Applications of ThermoCalc at the FZ Jülich

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Introduction

Use of simulation techniques for development of materials for energy applications

- ThermoCalc
- Dictra
- MICRESS

Experiments

- Ab initio
- ATAT
- Molecular Dynamics

ThermoCalc Users Meeting, September 2013, Aachen
Overall Work Strategy

EXPERIMENTS

Time

Applications

Materials properties

Calphad

Multicomponent systems

Thermodynamic properties

Equilibrium properties

Periodic structure

Multicomponent systems

Electronic structure

DFT

Band

Overall Work Strategy

ThermoCalc Users Meeting, September 2013, Aachen
Presentation Outline

• 1. Laves phase hardened ferritic steels – investigation and modeling of phase equilibria

• 2. Diffusion studies in Ni-base alloys
1. Steel - background

Crofer 22H – steel for fuel cell interconnects …


- good corrosion resistance
- Candidate for high temperature applications
- Laves-phase strengthened ferritic steel

<table>
<thead>
<tr>
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<th>At. %</th>
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<tbody>
<tr>
<td>Cr</td>
<td>21.12297</td>
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<tr>
<td>Fe</td>
<td>65.68136</td>
</tr>
<tr>
<td>C</td>
<td>0.006099</td>
</tr>
<tr>
<td>N</td>
<td>0.007113</td>
</tr>
<tr>
<td>S</td>
<td>0.003257</td>
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<td>Si</td>
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<td>Al</td>
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<tr>
<td>W</td>
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<tr>
<td>Nb</td>
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<tr>
<td>Ti</td>
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<td>La</td>
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<td>P</td>
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<tr>
<td>Cu</td>
<td>0.537813</td>
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</table>

1. Steel - Task

- Phase equilibria unclear - e.g. Fe-Nb-Si
  - ThermoCalc
  - TCFE6 database
  - 1050 °C

- microstructure evolution
  - corrosion resistance
  - lifetime stability

- Clarify phase equilibria
- CALPHAD modeling

- Use dataset for modeling of properties

Multiscale modeling
Key experiments
1. Steel - Fe-Nb-Si

Literature data: various versions of isothermal section ~1100 °C

- ThermoCalc
- TCFE6 database
- 1050 °C

Goldschmidt, JISI (1960), 169

Landoldt Börnstein database
Ab initio calculations

- ADF software (Amsterdam Density Functional)
  Density Functional Theory with Kohn Sham approach

- BAND (periodic system)
  Relativistic effect on the Dirac equation (Scalar) \(\rightarrow\) Useful for heavy elements

- Calculation of thermodynamic data at 0 K: \(\Delta_f H\)

\[
\Delta_f H (A_x B_y) = E_{A_x B_y} - \left[ \frac{x}{x+y} E_A + \frac{y}{x+y} E_B \right]
\]
Ab initio calculations

Fe-Si

Fe-Nb

\[ \Delta H \text{ (kJ mol}^{-1}\text{atom}^{-1}) \]

at. % Si

0 0.2 0.4 0.6 0.8 1

0 -5 -10 -15 -20 -25 -30 -35 -40 -45

\[ \Delta H \text{ (kJ mol}^{-1}\text{atom}^{-1}) \]

at. % Nb

0 0.2 0.4 0.6 0.8 1

-16 -14 -12 -10 -8 -6 -4 -2 0

Present work
Sommer (1988)
Meschel (1998)
Liang (2011), HT
Lacaze (1991)

Present work, HT
Chart (1973) (1971)
Liang (2011)
Tani (2003)
Du (2008)

Liu (2012), Ab initio
Mathon (2009), Ab Initio
Meschel (2006), exp
Liu (2012), Calphad
Khvan (2012), Calphad
### Ab initio calculations

#### C14 Laves phase end members

<table>
<thead>
<tr>
<th>End-members</th>
<th>$\Delta_f H$ (kJ.mol$^{-1}$.atom$^{-1}$) Present work</th>
<th>$\Delta_f H$ (kJ.mol$^{-1}$.atom$^{-1}$)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>a (Å), ref</th>
<th>c (Å), ref</th>
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</thead>
<tbody>
<tr>
<td>Nb:Fe$_2$</td>
<td>-12.23</td>
<td>-14.5$^1$, -13.16$^2$</td>
<td>4.82</td>
<td>7.88</td>
<td>4.82$^2$</td>
<td>7.839$^2$</td>
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<td>59.07</td>
<td>2.1$^1$, 60.01$^2$</td>
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<td>5.423$^2$</td>
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<td>7.615$^2$</td>
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<tr>
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<td>15.602$^1$, 16.54$^2$</td>
<td>5.58</td>
<td>8.54</td>
<td>5.467$^2$</td>
<td>8.869$^2$</td>
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<tr>
<td>Nb:Si$_2$</td>
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<td>-</td>
<td>5.26</td>
<td>8.08</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Si:Nb$_2$</td>
<td>76.34</td>
<td>-</td>
<td>5.50</td>
<td>8.54</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Si:Fe$_2$</td>
<td>17.89</td>
<td>19.91$^4$</td>
<td>4.70</td>
<td>7.61</td>
<td>4.55$^4$</td>
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<tr>
<td>Fe:Si$_2$</td>
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<td>48.92$^4$</td>
<td>4.84</td>
<td>7.91</td>
<td>5.11$^4$</td>
<td>6.93$^4$</td>
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<td>Si:Si$_2$</td>
<td>83.86</td>
<td>2.5$^3$, 56.52$^4$</td>
<td>5.50</td>
<td>8.39</td>
<td>5.60$^4$</td>
<td>6.91$^4$</td>
</tr>
</tbody>
</table>

1 M. Mathon et al., Calphad 33 (2009), pp. 136-161
2 Liu et al., Calphad 38 (2012), pp. 43-58
4 Pavlu et al., J. of Mining and Metallurgical (2012)
5 Pavlu et al., Calphad 33 (2009), pp. 179-186
Thermodynamics and Phase Diagrams

• CALPHAD: CALculation of PHAse Diagrams
  – Semiempirical method to describe phase equilibria on the basis of Gibbs free energy
    \[ \Delta G = f(p, T, x_i) \]

• Thermodynamic Assessment („Optimization“) to obtain thermodynamic dataset for the investigated system

• Input data from:
  – Phase diagram data
  – Thermodynamic data from calorimetry, KEMS, EMF
  – Experiments can be substituted by ab-initio calculations
Fe-Nb-Si
Experimental Phase Equilibria

- Induction levitation melting
- Equilibrium annealing
- Phase analysis SEM, XRD, EDX
- Thermal analysis DTA

1050 °C

80 at.% Si
Fe-Nb-Si – CALPHAD

- C14 – Fe$_2$Nb Laves Phase:
  - two sublattice model: (Fe,Si,Nb)$_2$: (Fe,Nb, Si)
  - end members from ab-initio

- $\mu$-phase Fe$_7$Nb$_6$:
  - 4 sublattice model: (Fe,Nb, Si): (Nb)$_4$: (Nb, Fe)$_2$: (Fe, Nb, Si)$_6$
  - end members from ab-initio (in progress) or estimated

- Ternary solubilities for Fe$_5$Si$_3$ and Nb$_5$Si$_3$
- Ternary compounds (line compounds)
Fe-Nb-Si – CALPHAD

THERMO-CALC (2013.09.03:15.42) : 
DATABASE: USER
T=1323, P=1E5, N=1;

- Phase diagram assessment in progress
Presentation Outline

• 1. Laves phase hardened ferritic steels – investigation and modeling of phase equilibria

• 2. Diffusion studies in Ni-base alloys
Many alloy systems contain precipitates which contain substantial amount of the element forming the oxide scale

Examples:

- Cr-carbide precipitates in Ni-base alloy
- β-NiAl phase in MCrAlY coatings
2. Ni-base alloys

Microstructure of a typical MCrAlY coating on a Ni-base alloy after 300 h. on air

\[ T = 1000 \, ^\circ\text{C} \]


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2. Ni-base alloys

Typical microstructure changes in MCrAlY-layers due to Al-depletion and interdiffusion

β-NiAl-depletion due to
✓ Al-consumption due to oxide growth (oxidation)
✓ interdiffusion between protective layer and base material

2. Ni-base alloys

NiCoCrAlY-layer on Ni-base superalloy after 5000 hrs. on air at 980 °C

etched metallographic cross section

- $\gamma'$-coarsening in superalloy by Al-diffusion out of the MCrAlY-layer


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Phase composition of NiCoCrAlY bond coat as function of temperature

Calculated in Thermo-Calc


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$\beta$-phase depletion in MCrAlY coating during oxidation: simulation in DICTRA (top coat side)

Metallographic cross-section

Al-depleted zone

Alumina scale

$\gamma/\beta$

Simulated using DICTRA

D. Naumenko, A. Chyrkin, V. Shemet, L. Singheiser and W.J. Quadakkers
International Conference on Metallurgical Coatings and Thin Films,
ICMCTF-2012, San-Diego, CA, USA, April 23-27, 2012
2. Ni-base alloys

DICRTA-simulation of interdiffusion between CoNiCrAlY and PWA 1483 after 300 h at 1050°C

Phase fraction

Distance / µm

Interdiffusion zone

Interdiffusion zone
2. Ni-base alloys

Interdiffusion between MCrAlY-layer and superalloy: pore formation

\[ f_{\text{porosity}} / \text{a.u.} \]

\[ -200 \quad -150 \quad -100 \quad -50 \quad 0 \quad 50 \quad 100 \quad 150 \quad 200 \]

Distance / µm

\[ 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \quad 1.2 \quad 1.4 \quad 1.6 \]

MCrAlY

\[ \text{DICTRA-simulation} \]

300h / 1050 °C

NiCoCrAlY-1

NiCoCrAlY-2

CoNiCrAlY

D. Naumenko, A. Chyrkin, V. Shemet, L. Singheiser and W.J. Quadakkers
International Conference on Metallurgical Coatings and Thin Films,
ICMCTF-2012, San-Diego, CA, USA, April 23-27, 2012
Subscale phase transformation in alloy system in which the precipitates do **NOT** contain substantial amounts of the element (Cr) forming the oxide scale

Example: Alloy 625

Reference:
A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
High temperature oxidation of INCONEL 625

*ADS-9, 900°C, 1000h, Ar-4%H₂-2%H₂O*
Main precipitate phase in INCONEL 625 at 900°C is $\delta$-Ni$_3$Nb

Only precipitate phase at 1000°C is (Ni,Mo,Cr)$_6$C

A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
GDOES element profiles in INCONEL 625

900°C / 1000 h / Ar-2%H₂O-4%H₂

A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
Why does chromium depletion result in formation of precipitate free zone, although chromium is not the main element in the precipitates?

Why are the precipitate phases enriched at the oxide/alloy interface?
What makes Nb diffuse towards the oxide/alloy interface?

INCONEL 625 after 1000h oxidation in air at 900°C

Cr concentration profiles (EDX)

A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
Chemical potential of Nb as function of Cr content at 900°C
Phase distribution prediction using DICTRA

INCONEL 625: 900°C, 100 h, Ar-2%H₂O-4%H₂

0.000 0.005 0.010 0.015 0.020
Phase fraction

0 10 20 30 40 50 60 70 80 90 100
Distance (µm)

δ-NbNi₃

δ-NbNi₃

0.82
Now at 1000°C:

\[ \delta\text{-NbNi}_3 \text{ phase is formed after prolonged oxidation of INCONEL 625 at 1000°C underneath the oxide although it is not present in the original alloy} \]

\[ \text{Uphill diffusion of Nb} \]

A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
Chemical potential of Nb as function of Cr content at 1000°C

\[ \mu(Nb) \]

A. Chyrkin, P. Huczkowski, V. Shemet, L. Singheiser, W. J. Quadakkers
Oxidation of Metals (2011), 75(3/4) 143-181
Further information on Corrosion of Ni-base alloys:

http://www.fz-juelich.de/iek/iek-2/DE/Forschung/Korrosion/Korrosion_node.html