Shaping the Future

The role of Oxygen and Hydrogen in Steels Processing

Dr. Michael AUINGER

GTT – Workshop 2015
Herzogenrath, Aachen, Germany
3rd July, 2015

The University of Warwick

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About myself

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M. Auinger

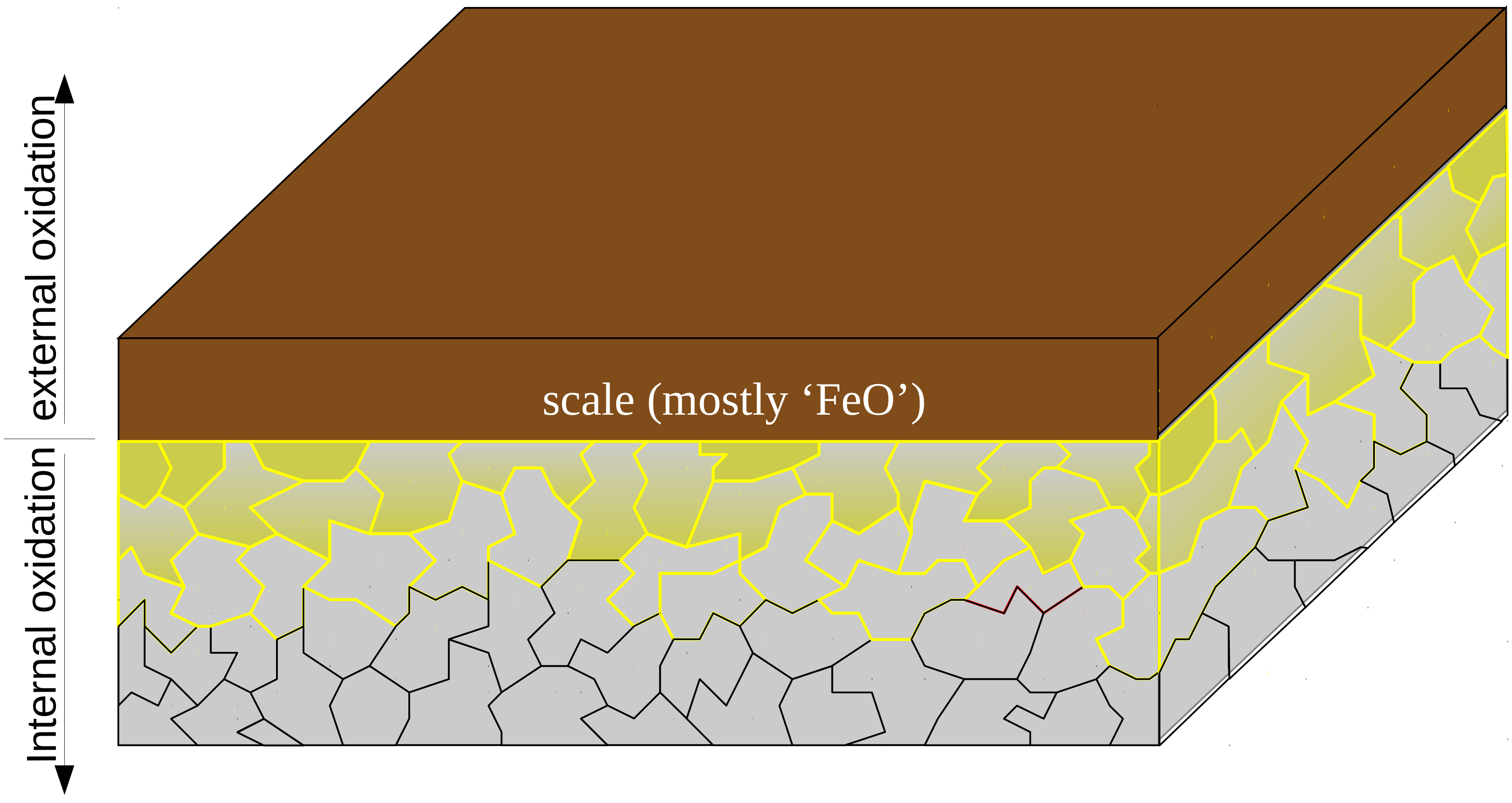
Education

2009	Doctorate at Johannes Kepler University (Austria) Chemical Technologies of Inorganic Materials
Postdoc	Max-Planck-Institute for Iron Research (Germany)
Now	Assistant Professor – Materials Modelling & Computation

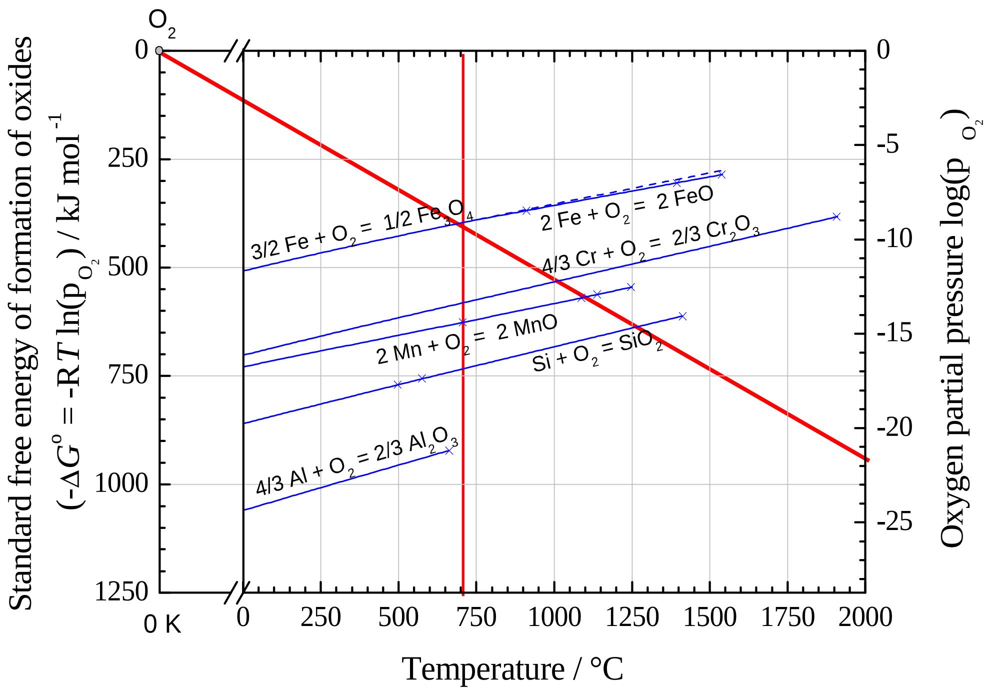
Interests

Thermodynamic modelling
High Temperature Reaction (e.g. Metal-Gas Reactions)
Transport-Defect- Interactions
Phase Field studies
Electrochemical Corrosion
CFD-Modelling
Solidification and Microstructure Evolution

(Internal) Oxidation Scheme



Properties of Oxygen



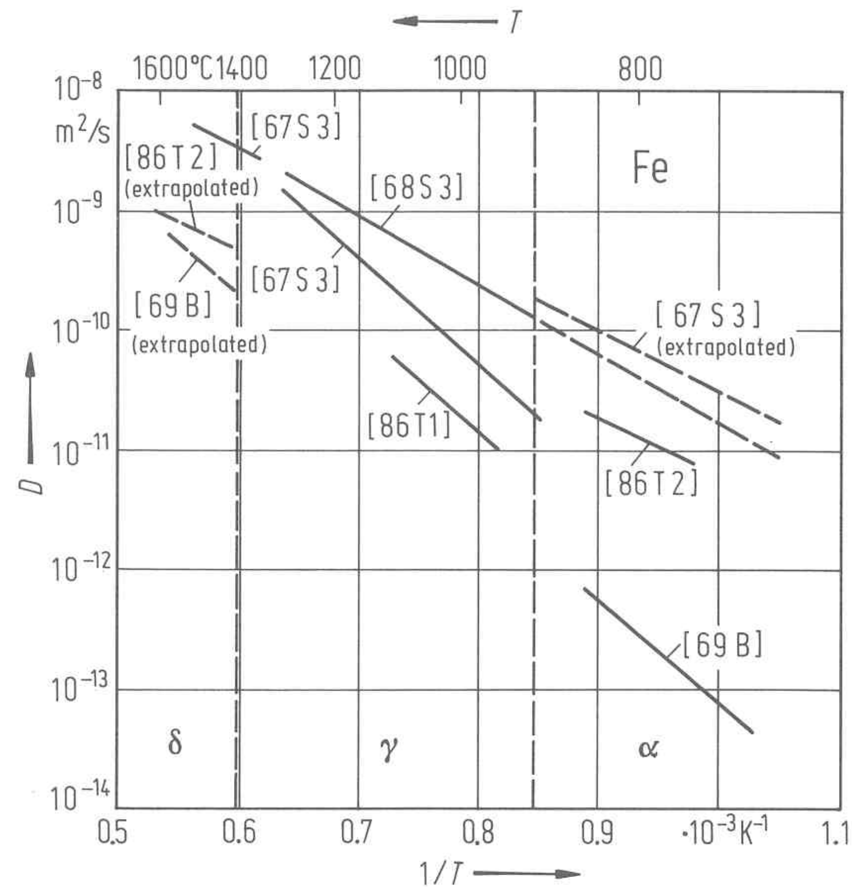


Fig. 23. Fe. Diffusion coefficient for O diffusion in α, γ and δ-phase Fe vs. (reciprocal) temperature.

FACTSage (left) and Landolt-Börnstein (right)

Binary Iron-based Alloys

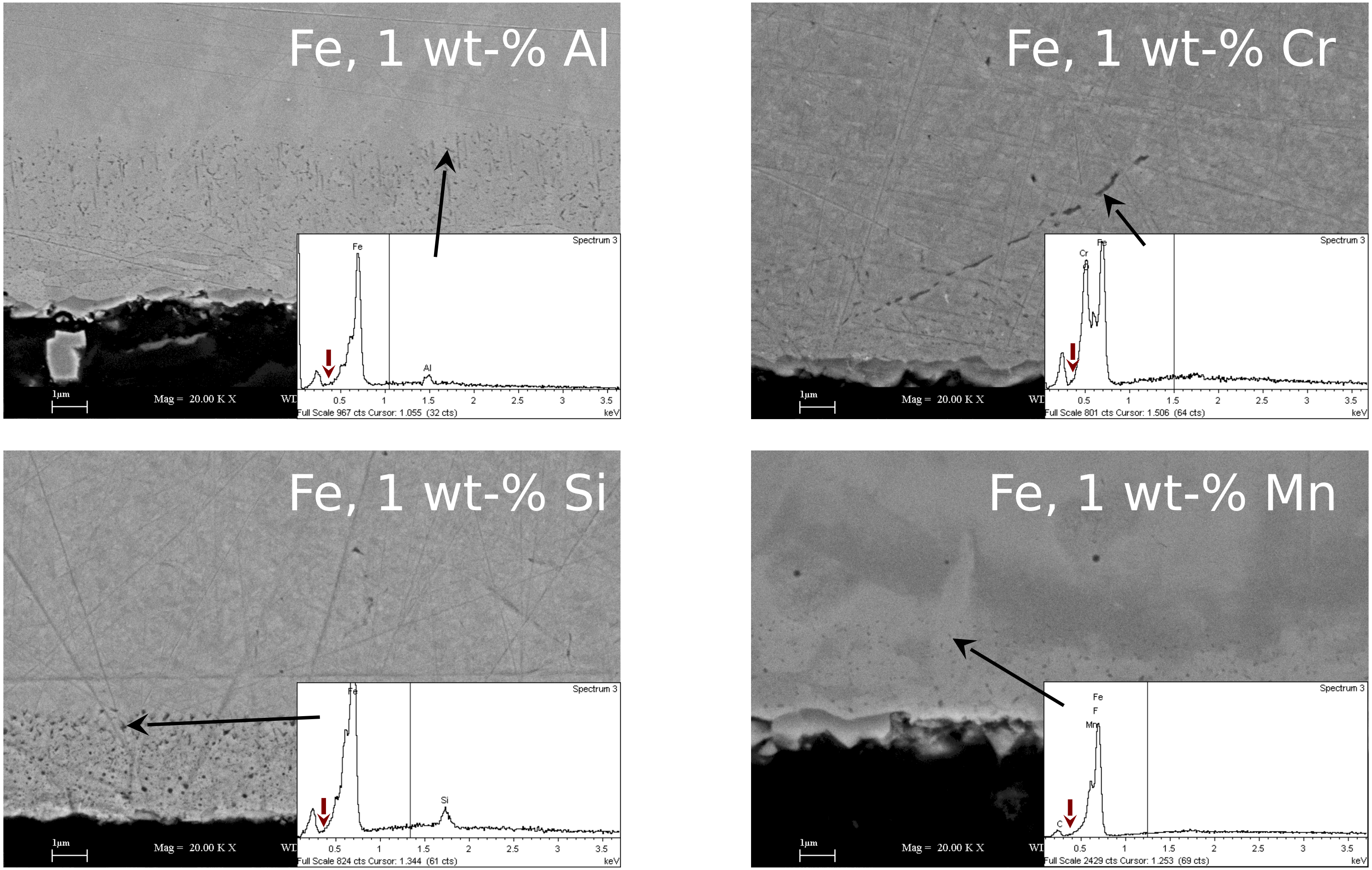
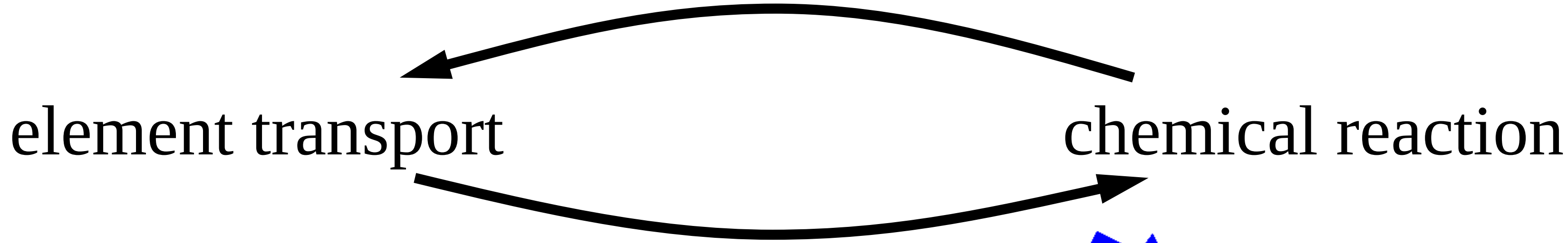


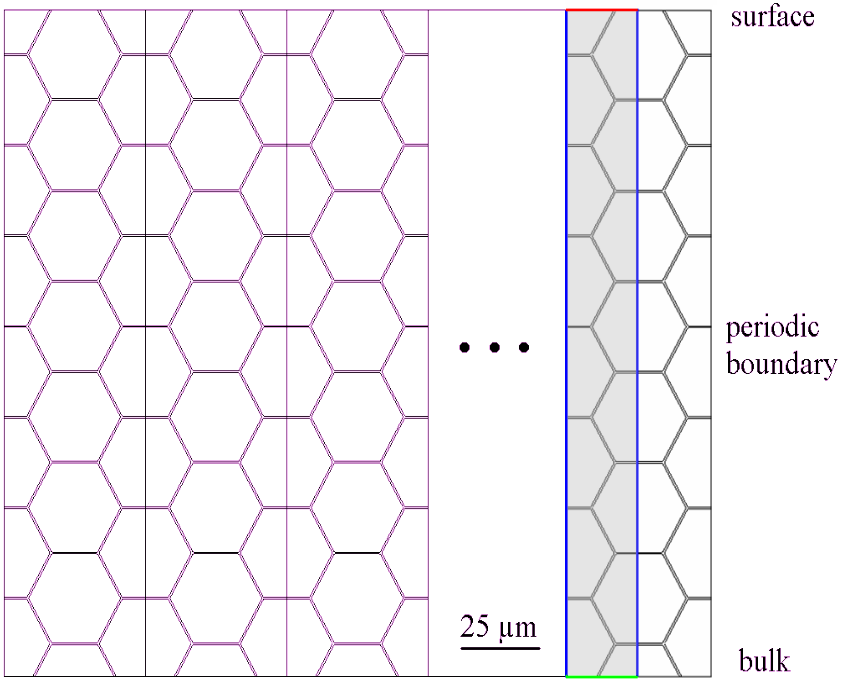
Figure: SEM and EDX-images of four different binary iron alloys, oxidised at 700 °C for 5 h in N_2 / 2.5 % H_2 / H_2O (DP +8 °C). The red arrow marks the N signal position.

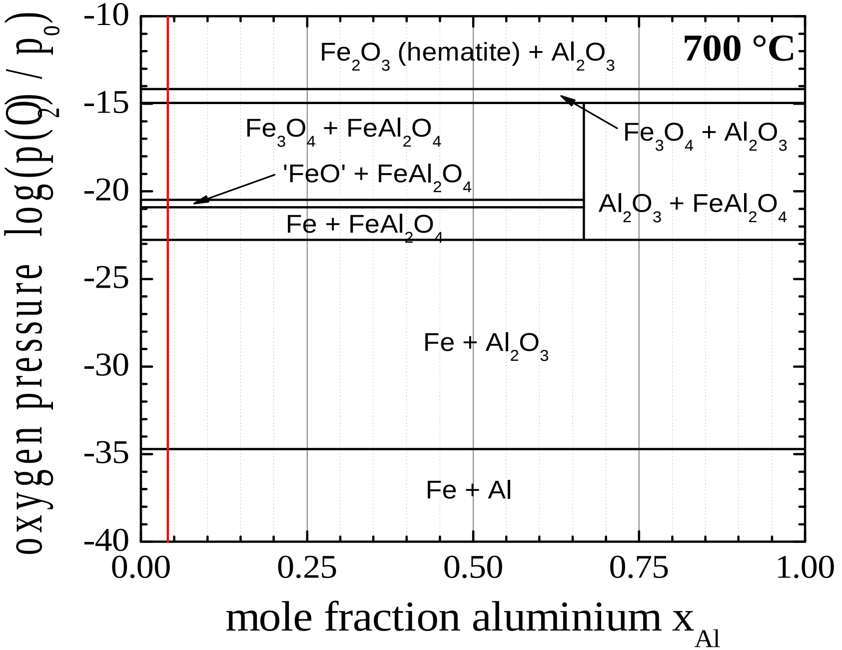
Corros. Sci. **90** (2015) 503-510.

Programme Algorithm



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





Oxid. Met. **76** (2011) 247-258.

Diffusion in Different Phases

$$J_A = -D\,\nabla c \qquad\qquad J_A = -L\,\nabla \mu$$

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

Figures: Shibuya (渋谷) crossing in Tokyo with green and red pedestrian lights.

(Oxide) Phase Distributions

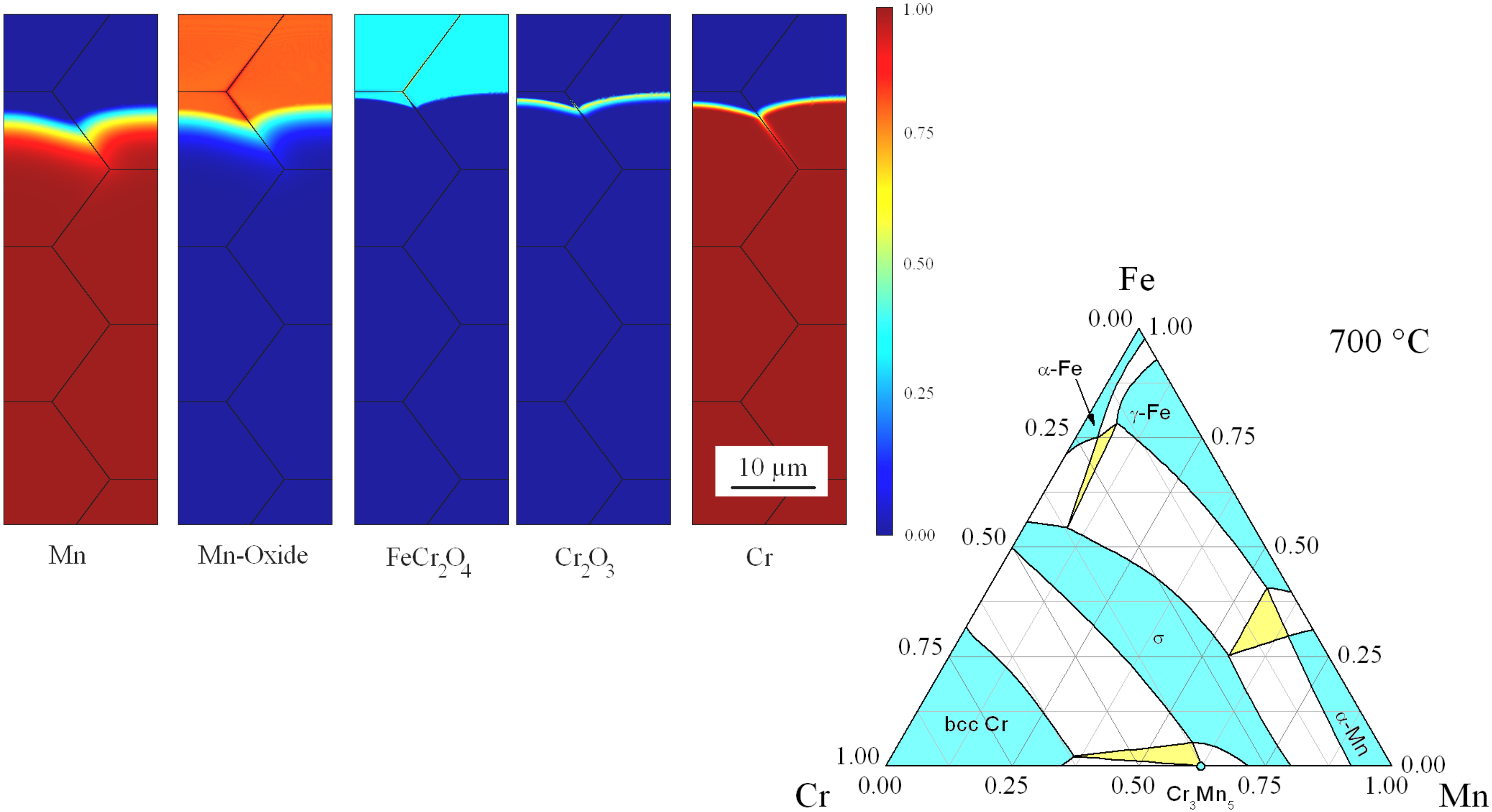


Figure: Spatial phase distribution in an Fe, 2 wt-% Mn, 0.8 wt-% Cr alloy after oxidation at $p(O_2)= 3 \cdot 10^{-22}$ bar and 700 °C for 120 min and ternary phase diagram.

Mater. Sci. Forum **969** (2011) 76-81.

Oxygen Isotope Distribution

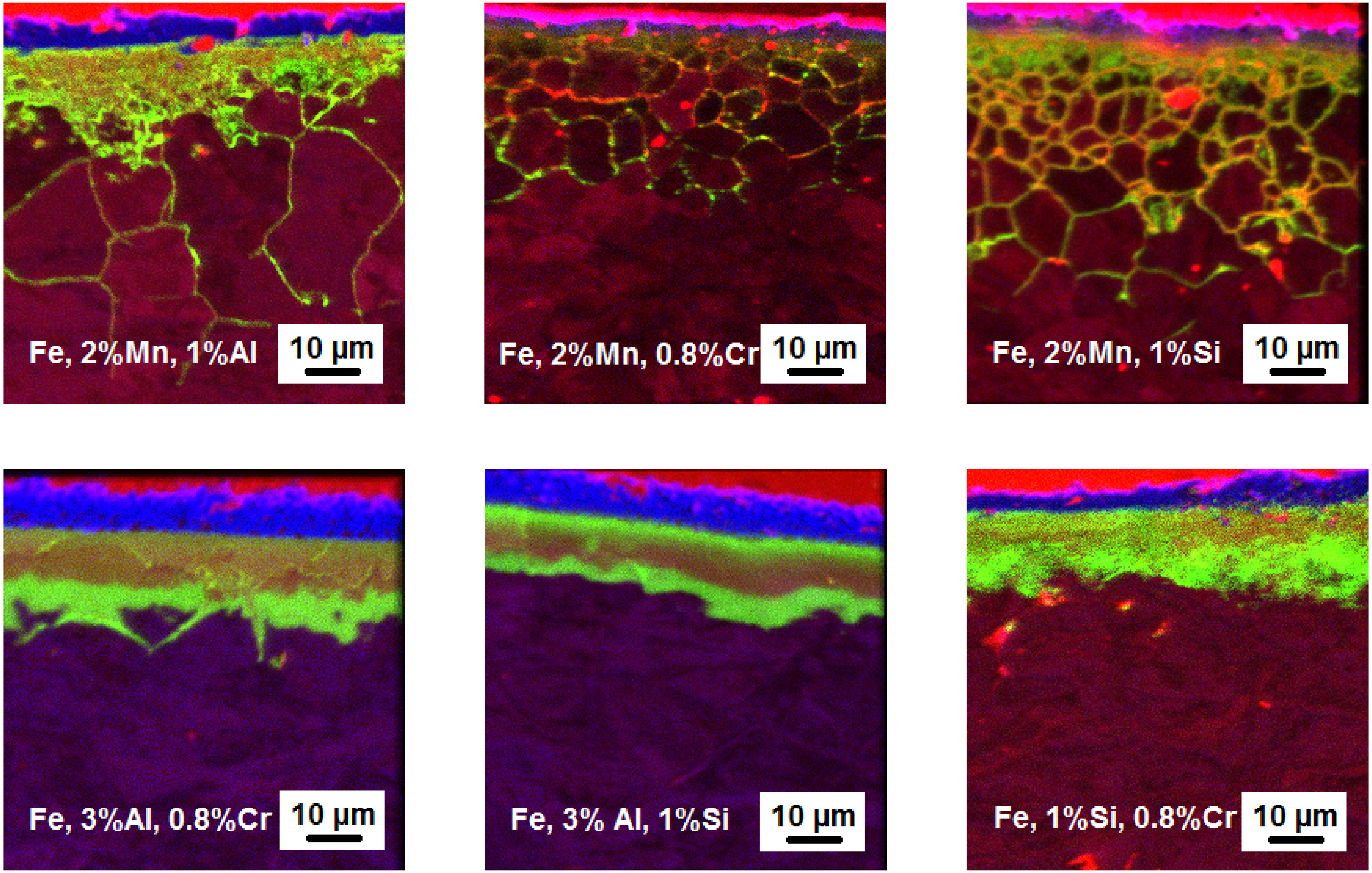


Figure: ToF-SIMS images of tilted angle (10°) polished ternary alloys after 60 min oxidation at 700°C in Ar / 2.5 vol-% H_2 / 0.9 vol-% H_2O (^{16}O – red, ^{18}O – green).

Corros. Sci. **96** (2015) 133-143.

Oxidation Depths

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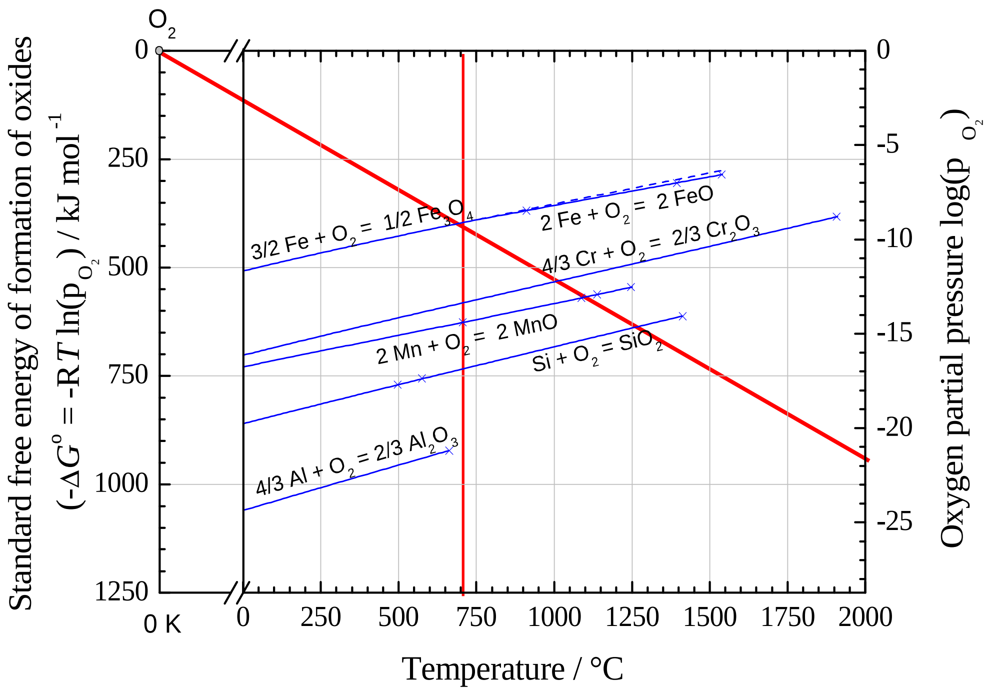
Alloy	GB-Oxidation	Oxidation depth *d* / µm		d_{exp} / d_{calc}
		experiment	calculation	
Fe-2Mn-1Al	Yes	8.2	8.9	0.920
Fe-2Mn-0.8Cr	Yes	7.4	9.2	0.800
Fe-2Mn-1Si	Yes	10.2	10.2	0.993
Fe-3Al-0.8Cr	Slightly	4.5	8.5	0.528
Fe-3Al-1Si	No	2.5	8.5	0.294
Fe-1Si-0.8Cr	No	2.5	9.9	0.252

Figure: Summary of measured and calculated corrosion depths in ternary alloys after 60 min oxidation at 700°C in Ar / 2.5 vol-% H_2 / 0.9 vol-% H_2O (^{16}O – red, ^{18}O – green).

Corros. Sci. **96** (2015) 133-143.

Properties of Oxygen



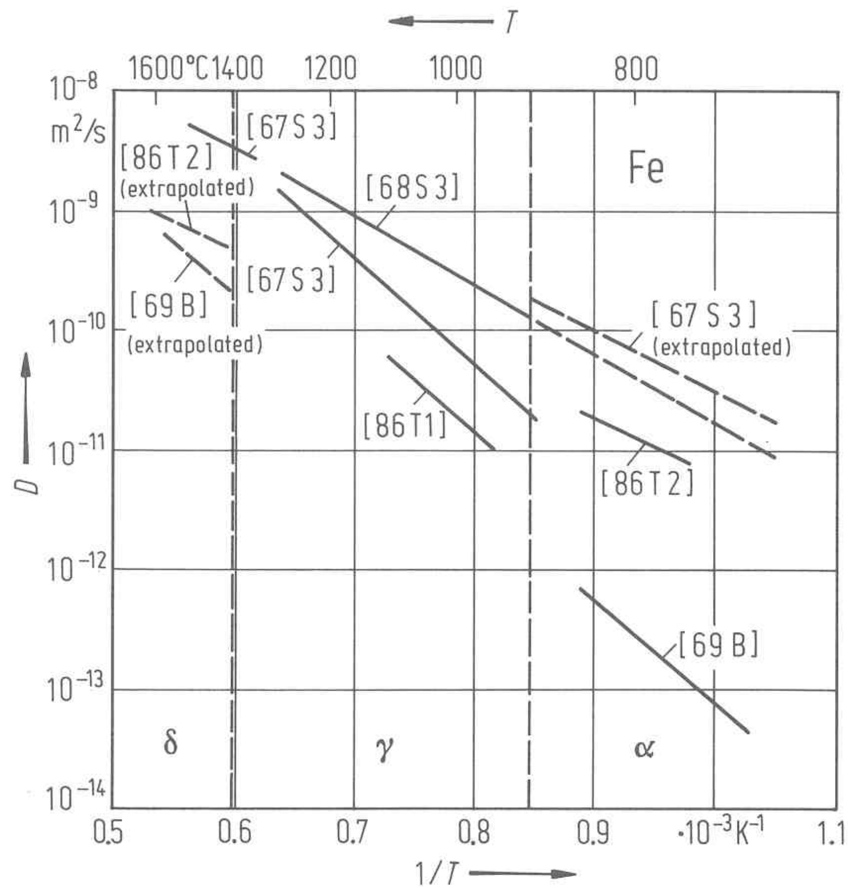
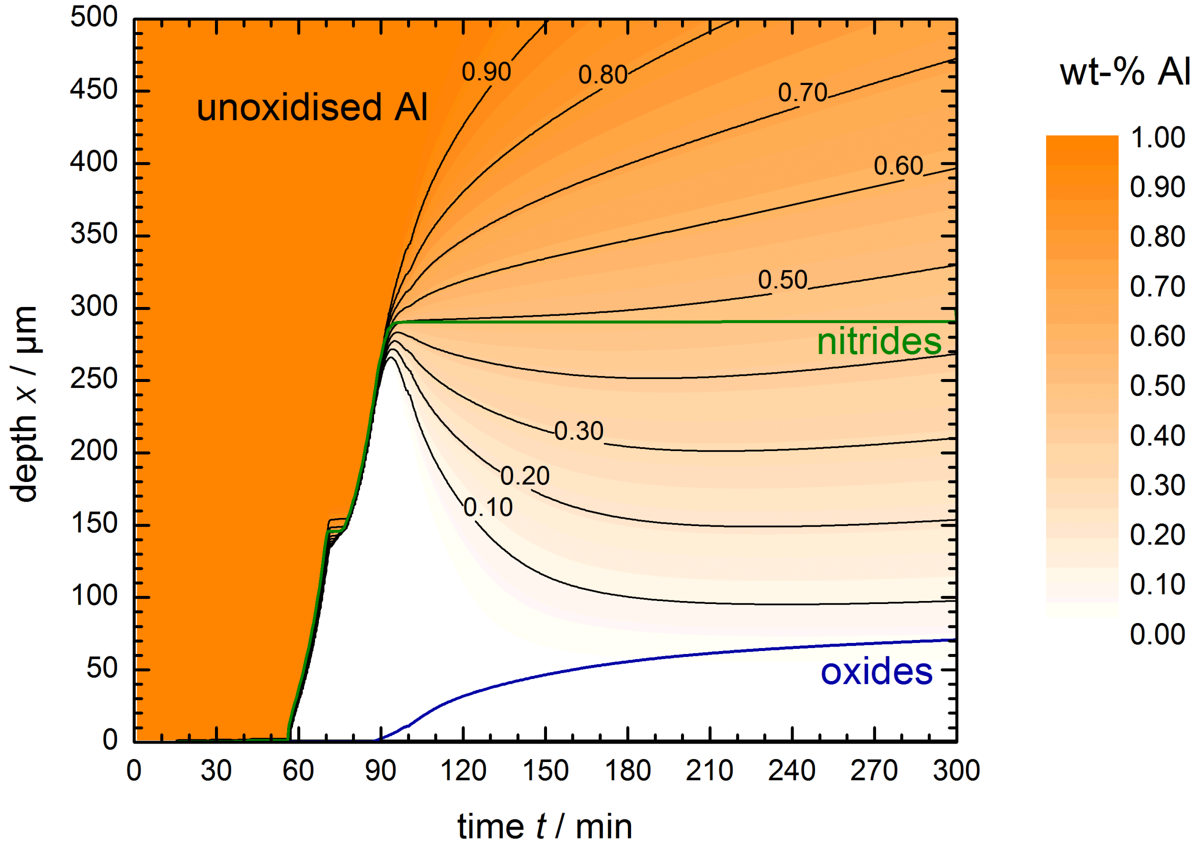


Fig. 23. Fe. Diffusion coefficient for O diffusion in α, γ and δ-phase Fe vs. (reciprocal) temperature.

FACTSage (left) and Landolt-Börnstein (right)

Oxides, Nitrides and Al Depletion



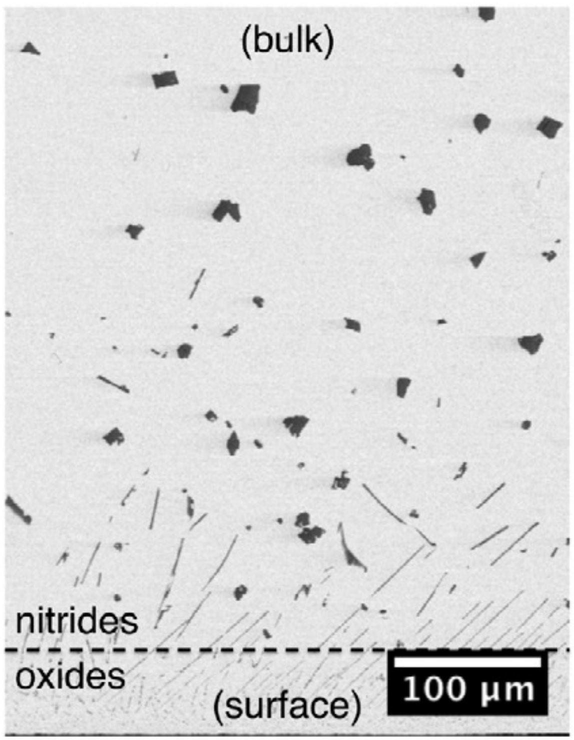
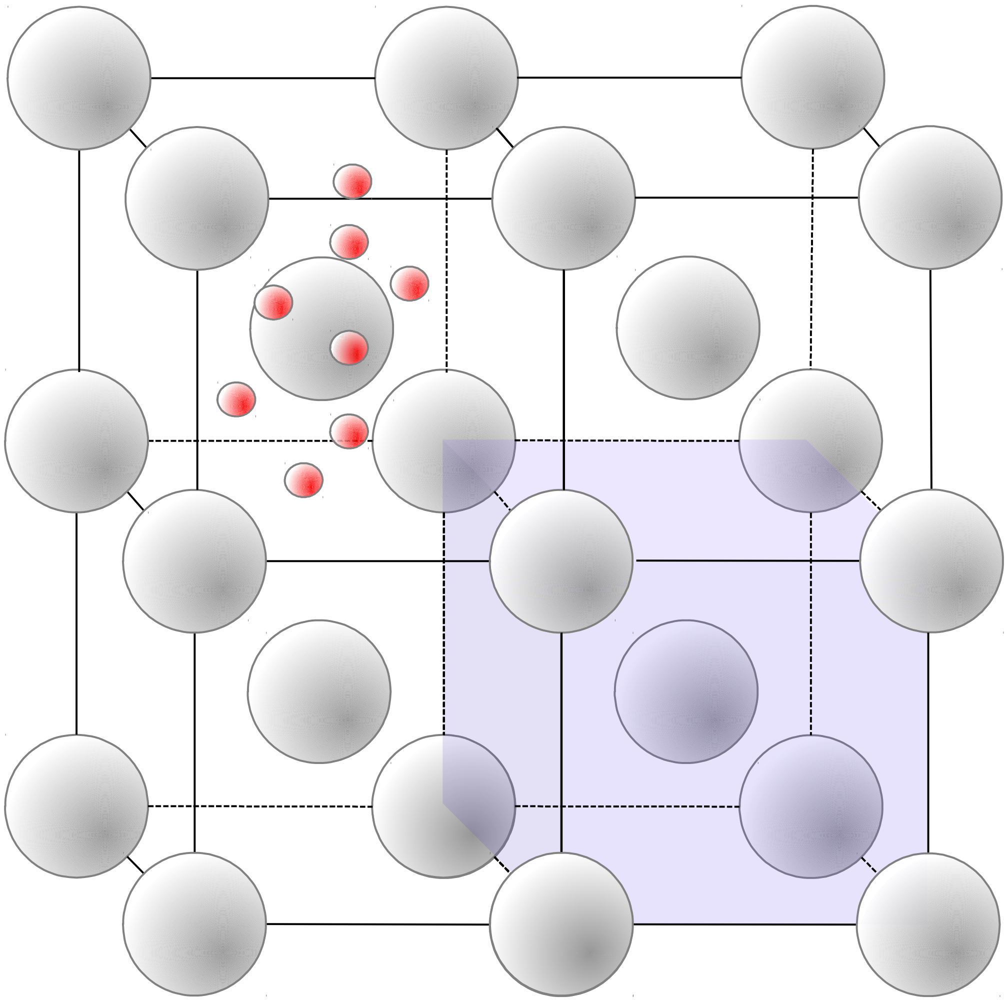


Figure: Calculated time evolution of phases and corrosion depth of Fe, 1wt-%Al slab in N_2 / 2.5 vol.% H_2 / 0.1 vol.% H_2O (left) and SEM image after 300min (right).

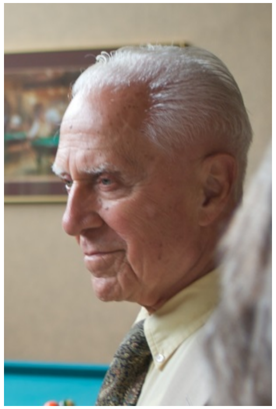
Hydrogen Trapping



$$H_i + \square_j \rightleftarrows \square_i + H_j$$

$$K_j = \frac{c_i^{max} - c_i}{c_i}\,\frac{c_j}{c_j^{max} - c_j} \stackrel{!}{=} e^{\frac{E_j}{RT}}$$

$$D = D_L \frac{c_L}{c_L + c_x(1 - \theta_x)}$$



R. Oriani, *Acta Metallurgica* **18** (1970), 147-157.

Constant Heating Rate

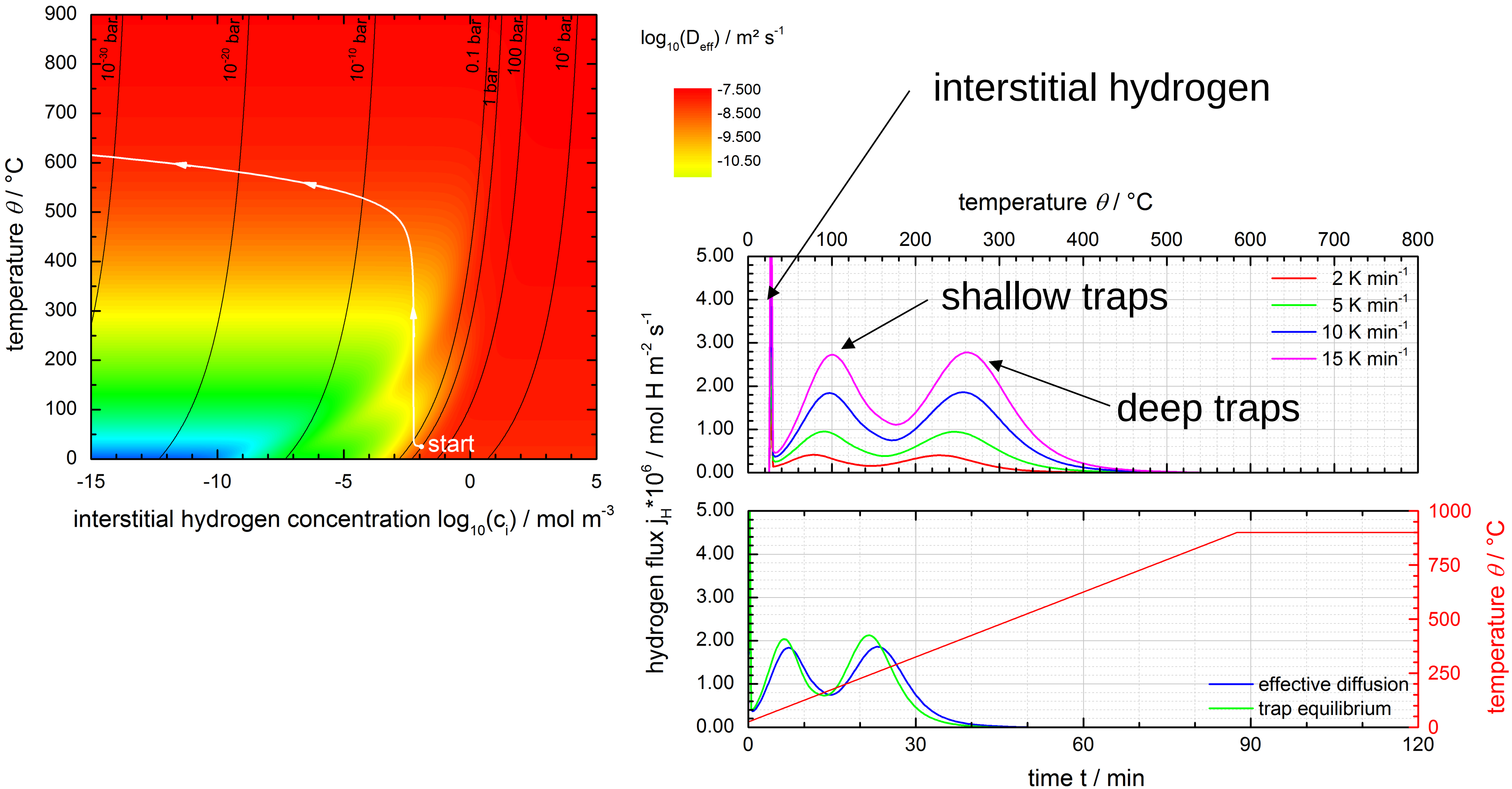
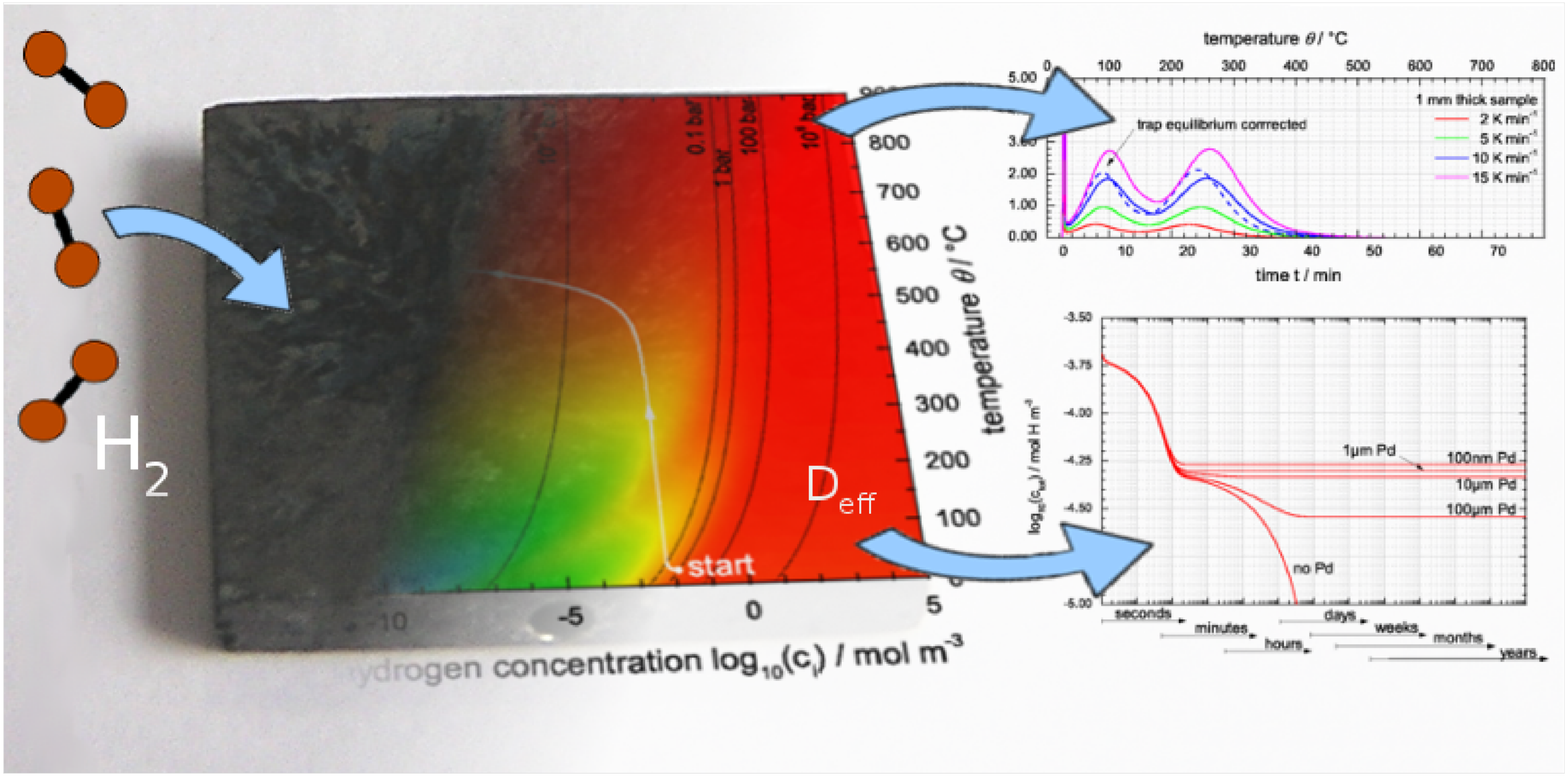


Figure: Effective diffusion coefficient in an idealised Fe-C alloy. Hydrogen trapping sites were calculated as H_1 = -58.6 kJ (10 molH m^{-3}), H_2 = -84 kJ (15 molH m^{-3}).

Chem. Phys. Chem. **15** (2014) 2893-2902.

Hydrogen Transport



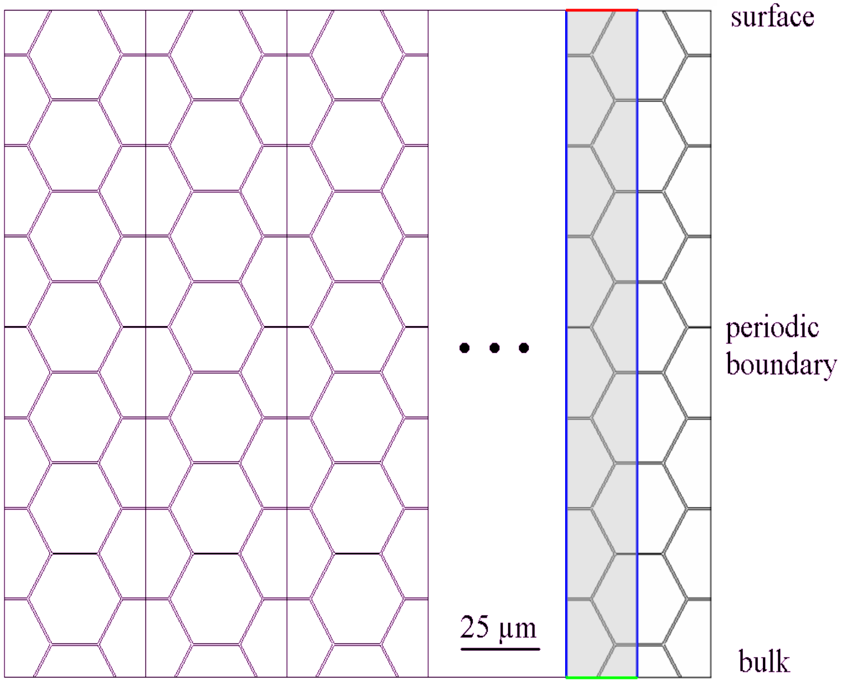
Chem. Phys. Chem. **15** (2014) 2893-2902.

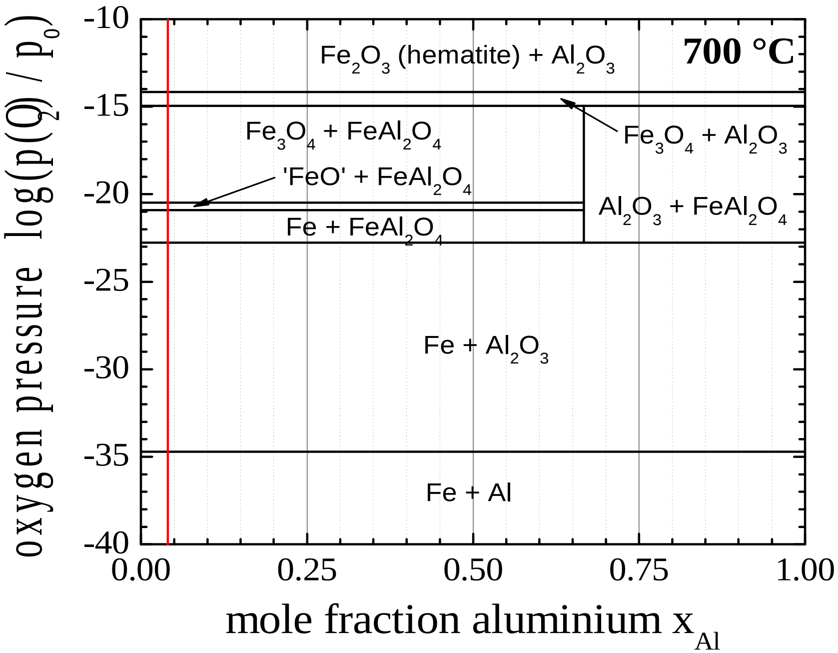
Programme Algorithm

element transport ⇄ chemical reaction

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

CHEMAPP





Oxid. Met. **76** (2011) 247-258.

Programme Algorithm

element transport ⇄ chemical reaction

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

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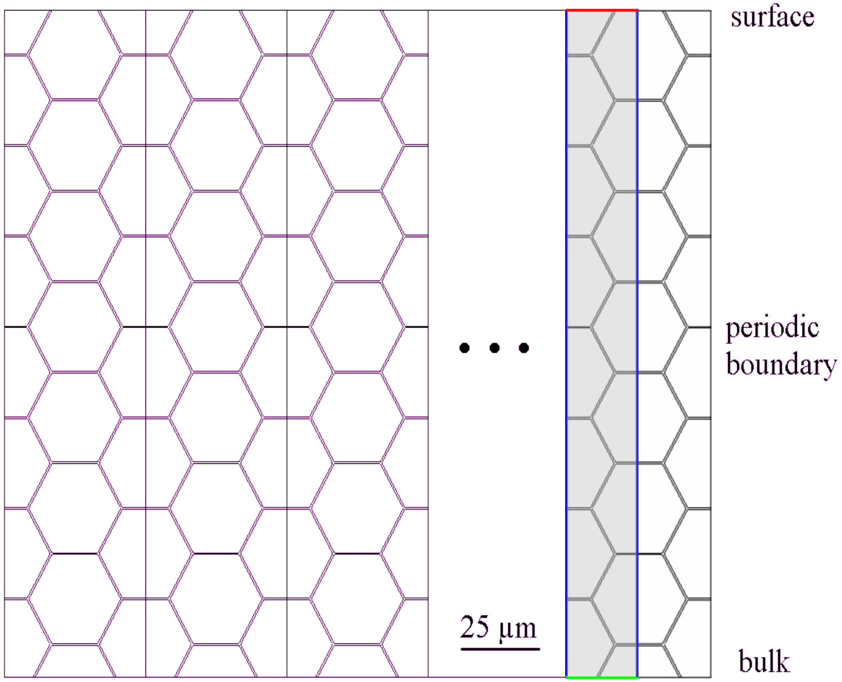
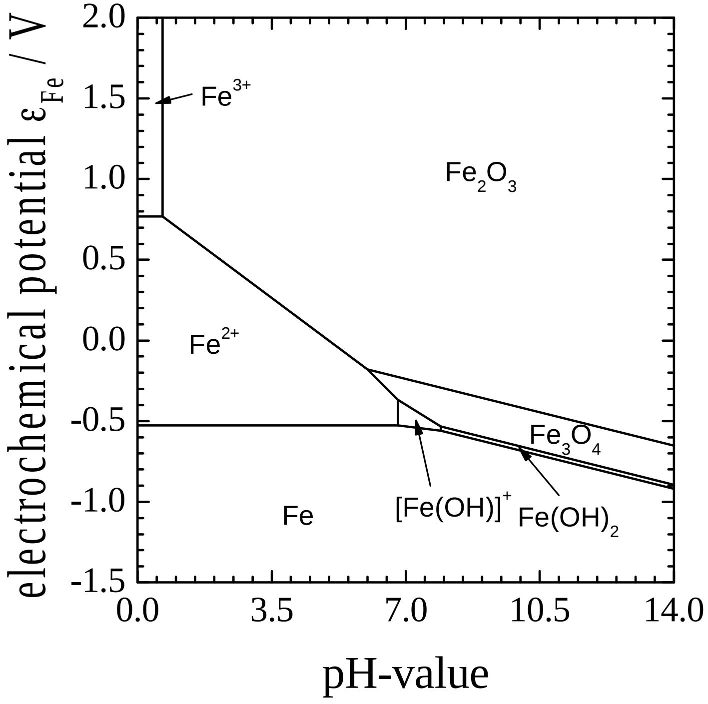




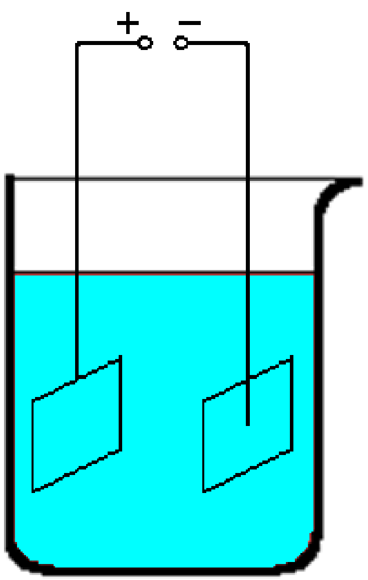
Oxid. Met. **76** (2011) 247-258.

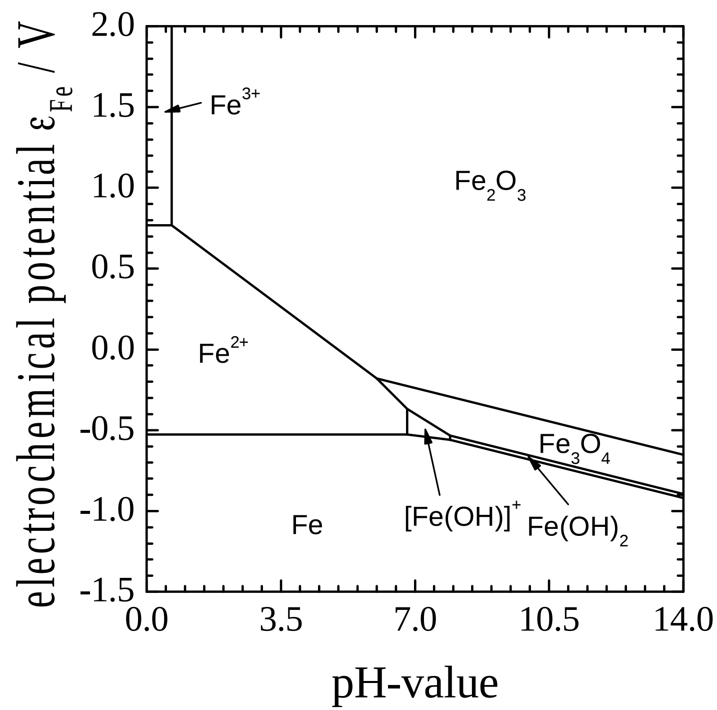
Programme Algorithm

element transport

chemical reaction

$$\frac{d c_{i(x,t)}}{d t} = \mathrm{div}\left(D_{i(x,T)} . \nabla c_{i(x,t)} + z_i . \mu_{i(x,T)} . c_{i(x,t)} . \nabla \phi_{(x,t)}\right)$$





Oxid. Met. **76** (2011) 247-258.

Electrochemistry & Pickling

$$\text{Nerst Equation} \quad E = E^o + \frac{RT}{zF} \ln\left(\frac{a_{Ox}}{a_{Red}}\right)$$

$$E = -58mV\,pH - (29mV \log(p(H_2)))$$

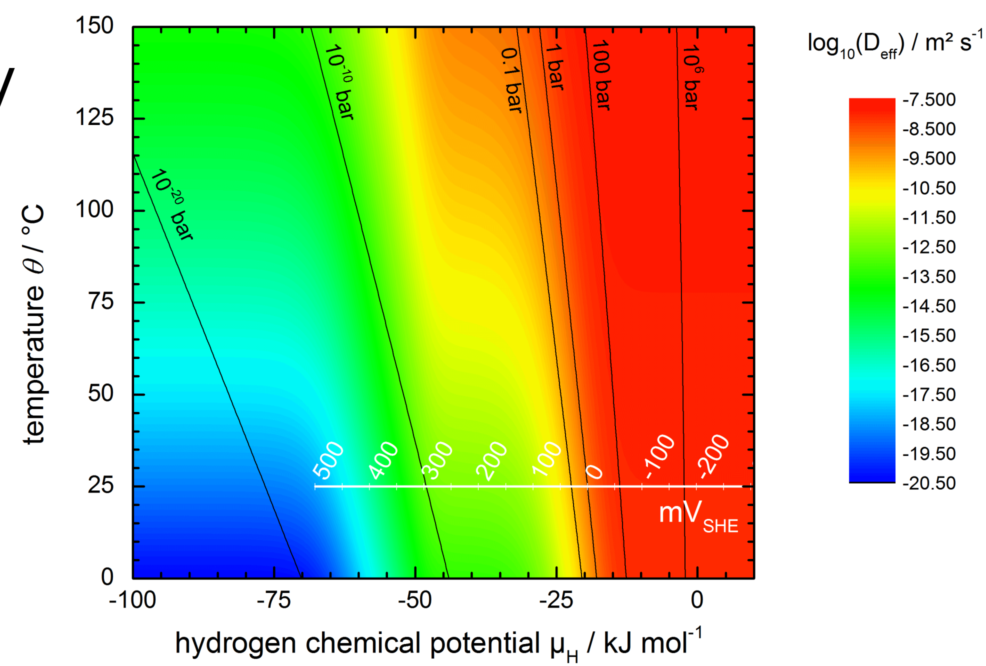
An applied voltage of -58 mV (vs SHE) corresponds to:

pH = 7 and 10^{-12} bar H_2

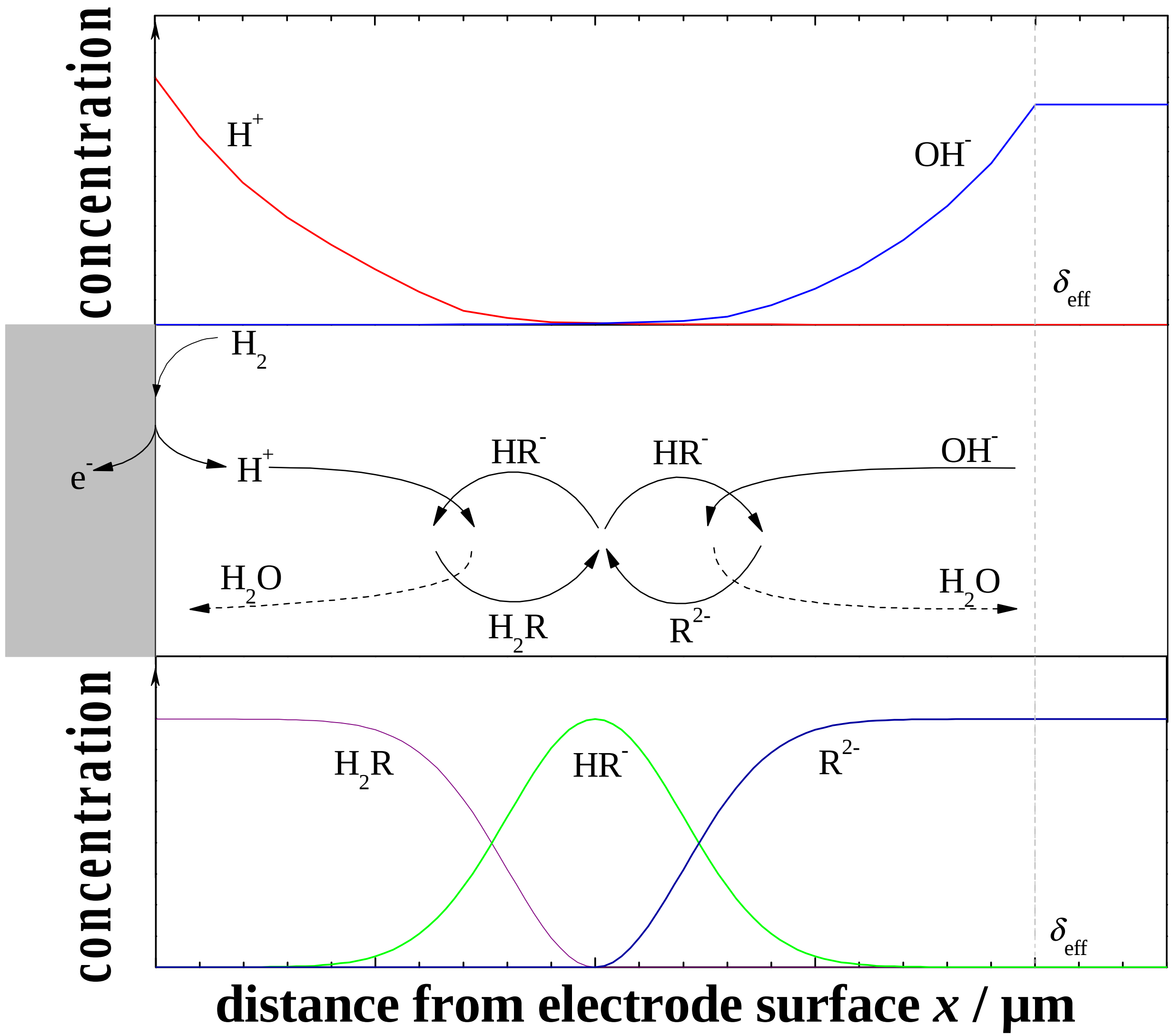
pH = 5 and 10^{-8} bar H_2

pH = 1 and 1 bar H_2

pH = 0 and 100 bar H_2



General Transport Scheme



PCCP **13** (2011) 16384-16394.

Local Corrosion Effects

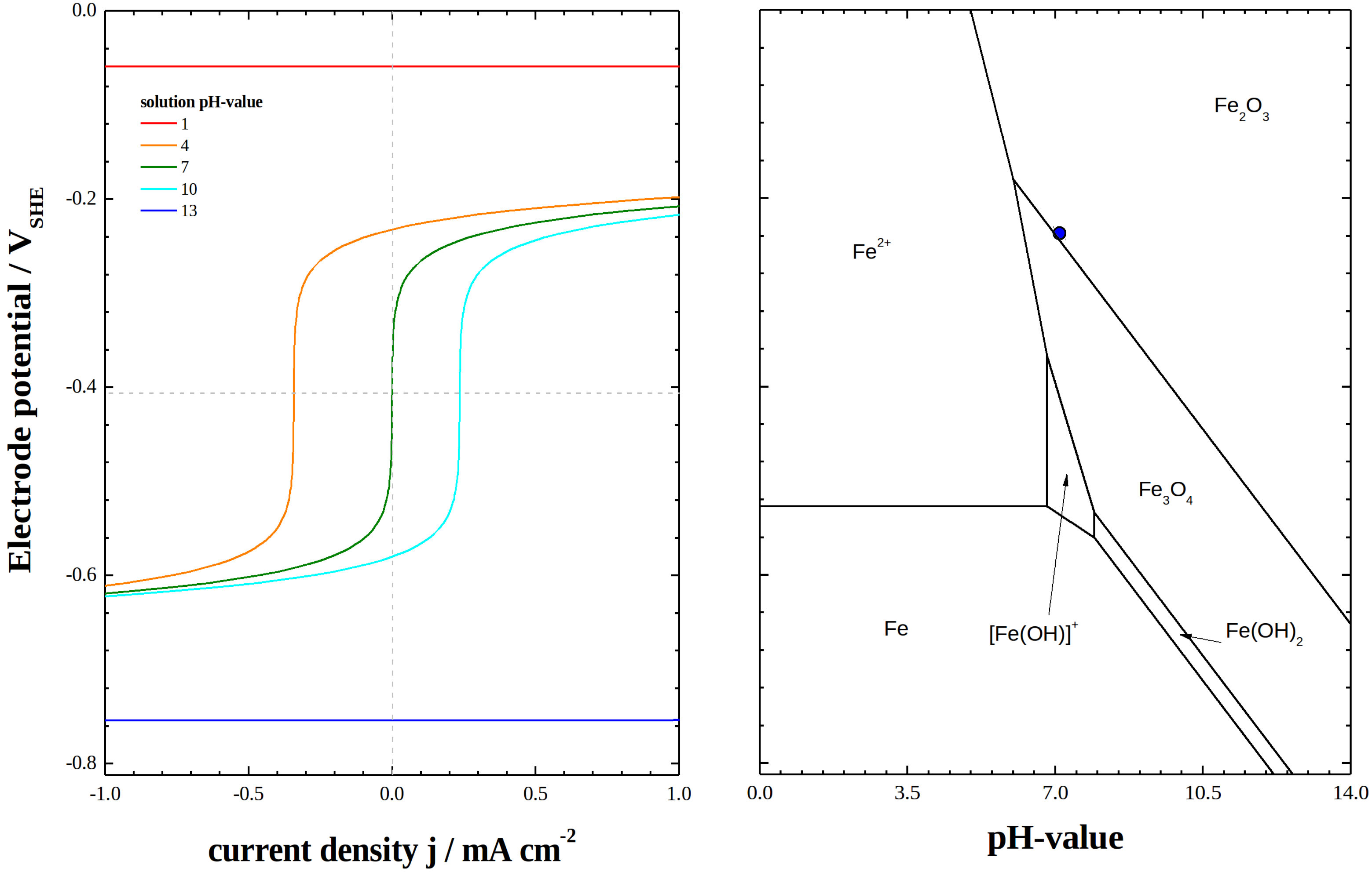


Figure: Cyclic voltammograms in unbuffered solutions of different pH-value.

Local Corrosion Effects

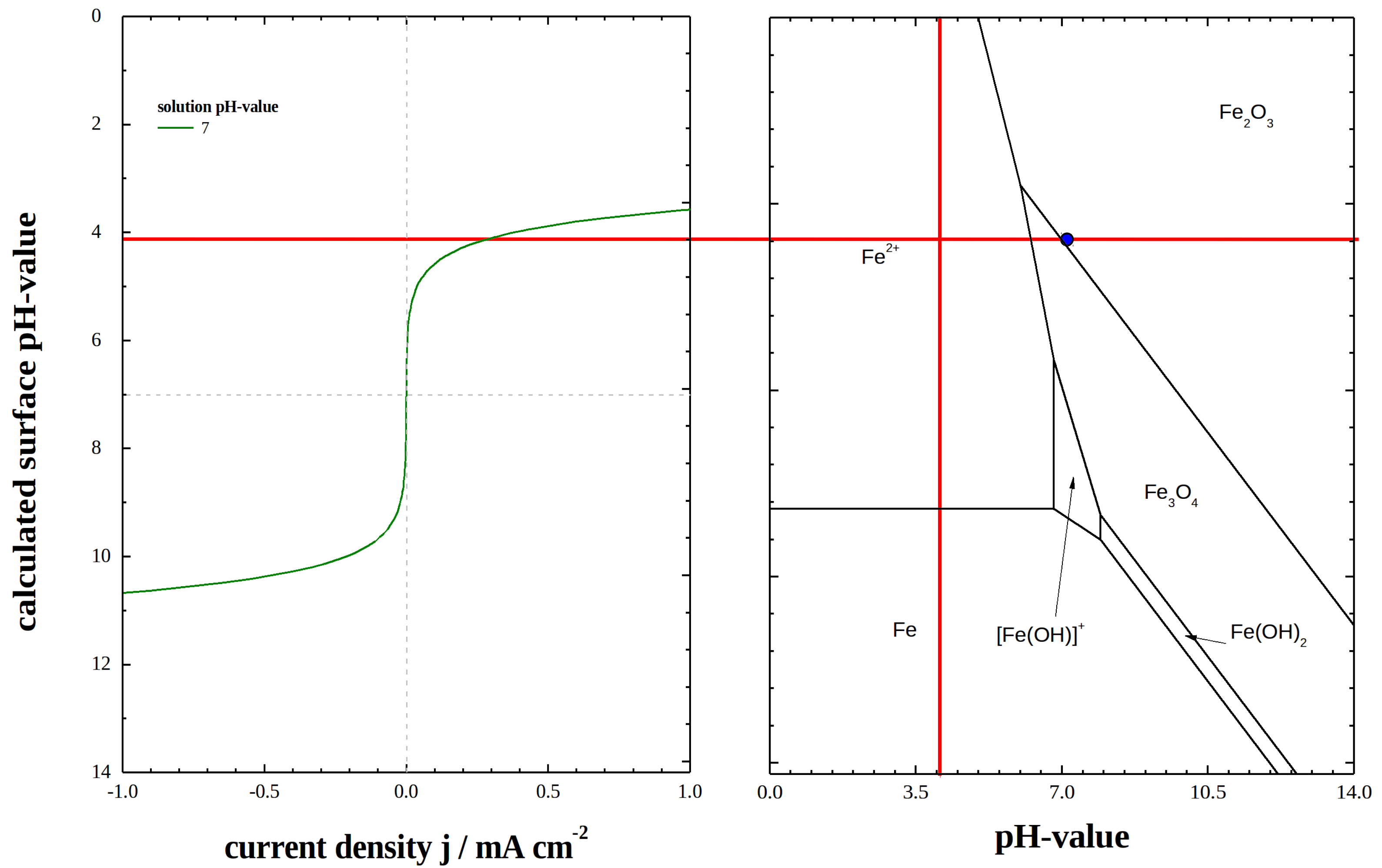
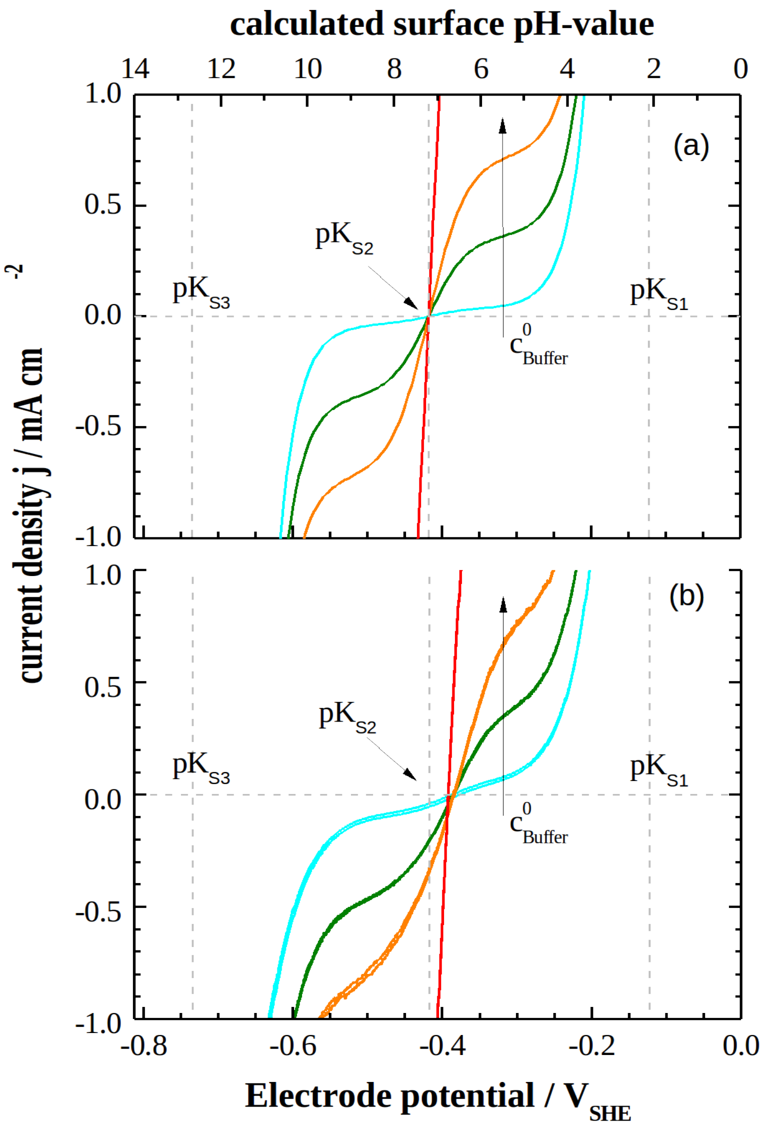
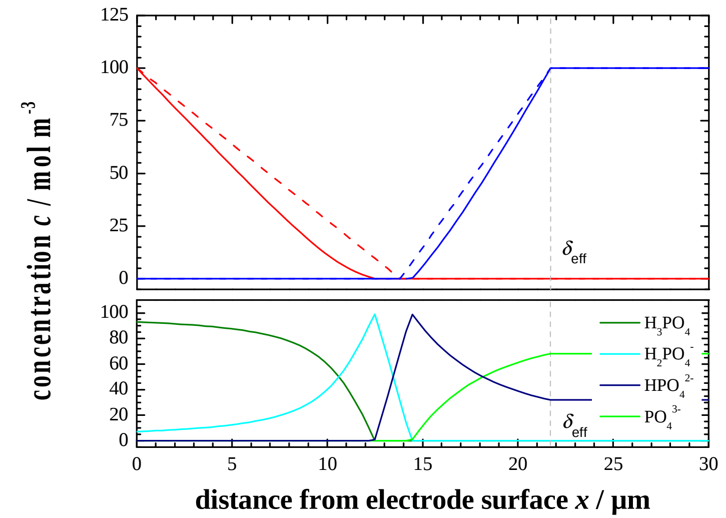


Figure: Cyclic voltammograms in unbuffered solution of pH 7.

Phosphate Buffered Solution



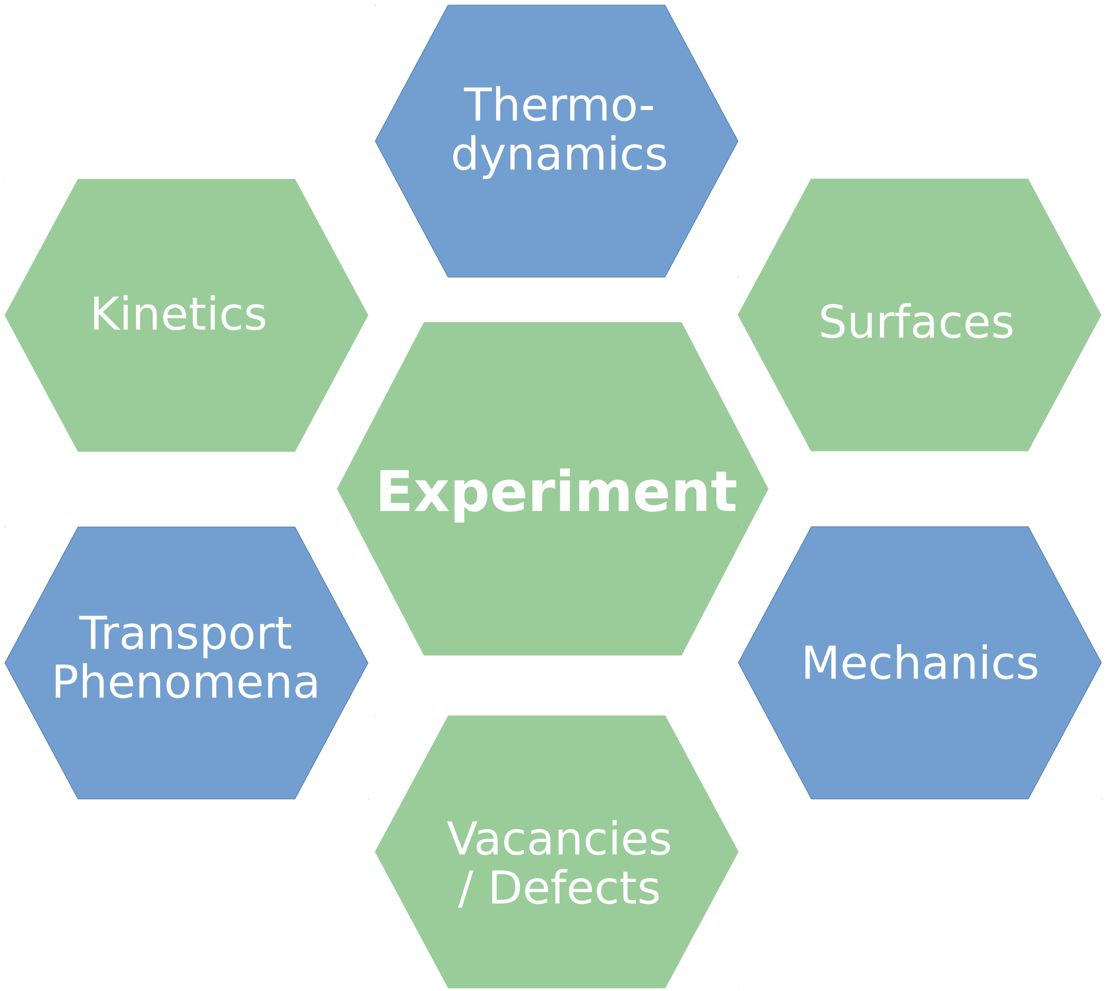


$$j = j_{H^+/OH^-} + j_{Buffer}$$

$$j_{Buffer} = \frac{c^0_{Buffer} F}{\delta_{eff}} \left(\frac{3D_1 + D_2 \frac{K_{S1}}{c_{(x)H^+}} - D_3 \frac{K_{S1}K_{S2}}{c^2_{(x)H^+}} - 3D_4 \frac{K_{S1}K_{S2}K_{S3}}{c^3_{(x)H^+}}}{1 + \frac{K_{S1}}{c_{(x)H^+}} + \frac{K_{S1}K_{S2}}{c^2_{(x)H^+}} + \frac{K_{S1}K_{S2}K_{S3}}{c^3_{(x)H^+}}} \right) \Bigg|_{x=\delta_{eff}}^{x=0}$$

PCCP **13** (2011) 16384-16394.

The General Modelling Idea



Acknowledgement

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Max-Planck-Institut für Eisenforschung GmbH

K. Mayrhofer, M. Rohwerder, A. Erbe, M. Nellessen, B. Hüning, E.-M. Müller-Lorenz, H. Bögershausen, J.C. Meier, A.A. Topalov, I. Katsounaros, D. & A. Vogel, B. Schönberger, M. Adamek, M. Kulse, D. Kurz, P. Ebbinghaus, S. Evers, A. Schüler

TECHNISCHE UNIVERSITÄT WIEN
Vienna University of Technology

Prof. Danninger, Prof. Hutter, Prof. Fleig
V. Praig, K. Piblits, M. DeBardi

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Prof. Seetharaman (now Uni Warwick)
J. Bott, J. Zhu

Financial Support

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