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

\[ \frac{dc_{i(x,t)}}{dt} = \text{div}(D_{i(x,T)} \nabla c_{i(x,t)}) \]

element migration (COMSOL Multiphysics)

chemical reaction (ChemApp)

\[
\begin{align*}
\text{Fe}_2\text{O}_3 & \text{ (hematite)} + \text{Al}_2\text{O}_3 \\
\text{Fe}_3\text{O}_4 & \text{ + FeAl}_2\text{O}_4 \\
\text{FeO} & \text{ (FeO') + FeAl}_2\text{O}_4 \\
\text{Fe} & \text{ + FeAl}_2\text{O}_4 \\
\text{Fe}_3\text{O}_4 & \text{ + Al}_2\text{O}_3 \\
\text{Al}_2\text{O}_3 & \text{ + FeAl}_2\text{O}_4 \\
\text{Fe} & \text{ + Al}_2\text{O}_3 \\
\text{Fe} & \text{ + Al} \\
\end{align*}
\]

\[0.00 \ 0.25 \ 0.50 \ 0.75 \ 1.00 \]

\[-40 \ -35 \ -30 \ -25 \ -20 \ -15 \ -10 \ -5 \ 0 \ 5 \ 10 \]

\[\log(p(O_2) / p_0)\]

\[\text{mole fraction aluminium } x_{\text{Al}}\]

700 °C

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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 Oxidation Depth - Distribution

Data: Data1_C
Model: SLogistic1
Equation:
y = a/(1 + exp(-k*(x-xc)))

Weighting: y
No weighting

Chi^2/DoF = 0.00721
R^2 = 0.99588

a = 3.20455 ± 0.00818
xc = 29.5835 ± 0.10386
k = 0.22165 ± 0.00442

Fraction of metallic Chromium

Oxides
metallic Cr

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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).

Fe  Si  O

10 μm

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).

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AES pictures by S. Borodin, MPIE
Figure: Thermodynamic stability (according to SGTE Pure Substance Data) of silicon and aluminium containing oxide phases in an iron alloy at 650 °C.
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.
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 $p(\text{O}_2) = 10^{-22}$ bar in a technical cooling programme.
Figure: Spatial phase distributions in a real alloy after oxidation at $p(\text{O}_2) = 10^{-22}$ bar in a technical cooling programme.
Part II

Introducing chemical Potentials
Figure: Shibuya (渋谷) crossing in Tokyo at night when pedestrian lights are green.
Figure: Shibuya crossing in Tokyo in the evening when pedestrian lights are red.
\[ \Delta G = V \Delta p - S \Delta T + \sum \mu \Delta n + \sum zF \varphi \Delta n \]

\[ J_A = -D \nabla c \] single phase

\[ J_A = -L \nabla \mu \] general description

\[ \mu = \mu^o + RT \ln(a) = \mu^o + RT \ln(\gamma c) = \bar{\mu}^o + RT \ln(c) \]

\[ J_A = -L \nabla \mu = -L \frac{\partial \mu}{\partial c} \nabla c = \cdots = -L \left( \frac{RT}{c} \nabla c - L \left( \nabla \mu^o + \frac{RT}{\gamma} \nabla \gamma \right) \right) \]
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).

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 cannot explain interphase transport phenomena
Again in real life...

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