Computational Design and Discovery of Ni-based Alloys and Coatings: Thermodynamic Approaches Validated by Experiments

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Outline

• Background
• Project Objectives and Tasks
• Approach
• Progress
  I. Thermodynamic modeling of Ni-Hf, Ni-Al-Hf, and Ni-Cr-Hf
  II. Prediction of Hf tolerance in NiCrAl bond coat alloys
  III. Preliminary results on the effect of Y
• Future work
• Acknowledgement
Extrinsic $\text{Al}_2\text{O}_3$ scale growth desired for the protection against high temperature corrosion

Effects of Reactive Elements (RE) on Alumina Scale Formation on Alloys


**Al₂O₃ scale growth is dominated by grain-boundary diffusion at the temperatures of interest**

![Diagram showing Al₂O₃ scale formation and the effects of RE](image)

<table>
<thead>
<tr>
<th>Comparisons</th>
<th>Effects on</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_p</td>
<td>Grain size</td>
<td>Outward transport</td>
</tr>
<tr>
<td>Fe, Ni-based with RE vs. Without</td>
<td>Down 2x</td>
<td>Down 1.5-2x</td>
</tr>
</tbody>
</table>

RE reduces $D_{b}^{Al}$ by 4x, has little effect on $D_{b}^{O}$

RE = Hf, Y, Zr, La, ...
Isothermal Oxidation Kinetics at 1150°C

*Single Doped*: Hf vs. Y

Base composition (at.%): Ni-20Al-5Cr

![Graph showing weight change vs. oxidation time for different dopants at 1150°C.](image)

- Ni-20Al-5Cr base
- -0.05Y
- -0.1Y
- -0.05Hf
- -0.1Hf

![Micrographs of oxidized materials.](image)
Thermodynamic considerations of oxidation

3Hf + 2Al₂O₃ → 3HfO₂ + 4Al

\[ \Delta G^\circ = -RT \times \ln K_{eq} \] and

\[ K = \frac{a_{Al}^4}{a_{Hf}^3} \]

In order to suppress HfO₂:

must have \( K < K_{eq} \)

Large composition space of bond coat alloys: Ni-Al-Co-Cr-Si-Hf-Y

Control the Hf activity \( a_{Hf} \) in the alloys is key!
Project Objectives

• Develop a thermodynamic database for accelerated design of Ni-base alloys and coatings: Ni-Al-Co-Cr-Si-Hf-Y

• Study effects of reactive elements on the phase stability and oxide scale formation of bond coat alloys: Hf and Y additions to Ni-systems

• Experimental verification of thermodynamic predictions

• Assist in the development of the automated thermodynamic modeling tool (ESPEI)
Modeling Approach - CALPHAD

Thermochemical data: enthalpy, entropy, heat capacity, activity…

Phase equilibria data: liquidus, solidus, phase boundary/composition

Fewer data points supplemented by first-principles calculations

Experimental data plenty, hard to predict using first-principles

http://www.calphad.org

Gibbs energy (parameterized)

Phase diagrams, direct applications

Pure elements → Binary → Ternary → Multi-component

Practical applications
First-principles methodology

- The CALPHAD framework requires data that is difficult to access with experimental work (stable & unstable phases)
- **First-principles couples with CALPHAD Naturally!**
- **Density Functional Theory (DFT)** is an efficient way to calculate the ground state energies of condensed matter systems

**Input**

- approximates interactions within the crystalline lattice for calculations

**Output**

- Properties:
  - Ground state energy of a lattice
  - Total energies of different states
  - Finite temperature properties

Efficient! Fewer calorimetric experiments, access metastable states

Shang et al. (2010) *Computational Materials Science*
Ni-Al-Cr-Co-Si-Hf-Y

Phase I

<table>
<thead>
<tr>
<th>Ni-Al</th>
<th>Ni-Cr</th>
<th>Ni-Co</th>
<th>Ni-Si</th>
<th>Ni-Hf</th>
<th>Ni-Y</th>
<th>Al-Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Co</td>
<td>Al-Si</td>
<td>Al-Hf</td>
<td>Al-Y</td>
<td>Cr-Co</td>
<td>Cr-Si</td>
<td>Cr-Hf</td>
</tr>
<tr>
<td>Cr-Y</td>
<td>Co-Si</td>
<td>Co-Hf</td>
<td>Co-Y</td>
<td>Si-Hf</td>
<td>Si-Y</td>
<td>Hf-Y</td>
</tr>
</tbody>
</table>

Ni-containing ternary systems

<table>
<thead>
<tr>
<th>Ni-Al-Cr</th>
<th>Ni-Al-Co</th>
<th>Ni-Al-Si</th>
<th>Ni-Al-Hf</th>
<th>Ni-Al-Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr-Co</td>
<td>Ni-Cr-Si</td>
<td>Ni-Cr-Hf</td>
<td>Ni-Cr-Y</td>
<td></td>
</tr>
<tr>
<td>Ni-Co-Si</td>
<td>Ni-Co-Hf</td>
<td>Ni-Co-Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Si-Hf</td>
<td>Ni-Si-Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Hf-Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Prioritized systems to model for studying of the Hf and Y effect

Modeled, compatible descriptions  No description available  Modeled/Partly modeled
• CALPHAD → self-consistency and the possibility to extrapolate to multicomponent systems

ESPEI
Extensible, Self-optimizing Phase Equilibrium Infrastructure

- Semi-automated model parameter optimization
- Statistical analysis of results
- Reusable storage of “raw” data for potential remodeling

Challenge
Revisions of lower order systems → re-modeling of higher order systems

Partly financed by DOE

- S. Shang, Y. Wang, Z-K. Liu
  Magnesium Technology (2010)
- www.materialsgenome.com
I. Thermodynamic modeling of Ni-Hf, Ni-Al-Hf, and Ni-Cr-Hf
Objectives

- Phase stabilities in base alloys: Al-Cr-Ni + Hf additions

![Diagram showing phase stabilities in base alloys: Al-Cr, Al-Hf, Al-Ni, Cr-Hf, Cr-Ni, Hf-Ni, Al-Cr-Hf, Al-Cr-Ni, Al-Hf-Ni, Cr-Hf-Ni, Al-Cr-Hf-Ni.]

Literature

DFT

N/A
Ni-Hf thermodynamic re-modeling

• Built upon the previous modeling work by Tao Wang et al. (2001) on Ni-Hf
• Remodeling with new data
  • DFT data for B2 phase
  • DFT data for intermetallic compounds
  • DFT SQS data for fcc and bcc solid solution
  PSU
• EPMA data for Hf solubility in Ni
• EPMA data for phase stability of compounds
• Optical microscopy, DSC and XRD data on B2 Hf$_{50}$Ni$_{50}$
  Pitt
Ni-Hf DFT calculations

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Ni$_3$Hf</th>
<th>Ni$_7$Hf$_2$</th>
<th>Ni$_3$Hf-L12</th>
<th>$\alpha$-Ni$_3$Hf</th>
<th>Ni$_{21}$Hf$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_7$H$_3$</td>
<td>Ni$_{10}$Hf$_7$</td>
<td>X$_1$Hf$_1$-B33</td>
<td>NiHf-B2</td>
<td>X$_1$Hf$_2$-C16</td>
<td>BCC_A2</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finite Temperature DFT

0K DFT

No DFT

Experimental Data:
- ▲ Yeremenko et al. [6]
- ✗ Svechnikov et. al. [4]
- ▼ Selhaoui et al. [10]
- + Present Work

Previous modeling from Tao Wang et al. (2001) Z. Metallkd. 92 (2001) 5
Ni-Hf: thermodynamics

Enthalpy of Formation, J/mol-atom

- Selhaoui, calorimetry
- Bencze, KEMS
- Guo, calorimetry
- Levy, DFT

Mole Fraction Hf

Activity

T=1423.15 K

DFT – HfNi₃, HfNi on convex hull

T=1418.15 K

Bencze & Hilpert (1996) - Knudsen cell effusion mass spectrometry
Ni-Hf: fcc phase

Enthalpy of Mixing, J/mol vs Mole Fraction Hf

- DFT (○)
- DFT-SQS (●)

Temperature [K] vs Mole Fraction Hf

- fcc+γ'

DATABASE: User data 2015. 4.22
N=1, P=1E5
Ni-Hf: bcc phase

Enthalpy of Mixing, J/mol-atom

Mole Fraction Hf

Temperature [K]

Mole Fraction Hf

bcc-A2

DFT (○)

DFT-SQS (●)

B2

B2+bcc-A2

bcc-A2

B2
Calculated Hf solubility in fcc Ni

- **Present work**
- **Hajjaji**
- **Reinbach**
- **Wang**
- **Svechnikov**

Previous modeling in the literature

Current modeling
Calculated Ni-Hf phase diagram

Temperature [K]

Mole Fraction Hf

Liquid

B2

fcc

hcp

Liquid

HfNi

HfNi

HfNi
New cast alloys - Ternaries

Micrographs, 1100 °C

Al-Hf-Ni

Cr-Hf-Ni
New cast alloys - Ternaries

Al-Hf-Ni

Cr-Hf-Ni

Model solubility of $\text{Ni}_7\text{Hf}_2$
Ni$_7$Hf$_2$ new sublattice model to include Al solubility

<table>
<thead>
<tr>
<th>Compound</th>
<th>Prototype Structure</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_7$Hf$_2$</td>
<td>Zr$_2$Ni$_7$</td>
<td>C2/m</td>
</tr>
</tbody>
</table>

New Sublattice Model
(Hf,Ni)$_2$(Al,Ni)$_7$

Assumption: all Al goes into the Ni site
DFT endmembers:
(Hf)$_2$(Ni)$_7$, (Hf)$_2$(Al)$_7$, (Ni)$_2$(Ni)$_7$, (Ni)$_2$(Al)$_7$

Al,Ni Interaction parameter from experiments
Calculated Al solubility in Ni$_7$Hf$_2$

Considering Al solubility in Hf$_2$Ni$_7$

Experimental tie-triangle

Not considering

T = 1100 °C
Phase compositions in NiCrAl-Hf alloys

- γ
- γ'

Experiments

Current thermodynamic modeling
II. Prediction of Hf tolerance in NiCrAl bond coat alloys
Thermodynamic considerations of oxidation

3Hf + 2Al₂O₃ → 3HfO₂ + 4Al

ΔG⁰ = -RT × lnKₑq and K = \( \frac{a_{Al}^4}{a_{Hf}^3} \)

In order to suppress HfO₂:
must have K < Kₑq

Large composition space of bond coat alloys: Ni-Al-Co-Cr-Si-Hf-Y
Control the Hf activity \( a_{Hf} \) in the alloys is key!
Oxidation of NiCrAl-Hf alloys

Three Ni-Al-Cr + 0.1 at. % Hf alloys

Predicted HfO$_2$ formation “boundary” at 1000 °C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Phase Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 °C</td>
<td>γ-γ'</td>
</tr>
<tr>
<td>1100 °C</td>
<td>γ-γ'</td>
</tr>
<tr>
<td>1200 °C</td>
<td>γ</td>
</tr>
</tbody>
</table>

Calculated Al-Cr-Ni isothermal section

- γ
- γ'
- γ + γ'
- B2 + γ'
- B2 + γ + γ'
- B2 + γ

Hf content for HfO$_2$ formation, at.%

- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
- 0.6

Cr concentration, at.%

- 0
- 5
- 10
- 15
- 20
- 25
- 30

Mole Fraction Al

- 0.05
- 0.1
- 0.15
- 0.2
- 0.25
- 0.3
- 0.35
- 0.4
- 0.45
- 0.5

Mole Fraction Cr

- 0
- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
Determination of whether Hf oxidized or not

- No Hf oxidation (traces present in middle of scale probably left from transient stage)

- Localized Hf oxidation (this is a subjective call)

- Hf oxidation
Oxidation of NiCrAl-Hf alloys

Note: all three alloys contained 0.1 at. % Hf

Predicted HfO₂ formation “boundary” at 1200 °C

1200 °C

Hf content for HfO₂ formation, at.%

0.6
0.5
0.4
0.3
0.2
0.1
0

Cr concentration, at.%

0 5 10 15 20 25 30

- γ
- γ′
- γ + γ′
- B2 + γ′
- B2 + γ + γ′
- B2 + γ

7.5Cr-13Al

7.5Cr-17Al

13Cr-17Al

HfO₂ pegs

10 µm
• Effect of **temperature**: tolerance reduced (larger driving force for HfO$_2$ formation) with increasing temperature

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature 1</th>
<th>Temperature 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQ8</td>
<td>1100 °C</td>
<td>1200 °C</td>
</tr>
<tr>
<td>HQ9</td>
<td>1000 °C</td>
<td>1100 °C</td>
</tr>
</tbody>
</table>

Less zones with no oxidation
• Effect of Hf (more Hf promotes HfO2 formation)

HQ10: Ni-8Cr-17Al-0.05Hf

HQ8: Ni-8Cr-17Al-0.1Hf

1000 °C

1100 °C

1200 °C
- Effect of Cr (prediction: Hf tolerance decreases when Cr increases)

HQ8: Ni-8Cr-17Al-0.1Hf

HQ9: Ni-13Cr-17Al-0.1Hf
III. Preliminary results on the effect of Y
Ternary Assessments of Y-containing systems in Literature

<table>
<thead>
<tr>
<th>Base</th>
<th>Al-Co-Cr</th>
<th>Al-Co-Ni</th>
<th>Al-Cr-Ni</th>
<th>Co-Cr-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X_1)-(X_2)-Y</td>
<td>Al-Co-Y</td>
<td>Al-Cr-Y</td>
<td>Al-Ni-Y</td>
<td>Co-Cr-Y</td>
</tr>
<tr>
<td>(X_1)-(X_2)-Hf</td>
<td>Al-Co-Hf</td>
<td>Al-Cr-Hf</td>
<td>Al-Ni-Hf</td>
<td>Co-Cr-Hf</td>
</tr>
<tr>
<td>(X_1)-(X_2)-Si</td>
<td>Al-Co-Si</td>
<td>Al-Cr-Si</td>
<td>Al-Ni-Si</td>
<td>Co-Cr-Si</td>
</tr>
<tr>
<td>(X_1)-Hf-Y</td>
<td>Al-Hf-Y</td>
<td>Co-Hf-Y</td>
<td>Cr-Hf-Y</td>
<td>Ni-Hf-Y</td>
</tr>
<tr>
<td>(X_1)-Hf-Si</td>
<td>Al-Hf-Si</td>
<td>Co-Hf-Si</td>
<td>Cr-Hf-Si</td>
<td>Ni-Hf-Si</td>
</tr>
<tr>
<td>(X_1)-Si-Y</td>
<td>Al-Si-Y</td>
<td>Co-Si-Y</td>
<td>Cr-Si-Y</td>
<td>Ni-Si-Y</td>
</tr>
</tbody>
</table>

| Additions | Hf-Si-Y |

- **Assessment available**: Good from binaries
- **Assessment not found**: Assessment under investigation
Y Solubility in Ni

Interactions in the fcc phase from Huang et al. (2015).

More work needs to be done to determine the Ni-Y interaction in fcc phase.


Stability of $Y_2O_3$

Hf tolerance concept not present: $Y_2O_3$ always more stable at low $P_{O2}$
Oxidation of Ni-Al-Cr-Y Alloys at 1200 °C: possible correlation between oxide scale formation and yittrides formation

Yittrides tolerance curves

Future Works in Phase II

• Continue to investigate the Y and Si effects on oxide scale formation in Phase II
• Study the \textit{Hf+Y co-doping} effects on oxide scale
• Planned publications so far:
  1. Hf-Ni Binary thermodynamic modeling
  2. Al-Hf-Ni, Cr-Hf-Ni Ternaries thermodynamic modeling
  3. Al-Cr-Hf-Ni prediction + Oxidation experiments
• The further development of ESPEI for automation of thermodynamic modeling
Acknowledgements

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Thank you for your attention.
Any questions?