Towards Predicting Reactive-element Tolerances in the Compositional Design of Al$_2$O$_3$-scale Forming Alloys and Coatings

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Key Questions

• Understand the controlling factors that affect the formation of Al$_2$O$_3$ scale vs internal oxidations

• Determine the effects of alloying elements on retardation of Al$_2$O$_3$ scale growth

• Explore new compositional design of Al$_2$O$_3$-scale forming alloys and coatings
• Thermally grown oxide (TGO)
  • Typically $\alpha$-$\text{Al}_2\text{O}_3$ for very high temperature applications (T > 1000 °C).
  • Established using **bulk alloys** and **metallic coatings**.

Alumina Scale Formation on Ni-Al Alloys

Oxidation carried out in 0.1 atm pure O₂


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Critical Al Concentration in $\gamma$–Ni$_{1-x}$Al$_x$

$N_{Al}^{*(0)}$ Using Zhao’s Model
$N_{Al}^{**(0)}$ Using Wagner’s Model

$N_{B}^{*(0)} = \sqrt{\pi N_{O}^{(s)} D_{O}} \cdot \frac{\pi}{\nu D_{B}} \beta$

$\beta = \left( \frac{1}{\left( \frac{V_{BO}^{*}}{g_{BO} V_{alloy}} - \frac{V_{BO}^{*}}{V_{alloy}^{*}} + 1 \right)^2 + g_{BO}^{*}} \right)$

Oxides Block Diffusion

Model for oxide blocking comes close to transition data

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

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

\[
\begin{align*}
\text{Al}_b^{3+} & \xrightarrow{\text{Al}_l^{3+}} \text{Al}_b^{3+} \\
\text{O}_l^{2-} & \xrightarrow{\text{O}_b^{2-}} \text{O}_l^{2-}
\end{align*}
\]

Oxygen

Al₂O₃ Scale

Alloy

\[k_p\] Outward transport

Fe, Ni-based with RE vs. Without

- Down 2x
- RE reduces \(D_b^{Al}\) by 4x

RE = Hf, Y, Zr, La, ...

Oxidation of Ni-20Al-20Pt-xHf at 1150°C

- Reactive elements offer added oxidation resistance.
- High concentrations results in over-doping.

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Cross-sectional Images After 100 h Oxidation at 1150°C

- This over-doping concentration is usually found by trial and error and depends on alloys.
- Can it be determined by the thermodynamic criteria for this event?

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Computational Thermodynamics and Materials Design

\[ dU = TdS - PdV + \sum \mu_i dN_i = \sum Y^a dX^a \]

- Equilibrium thermodynamics

\[ dU = \sum Y^a dX^a - D_{ip} d\xi + 0.5D_2 (d\xi)^2 \]

- Irreversible/non-equilibrium thermodynamics

\[ S = -k_B \sum p_i \ln p_i \]

- Statistical: Entropy for probability of configurations/states by Boltzmann/Plank/Gibbs.
CALPHAD modeling: Individual phases

Thermochemical data: enthalpy, entropy, heat capacity, activity

Phase equilibrium data: phase boundary, phase stability

Gibbs Energy of Individual Phases

Applications

Pure elements → Binary → Ternary → Multicomponent

Thermochemical and phase equilibrium data are not independent!

First-Principles Calculations and CALPHAD Modeling of Thermodynamics

Zi-Kui Liu

Predictability
First-principles
Modeling
Experiments
Statistical Mechanics

Liu, J. Phase Equilib. Diffus., 30 (2009), 517
Properties of Individual Phases and Interfaces: Dependence on T, P, xi

- Electronic structures
- Thermal Properties
  - Heat capacity
  - Enthalpy, entropy, free energy
  - Thermal expansion/contraction
- Transport Properties
  - Diffusion coefficient
  - Seebeck coefficients
  - Heat of transport
- Interfacial properties
  - Stacking fault energy
  - Anti-phase boundary energy
  - Grain boundary and interfacial energy
- Mechanical properties
  - Elastic moduli/Compressibility
  - Dislocations mobility
  - Relative creep rate
- Kinetic Properties
  - Interface mobility
- Physical properties
  - Melting and Glass transition
  - Electrical properties
    - Magnetic properties
  - Optical properties
- Mechanical properties
  - Fracture toughness
  - Plasticity of single crystal
  - Ductility and formability
  - Hardness
  - Yield strength
  - Fatigue strength

Liu, J. Phase Equilib. Diffus., 30 (2009), 517
Ni-Al-Cr-Hf-O

Modeled in the Literature

Modeled by PSU

X=Al,Cr,Hf
HfO$_2$ Stability in an Al$_2$O$_3$ Forming Alloy

\[ \text{Gheno, Zhou, Ross, et al. (2017). Oxidation of Metals.} \]
Hf Activity Changes with Hf Concentration, Al Concentration and Phases Present

In single phase

\[ \frac{\partial \mu_{Hf}}{\partial N_{Al}} > 0 \]

In two-phase region: average of two phases

Ni-xAl-5Cr-yHf

T=1150 °C
Defining Hf tolerance

\[ T = 1150 \, ^\circ \text{C} \]

\[ \frac{\text{ACR(O}_2\text{,GAS)}}{\text{Al}} = 6.7 \cdot 10^{-8} \]

\[ x_{\text{Hf}}^\text{max} = 0.24 \, \text{at\%} \]
HfTolerance: Engineering in Composition Space

T=1150 °C
Ni-xAl-5Cr-yHf

HfO₂ stable

γ
γ' + γ'
β + γ'

Only Al₂O₃

Hf content for HfO₂ formation, at.%

Al concentration, at.%
Reactive Element Doping: Ni-20Al-5Cr-0.1Hf (at\%)

- Air, 1150 °C

\[ \Delta m / A \text{ (mg/cm}^2\text{)} \]

- Time (h)

\[ \text{Ni-20Al-5Cr} \]

- Only Al\(_2\)O\(_3\) is stable

- Hf content for HfO\(_2\) formation, at.\%

- Al concentration, at.\%

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Experimental Results

Two Major Factors Affecting Hf Tolerance In The Design of High Temperature Alloys

• **γ’ phase stability:** In Ni-Al-X systems, elements can be added which increase the γ’ phase fraction when substituting Ni or Al.

• **Hf-X chemical interaction:** In the Al-Hf-Ni-X systems, elements can be added which decrease the Hf activity in γ and γ’.
  • Effect of X on activity of Hf can be found by determining the enthalpy of mixing between Hf and X.
Alloying Effects on $\gamma'$ Phase Stability in Ni-Al-X

Mole fraction, X

Mole fraction, Al

T=1000°C

Elements: Cr, Co, Cu, Fe, Ga, Hf, Mn, Pt, Re, Si, Ti, W

Calculations Using Special Quasi-random Structures to Calculate Hf-X Mixing Enthalpy

![Diagram showing mixing enthalpies for various Hf-X pairs.]
Calculated Effect of Pt on Hf Activity

T = 1000 °C

Ni-xAl-5Cr-0.1Hf

Ni-xAl-5Cr-0.1Hf-1Pt
Calculated Effect of Si on Hf Activity

T = 1000 °C

Ni-xAl-5Cr-0.1Hf

Ni-xAl-5Cr-0.1Hf-1Si
Calculated Effect of Cr on Hf Activity

Ni-xAl-5Cr-0.1Hf

Ni-xAl-6Cr-0.1Hf

T=1150 °C
Cross-Sectional Images of Ni-20at.%Al-Pt-Hf γ/γ' Alloys After 500 Oxidation Cycles at 1150°C in Air
Hf Tolerance: Ni-20Al-5Pt-0.5Hf

![Graph showing Hf content for HfO2 formation vs Al concentration, with NiAl2O4, Al2O3, and HfO2 phases indicated.]

- Hf content for HfO2 formation, at.%
- Al concentration, at.%
Hf Tolerance: Ni-20Al-20Pt-0.5Hf

Provided by Dr. Brian Gleeson at the University of Pittsburg
Parameters:

\( f^\gamma = 0.57 \)

\( \chi_{Al} = 17 \text{ at}\% \)

\( \chi_{Cr} = 8 \text{ at}\% \)

Alloy:

Ni-17Al-8Cr
Engineering a RE-doped Alloy/Coating: Doping with Hf

Parameters:

\[
\begin{align*}
\chi_{Al} &= 17 \text{ at}\% \\
\chi_{Cr} &= 8 \text{ at}\%
\end{align*}
\]

Alloy:

Ni-17Al-8Cr-(<0.15)Hf

T = 1100 °C
Experimental Results for Hf Doped Alloy

Alloy: Ni-17Al-8Cr-(0.1)Hf

• The $\gamma'$ phase in Ni-superalloys produces an appreciable decrease in Hf activity compared to the $\gamma$ phase, resulting in a high solubility of Hf in $\gamma'$.
• The Hf tolerance, a thermodynamic criterion for Hf over-doping, was established in terms of the relative stabilities of HfO$_2$ and Al$_2$O$_3$ and , showing excellent agreement with observations in oxidation experiments.
• First-principles calculations were used to predict the effects of alloying elements on Hf tolerance, with favorable results demonstrated for an alloy.
• The developed approach has the potential for applications such as the effects of CO$_2$, steam, and other service conditions.
• Similar approaches may be developed for the Cr$_2$O$_3$ scale growth.