Phase Diagrams with FACTSage
Speaking different Languages for Thermochemical Properties

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Outlook

– Motivation

– Thermochemical Properties in Oxides
  – Ellingham-Richardson Diagrams
  – Stability Diagrams

– Thermochemistry of Oxides and Nitrides
  – Nitrides in the System Iron - Chromium - Carbon
  – Nitrogen and Oxygen in Iron - Silicon

– Summary
Oxidation Processes in Steels

scale (mainly ‘FeO’)

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Figure 18. Cross-section SEM micrographs of Fe–10Cr after isothermal oxidation for 72 h at temperatures between 800 and 900 °C in Ar–4%H₂–2%H₂O
The Problem

pictures from various internet sources and FACTSage
Lost in Translation?

„아미 타পগতিবিদ্যা পছন্দ“

أنا أحب الديناميكا الحرارية

„Мне нравится термодинамики“

„我喜歡熱力學“

„Мou арέσει θερμοδυναμική“

„나는 열역학을 좋아“
An Effective Solution

I love thermodynamics.

I like thermodynamics.

I love thermodynamics.

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An Effective Solution

"I like thermodynamics"

„Мне нравится термодинамики“

„أنا أحب الديناميكا الحرارية“

„آمي تآپگتیبیدا پخند“

„Mou aréssei theromodúnamikí“

„我喜歡熱力學“

„나는 열역학을 좋아“
Part I

Thermochemical Properties of Oxides
**Figure 12.13** The Ellingham diagram for selected oxides.
2 Fe + O₂ ⇄ 2 FeO

\[-2G^{o, FeO}_T + 2G^{o, Fe}_T + G^{o, O}_T = -RT \ln \left( \frac{p_{O_2}}{p_o} \right) T\]
Ellingham Diagram with FACTSage

\[ 2 \text{Fe} + \text{O}_2 \rightleftharpoons 2 \text{FeO} \]

\[-2G^o_{(T)} + 2G^o_{(T)} + G^o_{(T)} = -R \ln \left( \frac{p_{O_2}}{p_o} \right) T\]
2 Fe + O₂ ⇔ 2 FeO

\[-2 G^o_{FeO} + 2 G^o_{Fe} + G^o_{O_2} = -R \ln \left( \frac{p_{O_2}}{p_o} \right) T\]
Ellingham Diagrams for Oxide Formation

ΔG° = RT ln P_O₂ (kJ)

Temperature, °C

Fe - O₂
1 atm

Fe₂O₃(s)
Fe₃O₄(s)
FeO(lq)

FeO(s)

Ferrite
Austenite
Ferrite
liquid

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2 Fe + O₂ ⇌ 2 FeO
Stability Diagrams with FACTSage

\[ 2 \text{ Fe} + \text{O}_2 \rightleftharpoons 2 \text{ FeO} \]
Stability Diagrams with FACTSage

\[ 2 \text{Fe} + \text{O}_2 \rightleftharpoons 2 \text{FeO} \]
\[
-2 G_{(T)}^{o, FeO} + 2 G_{(T)}^{o, Fe} + G_{(T)}^{o, O_2} = -R \ln \left( \frac{p_{O_2}}{p_o} \right) T
\]

\[
- \frac{2 G_{(T)}^{o, FeO} - 2 G_{(T)}^{o, Fe} - G_{(T)}^{o, O_2}}{RT} = \ln \left( \frac{p_{O_2}}{p_o} \right)
\]
Properties of Oxygen

Oxide Stability

Standard free energy of formation of oxides

\(-\Delta G^0 = -RT \ln(p_{O_2}) / \text{kJ mol}^{-1}\)

Temperature / °C

Oxygen partial pressure log\(\left(p_{O_2}/p_0\right)\)

\(3/2 \text{Fe} + O_2 = \frac{1}{2} \text{Fe}_3\text{O}_4\)

\(2 \text{Fe} + O_2 = 2 \text{FeO}\)

\(4/3 \text{Cr} + O_2 = 2/3 \text{Cr}_2\text{O}_3\)

\(2 \text{Mn} + O_2 = 2 \text{MnO}\)

\(\text{Si} + O_2 = \text{SiO}_2\)

\(4/3 \text{Al} + O_2 = 2/3 \text{Al}_2\text{O}_3\)
Iron – Manganese – Chromium alloy

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.

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Part II

Gaseous Nitriding in the system Fe – Cr – C

Nitriding of Fe, 1 wt-% Cr, 0.10 wt-% C and

Conditions: 48 h at 500 °C
p(NH₃) : p(H₂) = 100 (K_N = 1 000)
Gaseous Nitriding Process

- $\varepsilon$-Phase ($Fe_2N$)
- $\gamma'$-Phase ($Fe_4N$)
- Diffusion Zone
Figure: Lehrer-Diagram of iron nitrides according to literature (left) and calculated with the programme FactSage (right).
Figure: Spatial phase distribution in an Fe, 1 wt-% Cr, 0.1 wt-% C alloy after gas nitriding at $K_N = 2.4$ and 500 °C for 48 h and phase stability diagram.
Binary Phase Diagrams

C - Fe
Data from SGTE 2011 alloy database

LIQUID + GRAPHITE

FCC_A1 + GRAPHITE

BCC_A2 + GRAPHITE

Cr - Fe
Data from BINARY (SGTE) alloy databases

BCC_A2(Fe,C,H,N,V)

SIGMA

BCC_A2(Fe,C,H,N,V) + BCC_A2(Fe,C,H,N,V)

mole Fe/(Cr+Fe)
The System Iron – Nitrogen

Figure: Nitrogen Solubility in Iron at 1 bar (left) and binary Iron-Nitrogen phase diagram, calculated with FACTSage (right).

Figure: Nitrogen Solubility in Iron at 1 bar (left) and binary Iron-Nitrogen phase diagram, calculated with FACTSage (right).
The System Iron – Nitrogen

Figure: Nitrogen Solubility in Iron at 1 bar (left) and binary Iron-Nitrogen phase diagram, calculated with FACTSage (right).
Part III

Gaseous Nitriding and Oxidation in the system Fe – Si

Nitriding of Fe, 1 wt-% Si

Conditions: 20 h at 550 °C ($K_N = 1000$)
4 h at 550 °C ($K_O \approx 0.01$)
Figure: Stability diagram of an Fe, 1 wt-% Si alloy at 550 °C with respect to the partial pressures of nitrogen and oxygen (SGTE Pure Substance Database).
Simulation Results with ASTRID

**Figure**: Spatial phase distribution in Fe, 1 wt-% Si after gaseous nitriding for 20 h at $K_N = 1000$ and oxidation for 4 h and $K_O \approx 0.01$ ($p_{tot} = 1$ atm, 550 °C).
Ternary Phase Diagrams

700 °C
Ternary Phase Diagrams

700 °C

N - Si - O
973 K, 1 atm

Fe - Al - O
973 K, 1 atm

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Conclusions - The Problem

pictures from various internet sources and FACTSage
Conclusions – An Effective Solution

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Backup Slides

Additional Slides for the Presentation
Where we work…

Max-Planck-Institut für Eisenforschung GmbH

Head: Prof. Dierk Raabe

Founded in 1917 from the “Kaiser Wilhelm Institute” by Fritz Wüst.

3 Departments:
- Computational Materials Design
- Interface Chemistry and Surface Engineering
- Microstructure Physics and Alloy Design
Austria

Area: 83 879 km²
Inhabitants: ~ 8 405 000
Language: German
Capital: Vienna
Fisher’s Model of Diffusion

Whipple – Le Claire equation

\[ s \delta D_{GB} = 0.3292 \sqrt{\frac{D}{t}} \left( \frac{\partial \log \bar{c}}{\partial z} \right)^{5/3} \]

Levine – MacCallum equation

\[ s \delta D_{GB} = 0.4704 \sqrt{\frac{D}{t}} \left( \frac{\partial \log \bar{c}}{\partial z} \right)^{5/3} \]
Internal Corrosion of Engineering Alloys: Experiment and Computer Simulation

Ulrich Krupp and Hans J. Christ

(Submitted July 18, 2005)

High-temperature corrosion is generally known as a material degradation process that occurs at the surface of engineering components. In the case of internal corrosion, the corrosive species penetrates into the material by solid-state diffusion leading to the formation of internal precipitates, for instance, oxides (internal oxidation), nitrides (internal nitridation), and carbides (carburization). It is known from numerous publications and technical failure cases that internal corrosion results in a strong deterioration of the properties of a material (i.e., near-surface embrittlement or the dissolution of strengthening phases). The present article introduces the classic theory of internal oxidation and reviews some recent research on internal corrosion phenomena that are closely related to the failure mechanisms of thermally grown protective oxide scales on several commercial high-temperature alloys (e.g., single-crystalline and polycrystalline Ni-base alloys and Cr steels). The mechanisms and kinetics of internal corrosion processes are determined by the temperature, the local chemical composition of the material, the solubility and diffusivity of the corrosive species, as well as the mechanical loading conditions. These influence factors are taken into account by means of a computer model combining a numerical finite-difference approach with the solution of the diffusion differential equations with the thermodynamic tool ChemApp. Using several examples, it is shown that the model has been applied successfully to simulate the internal nitridation, carburization, and oxidation of high-temperature alloys.

1. Introduction

Internal corrosion is a generic kind of material degradation occurring at high temperatures that is driven by the inward diffusion of a corrosive species (i.e., oxygen, nitrogen, carbon, or sulfur), followed by internal precipitation of the respective oxides, nitrides, carbides, and sulfides. Contrary to the formation of superficial scales, which in the case of Cr₂O₃ and Al₂O₃ protect the substrate against excessive corrosion attack, internal corrosion may result in a deep deterioration of the physical properties of the material (e.g., creep resistance and high-temperature fatigue strength). Figure 1 shows an example of internal oxidation (Al₂O₃) and nitridation (AlN; penetration depth \( \xi = 600 \mu \text{m} \)) underneath a thin Cr₂O₃ scale.

The mechanism of internal corrosion depends on the local concentrations and the diffusivities of the corrosive species and the metallic elements in the substrate. For the example shown in Fig. 1, a low oxygen partial pressure, \( p(O_2) \), relative to the nitrogen partial pressure \( p(N_2) \) in the combustion gas leads to conditions in the material interior, for

\[ \text{Cr}_2\text{O}_3 \]

which AlN instead of Al₂O₃ is the thermodynamically most stable compound.

Even in the case of Al₂O₃-scale-forming Ni-base super-
element migration

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

chemical reaction

\[
\text{Fe}_2\text{O}_3 (\text{hematite}) + \text{Al}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 + \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe}_3\text{O}_4 + \text{FeAl}_2\text{O}_4 \rightarrow \text{'FeO'} + \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe} + \text{FeAl}_2\text{O}_4 \rightarrow \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe} + \text{Al} \rightarrow \text{FeAl}_2\text{O}_4
\]

\[
\text{Fe} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4
\]

\[
700 \, ^\circ\text{C}
\]
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.
Figure: Spatial distribution of chromium oxides $\text{Cr}_2\text{O}_3$ and $\text{FeCr}_2\text{O}_4$ along a grain boundary in Fe, 3 wt-% Cr after finished cooling from 650 °C.
Diffusion between different Phases

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

\[ J_A = -D \nabla c \]

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

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

Calculation of the Oxidation Depth

Data: Data1_C
Model: SLogistic1
Equation: 
\[ y = \frac{a}{1 + \exp(-k(x-xc))} \]
Weighting: 
\( y \) No weighting

\( \chi^2/\text{DoF} = 0.00721 \)
\( R^2 = 0.99588 \)

\( a = 3.20455 \pm 0.00818 \)
\( xc = 29.5835 \pm 0.10386 \)
\( k = 0.22165 \pm 0.00442 \)

Fraction of metallic Chromium
Depth into Steel Sample x / µm

Cr- oxides
metallic Cr
**Abbildung:** Phasenverteilung einer industrienahen Legierungszusammensetzung nach erfolgter Oxidation bei $p(O_2) = 10^{-22}$ bar und einer technischen Abkühlkurve.
Temperature Dependence

The diffusion equation for the concentration $c_i(x,t)$ of an impurity $i$ is given by:

$$\frac{dc_i(x,t)}{dt} = \text{div}(D_i(x,T) \cdot \nabla c_i(x,t)) + f(x,T,c_i(x,t))$$

where $D_i(x,T)$ is the diffusion coefficient, and $f(x,T,c_i(x,t))$ represents an additional source term.

The diffusion coefficient $D_i(T)$ is temperature-dependent and can be expressed as:

$$D_i(T) = D_i^o e^{-\frac{Q}{RT}}$$

where $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature in Kelvin.

**Figure:** Temperature dependence of phosphorous diffusion in iron.
Figure: State diagram of water [2] (left) and schematic temperature evolution with constant heating (right).
Efficiency of the Calculation

Figure: Distribution of Cr$_2$O$_3$ in Fe, 0.67 wt-% Cr at 700 °C after 90 min. Simulation with InCorr (left) and with self-written programme (right).

300 FEM-points
Calculation time: 90 min

63 000 FEM-points
Calculation time: 120 min
Abbildung: Abhängigkeit der Rechenzeit zur Simulation des Oxidationsverhaltens von Fe, 3 wt-% Cr bei verwendetem Kühlprogramm ab 650 °C (B).
Grain Boundary Diffusion Regimes

Coarse grained

C – regime

B – regime

A – regime

Fine grained

C’ – regime

B’ – regime

A’ – regime

**Figure:** Illustration of different diffusion regimes, depending on total diffusion time and ratio of $D_{\text{GB}}/D$. 
Experimental Set-up

- N\textsubscript{2}
- Ar
- H\textsubscript{2}

Dew-Point Sensor

H\textsubscript{2}O-Dosage

Gas Mixing Chamber

Reaction Chamber

Gas Analysis (H\textsubscript{2}O, O\textsubscript{2}-Content)
Selective Decarburisation at 800 °C

Figure: Experimental parameters during selective decarburisation of Fe, 0.8 wt-% C at 800°C in Ar / 2.5 vol-% H₂ / H₂O.
Selective Decarburisation at 800 °C

Fe, 0.8 wt-% C, 800 °C, Ar/2.5% H₂, DP+13°C

Figure: Mass change during selective decarburisation of Fe, 0.8 wt-% C at 800°C in Ar / 2.5 vol-% H₂ / H₂O.
Figure: Cross section of Fe, 0.8 wt-% C after oxidation at 800 °C in Ar / 2.5 % H₂ / H₂O for 60 min. The cross section was etched with 1 % HNO₃ / Ethanol for 15 s.
Selective Decarburisation at 800 °C

Figure: Evolution of the decarburised zone depth in Fe, 0.8 wt-% C after oxidation at 800 °C in Ar / 2.5 % H₂ / H₂O. The solid lines represent theoretical results.

M. Auinger, V.G. Praig, et.al., Corros. Sci., submitted
Figure: Evolution of the mass change in Fe, 0.8 wt-% C during oxidation at 800 °C in Ar / 2.5 % H₂ / H₂O. The solid lines represent the theoretical results.
2 Fe + O$_2$ $\rightleftharpoons$ 2 FeO

$\Delta G_{\text{Formation}}^{(T)} \approx 2 \mu_{\text{FeO}}^{(T)} - 2 \mu_{\text{Fe}}^{(T)} - \mu_{\text{O}_2}^{(T)} = 0$

$0 = 2 G_{\text{FeO}}^{(T)} + 2 RT \ln(a_{\text{FeO}}) - 2 G_{\text{Fe}}^{(T)} - 2 RT \ln(a_{\text{Fe}}) - G_{\text{O}_2}^{(T)} - RT \ln \left( \frac{p_{\text{O}_2}}{p_o} \right)$

$\Delta G_{\text{o,Formation}}^{(T)} = 2 G_{\text{FeO}}^{(T)} - 2 G_{\text{Fe}}^{(T)} - G_{\text{O}_2}^{(T)} = -RT \ln \left( \frac{p_{\text{O}_2}}{p_o} \right) + 2 \left( RT \ln(a_{\text{FeO}}) - RT \ln(a_{\text{Fe}}) \right)$

$2 G_{\text{FeO}}^{(T)} - 2 G_{\text{Fe}}^{(T)} - G_{\text{O}_2}^{(T)} = -RT \left( \frac{p_{\text{O}_2}}{p_o} \right) T + \frac{y}{d} 0$
Properties of Nitrogen

Nitride Stability

Standard free energy of formation of nitrides
\( -\Delta G^0 = R \cdot T \cdot \ln (p_{N_2}) / \text{kJ mol}^{-1} \)

Temperature / °C

Nitrogen partial pressure \( \log (p_{N_2}) \)

Fig. 22. Fe. Diffusion coefficient for N diffusion in \( \alpha, \gamma \) and \( \delta \)-phase Fe vs. (reciprocal) temperature. Circles: calculated from equation quoted from [76S3].

figures from Landoldt-Börnstein (right) and FACTSage (left)
Theoretical Principles

\[ \frac{3}{2} H_2 + \frac{1}{2} N_2 \xrightarrow{p, T} NH_3 \]

\[ G_{NH_3}^{(T)} - \frac{3}{2} G_{H_2}^{(T)} - \frac{1}{2} G_{N_2}^{(T)} = 0 \]

\[ K_{p(T)} = e^{-\frac{G_{NH_3}^0(T) - \frac{3}{2} G_{H_2}^0(T) - \frac{1}{2} G_{N_2}^0(T)}{RT}} \]

\[ K_p = \frac{p_{NH_3}}{p_{H_2}^{1.5} p_{N_2}^{0.5} p_0} \]

\[ K_N = \frac{p_{NH_3}}{p_{H_2}^{1.5}} \sqrt{p_0} \]

\[ K_N = \sqrt{p_{N_2}} \frac{K_{p(T)}}{\sqrt{p_0}} \]
Figure: Lehrer-Diagram of iron nitrides according to literature (left) and stability diagram calculated with the programme FactSage (right).