Coupled thermodynamic and kinetic modelling to predict oxidation induced thermal degradation of high temperature materials

R. Pillai, T. Galiullin and W. J. Quadakkers

Thermo-Calc Anwendertreffen 2017, Aachen
Outline

• Applications of high temperature materials

• Modelling approach

• Case study:
  • microstructural changes in multilayered coating system during exposure at elevated temperatures

• Conclusions
High temperature materials

Gas turbine technology

- Coated/uncoated turbine blades and vanes, turbine discs, combustion liners, honeycomb sealings
  **Materials:** Ni-base and Co-base superalloys, NiCrFe-base and TiAl-base alloys

Power generation systems

- Boiler components (e.g. heat exchangers, burners), components of steam turbines
  **Materials:** ferritic, martensitic and austenitic stainless steels, Ni-base alloys

Fuel cells and Power-to-X

- Solid oxide fuel cells (SOFC) and electrolysers (SOEC)
  **Materials for interconnect:** High Cr ferritic steels
Examples of oxidation induced thermal degradation

Wrought Ni-base alloy after 300 h at 1200 °C in air

- External (I.) and internal (II.) oxide formation - metal loss
- Dissolution of strengthening carbides (III.) - affected mechanical properties

BSE-image

MCrAlY coating (1) on Ni-base superalloy (2) after 2000 h at 1050 °C in air

- Loss of Al in the coating on protective oxide formation
- Microstructural evolution of the coating (phase transformation/dissolution)
- Interaction between the coating (1) and the substrate material (2) - Interdiffusion

Etched optical micrograph

100 µm
Aimed applications for modelling

• Prediction of chemical *life time of coated/uncoated materials* due to simultaneous oxidation and diffusion processes

• Prediction of *oxidation induced element depletion* in alloys during high temperature exposure

• *Microstructural evolution* of materials during high temperature exposure
  • precipitation of detrimental phases
  • dissolution/redistribution of strengthening precipitates

• *Microstructural evolution* of materials during *diffusion coating process* (e.g. aluminizing, chromizing) for process optimization
Modelling tools

- Thermodynamic and kinetic databases available in *Thermo-Calc* for FeCr-, FeCrAl-, NiCr-, NiCrAl-base alloys and coating systems

- Diffusion module (*DICTRA*)

  - **In-house developed diffusion model** for multi-component and -phase systems:
    - access to commercial thermodynamic and kinetic data of *Thermo-Calc* via TQ-Interface
    - possible implementation of an independent mobility data
    - flexible boundary conditions (e.g. modelling of internal oxidation)
    - improved computation time due to parallel multi-core simulations
In-house developed diffusion model

Simulation workflow

**Modelling input**

- Global and boundary conditions
- Domain discretization
- Initial concentration profiles

**Equilibrium calculation**

- TQ-Interface
- TQ-Interface to extract thermodynamic and kinetic data:
  - Chemical potentials $\mu_c$
  - Phase fractions $f_\phi$
  - Mobilities $M_c$

**Homogenization model**

- Effective mobilities
- Fluxes of elements

**Output**

- Concentrations/Phase fractions

Increasing computational efficiency

Serial vs. Parallel calculation

Computational domain (n cells)

\[ t_1 + t_2 + t_3 + \ldots \]

\[ \ldots + t_n = t_{EQ} \]

Time to calculate phase equilibria of the domain (\( t_{EQ} \))

Serial calculation (single core)

\[ t_{EQ} = t_1 + t_2 + \ldots + t_n \]

Parallel calculation

\[ t_{EQ} = t_n \]

Serial vs. Parallel calculation

Commercial MCrAlY-coated Ni-base superalloy

(9 elements, 3 phases)

- Almost linear gain in the computational speed
- Maximum speed is limited to one grid node (or eq. calculation) per core

Outline

• Applications of high temperature materials

• Modelling approach

• Case study:
  • microstructural changes in multilayered coating system during exposure at elevated temperatures

• Conclusions
Multilayered coatings (SMARTCOAT)

- Alternating Cr/Al rich layers
- Bond coat (MCrAlY)
- Superalloy substrate

SMARTCOAT*

- Chemically graded coatings
- Combined resistance to oxidation and salt-induced corrosion

- Microstructural changes during high temperature exposure:
  - Interdiffusion between different layers
  - Enrichment of phases at coating interfaces
  - Phase transformations

* Cooperation University of Birmingham, UK

Microstructure of as-received coating system on CMSX-4

- Phases identified by means of EDX-point analysis and EBSD

Nominal composition (wt.%):

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>Ta</th>
<th>W</th>
<th>Ti</th>
<th>Mo</th>
<th>Re</th>
<th>Si</th>
<th>Y</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr layer</td>
<td>-</td>
<td>49.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>0.3</td>
<td>49.0</td>
</tr>
<tr>
<td>NiCrAlY layer</td>
<td>-</td>
<td>22.0</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Substrate CMSX-4</td>
<td>9.6</td>
<td>6.5</td>
<td>5.6</td>
<td>6.5</td>
<td>6.4</td>
<td>1.0</td>
<td>0.6</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Microstructure after exposure at 800°C for 3000 h in air

- Coupled thermodynamic and kinetic diffusion modelling to describe microstructural evolution in the multiphase coating system

- Oxidation induced depletion of Cr: $\uparrow J_{Cr}$
- Interdiffusion of Ni, Cr, Si and Al: $\uparrow \downarrow J_i$
- Enrichment of phases at the interfaces
- Phase transformations
- Interdiffusion between NiCrAlY and substrate: $\uparrow \downarrow J_i$

Initial Ni-Cr layer

Initial aluminide layer

Initial NiCrAlY layer

Substrate CMSX-4

800 °C, 3000 h

50 µm
Ni:Cr/Aluminide interface after 3000 h at 800°C

EBSD analysis to identify phases at the interface

- Enrichment of $\alpha$-Cr at the initial Ni-Cr-aluminide layer interface
- Complete depletion of $\beta$-NiAl in aluminide layer which is now $\gamma'$+$\alpha$-Cr
- Formation of $\text{Cr}_3\text{Ni}_2\text{Si}$ at the interface
Calculated chemical activities
Driving forces for interdiffusion

Ni diffusion: Ni-Cr → Aluminide layer; NiCrAlY → Aluminide layer; Substrate → NiCrAlY

Al diffusion: Aluminide → Ni-Cr; Aluminide → NiCrAlY; NiCrAlY → Substrate

Cr diffusion: Ni-Cr → Aluminide layer; NiCrAlY → Aluminide layer; Substrate → NiCrAlY
Calculated phase distribution after 3000 h at 800 °C in air

- Enrichment of \( \alpha \)-Cr at the Ni-Cr/Aluminide interface and \( \beta \)-NiAl dissolution in the aluminide layer is correctly predicted.
- Formation of \( \text{Cr}_2\text{Ni}_2\text{Si} \) could not be modelled (no thermodynamic description in current databases from TC)
Calculated phase distribution after 3000 h at 800 °C in air

**SE-image**

- Initial NiCr layer
- Initial aluminide layer

**EBSD phase map**

- α-Cr
- Cr$_3$Ni$_2$Si
- Ni-FCC ($\gamma'$)

![Graph showing phase fractions](image)

- **Molar phase fraction**
- **Exposure time (h)**

- **α-Cr fraction at the interface**
- **max. β-NiAl fraction in the NiAl layer**

- Enrichment of α-Cr at the Ni-Cr/Aluminide interface and β-NiAl dissolution in the aluminide layer is correctly predicted.
- Formation of Cr$_3$Ni$_2$Si could not be modelled (no thermodynamic description in current databases from TC)
Outline

• Applications of high temperature materials

• Modelling approach

• Case study:
  • microstructural changes in multilayered coating system during exposure at elevated temperatures

• Conclusions
Conclusions

• Implemented coupled thermodynamic-kinetic diffusion model is able to predict with reasonable accuracy:
  - microstructural evolution during long-term high temperature exposure
  - phase transformations

in multilayer complex coating system

• Limitations:
  availability of thermodynamic and kinetic data, assumption of uniform diffusion, reliance on experimentally measured oxidation kinetics
Related published work

• A new computational approach for modelling the microstructural evolution and residual lifetime assessment of MCrAlY coatings, 
  *Materials at High Temperatures (32)*, 2015, 57-67

• Methods to increase computational efficiency of CALPHAD-based thermodynamic and kinetic models employed in describing high temperature material degradation, 
  *CALPHAD(53)*, 2016, 62-71

• Carbides in an aluminised single crystal superalloy: tracing the source of carbon 
  *Surface and Coatings Technology (288)*, 2016, 15-24

• Predicting the microstructural evolution in a multi-layered corrosion resistant coating on a Ni-base superalloy 
  *Materials at High Temperatures, in press*
Thank you!