Oxidation and diffusion in oxides – a progress report

John Ågren

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

Acknowledgement: Reza Naraghi, Samuel Hallström, Lars Höglund and Malin Selleby
New Research directions in Materials science and Engineering:
Content

1. Aim of work
2. Issues in modelling of oxidation
3. Bulk diffusion in oxides
   a) Summary and present stage
   b) Some issues in the diffusion modelling
   c) Defect structures for oxygen diffusion and results
4. Grain boundary diffusion
5. Kirkendall porosity
1. 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 oxidation rate in terms of diffusional flux as function of gradients in composition or chemical potentials.
- Parameters that characterize a given material
2. Issues in modelling of oxidation

Predict:

- **Rate of oxidation**
  - External (growth of external layers)
  - Internal (internal oxide particles)
  - Grain boundaries in metal and in oxides
- **What oxides form?**
- **Porosity**
  - Kirkendall effect

Jonsson et al. 2006

Giggins and Pettit 1971

Internal oxidation of Mn, Si, Cr etc during carburization (Holm et al. 2010)
External oxidation - general
Inward and outward growth

- Oxygen diffusion in the oxide layer gives inward growth
- Metal diffusion in the oxide layer gives outward growth
Growth of external layers

Atmosphere with O\textsubscript{2}

Oxide $\beta$

Metal $\alpha$

Oxygen content

Distance

Diffusion and flux balances in sharp-interface modelling!
Growth of internal oxide particles

- Oxygen must diffuse through external oxide layers and dissolve in the metallic matrix.
- Rate may be controlled by oxygen diffusion, alloy element diffusion or both.
3. Bulk diffusion in oxides
3.a) Summary and present stage

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!
Present stage

The models have been implemented in DICTRA.

Data base now contains diffusional mobilities of

- Wüstite (Halite)
  - Fe and O
- Magnetite (Spinel)
  - Fe Cr O
- Hematite (Corundum)
  - Fe, Cr, O
3.b) Some issues in the diffusion modelling

- Phase equilibria and driving forces – Calphad thermodynamics
- Defect structures
  - Vacancies and interstitials
  - Oxygen substitutional
  - Fe, Cr etc interstitial
- Diffusing species
  - Ions
  - Neutral atoms
  - Positive holes
- Rate equations

Fe-O Calculated from Sundman 1991.
Diffusing species: in 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, Hallström et al. 2011)

Thermodynamic model (Sundman 1991):

\[
(\text{Fe}^{2+}, \text{Fe}^{3+})_1 \quad (\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Va})_2 \quad (\text{Va}, \text{Fe}^{2+})_2 \quad (\text{O}^{-2})_4
\]

- tetrahedral
- octahedral
- fcc

Interststitial sites

1/8*8 sites

4 sites
Absolute reaction rate arguments:

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

\[ L_{Fe} \]

\[ RTM_k = \delta^2 v \exp(-\Delta G_k / RT) \]

\[ D_{Fe^*} \approx RT \frac{1}{2} \left[ y''_{Va} y''_{Fe} M''_{FeVa} + y'''_{Fe} y'''_{Va} M'''_{FeVa} \right] \frac{1}{u_{Fe}} \]
Experimental data on Fe tracer diffusion in spinel - Optimization of Fe mobilities

(Hallström et al. 2011)
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.

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

\[
D_{Cr}^* = RT \left[ y_{Va} y_{Cr} M_{CrVa} + y_{Cr} y_{Va} M_{CrVa} \right] / u_{Cr}
\]
3.c) Defect structures for oxygen diffusion and results

Wüstite (Halite)

Sundman's model:

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

Yamagochi et al. 1982 found that oxygen diffusion rate increases with oxygen potential. Thus oxygen vacancies cannot be the dominating mechanism. We thus postulate that oxygen diffuses on interstitial (cation) sites:

\[ J_O = -\left[ y_{Va} y'_O M_{Ova}^i \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z} \]

\[ D_O^* = \left[ y_{Va} y'_O M_{Ova}^i \right] \frac{1}{n_O} \]
Oxygen tracer diffusion in Wüstite.

Experiments from Yamaguchi et al 1982
3.c) Defect structures for oxygen diffusion and results
Magnetite (Spinel)

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

Millot and Niu 1996

T = 1150°C
At low oxygen potentials it seems reasonable that oxygen diffusion is assisted by anion vacancies. The lower the oxygen potential, the higher fraction of vacancies and rate of diffusion.

Modification of Sundman’s thermodynamic model:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Formula</th>
<th>Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrahedral</td>
<td>(Fe$^{+2}$,Fe$^{+3}$)$_1$</td>
<td>1/8*8 sites</td>
</tr>
<tr>
<td>octahedral</td>
<td>(Fe$^{+2}$,Fe$^{+3}$,Va)$_2$ (Va,Fe$^{+2}$)$_2$</td>
<td>4 sites</td>
</tr>
<tr>
<td>fcc</td>
<td>(O$_2^-$,Va)$_4$</td>
<td>4 sites</td>
</tr>
</tbody>
</table>

Interstitial sites
At high oxygen potentials this model predicts very low vacancy fractions. The lower the oxygen potential, the higher fraction of vacancies and rate of diffusion. This is not in agreement with experiments!

Modification of Sundman’s thermodynamic model:

Alternativ 1

\[
\begin{array}{ccc}
(\text{Fe}^{+2}, \text{Fe}^{+3})_1 & (\text{Fe}^{+2}, \text{Fe}^{+3}, \text{Va})_2 & (\text{Va}, \text{Fe}^{+2}, \text{O}^{-2})_2 \\
\text{tetrahedral} & \text{octahedral} & (\text{O}^{-2}, \text{Va})_4 \\
1/8*8 \text{ sites} & 4 \text{ sites} & \text{fcc}
\end{array}
\]

Interstitial sites
This may work but gives too a strong increase in vacancy content at high oxygen potentials. It also requires a complete re-assessment of Fe-O!

\[
d \ln y_{Va}^a / d \ln P_{O_2} = -\frac{1}{2}
\]

\[
d \ln y_{O}^i / d \ln P_{O_2} = \frac{1}{2}
\]

\[
d \ln D_{O} / d \ln P_{O_2} \approx -10.6
\]

(Millot and Niu 1996)

\[
J_O = -\left[ y_{Va}^a y_{O}^a M_{OVa}^a + y_{O}^i y_{Va}^i M_{OVa}^i \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z}
\]

(Millot and Niu 1996)
Modification of Sundman’s thermodynamic model:

Alternativ 2

\[
\begin{array}{|c|c|c|}
\hline
(\text{Fe}^{+2},\text{Fe}^{+3})_1 & (\text{Fe}^{+2},\text{Fe}^{+3},\text{Va})_2 & (\text{Va},\text{Fe}^{+2})_2 \\
\text{tetrahedral} & \text{octahedral} & (\text{O}_{-2},\text{Va})_4 \\
1/8*8 \text{ sites} & 4 \text{ sites} & \text{fcc} \\
\hline
\end{array}
\]

Could the vacancy formation energy be chosen such that:

\[
\log \gamma^a_{Va}
\]
At present we have

\[ J_O = -y_O^a \left[ y_{Va}^a M_{OVA}^a + y_{Va}^i M_{OVA}^i \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z} \]

\[ D_O^* = -y_O^a RT \left[ y_{Va}^a M_{OVA}^a + y_{Va}^i M_{OVA}^i \right] \frac{1}{n_O} \]

\[ M_{OVA}^g = 6.995057e - 10 \exp(-9.774850e4/RT)/RT \]

\[ M_{OVA}^i = 2.218464e - 5 \exp(-2.151230e5/RT)/RT \]
3.c) Defect structures for oxygen diffusion and results
Hematite (Corundum)

Kjellqvist et al. 2008

\[(Fe^{+3}, Fe^{+2})_2(Va, Fe^{+3})_1(O^{−2}, Va)_3\]

“End members” and plane of electro neutrality

\[G_{2vv} + G_{23o} = G_{2vO} + G_{23v}\]

\[G_{3vO} + G_{2vv} = G_{3vv} + G_{2vO}\]

\[G_{2vv} = G_{3vv}\]

\[\frac{2}{3} G_{2vO} + \frac{1}{3} G_{2vv} = G_{3vO} + a' + b'T\]

\[a' = 1200000, \ b' = 0\]

where 2 denotes Fe^{12}, 3 Fe^{+3}, Va vacancies, and finally O denotes O^{−2}. 
\[(Fe^{+3},Fe^{+2})_2(Va,Fe^{+3})_1(O^{-2},Va)_3\]

We postulate

\[J_O = -\left[ y^{a}_{Va} y^{a}_{O} M^{a}_{Ova} \right] \frac{1}{V_m} \frac{\partial \mu_O}{\partial z} \]

\[D^*_O = \left[ y^{a}_{Va} y^{a}_{O} M^{a}_{Ova} \right] \frac{1}{n_O} \]
Experiments: Amami et al. 1999

\[ P_{O_2} = 6.5 \times 10^{-2} \text{ atm} \]

\[ T = 1423 \text{ K} \]
4. Grain boundary diffusion

Simplified approach:

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

\[ Q_{gb} \cong \alpha Q_{bulk} \quad 0.3 < \alpha < 0.5 \]
5. Kirkendall porosity

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

\[
\frac{v}{V_m} = -J = -J'_{O_2} / x_{O_2} \quad V_m = \text{molar volume/mole of atoms}
\]

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

\[
\frac{1}{V_m^2} \dot{V}_m = \text{div}(J)
\]

No porosity \(\Rightarrow\) Strain rate:

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

Only porosity (volume fraction \(f_p\)):

\[
\frac{\dot{f}_p}{(1 - f_p)^2} = -V_m \text{div}(J)
\]
Voids form as a consequence of a divergence in the oxygen flux.
Schematics of Kirkendall effect in magnetite

\[ \mu_{Fe} \]

\[ \frac{\partial \mu_{Fe}}{\partial z} \]

Distance

Distance
\[ \frac{\partial y_{Va}}{\partial t} = \frac{\partial J_O}{\partial z} \]
Summary

• DICTRA can now handle diffusion in oxides allowing prediction of oxidation.
• Data base now contains diffusional mobilities of
  Wüstite (Halite): Fe and O
  Magnetite (spinel): Fe Cr O
  Hematite (Corundum): Fe, Cr, O
• Grain boundary diffusion is taken into account in a simplified manner.
• Oxygen diffusion may cause Kirkendall effect and porosity.