Update on Diffusion Mobilities in Oxide Systems

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Diffusion workshop
25-26 March 2009
NIST, USA

Aim of work

Predict oxidation:

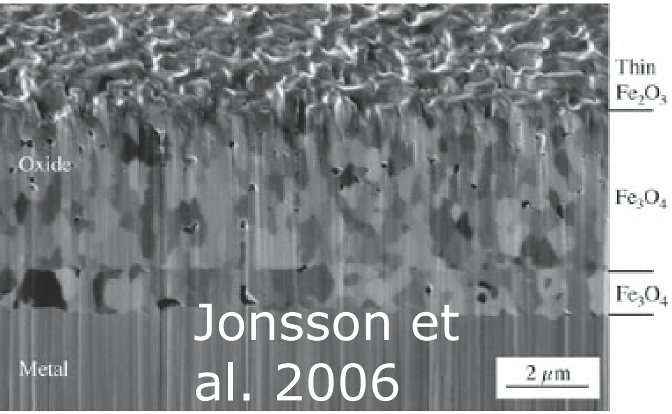
- Sharp-interface methods – DICTRA
- Diffuse-interface methods – phase-field

For example:

- Oxidation of steels
- Degradation of superalloy coatings

We need:

- Mathematical expressions for flux as function of gradients in composition or chemical potentials.
- Parameters that characterize a given material



Jonsson et al. 2006

Background

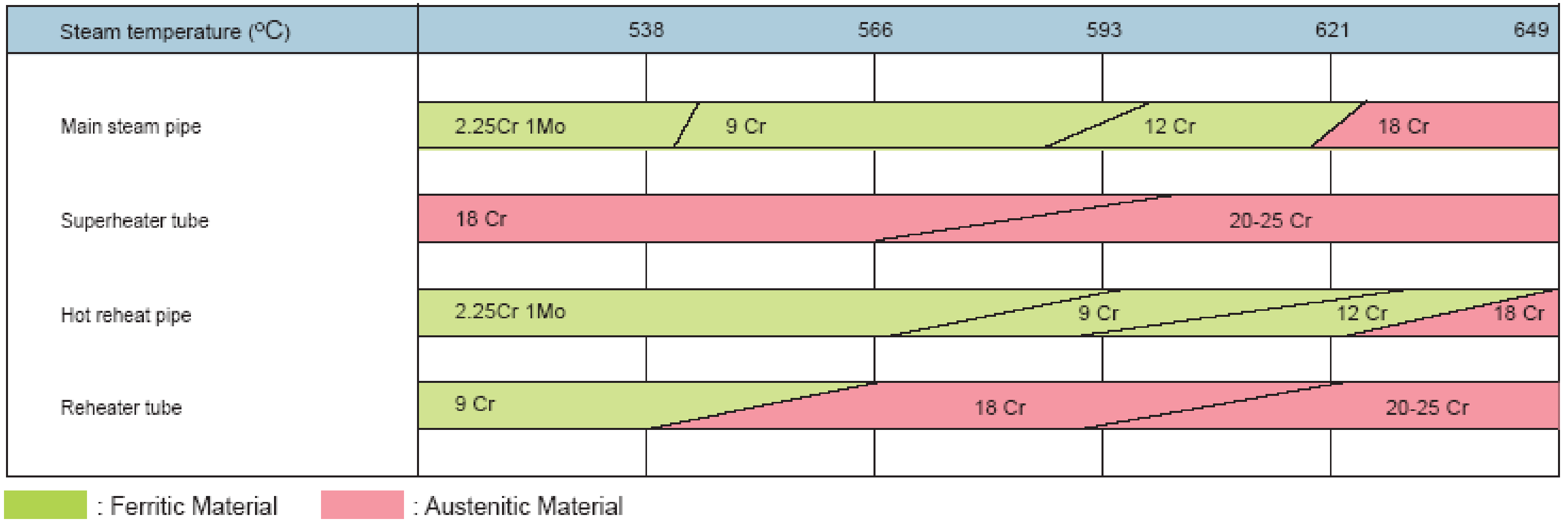
Ferritic 9-12 % Cr steels

Avedøre (Copenhagen)

The life-time of is limited by:
- Creep
- Oxidation.

Design requirement: at least 100 000 h at 100 MPa

Fig. 3 Steam conditions and high temperature materials



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Content

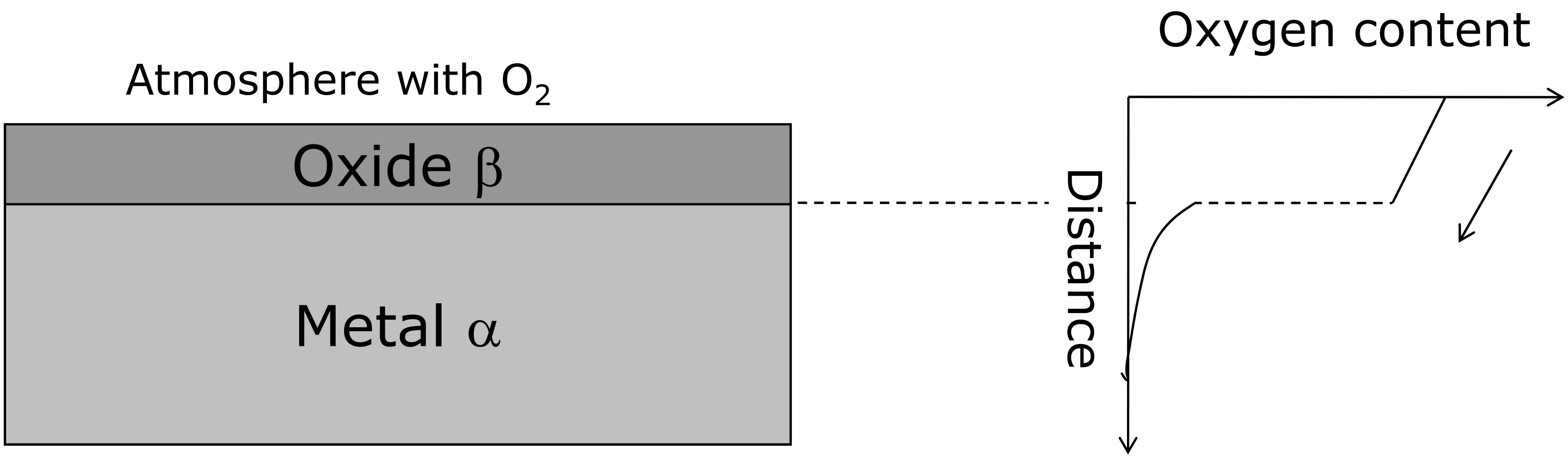
- Background
- Modelling of oxidation
- Bulk diffusion in oxides
- Grain boundary diffusion
- Kirkendall porosity
- Effect of water vapour

Modelling of oxidation - issues

Predict:

- Rate of oxidation
- What oxides form
- Porosity

Growth of oxide layers – how fast do the layers grow?



Flux balances in sharp-interface modelling!

General approach

Flux :

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

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

Kinetic parameters from model.

Darken's thermodynamic factor, e.g. from Calphad analysis.

Base models on a vacancy mechanism!

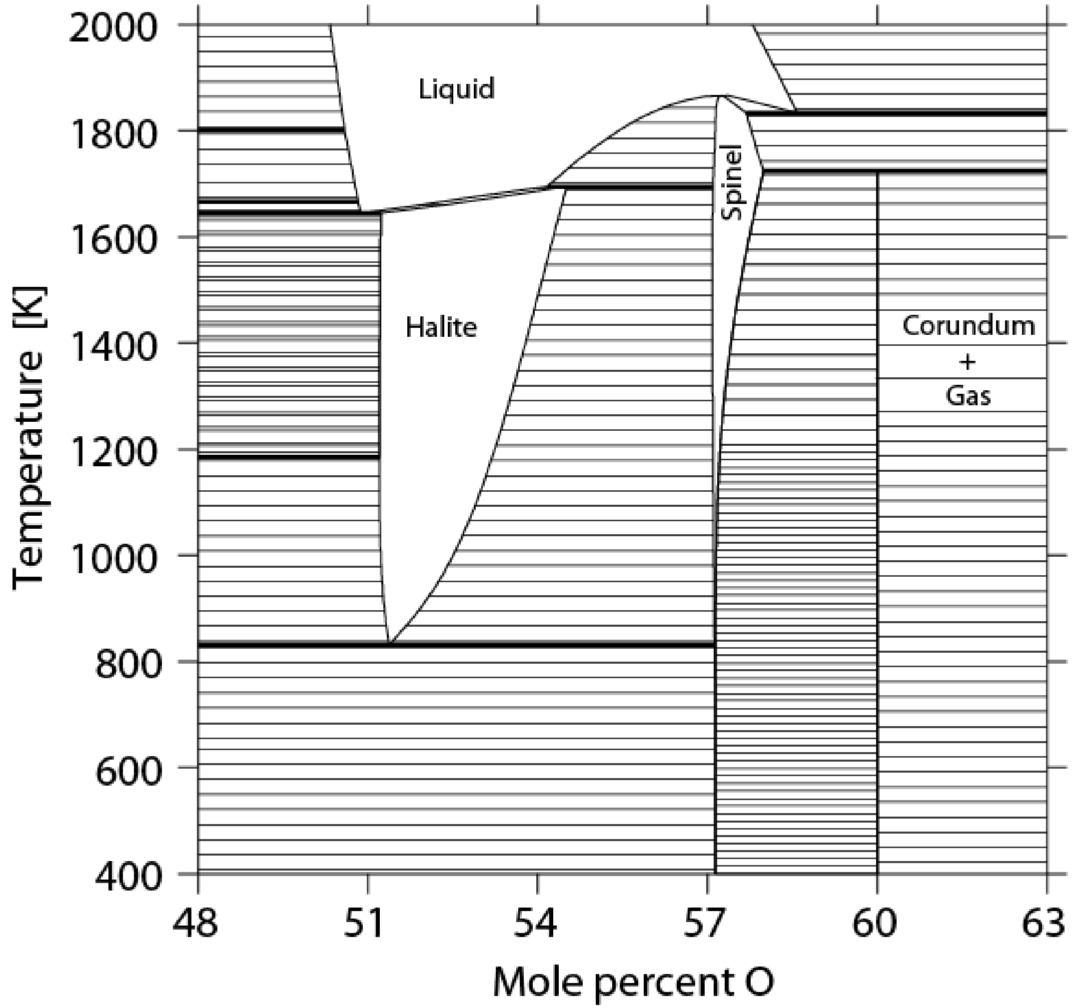
At present:

- Models included in DICTRA

  Our data base now contains diffusional mobilities of
- Wustite
  - Fe
  - O missing but probably very small
- Magnetite (spinel)
  - Fe, Cr ongoing
  - O
- Hematite (Corundum)
  - Fe, Cr
  - O missing but similar to Fe

The Fe-O system

- Calculated from Sundman 1991.



Ionic systems – two extremes

- Electronic conduction compared to diffusion:
  - Much faster (charge does not need to be included)
  - Much slower (ions diffuse as species)

If electronic conduction and diffusion are about the same rate (electronic conduction needs to be accounted for)

Fe diffusion in spinel (lattice-fixed frame of reference)

Absolute reaction rate arguments:

$$J_{Fe}' = -\tfrac{1}{2}\left[y''_{Va}y''_{Fe}M''_{FeVa} + y'''_{Fe}y'''_{Va}M'''_{FeVa}\right]\frac{1}{V_s}\frac{\partial \mu_{Fe}}{\partial z}$$

L_{Fe}

Normal octahedral sites

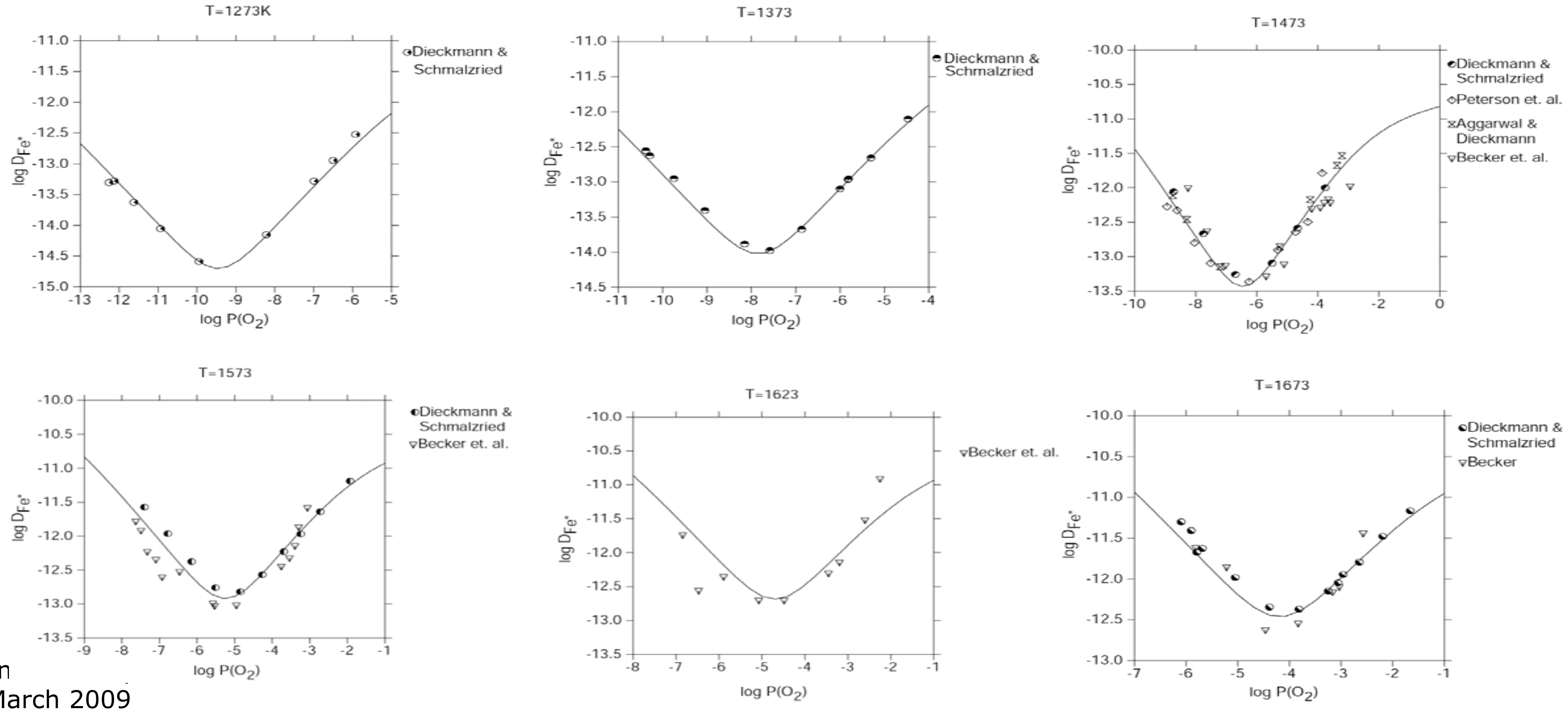
extra octahedral sites

$$RTM_k = \delta^2 \nu \exp(-\Delta G_k / RT)$$

$$D_{Fe^*} \cong RT\,\tfrac{1}{2}\left[y''_{Va}y''_{Fe}M''_{FeVa} + y'''_{Fe}y'''_{Va}M'''_{FeVa}\right]\frac{1}{u_{Fe}}$$

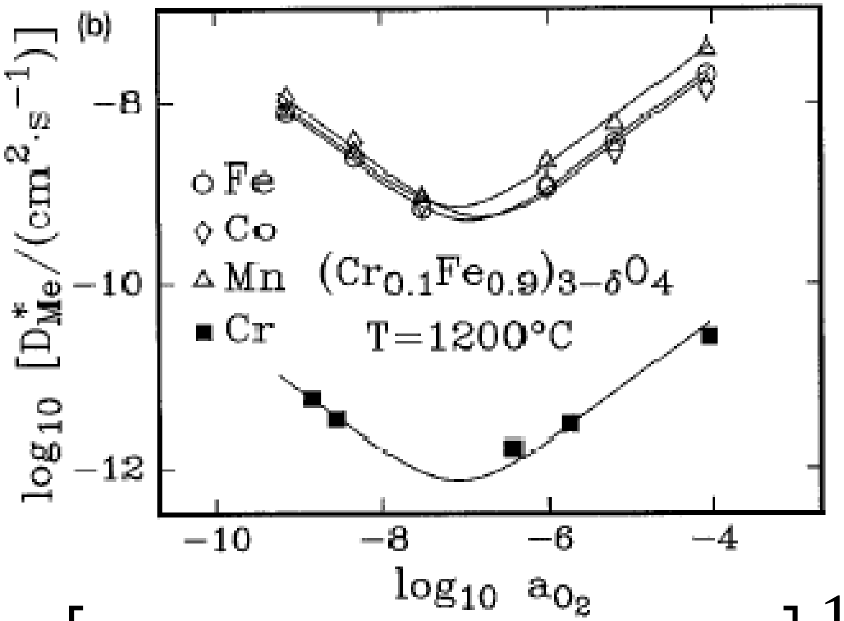
Experimental data on Fe tracer diffusion in spinel - Optimization of Fe mobilities

(Hallström et al. 2008)



Alloy elements in spinel (lattice fixed frame of reference)

Töpfer et.al. 1995

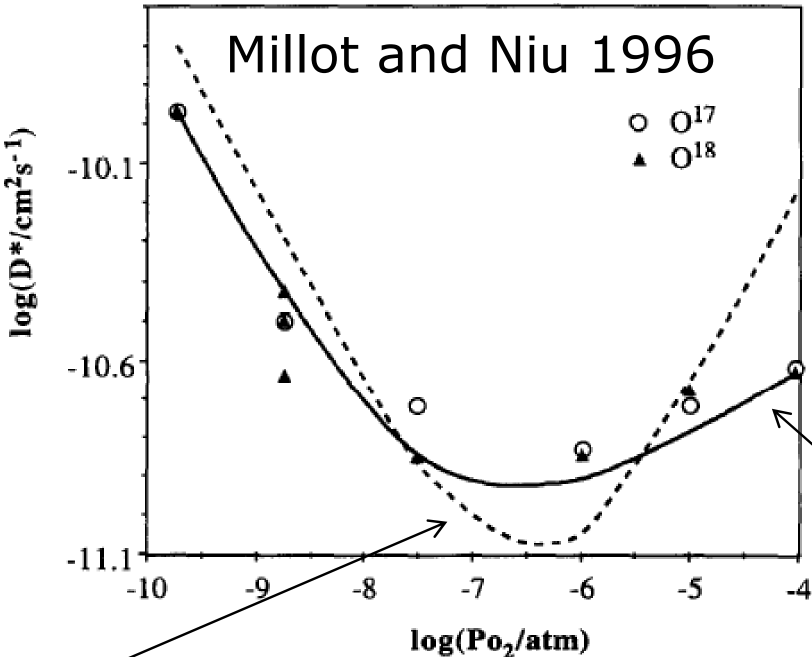


Cr content of inward growing spinel will inherit Cr content of alloy.

$$J_{Cr}' = -\left[y''_{Va} y''_{Cr} M''_{CrVa} + y'''_{Cr} y'''_{Va} M'''_{CrVa}\right] \frac{1}{V_s} \frac{\partial \mu_{Cr}}{\partial z}$$

$$D_{Cr^*} = RT\left[y''_{Va} y''_{Cr} M''_{CrVa} + y'''_{Cr} y'''_{Va} M'''_{CrVa}\right] / u_{Cr}$$

O tracer diffusion in spinel (lattice-fixed frame of reference)



T= 1150°C

$$J_O = -\left[y^a_{Va} y^a_O M^a_{OVa} + y^i_O y^i_{Va} M^i_{OVa} \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

or $$J_O = -y^a_{Va} y^a_O M^a_{OVa} \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}$$

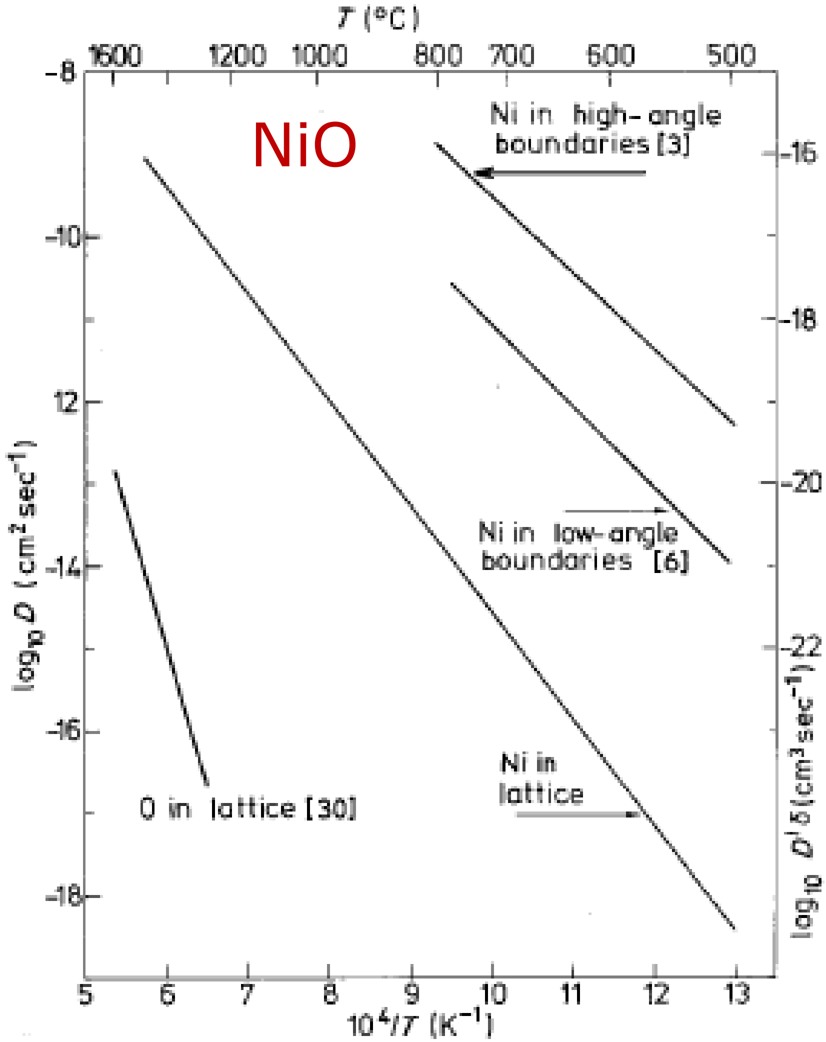
$$y^a_{Va} = \left[y^{''}_{Va} y^{''}_{Fe} k^{''}_{FeVa} + y^{'''}_{Va} y^{'''}_{Fe} k^{'''}_{FeVa} \right]$$

Effect of grain boundaries

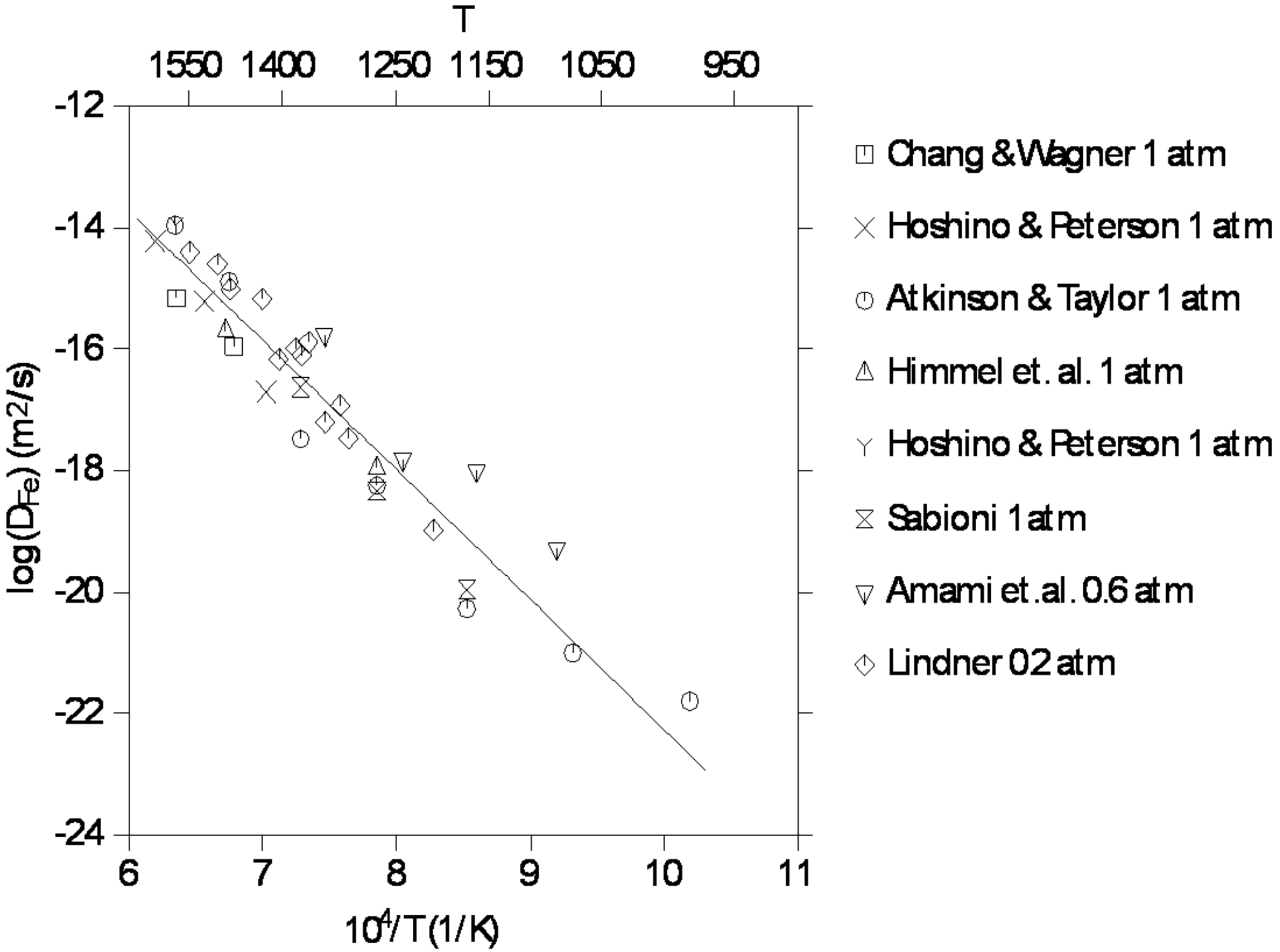
Simplified approach:

$$D_{eff} = (1 - \delta / d) D_{bulk} + \delta / d \; D_{gb}$$

$$Q_{gb} \cong \alpha \, Q_{bulk} \quad 0.3 < \alpha < 0.5$$

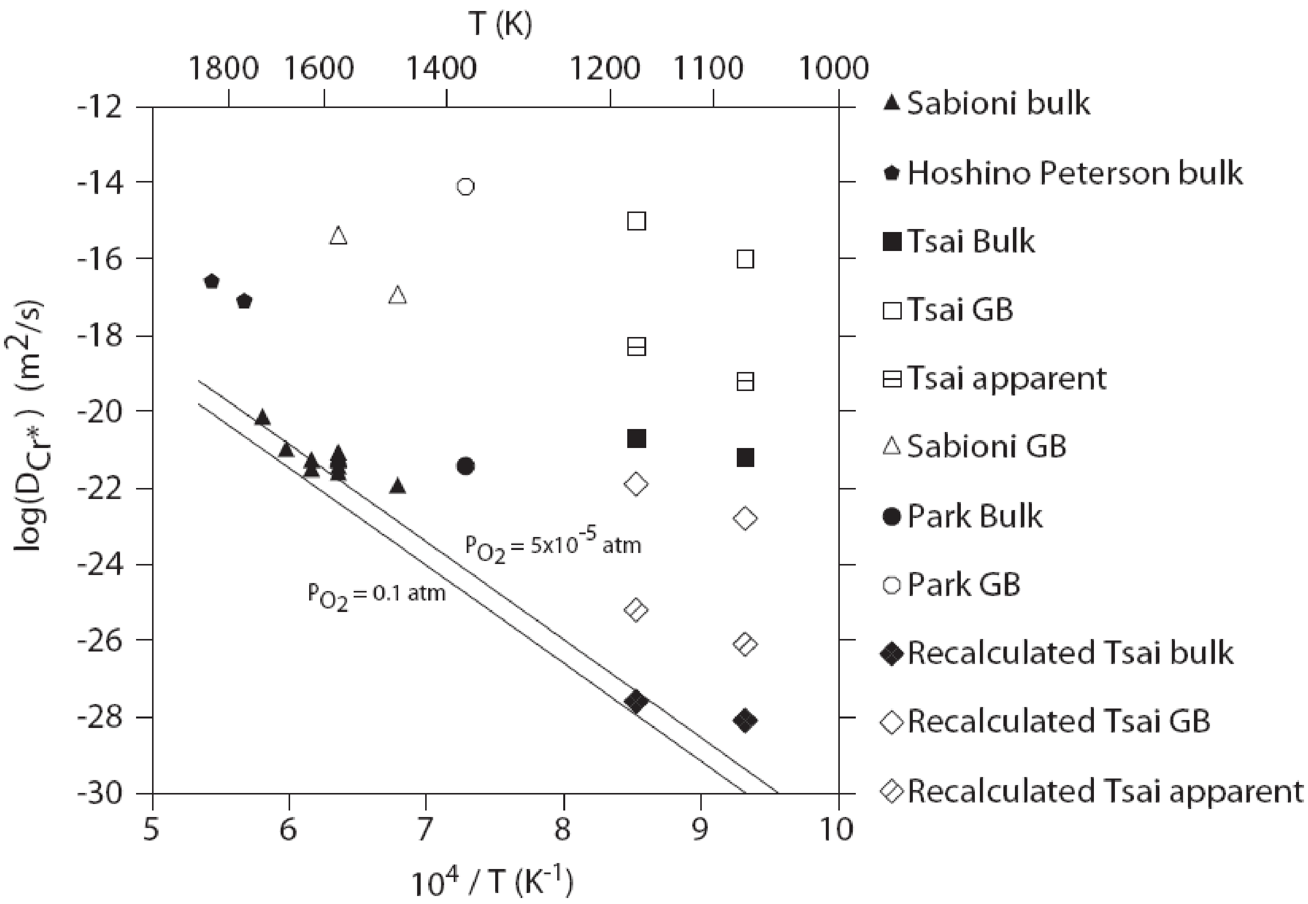


Fe tracer in Fe_2O_3



Cr tracer in Cr_2O_3

- Q estimated from diffusion of Fe in hematite (isostructural).
- Lowest values should correspond to the most pure material.
- Values from Sabioni and Tsai (recalculated to tracer) used in optimization.



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Simulations of oxidation of pure Fe at 600°C in dry atmosphere

- 600°C, P_{02}=0.05, 24h.
- $d^{mag} \approx$ 3μm, $d^{cor} \approx$ 0.1μm, δ=5 nm
- Gb diffusion accounted for in magnetite and hematite.

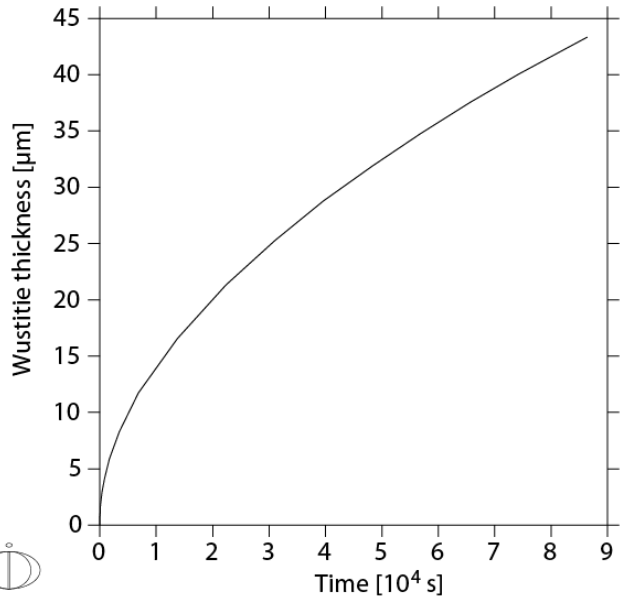
$$D_{eff} = (1-\delta/d)D_{bulk} + \delta/d\ D_{gb}$$

$$Q_{gb} \cong \alpha\ Q_{bulk} \quad 0.3 < \alpha < 0.5$$

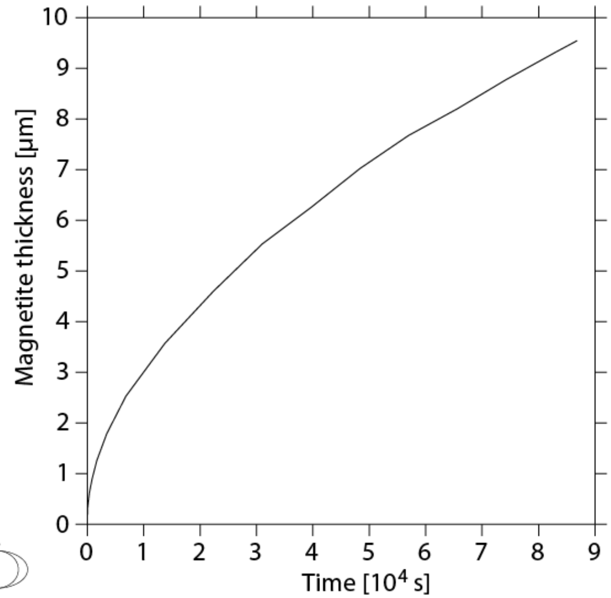
- Oxygen diffusion neglected

Simulation: α=0.33 oxide thicknesses

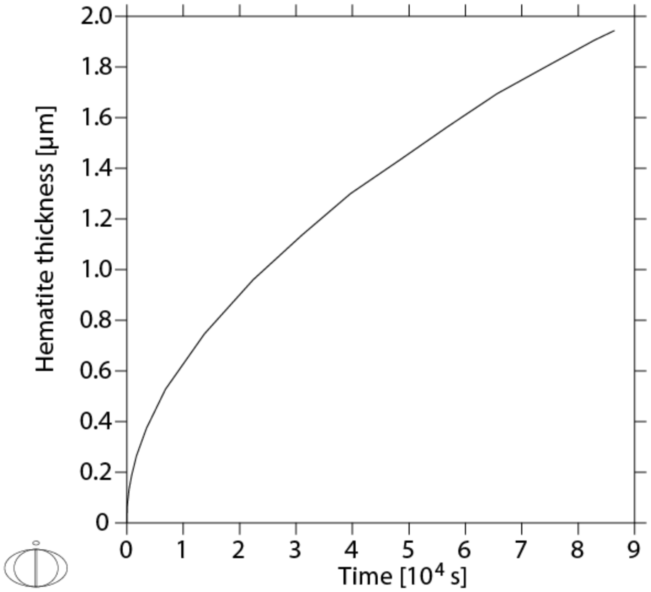
Wustite



Magnetite



Hematite



	Wustite	Magnetite	Hematite
Calculated:	45 μm	10 μm	2 μm
Experimental:	21 μm	11 μm	2 μm

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Kirkendall effect - porosity

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

$$\frac{v}{V_m} = -J = -J'_{O^{-2}} / x_{O^{-2}}$$

V_m = molar volume/mole of atoms

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

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

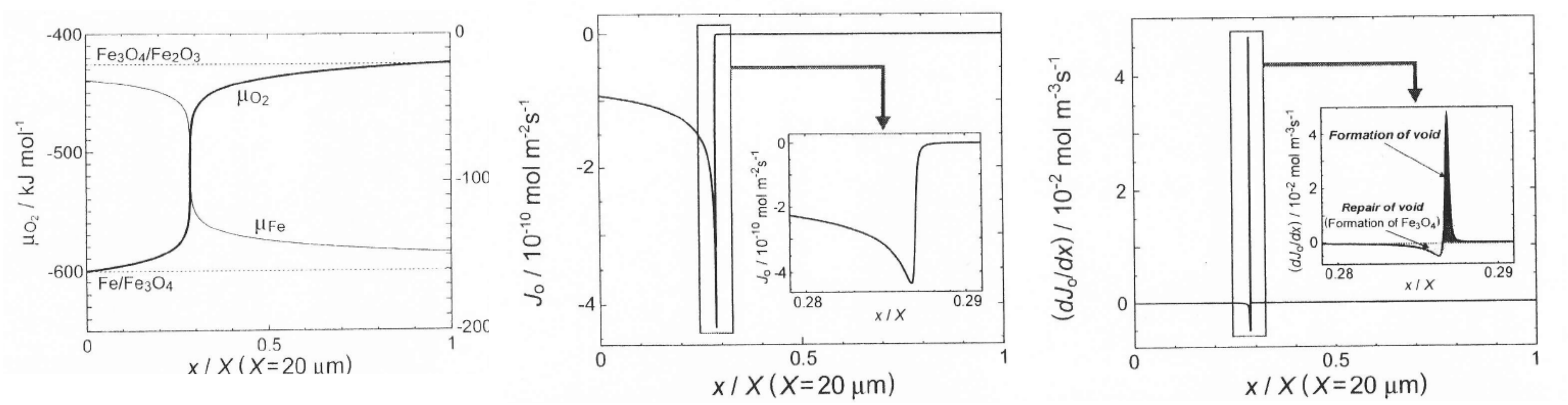
No porosity $\Rightarrow$ Strain rate:

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

Only porosity (volume fraction f_p):

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

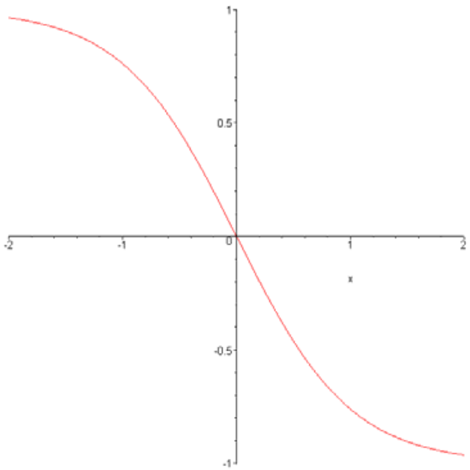
Maruyama et al. 2004



Voids form as a consequence of a divergence in the oxygen flux.

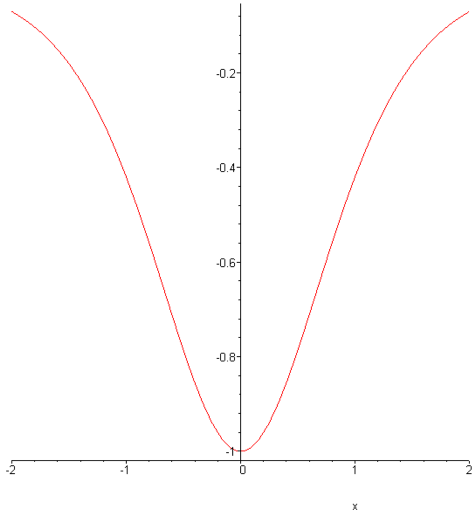
Schematics of Kirkendall effect in magnetite

μ_{Fe}



Distance

$$\frac{\partial \mu_{Fe}}{\partial z}$$



Distance

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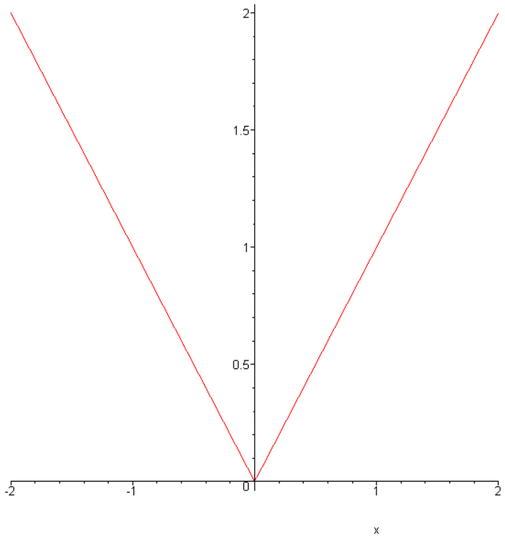
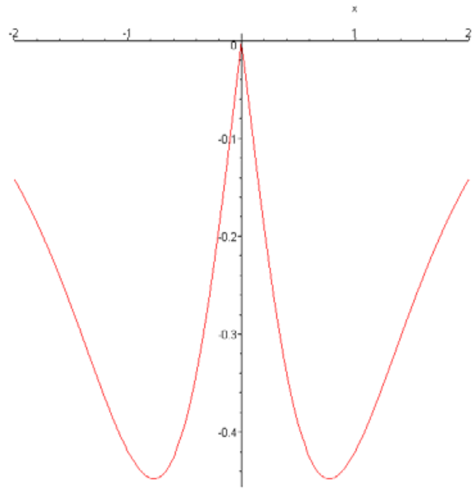
Oxygen mobility



Distance

Oxygen flux



Distance

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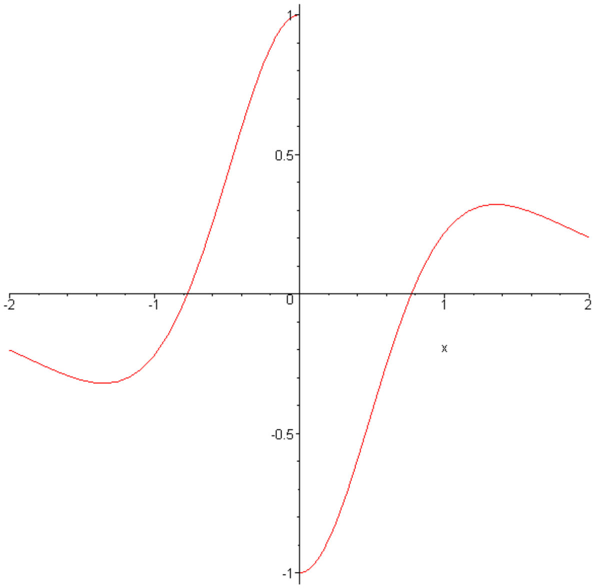
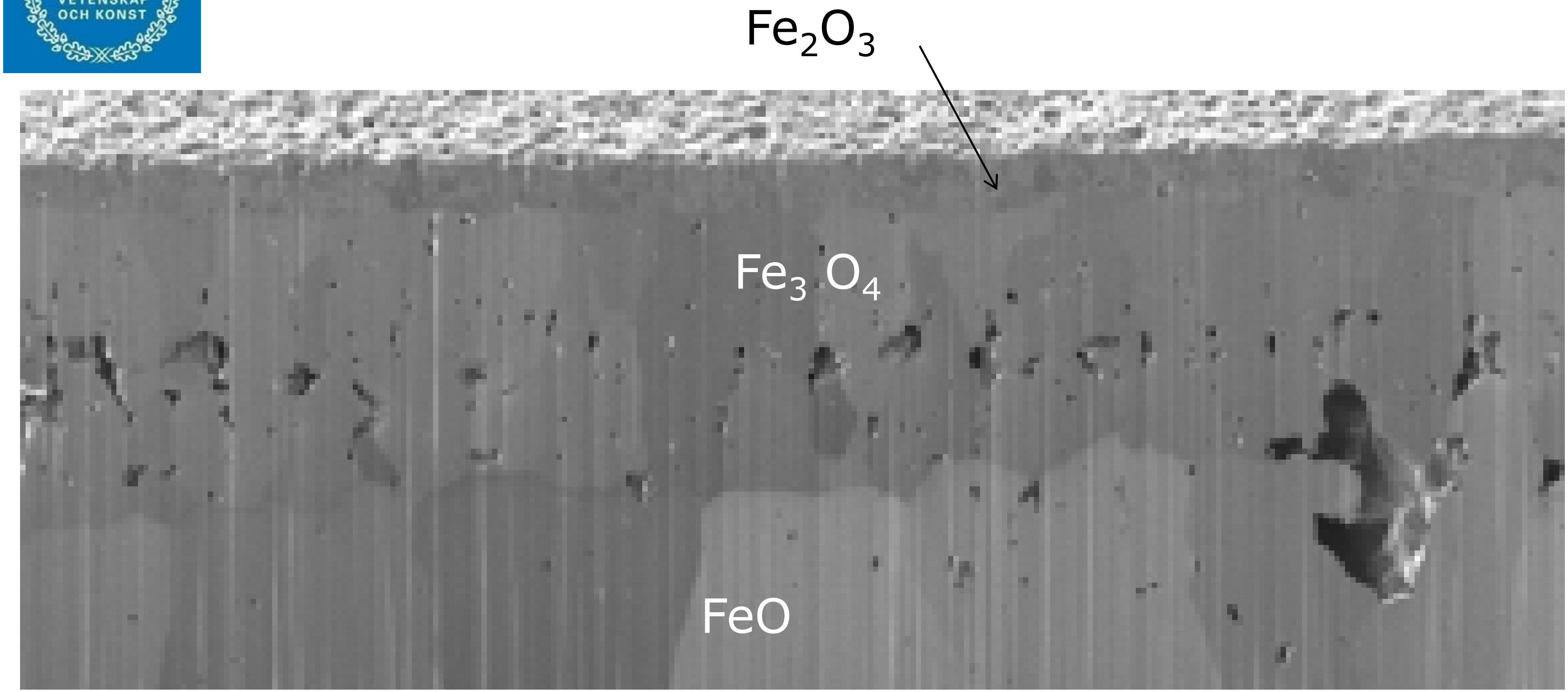
$$\partial y_{Va} / \partial t = \partial J_O / \partial z$$

Pores Pores



Distance



T. Jonsson et al. 2008

Simulations of oxidation of pure Fe at 500°C in dry atmosphere

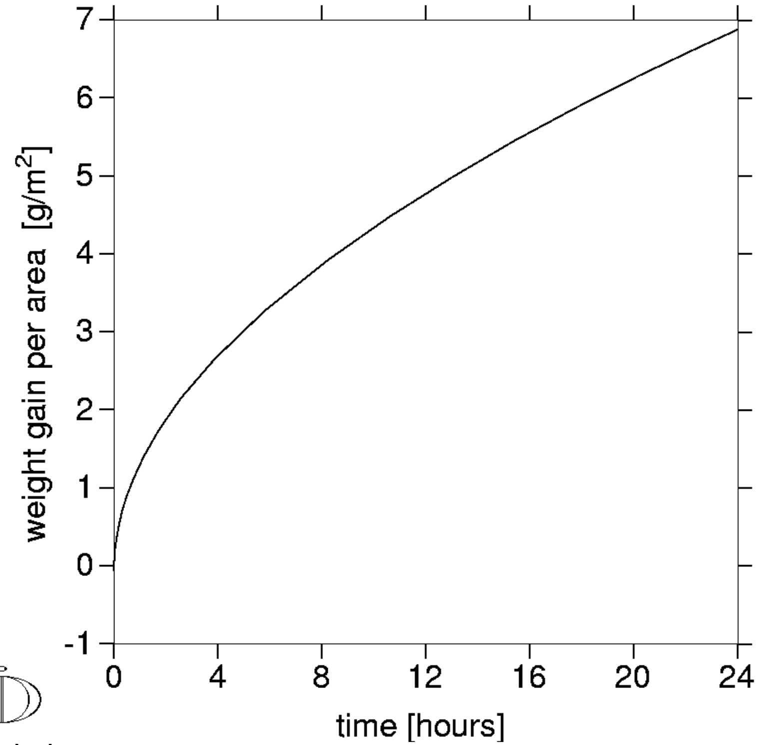
- 500°C, P_{02}=1 atm
- $d^{mag} \approx 3\mu m$, $d^{cor} \approx 0.1\mu m$, δ=5 nm
- Gb diffusion accounted for in magnetite and hematite.

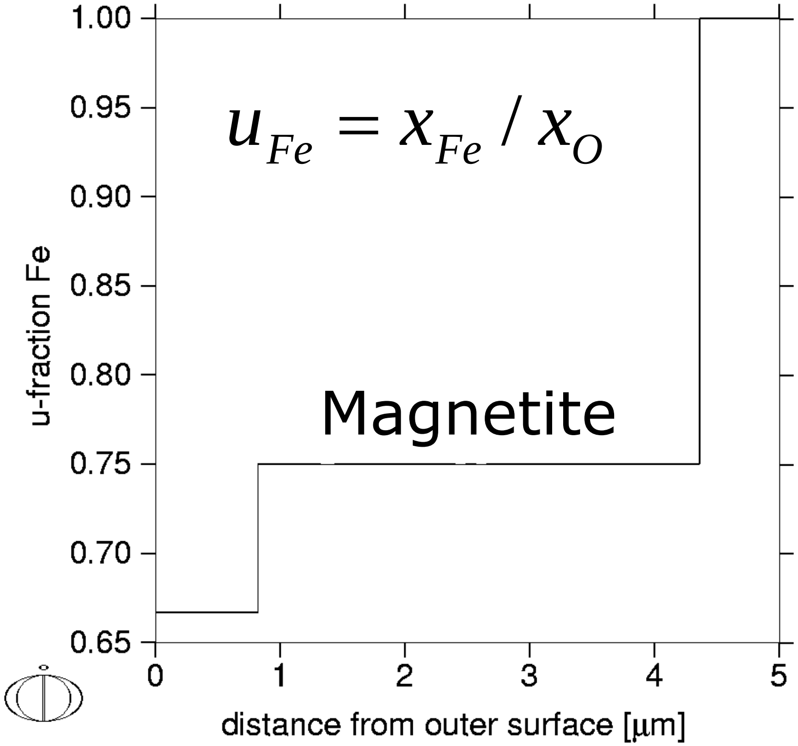
$$D_{eff} = (1-\delta/d)D_{bulk} + \delta/d\ D_{gb}$$

$$Q_{gb} \cong \alpha\ Q_{bulk} \quad 0.3 < \alpha < 0.5$$

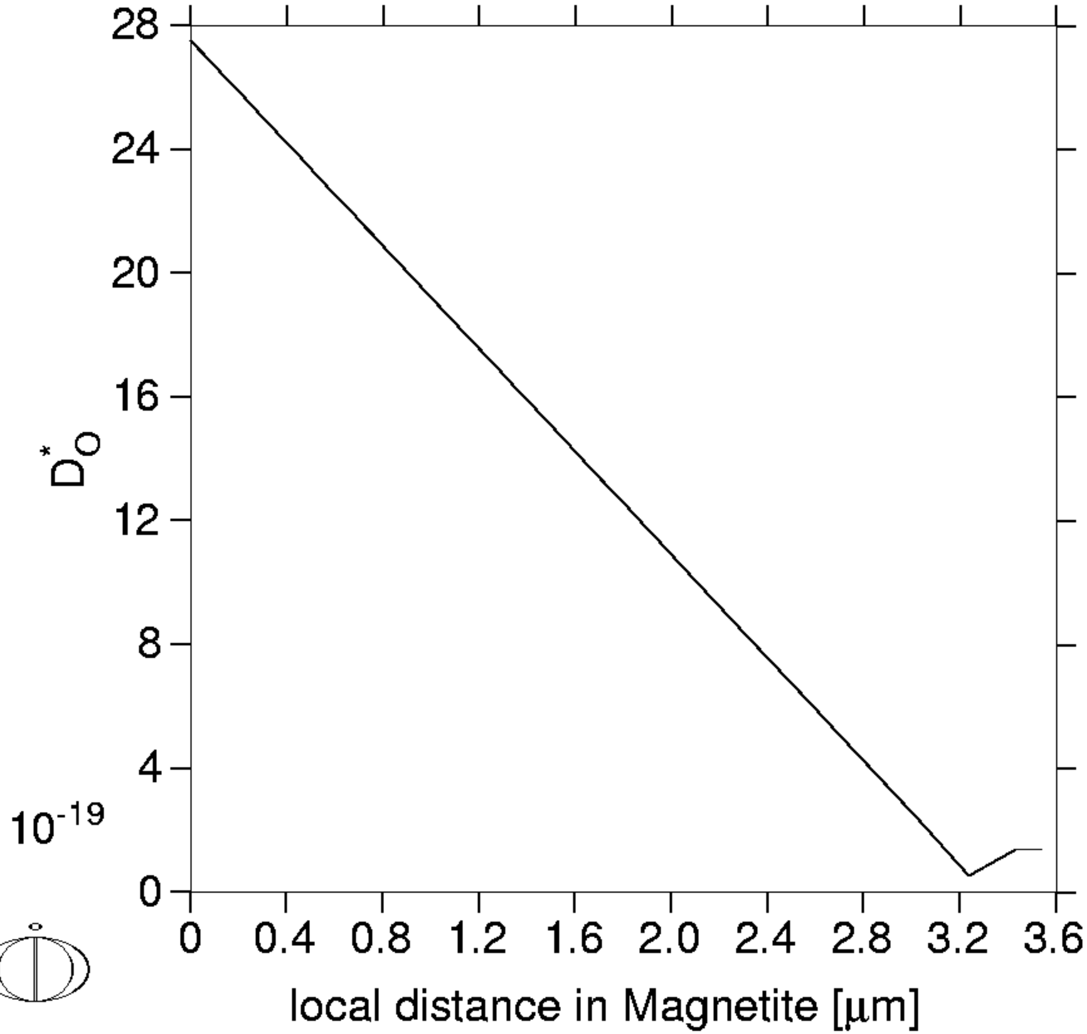
- Oxygen diffusion included

Fe-profile after 24 h





Interface Fe Interface hematite



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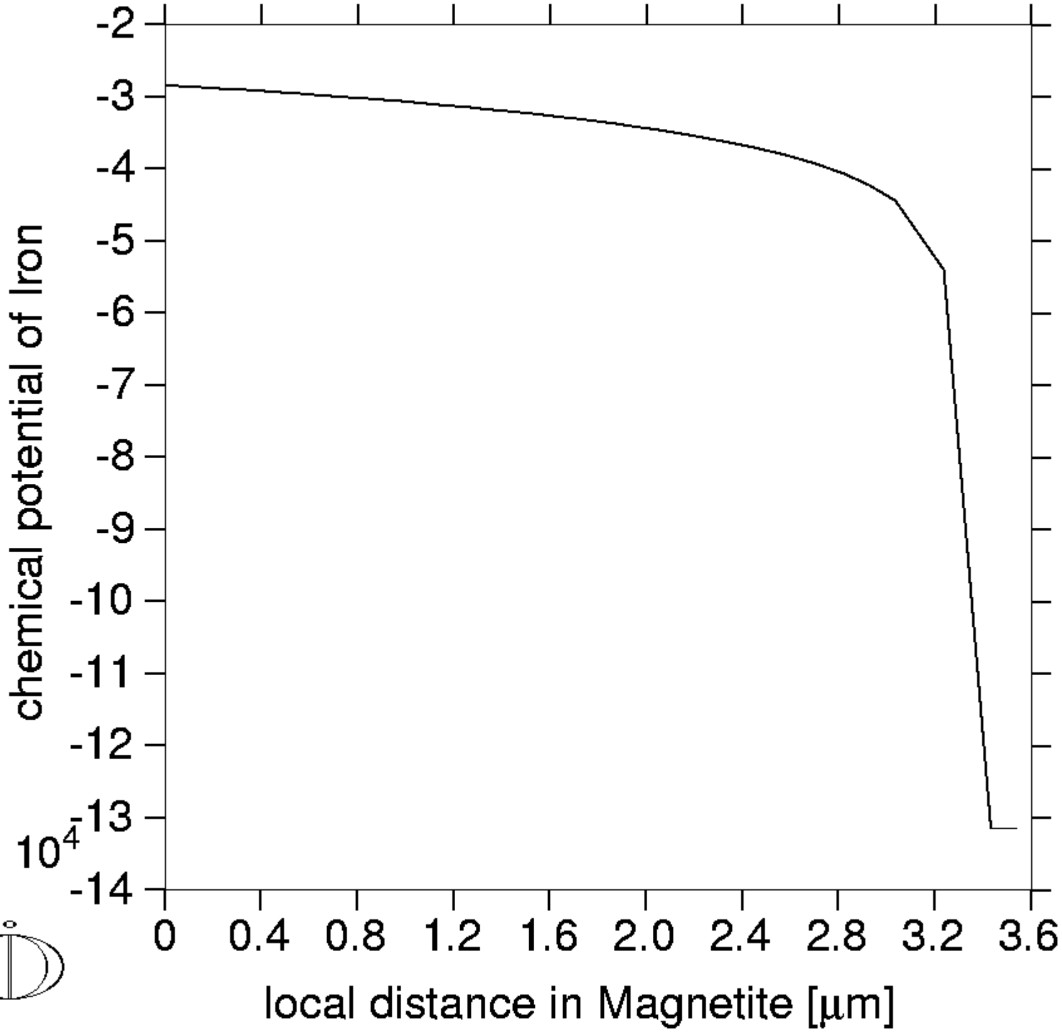
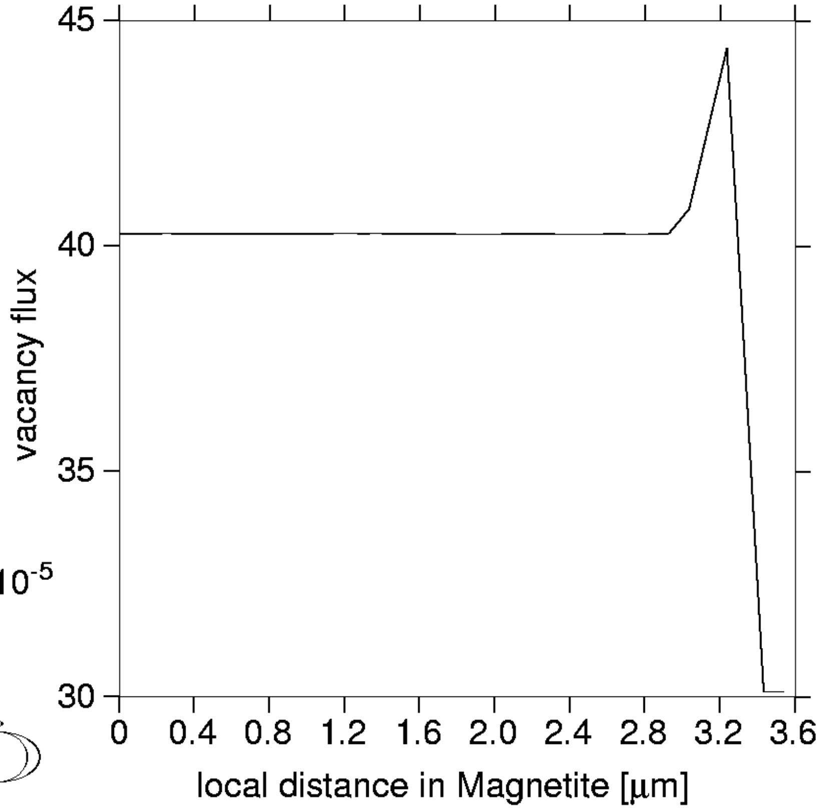
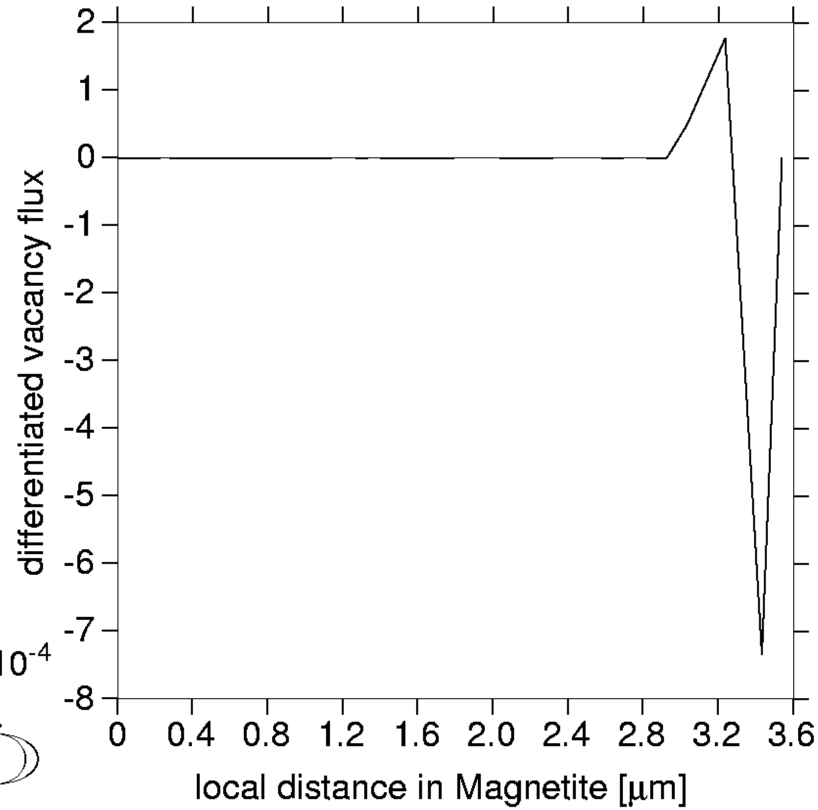

chemical potential of Iron
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
10^4
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
local distance in Magnetite [μm]





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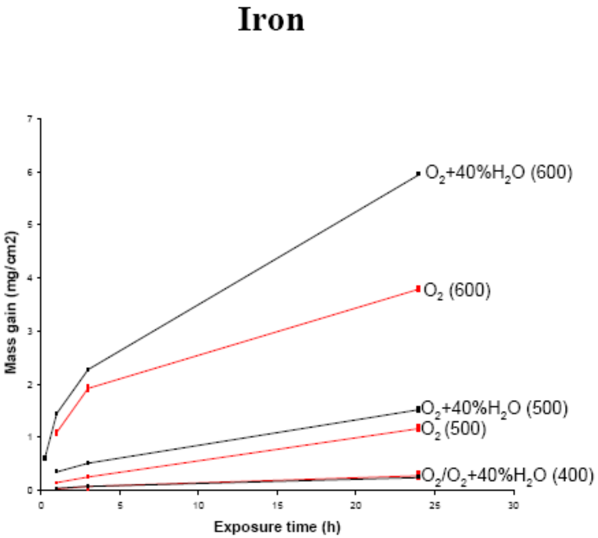
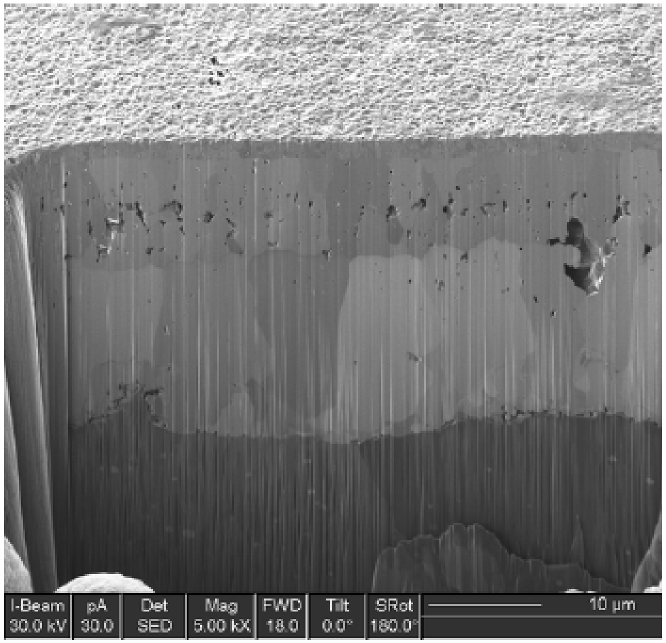
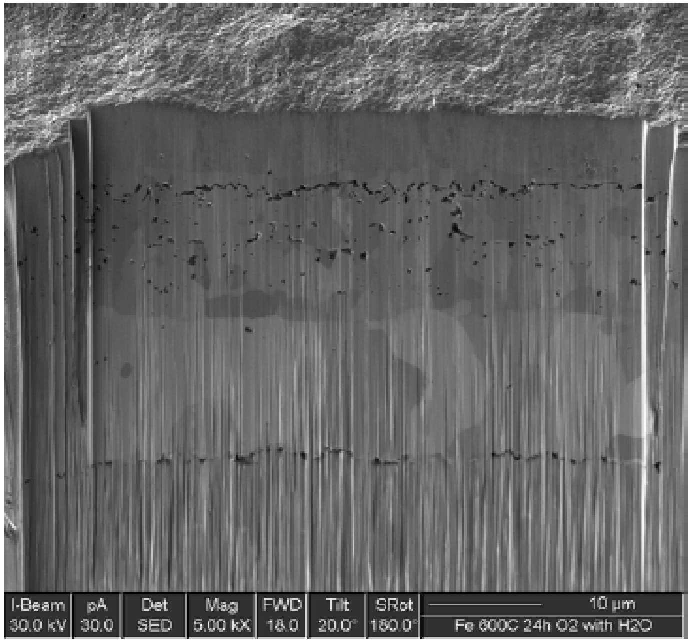
The steam effect in oxidation of Fe



600°C O_2 24h



600°C O_2+H_2O 24h



T. Jonsson et al. 2008

- Dry atmosphere:
  - Inward growth of magnetite about 20-30 % of magnetite thickness.
  - Some porosity adjacent to the original steel surface
- Wet atmosphere:
  - Hematite layer much thicker due to much stronger outward growth (ca 50% of magnetite layer).
  - No porosity in hematite layer
  - High porosity in the inward growing magnetite layer.
  - Porosity at wustite/metal interface

The observations indicate that outward iron diffusion in hematite is accelerated by the steam.

Summary

- DICTRA can now handle diffusion in oxides allowing prediction of oxidation.
- Oxide moblities in Fe-Cr oxides being assessed.
- Grain boundary diffusion is taken into account in a simplified manner.
- Oxygen diffusion may cause Kirkendall effect and porosity.