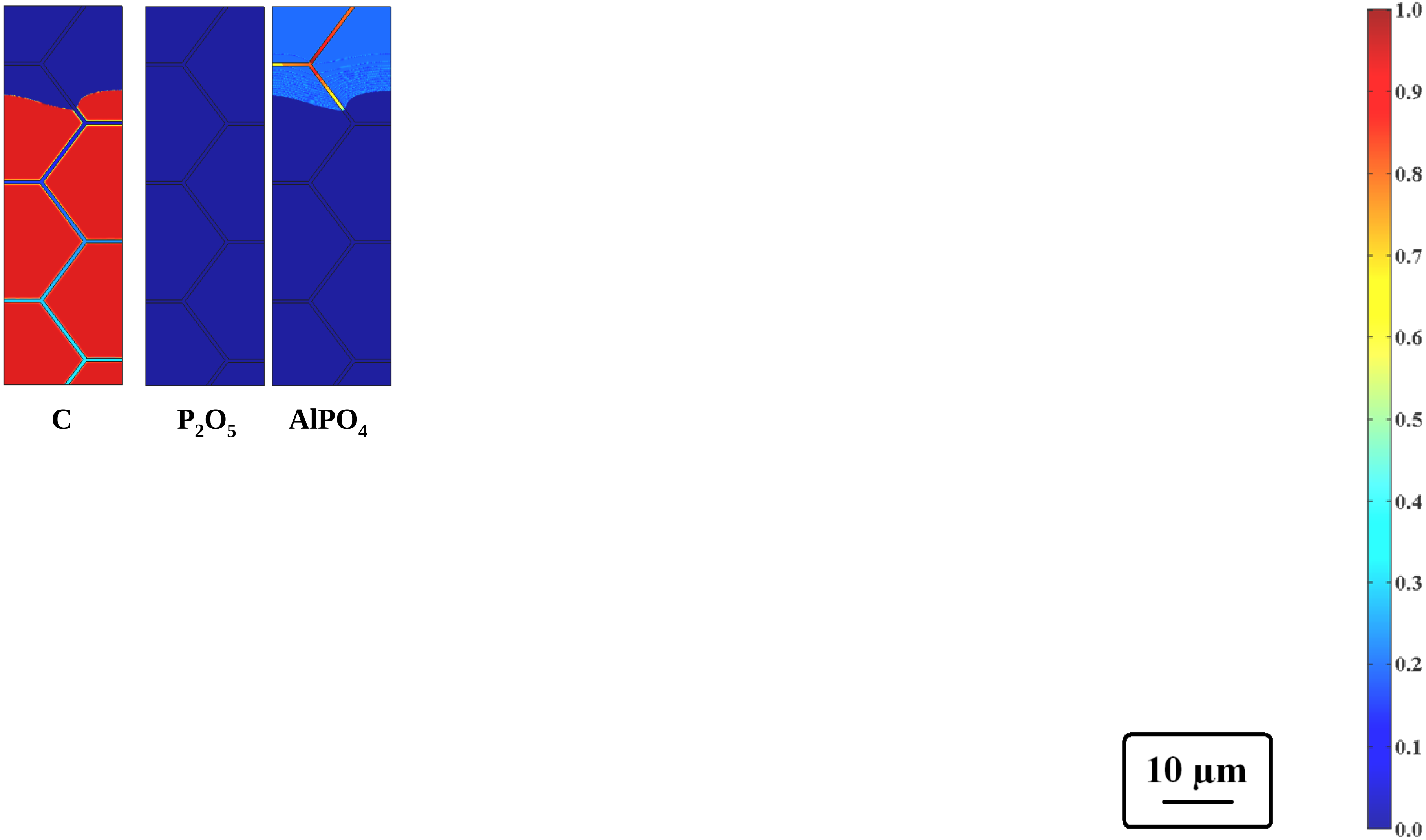


Figure: Spatial phase distributions in a real alloy after oxidation at $p(O_2) = 10^{-22}$ bar in a technical cooling programme.

Part II

Introducing chemical Potentials

Thermodynamics in normal life

Figure: Shibuya (渋谷) crossing in Tokyo at night when pedestrian lights are green.

http://adsjapan.blogspot.com (dl 10.06.2010)

Thermodynamics in normal life

Figure: Shibuya crossing in Tokyo in the evening when pedestrian lights are red.

http://www.gettyimages.com (dl 10.06.2010)

Some Formulas

$$\Delta G = V\,\Delta p - S\,\Delta T + \sum \mu\,\Delta n + \sum zF\varphi\,\Delta n$$

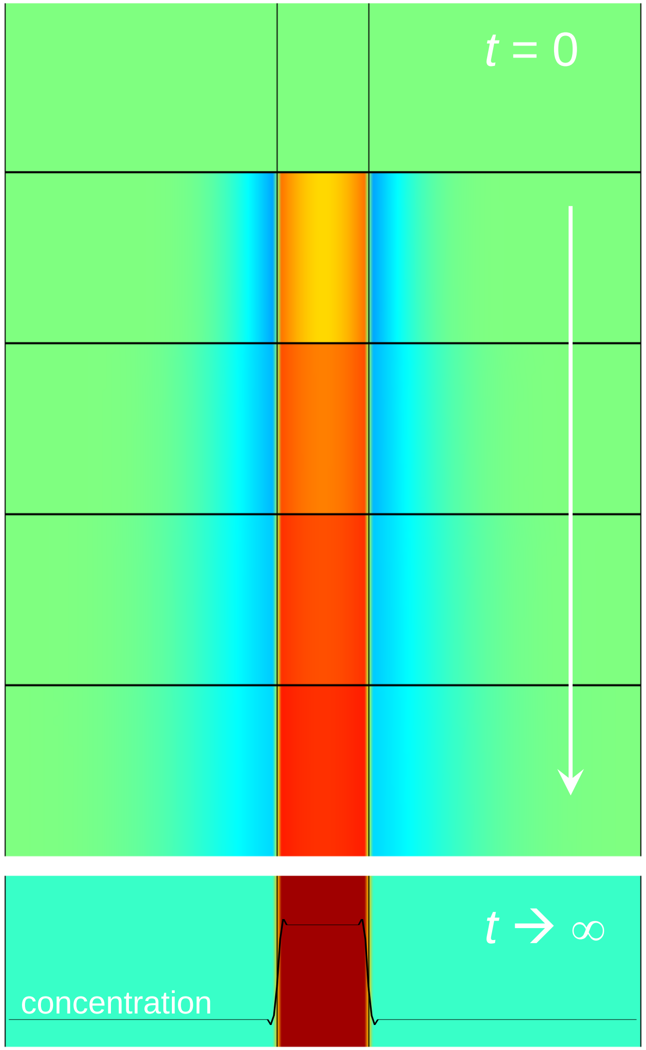
$$J_A = -D\,\nabla c$$ single phase

$$J_A = -L\,\nabla \mu$$ general description

$$\mu = \mu^o + RT\ln(a) = \mu^o + RT\ln(\gamma c) = \tilde{\mu}^o + RT\ln(c)$$

$$J_A = -L\,\nabla\mu = -L\frac{\partial\mu}{\partial c}\nabla c = \cdots = \underbrace{-L\frac{RT}{c}}_{D}\nabla c - \underline{L\left(\nabla\mu^o + \frac{RT}{\gamma}\nabla\gamma\right)}$$

Simulation Results



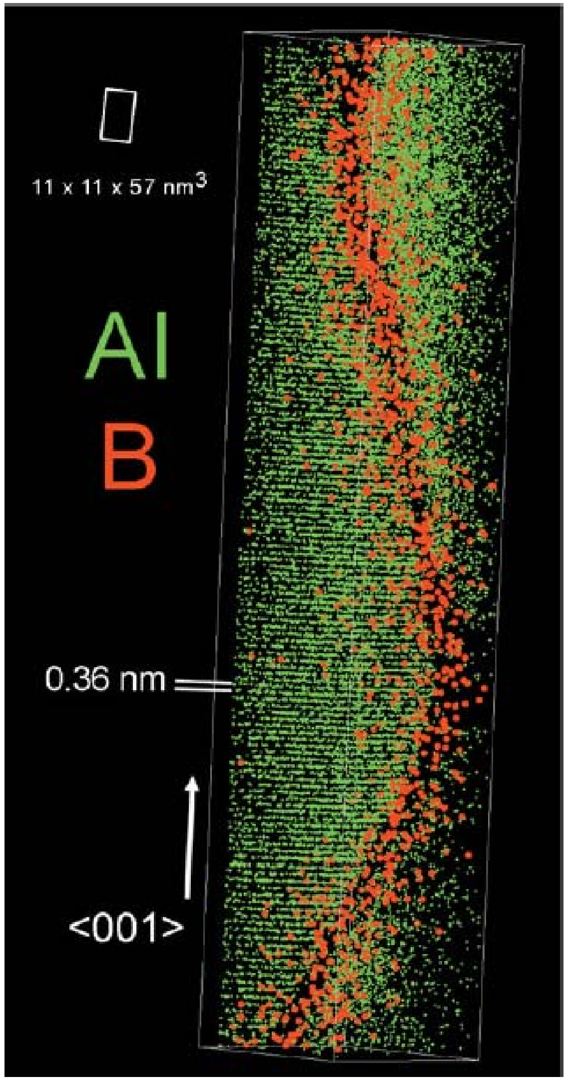


Figure: Numerical simulation of segregation (left) and 3D atom probe tomography of segregated boron atoms along the grain boundary in a NiAl superalloy [1] (right).

[1] Blavette et al. *Microsc. Microanal.* **13** (2007) 464

Summary

- simulations of (oxide) phase distributions in local thermodynamic equilibrium with ChemApp
- good agreement within experimental error for binary alloys
- some deviations for ternary systems
- concentration gradients alone can not explain interphase transport phenomena

Again in real life…

Figure: Castle Schönbrunn (Vienna, Austria) in the summer time.

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