Update on Diffusion Mobilities in Oxide Systems

Samuel Hallström, Lars Höglund, John Ågren

Dept. of Matls. Sci. & Engg.
Royal Institute of Technology
Stockholm, 100 44 Sweden

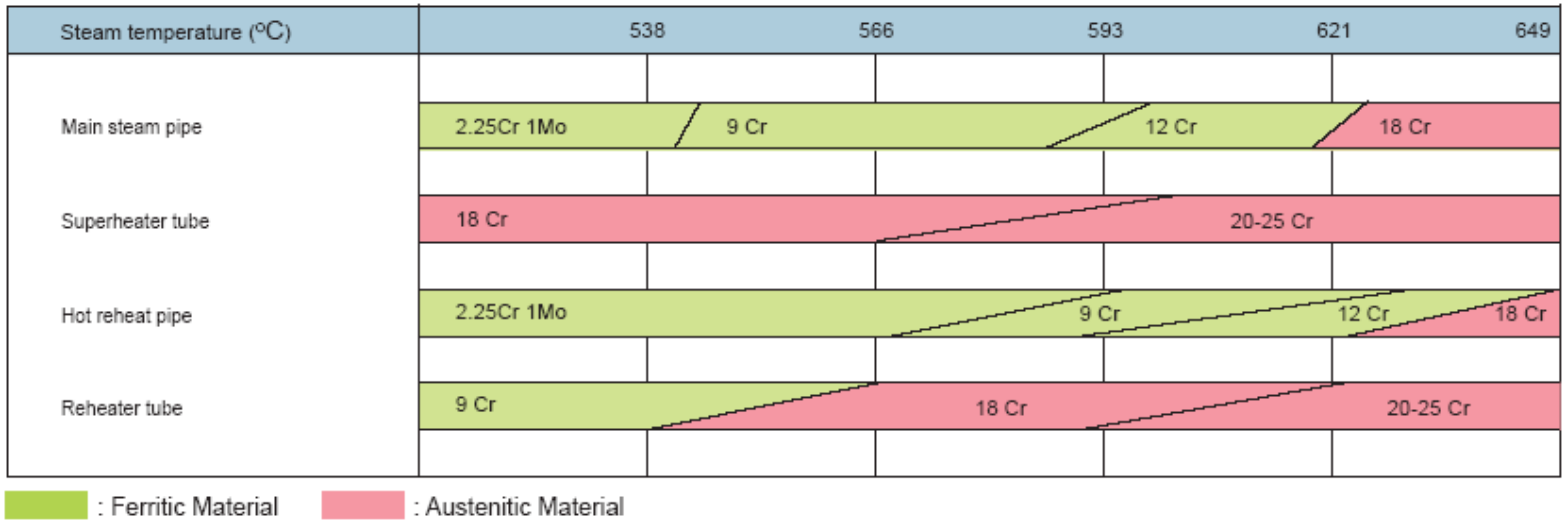
Diffusion workshop
12-13 May 2008
NIST, USA

Background

Ferritic 9-12 % Cr steels

Avedøre (Copenhagen)

Fig. 3 Steam conditions and high temperature materials



The life-time of is limited by

- Creep
- Oxidation.

Design requirement: at least 100 000 h at 100 MPa

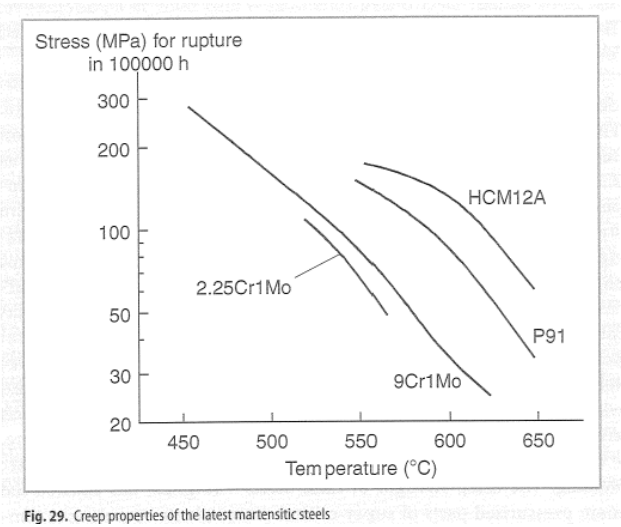
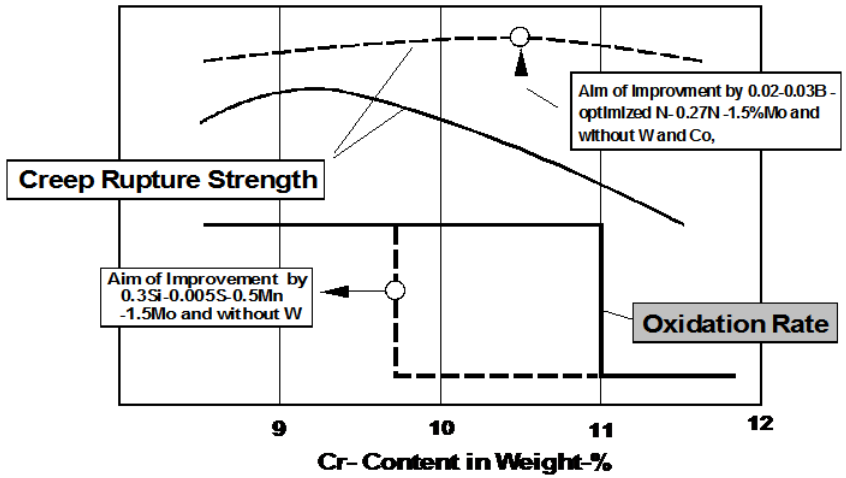


Fig. 29. Creep properties of the latest martensitic steels



Aim of work

Jonsson et al. 2006

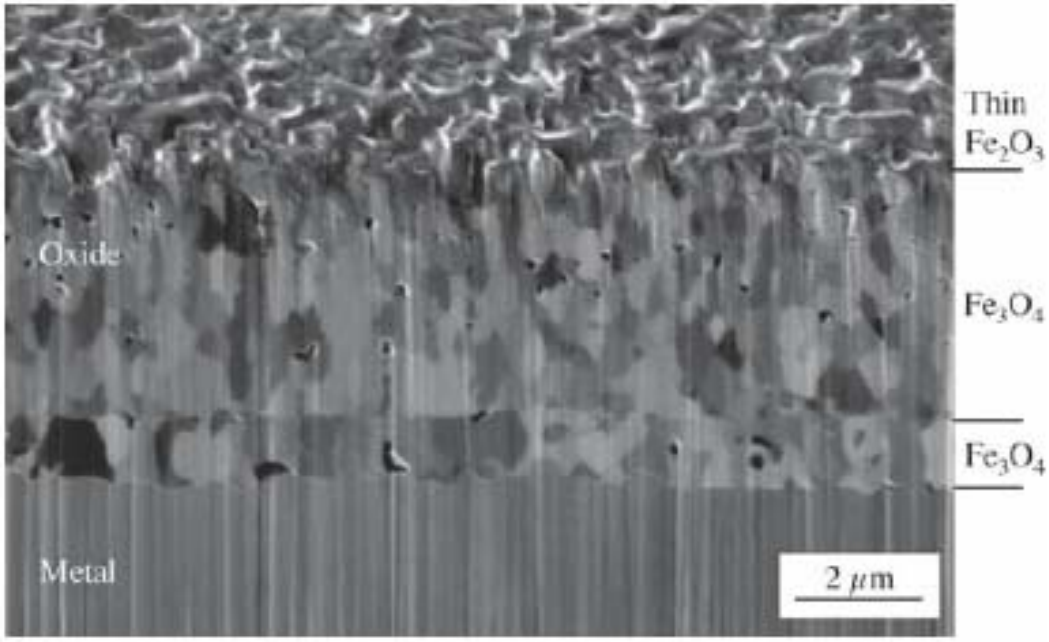


Fig. 6 A FIB image of an ion milled cross-section of the sample exposed for 1 h in O_2. The sample is tilted 50°. The total thickness of the oxide scale is 6 μm and it can be divided into two parts, a 1 μm thick inner part and a 5 μm thick outer part. The interfaces between the different layers are marked in the image

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

Contents

- General approach.
- Model for diffusion in magnetite.
- Optimization of mobilities in magnetite.
- Modelling of diffusion in hematite, Fe_2O_3.
- Modelling of diffusion in wustite, FeO.
- Chemical diffusivity in magnetite and wustite.
- Simulations of oxidation at 600°C.

General approach

Flux :

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

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

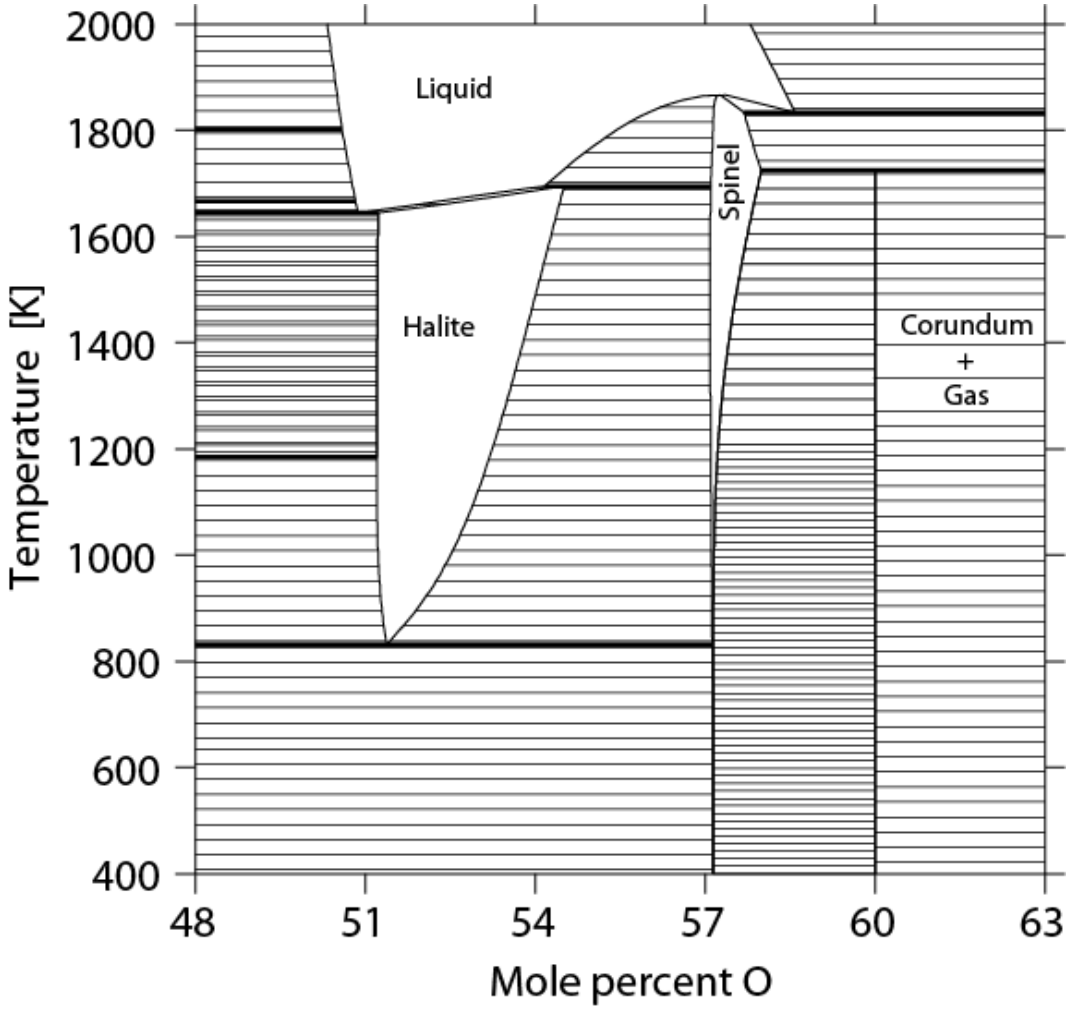
Kinetic parameters from model.

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

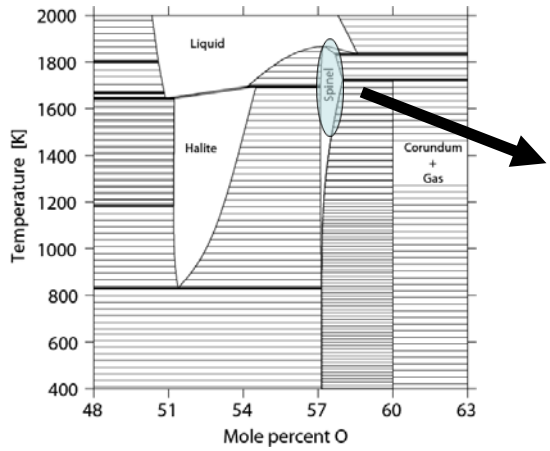
Base models on a vacancy mechanism!

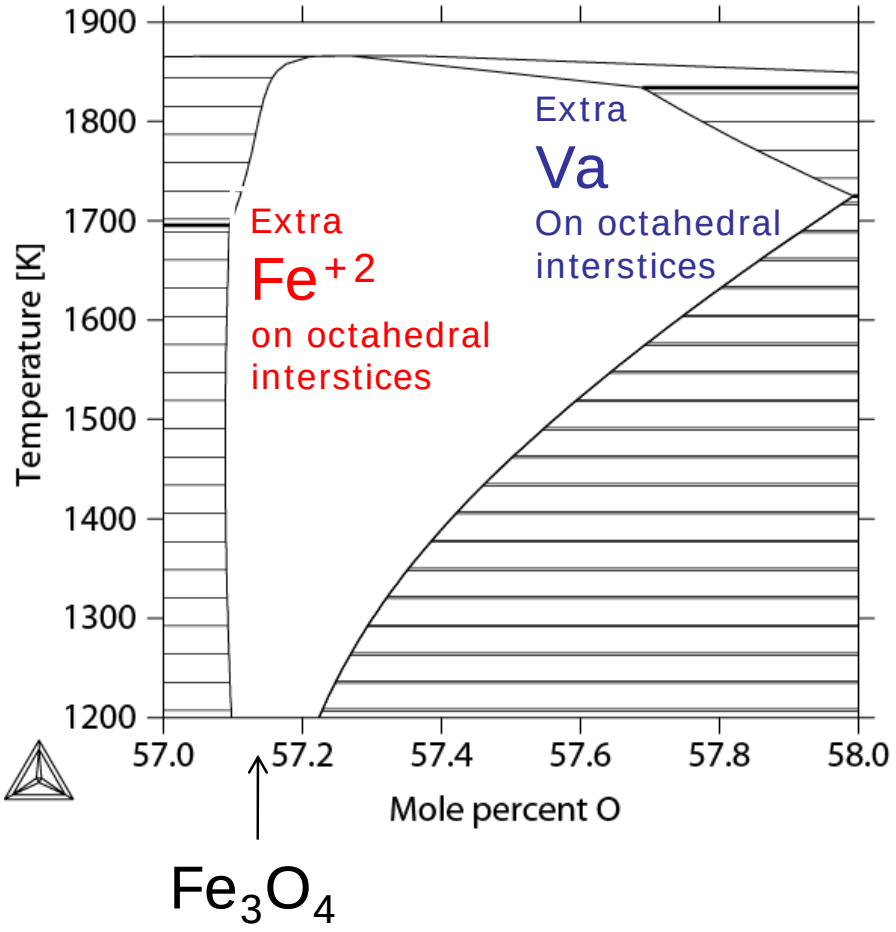
The Fe-O system

- Calculated from Sundman 1991.



Major contributions to diffusion in magnetite





Thermodynamic model (Sundman 1991):

$(Fe^{+2},Fe^{+3})_1$	$(Fe^{+2},Fe^{+3},Va)_2$ $(Va,Fe^{+2})_2$	$(O^{-2})_4$
tetrahedral	octahedral	fcc
1/8*8 sites	4 sites	

Interstitial sites

Fe diffusion in lattice-fixed frame of reference

$$J_{Fe} = -\left[y_{Va}^{''} y_{Fe}^{''} M_{FeVa}^{''} + y_{Fe}^{'''} y_{Va}^{'''} M_{FeVa}^{'''}\right] \frac{1}{V_m} \frac{\partial \mu_{Fe}}{\partial z}$$

Normal octahedral sites

extra octahedral sites

$$D_{Fe^*} = RT\left[y_{Va}^{''} y_{Fe}^{''} M_{FeVa}^{''} + y_{Va}^{'''} y_{Fe}^{'''} M_{FeVa}^{'''}\right] / n_{Fe}$$

Optimization in magnetite

- Jump distance on 3rd sublattice twice that on 2nd.
- Constraint on frequency factors!

$(Fe^{+2},Fe^{+3})_1$	$(Fe^{+2},Fe^{+3},Va)_2$ $(Va,Fe^{+2})_2$	$(O^{-2})_4$
tetrahedral	octahedral	fcc

Absolute reaction rate theory:

$$RTM_{FeVa} = \nu\delta^2 \exp(-\Delta G / RT)$$

$$M_0''' = 4M_0''$$

Optimized parameters:

$$RTM_{FeVa}'' = 1.57\times10^{-6} \exp(-114000 / RT)$$

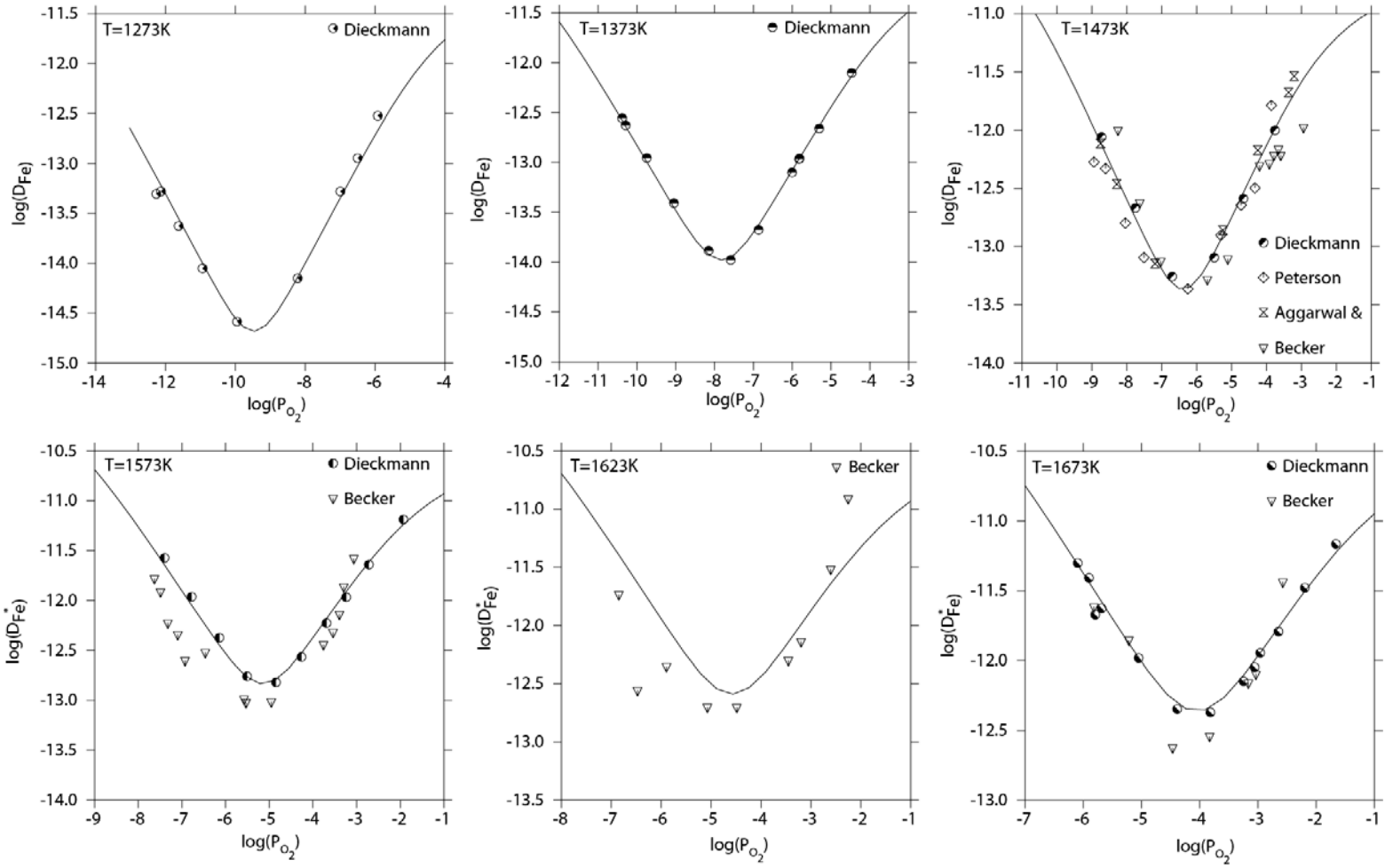
$$RTM_{FeVa}''' = 6.28\times10^{-6} \exp(-120000 / RT)$$

Experimental data

Tracer diffusion coefficients in magnetite

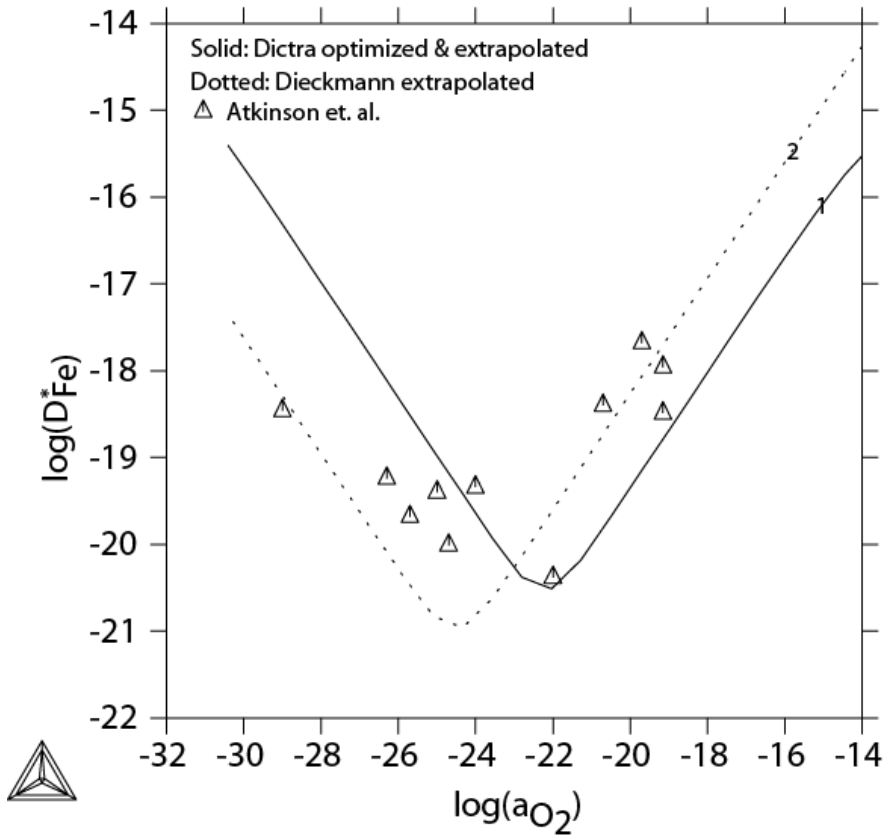
• Dieckmann & Schmalzried	900-1400°C
• Peterson et. al.	1200°C
• Aggarwal & Dieckmann	1200°C
• Becker et. al.	1200-1400°C

Optimization of mobilities



Extrapolation to low temperature

- Calculated bulk tracer diffusion at 500°C compared to experimental values (single crystal).
- Not used in optimization.
- Bulk high T data extrapolates well to low temperature.



Oxygen diffusion in magnetite

Yields a Kirkendall effect and porosity!

Yields the ”inward growing” oxide!

The experimental information shows a similar behaviour as for Fe.

This cannot be represented by random oxygen vacancies and a constant oxygen mobility.

Possible physical picture:

Low oxygen potentials favours oxygen vacancies -> higher diffusivity.

High oxygen potentials lead to less Fe on the interstials which favours oxygen vacancies (vacancy-vacancy coupling)-> higher diffusivity.

O diffusion in lattice-fixed frame of reference

$$J_{O^{-2}} = -y_{Va} y_O M_{OVa} \frac{1}{V_m} \frac{\partial \mu_O}{\partial z} = y_{Va} y_O M_{OVa} \frac{u_{Fe}}{V_m} \frac{\partial \mu_{Fe}}{\partial z}$$

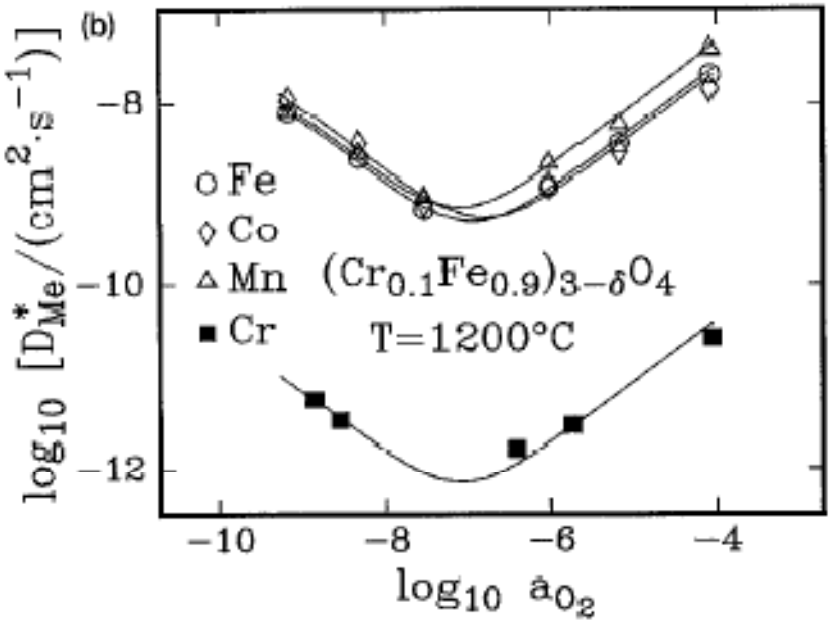
$$y_{Va} = \left[y_{Va}^{''} y_{Fe}^{''} k_{FeVa}^{''} + y_{Va}^{'''} y_{Fe}^{'''} k_{FeVa}^{'''} \right]$$

$$J_{O^{-2}} = \left[y_{Va}^{''} y_{Fe}^{''} k_{FeVa}^{''} + y_{Va}^{'''} y_{Fe}^{'''} k_{FeVa}^{'''} \right] y_O M_{OVa} \frac{u_{Fe}}{V_m} \frac{\partial \mu_{Fe}}{\partial z}$$

$$D_{O^*} \cong RT \left[y_{Va}^{''} y_{Fe}^{''} M_{OVa}^{''} + y_{Va}^{'''} y_{Fe}^{'''} M_{OVa}^{'''} \right] / n_O$$

Alloy elements in magnetite – lattice fixed frame of reference

Töpfer et.al. 1995



$$J_{Cr} = -\left[y_{Va}^{''} y_{Cr}^{''} M_{CrVa}^{''} + y_{Cr}^{'''} y_{Va}^{'''} M_{CrVa}^{'''}\right] \frac{1}{V_m} \frac{\partial \mu_{Cr}}{\partial z}$$

$$D_{Cr^*} = RT\left[y_{Va}^{''} y_{Cr}^{''} M_{CrVa}^{''} + y_{Cr}^{'''} y_{Va}^{'''} M_{CrVa}^{'''}\right] / n_{Cr}$$

Diffusion in hematite

- Same approach as for spinel
- Thermodynamic model:

  $(Fe^{+2},Fe^{+3})_2(Va,Fe^{+3})_1\ (O^{-2})_3$

- For vacancy mechanism on interstitial sublattice in the anion fixed frame of reference:

$$J_{Fe} = -y_{Va}^{''} y_{Fe}^{''} M_{FeVa}^{''} \frac{1}{V_m} \frac{\partial \mu_{Fe}}{\partial z}$$

$$D_{Fe^*} \cong RT y_{Va}^{''} y_{Fe}^{''} M_{FeVa}^{''}$$

Literature data Fe_2O_3

- Atkinson and Taylor (m^2/s):

  High T > 900°C

  $D^* = 1.6\times10^{+5}\ \exp(-579000/RT)$

  Low T < 900°C

  $D^* = 2.8\times10^{-5}\ \exp(-174000/RT)$

- Hoshino and Peterson (m^2/s):

  $D^* = 1.9\times10^{+5}\ \exp(-592000/RT)$

- Amami et. al (m^2/s):

  $D^* = 9.2\times10^{+6}\ \exp(-578000/RT)$

- Comparison Cr in Cr_2O_3 Sabioni et. al.:

  $D^* = 5.84\times10^{-5}\ \exp(-280000/RT)$

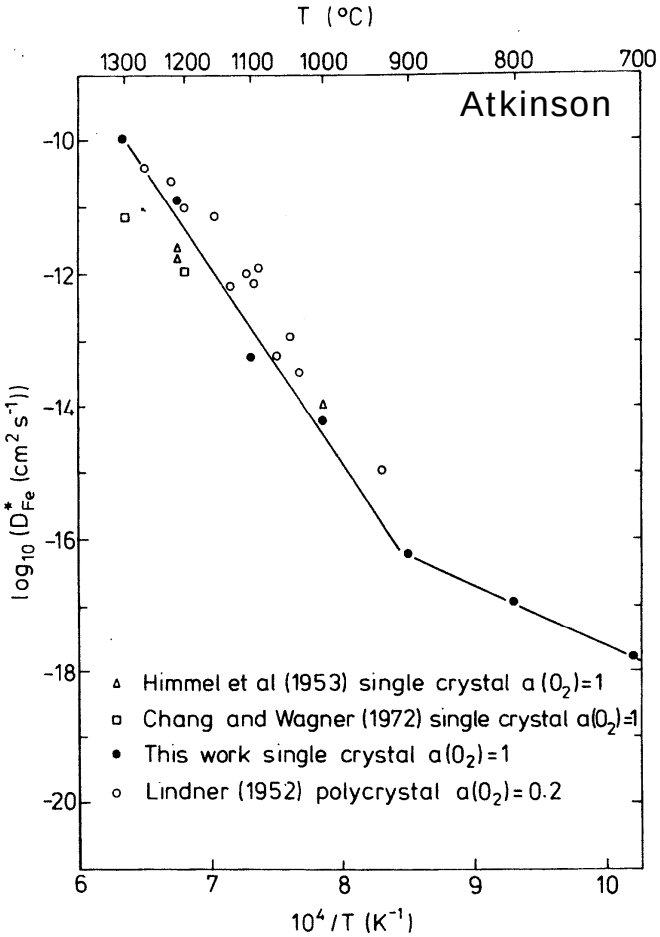


Fig. 1. Arrhenius plot summarizing data for the tracer diffusion coefficient of Fe in Fe_2O_3 at constant oxygen activity.

Literature data Fe_2O_3

- Himmel, and Chang and Wagner gives (red line):

$$RTM = 3.7 \times 10^{-3} \exp(-271600/RT)$$

- Fixing freq. factor to 10^{-6} gives (blue line):

$$RTM = 10^{-6} \exp(-172900/RT)$$

Absolute reaction rate reminder:

$$RTM_{FeVa} = \nu\delta^2 \exp(-\Delta G / RT)$$

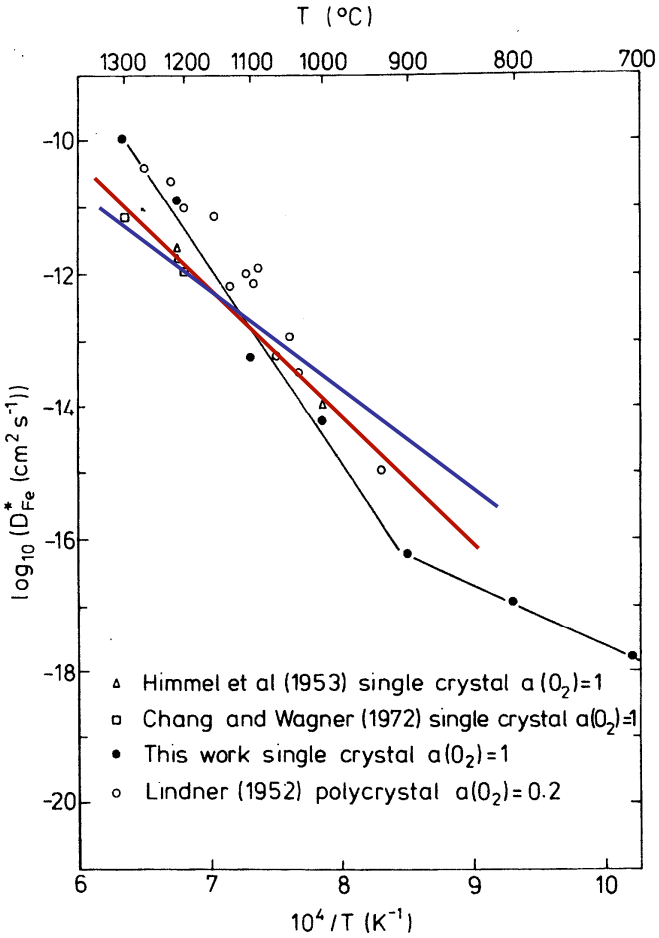


Fig. 1. Arrhenius plot summarizing data for the tracer diffusion coefficient of Fe in Fe_2O_3 at constant oxygen activity.

- Why the anomolous activation energy and prefactor?
  - Large scatter in experimental information.
  - Cr diffusion in Cr_2O_3 more complex temperature dependence.
  - More complex defects?

Diffusion in FeO

- Thermodynamic model

$(Fe^{+2},Fe^{+3},Va)_1\ (O^{-2})_1$

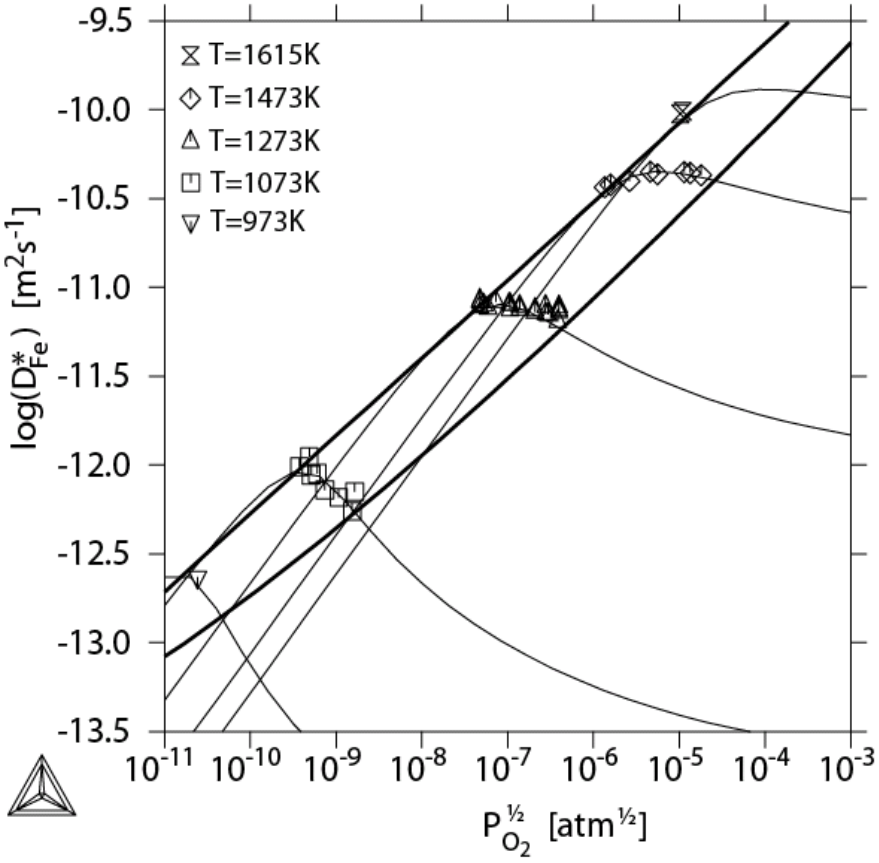
- For vacancy mechanism on cation sublattice in the anion fixed frame of reference:

$$J_{Fe} = -y'_{Va} y'_{Fe} M'_{BVa} \frac{1}{V_m} \frac{\partial \mu_{Fe}}{\partial z}$$

$$D_{Fe^*} \cong RT y'_{Va} y'_{Fe} M'_{FeVa}$$

Tracer diffusion in FeO

$$M_{Fe} = 3.15 \cdot 10^{-5} \exp\left(\frac{-89280 + u_{Fe} u_{Va} \left(-585900 + 188.7 \cdot T\right)}{RT} \right) m^2 s^{-1}$$



Experiments from Chen and Peterson, J. Phys. Solids, 36, 1975.

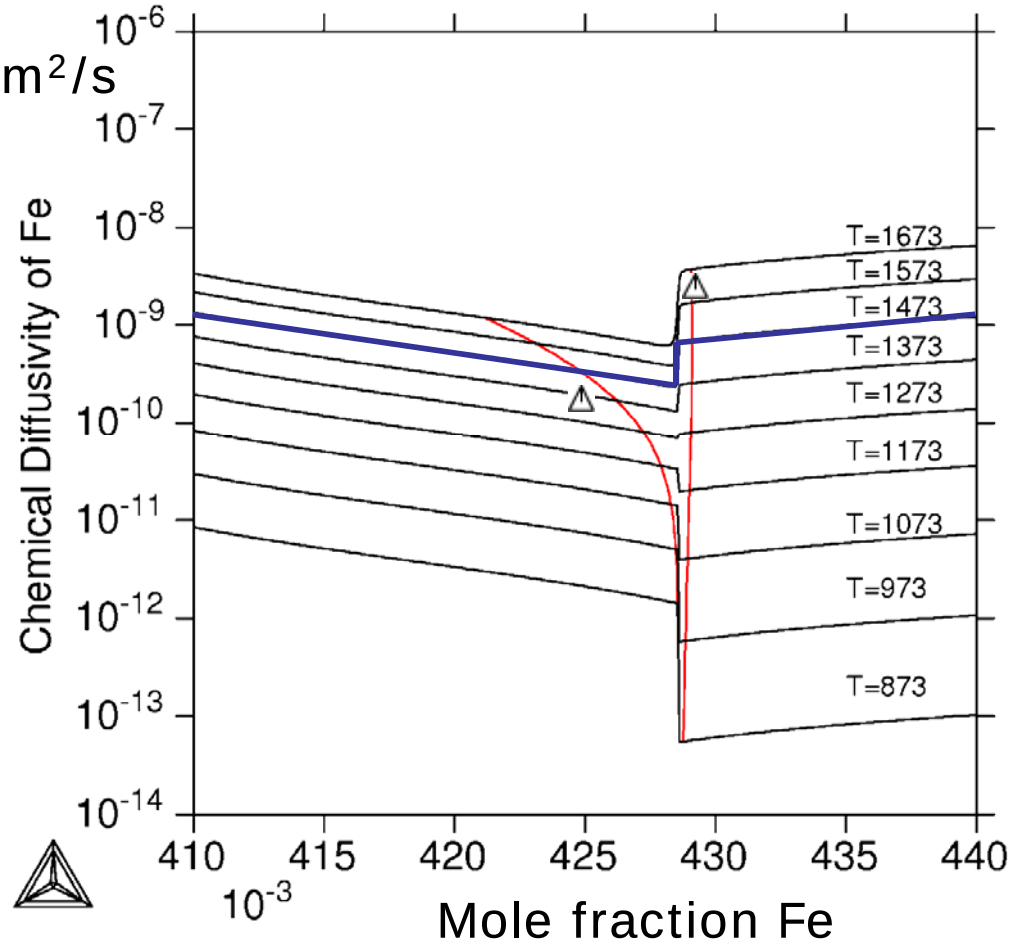
Diffusion workshop
12-13 May 2008
NIST, USA

Chemical diffusivity

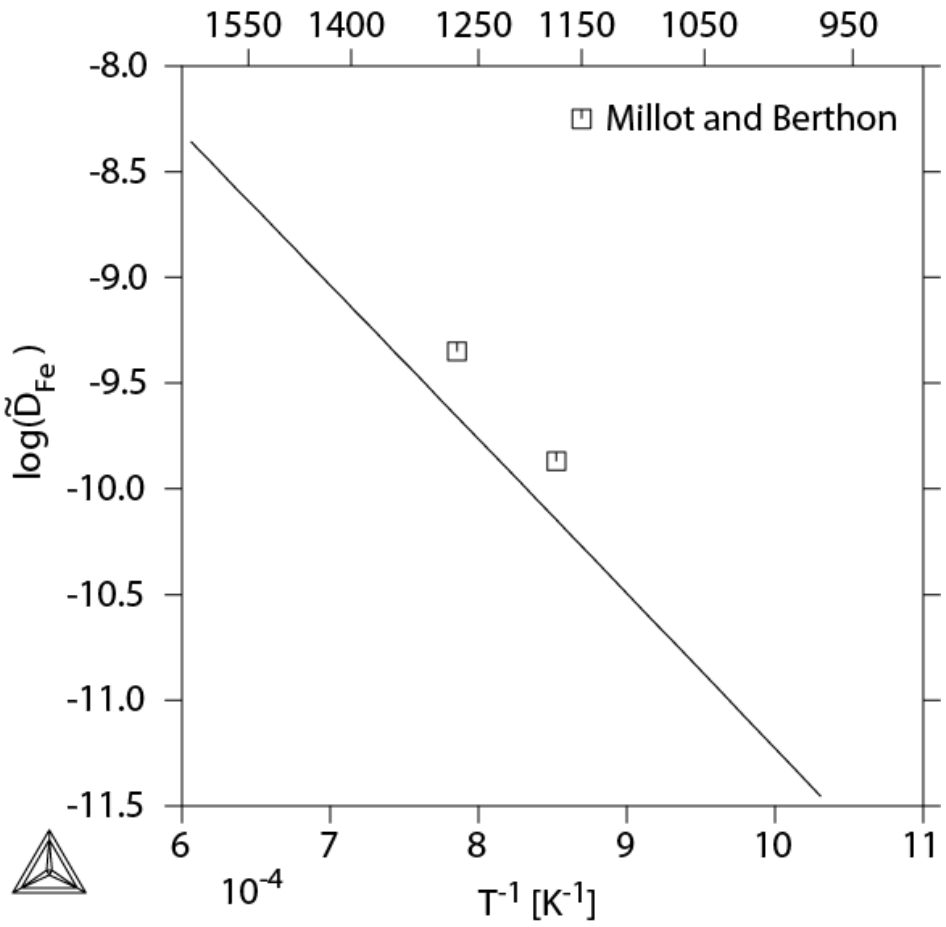
$$\tilde{D}_{Fe} = \frac{M_{Fe}}{RT} c_{Fe} \frac{\partial \mu_{Fe}}{\partial c_{Fe}}$$

Calculated chemical diffusivity in magnetite

- Red line shows stable composition range of spinel.
- Triangles show measured chemical diffusivities at 1508K.
- Blue line shows experimental temperature.
- Values are high, but still in reasonable agreement with experiments.



Calculated chemical diffusivity in wustite



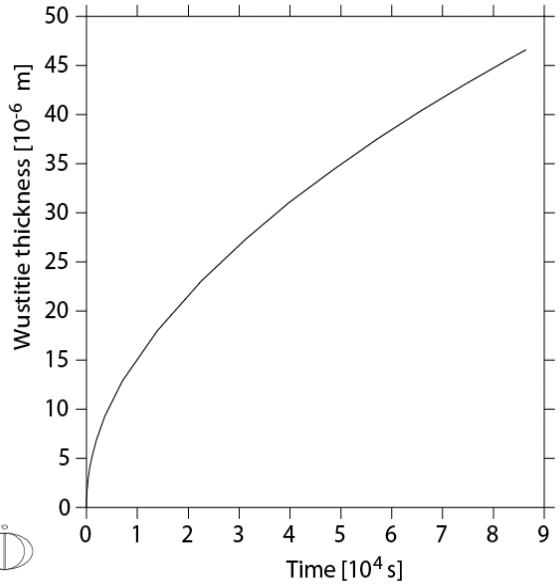
Diffusion workshop
12-13 May 2008
NIST, USA

Simulation 1: Fe-O, 600°C

- 600°C, P_{02}=0.05, 24h.
- $f^{gb=}=\delta/D$, D grain size, $\delta\approx 5$Å gb thickness.
- $D^{mag} \approx$ 3µm, $D^{cor} \approx$ 0.1µm.
- Assumption: Activation energy for diffusion in gb is half that of bulk diffusion.
- $D^{eff}=(1- f^{gb})D^{bulk}+ f^{gb}D^{gb}$
- Gb diffusion assumed only in magnetite and hematite.
- No diffusion of oxygen.

Simulation 1: oxide thicknesses

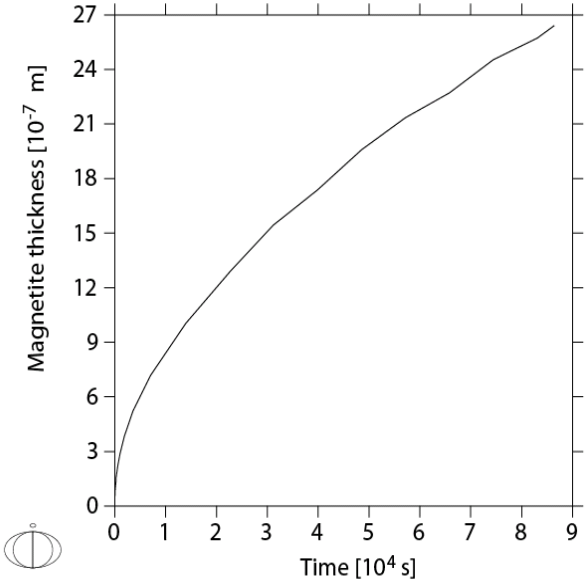
Wustite



Calculated: 45 µm

Experimental: 21 µm

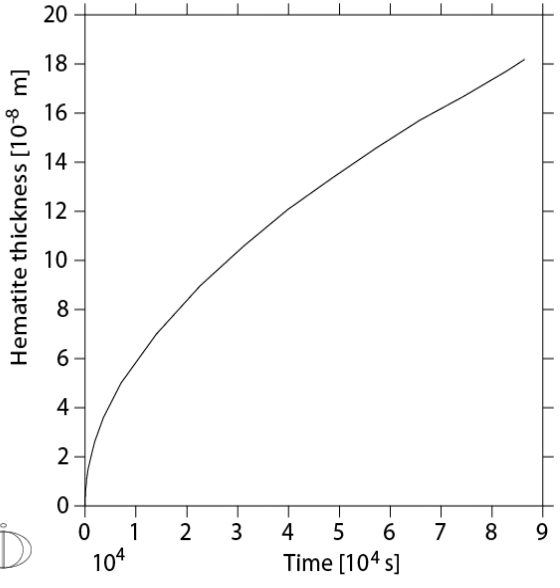
Magnetite



27 µm

11 µm

Hematite



0.18 µm

2 µm

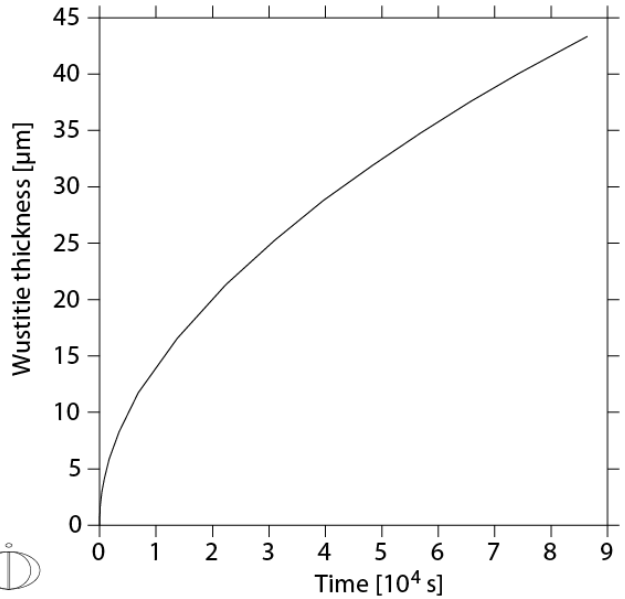
Diffusion workshop
12-13 May 2008
NIST, USA

Simulation 2: Fe-O, 600°C

- Conditions almost identical to simulation 1.
- Assumption: Activation energy for diffusion in gb is about 1/3 of that of bulk diffusion (instead of ½).

Simulation 2: oxide thicknesses

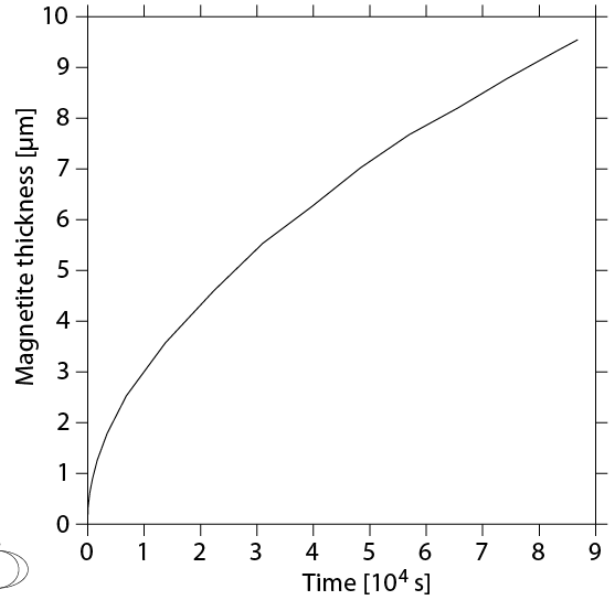
Wustite



Calculated: 45 µm

Experimental: 21 µm

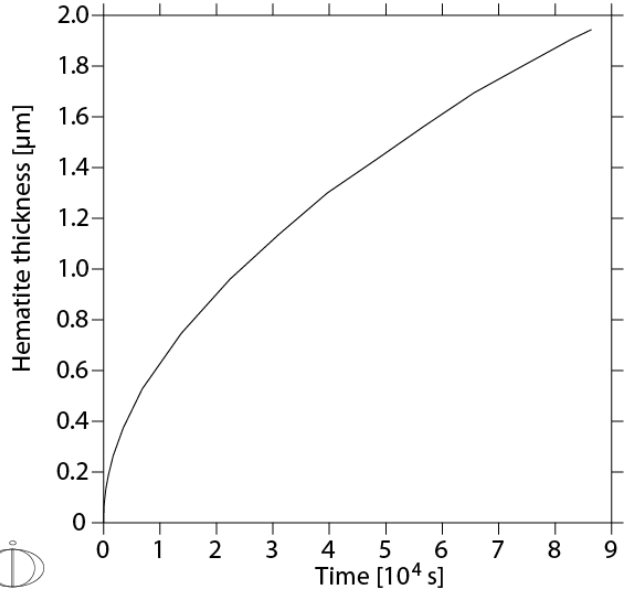
Magnetite



10 µm

11 µm

Hematite



2 µm

2 µm

Diffusion workshop
12-13 May 2008
NIST, USA

Conclusions

- DICTRA can now handle diffusion in complex phases, e.g. oxides.
- Cation diffusion in the three iron oxides has been critically assessed.
- Grain boundary diffusion is taken into account in a simplified manner.
- Cr and oxygen diffusion is currently being added.