Towards Predicting Reactive-element Tolerances in the Compositional Design of Al_2O_3-scale Forming Alloys and Coatings

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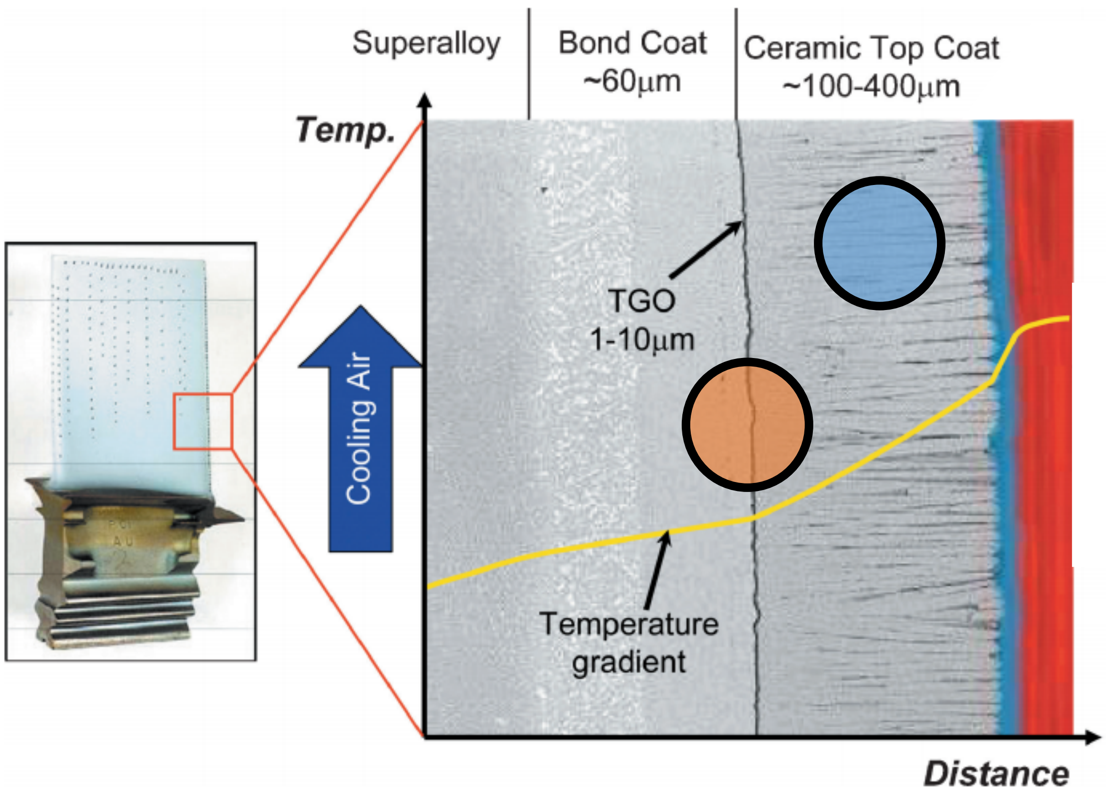
Key Questions

- Understand the controlling factors that affect the formation of Al_2O_3 scale vs internal oxidations
- Determine the effects of alloying elements on retardation of Al_2O_3 scale growth
- Explore new compositional design of Al_2O_3-scale forming alloys and coatings

Bond Coats in Turbines

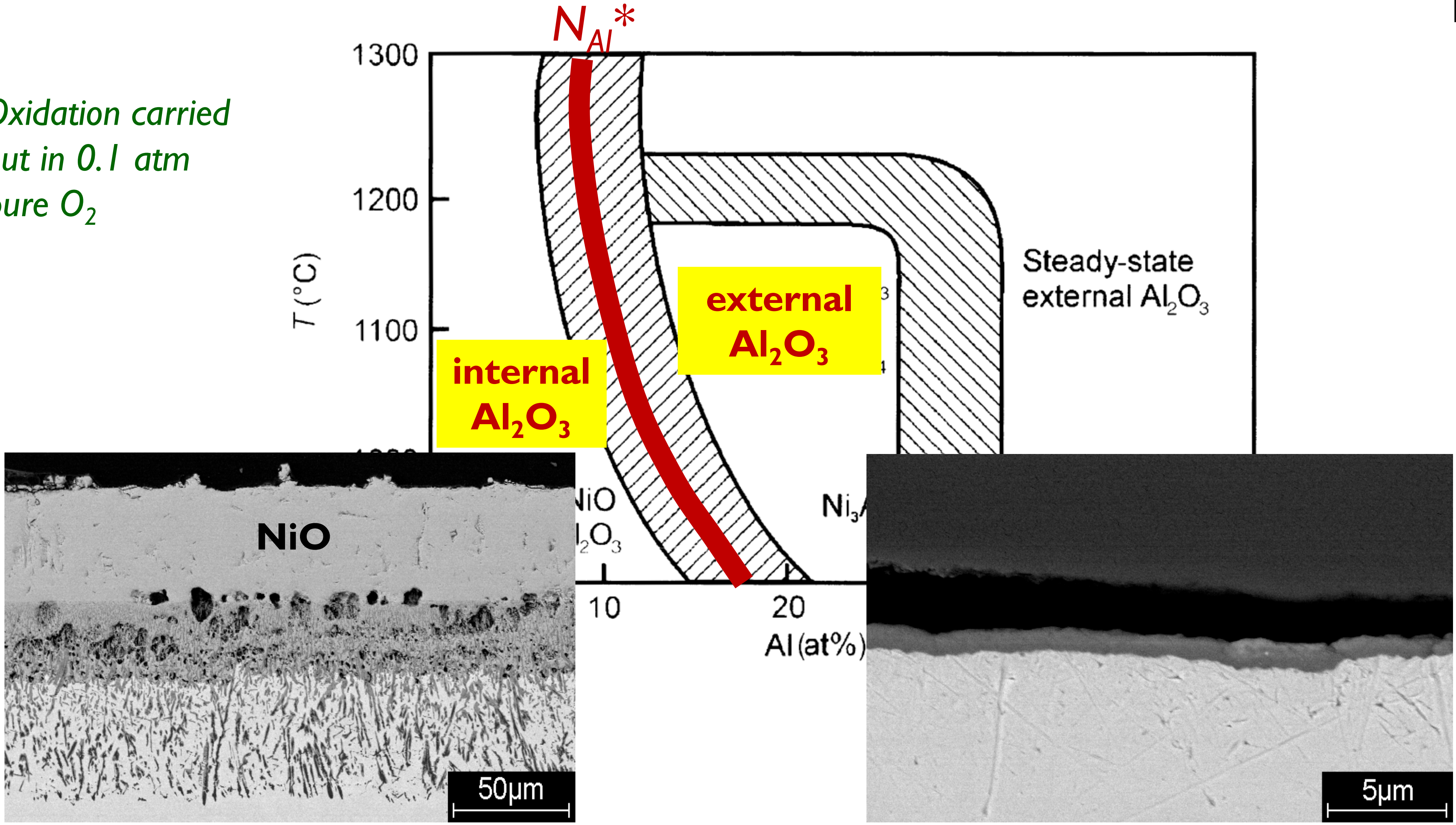


- **Thermally grown oxide (TGO)**
  - Typically α-Al_2O_3 for very high temperature applications (T> 1000 °C).
  - Established using **bulk alloys** and **metallic coatings**.

Gleeson, B. (2006). *Journal of Propulsion and Power*, *22*(2), 375–383.

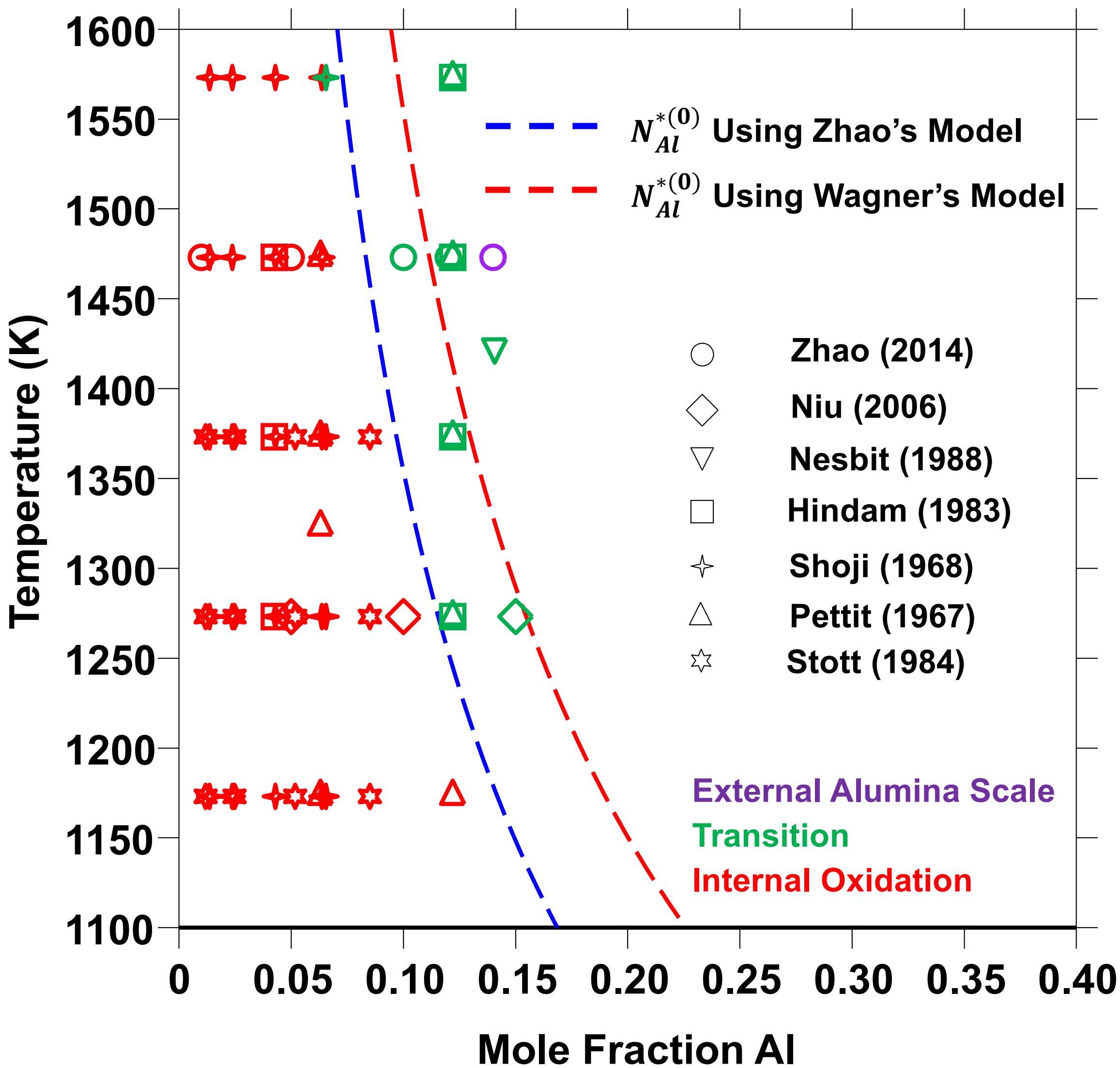
Alumina Scale Formation on Ni-Al Alloys

Oxidation carried out in 0.1 atm pure O_2



F.S. Pettit, "Oxidation mechanisms for Ni-Al Alloys at temperatures between 900 and 1300°C," *AIME Met. Soc. Trans.*, **239** (1967) 1296.

Critical Al Concentration in γ –$Ni_{1-x}Al_x$



$$N_B^{*(0)} = \sqrt{g^*_{BO_\nu},\frac{V_{alloy}}{V_{BO_\nu}}\frac{D_O N_O^{(s)}}{D_B}\frac{\pi}{2\nu}}$$

Oxides Block Diffusion

$$N_B^{*(0)} = \sqrt{\frac{\pi N_O^{(s)} D_O}{\nu D_B}\beta}$$

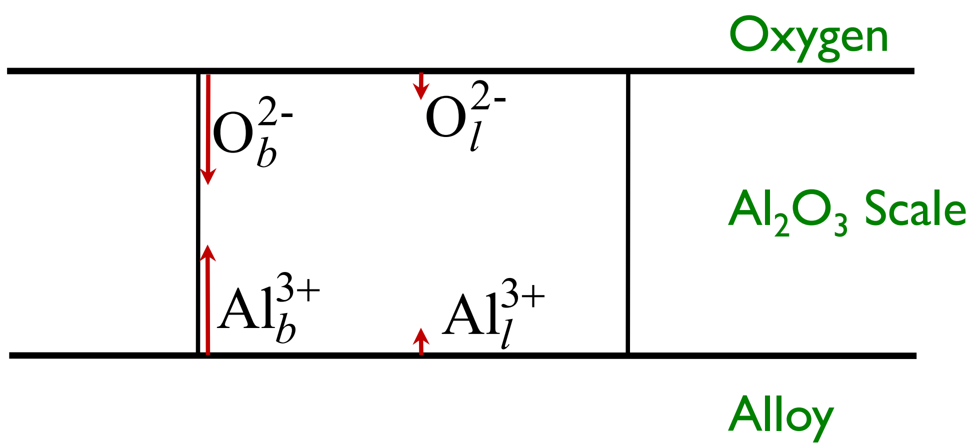
$$\beta = \left(\frac{1}{\left(\frac{V_{BO_\nu}}{g_{BO_\nu}V_{alloy}} - \frac{V_{BO_\nu}}{V_{alloy}} + 1\right)\frac{2+g_{BO_\nu}}{1-g_{BO_\nu}}}\right)$$

Model for oxide blocking comes close to transition data

Ross, AJ. Master Thesis Dissertation. The Pennsylvania State University, 2015.

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

Al_2O_3 scale growth is dominated by grain-boundary diffusion at the temperatures of interest

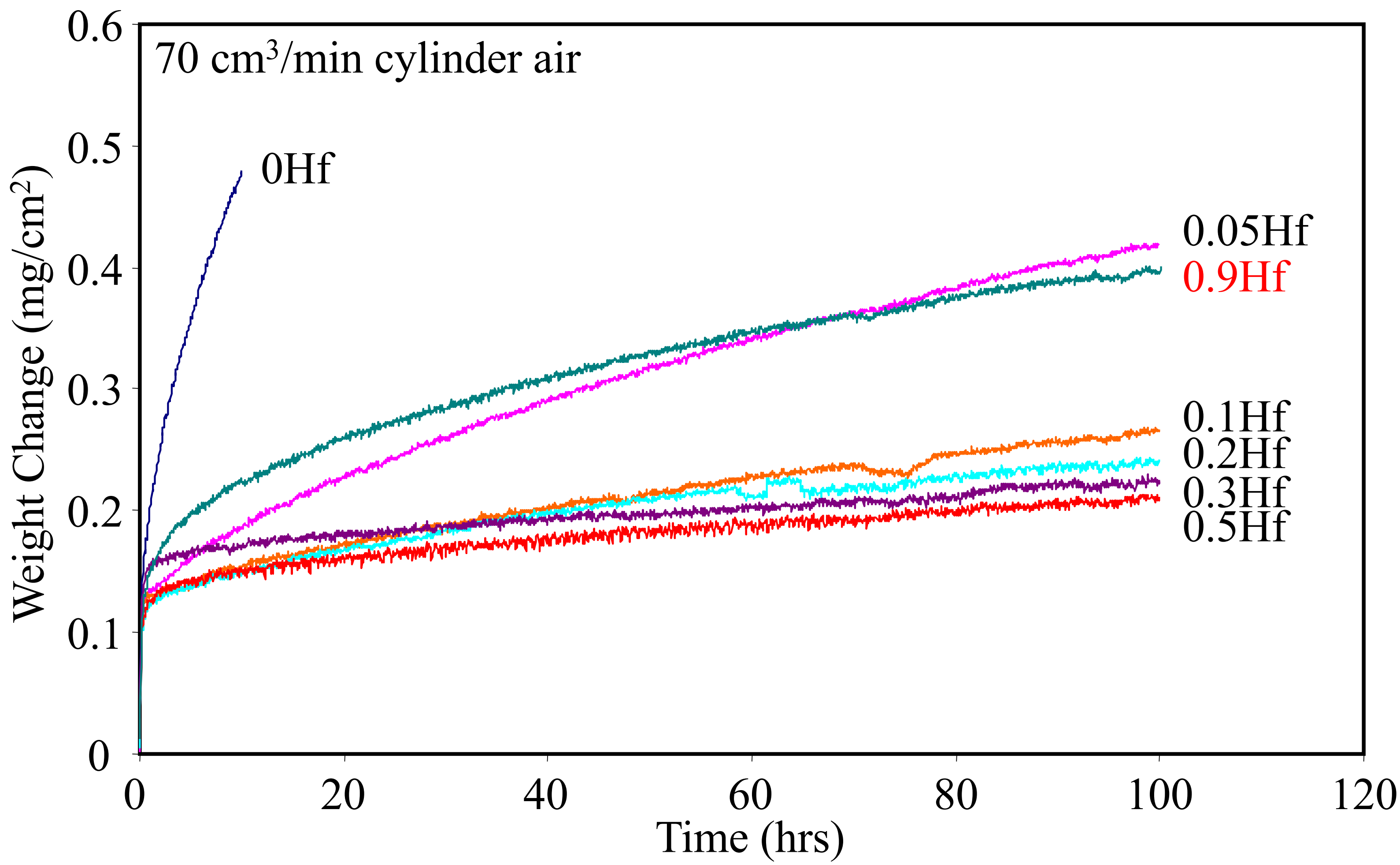


	k_p	Outward transport
Fe, Ni-based with RE *vs.* Without	**Down 2×**	**RE reduces D_b^{Al} by 4×**

RE = Hf, Y, Zr, La, …

P.Y. Hou, "Impurity effects on alumina scale growth," *J. Am. Ceram. Soc.*, **86** (2003) 660.

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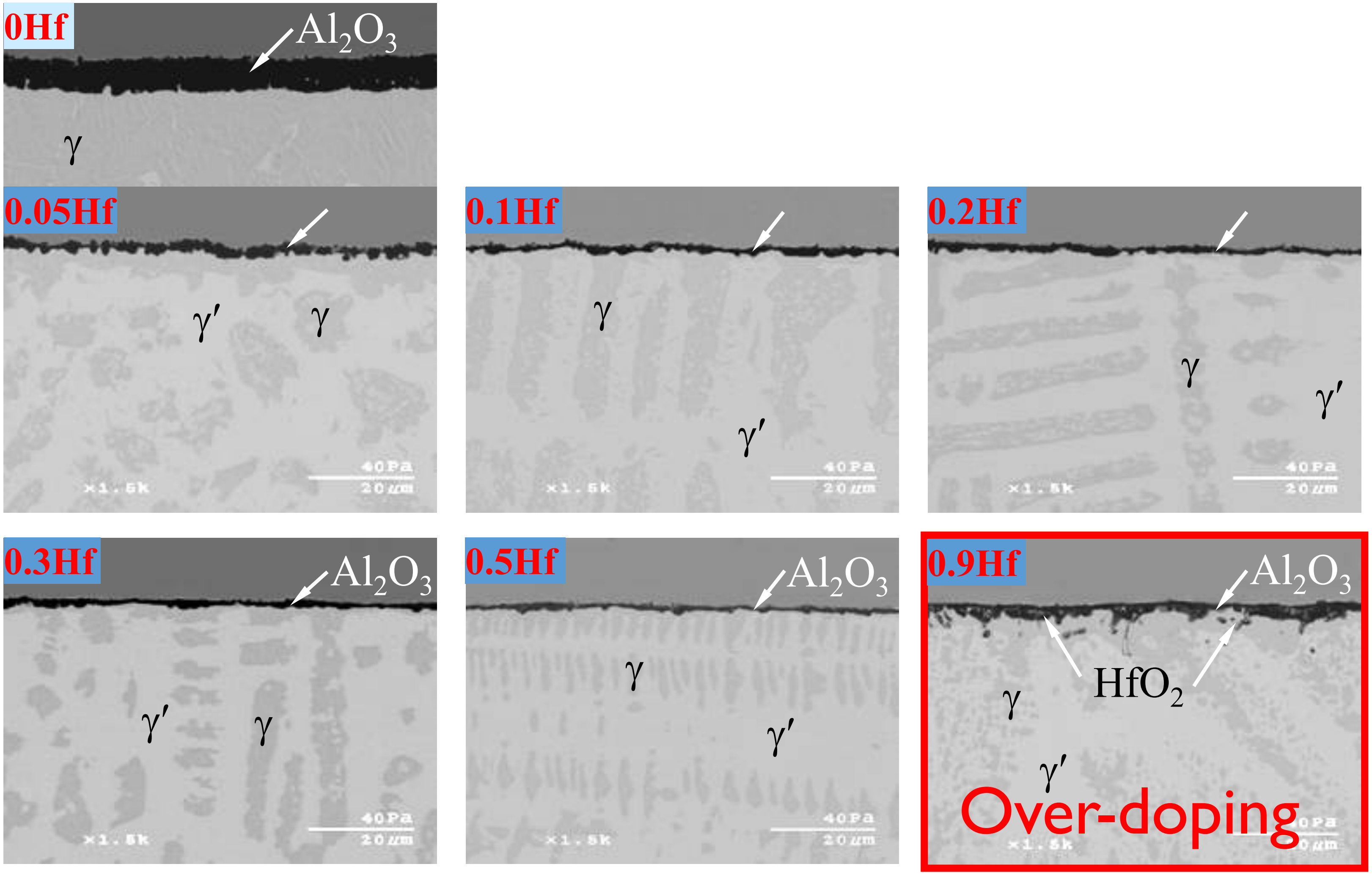
Cross-sectional Images After 100 h Oxidation at 1150°C



- 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?

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

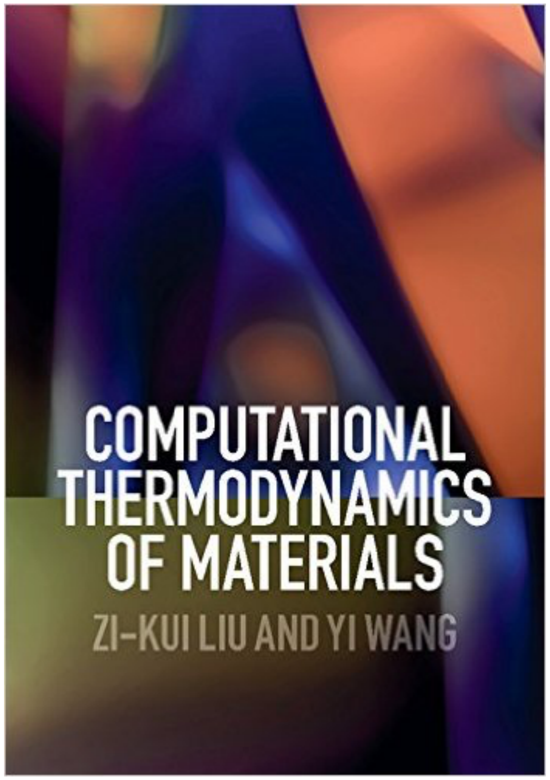
- Equilibrium thermodynamics

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

- Irreversible/non-equilibrium thermodynamics

$$S = -k_B \sum p_i ln p_i$$

- Statistical: Entropy for probability of configurations/states by Boltzmann/Plank/Gibbs.



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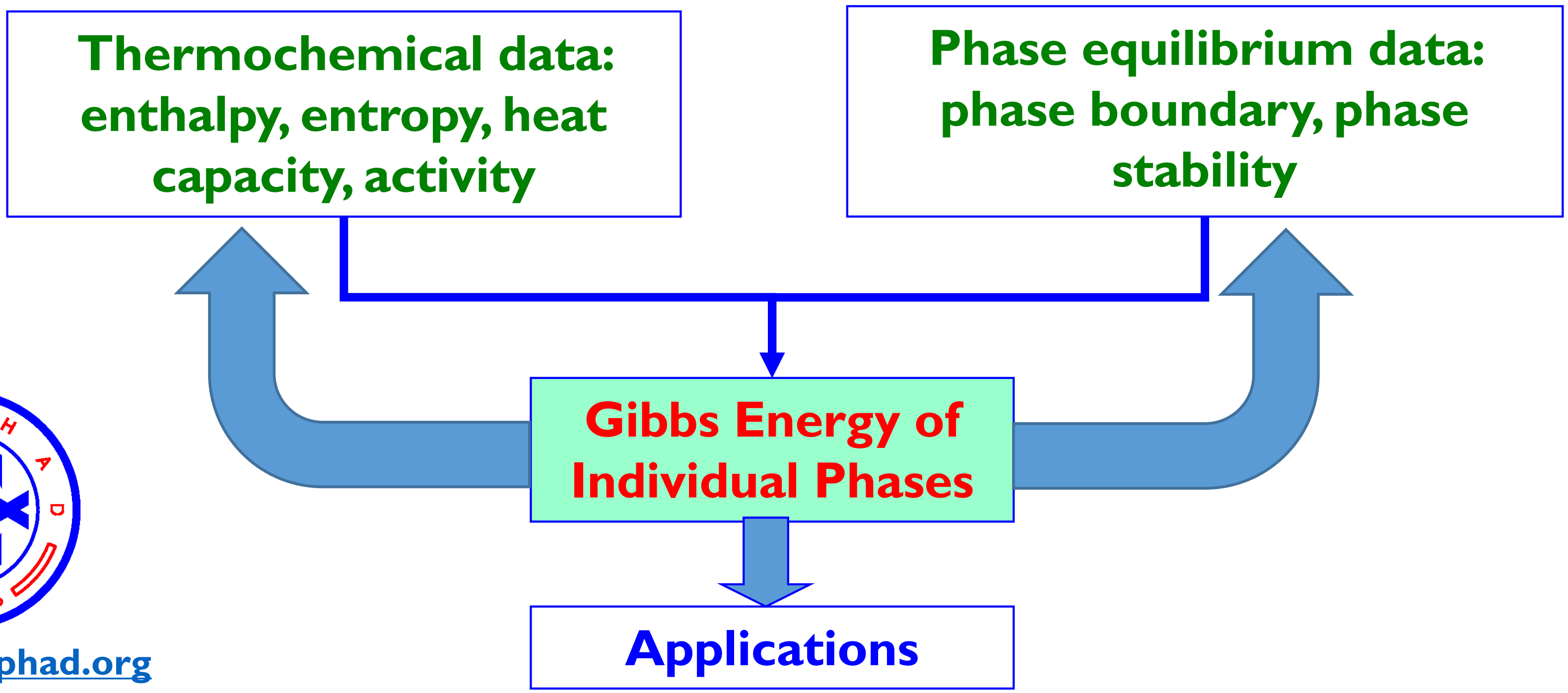
CALPHAD modeling: Individual phases



www.calphad.org
www.journals.elsevier.com/calphad

Pure elements → Binary → Ternary → Multicomponent

Thermochemical and phase equilibrium data are not independent!

Kaufman & Bernstein: *Computer Calculation of Phase Diagram. 1970*

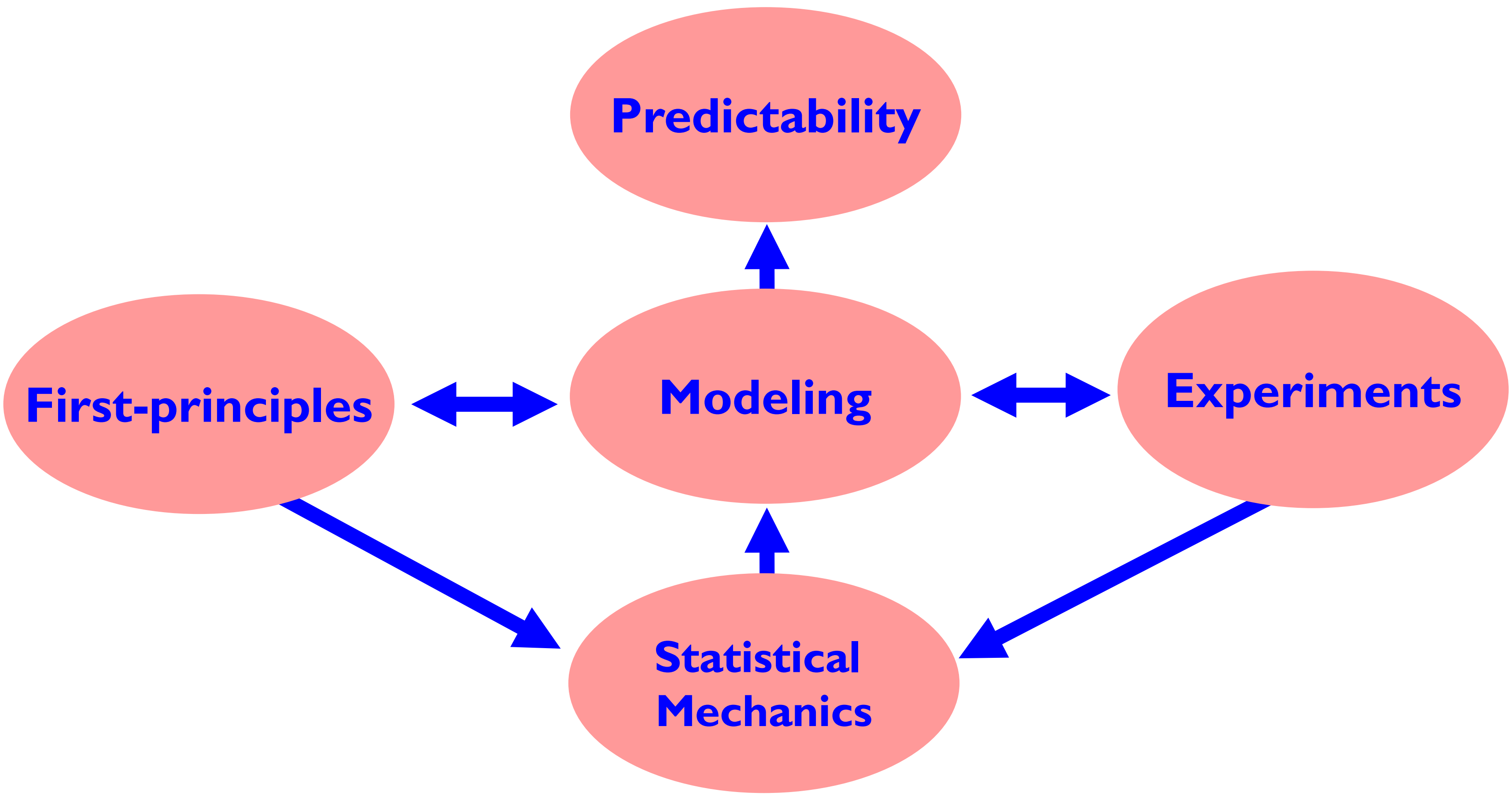
DFT and Thermodynamic modeling

JPEDAV (2009) 30:517–534
DOI: 10.1007/s11669-009-9570-6

Basic and Applied Research: Section I

First-Principles Calculations and CALPHAD Modeling of Thermodynamics

Zi-Kui Liu



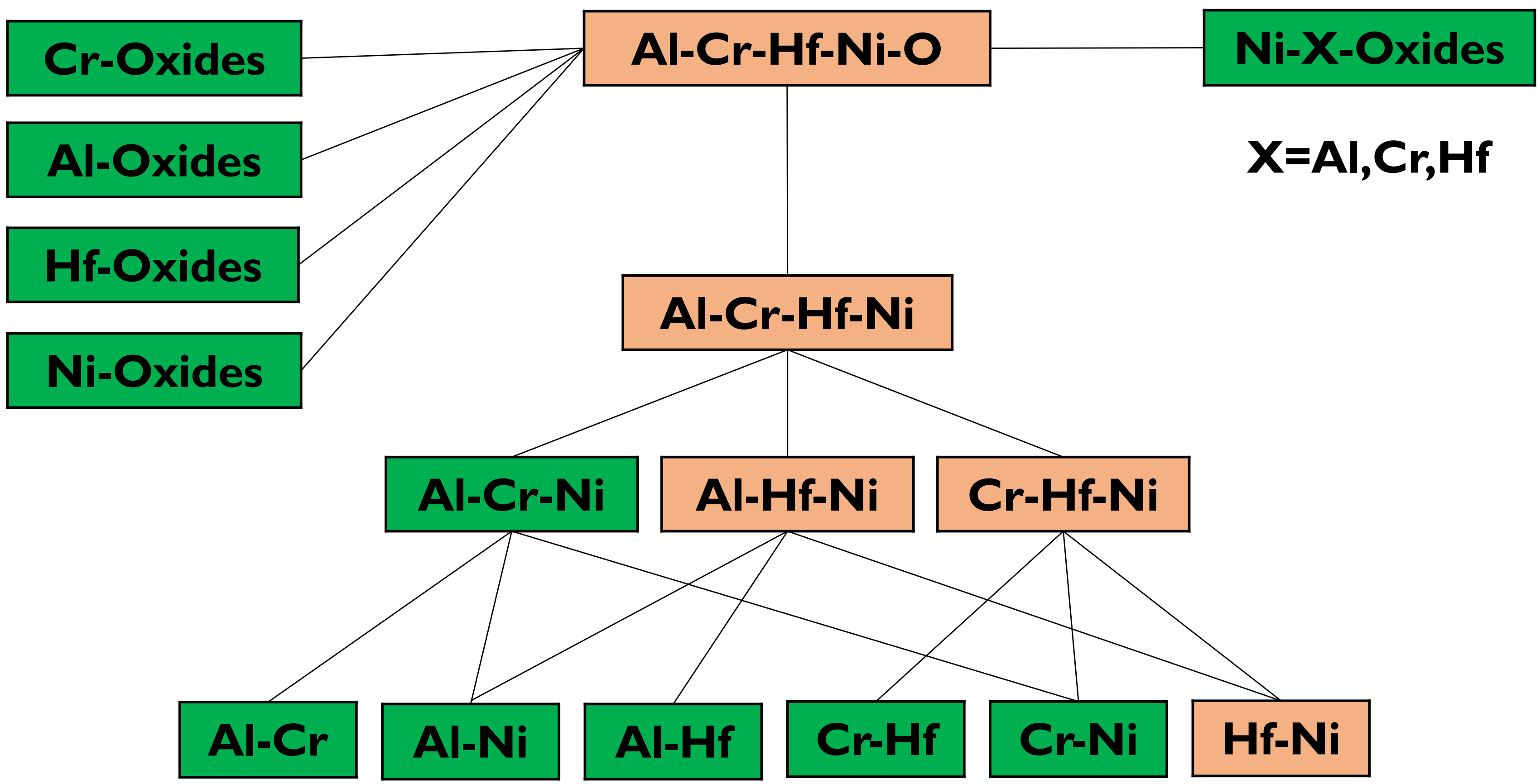
Liu, *J. Phase Equilib. Diffus.*, 30 (2009), 517

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

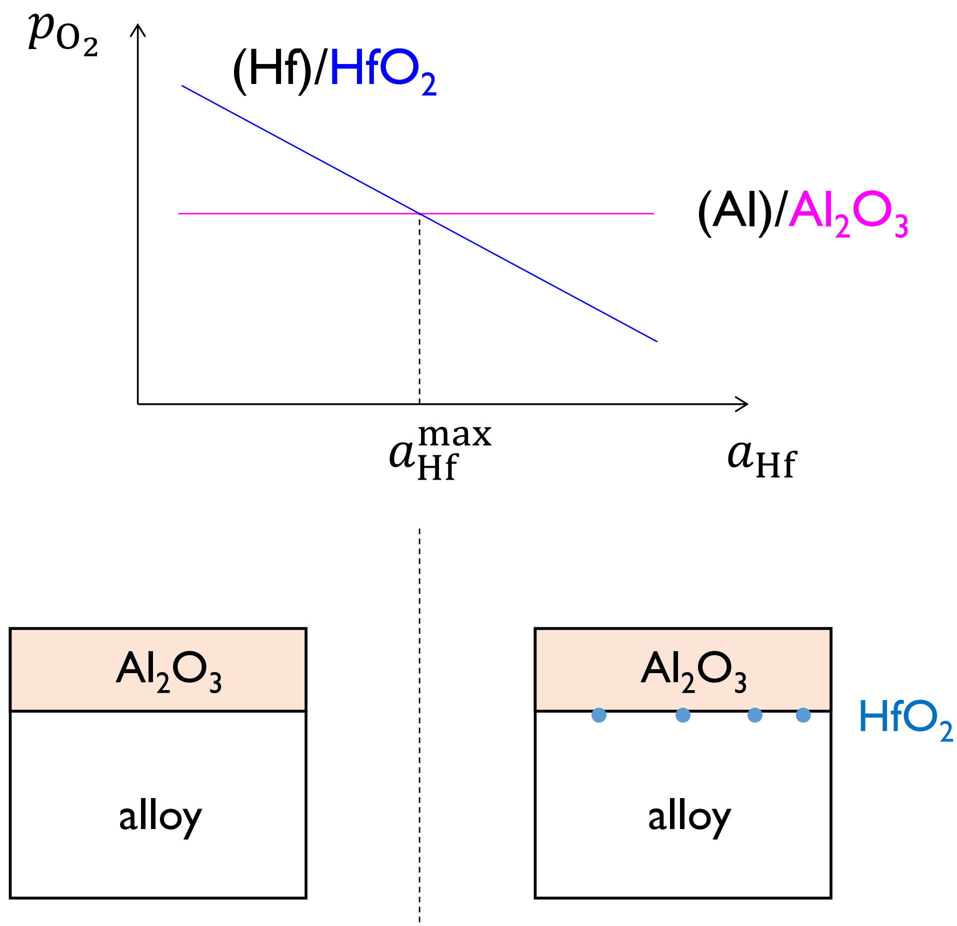
Ni-Al-Cr-Hf-O



Modeled in the Literature

Modeled by PSU

HfO_2 Stability in an Al_2O_3 Forming Alloy



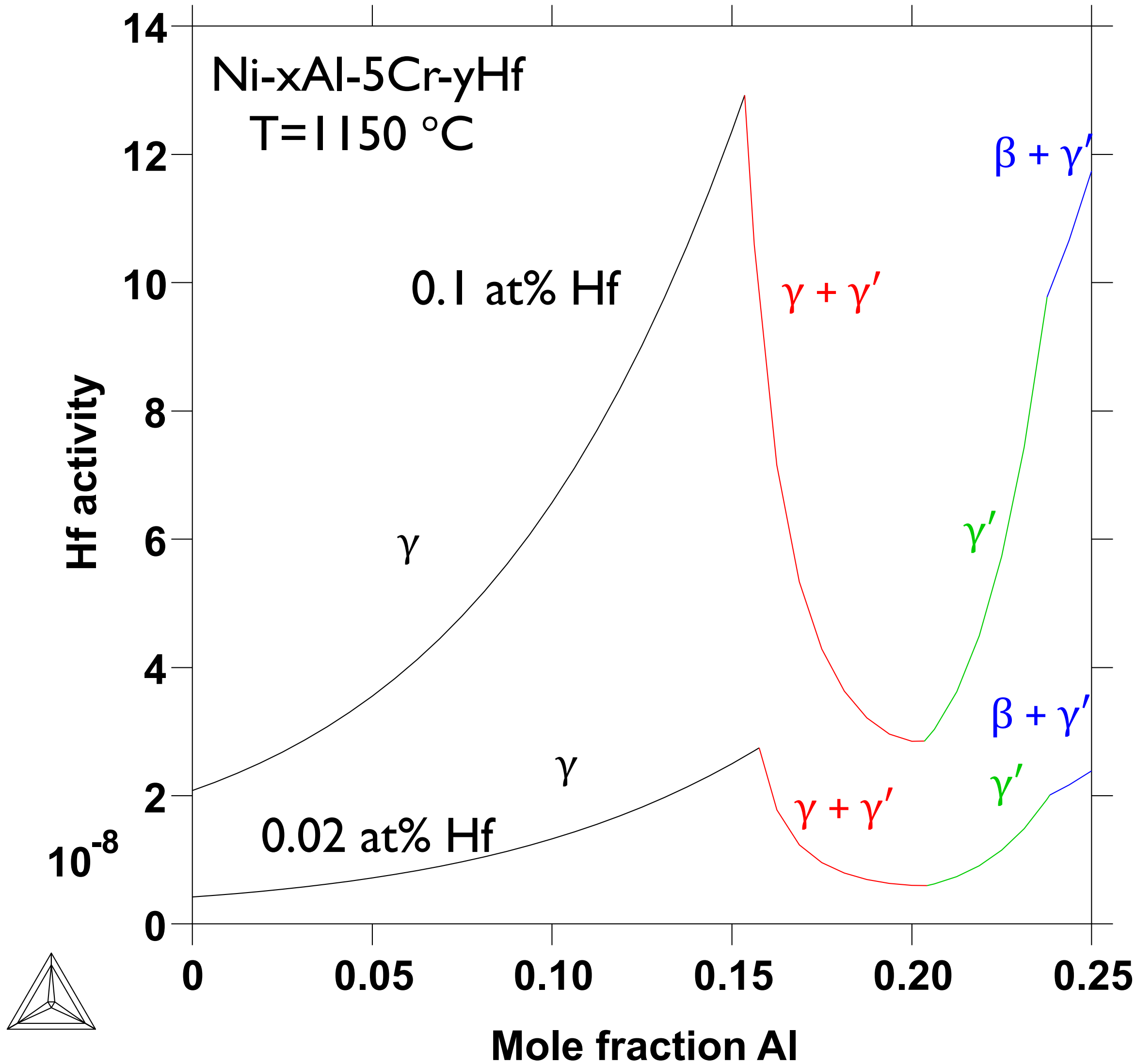
Gheno, Zhou, Ross, et al. (2017). *Oxidation of Metals*.

Hf Activity Changes with Hf Concentration, Al Concentration and Phases Present

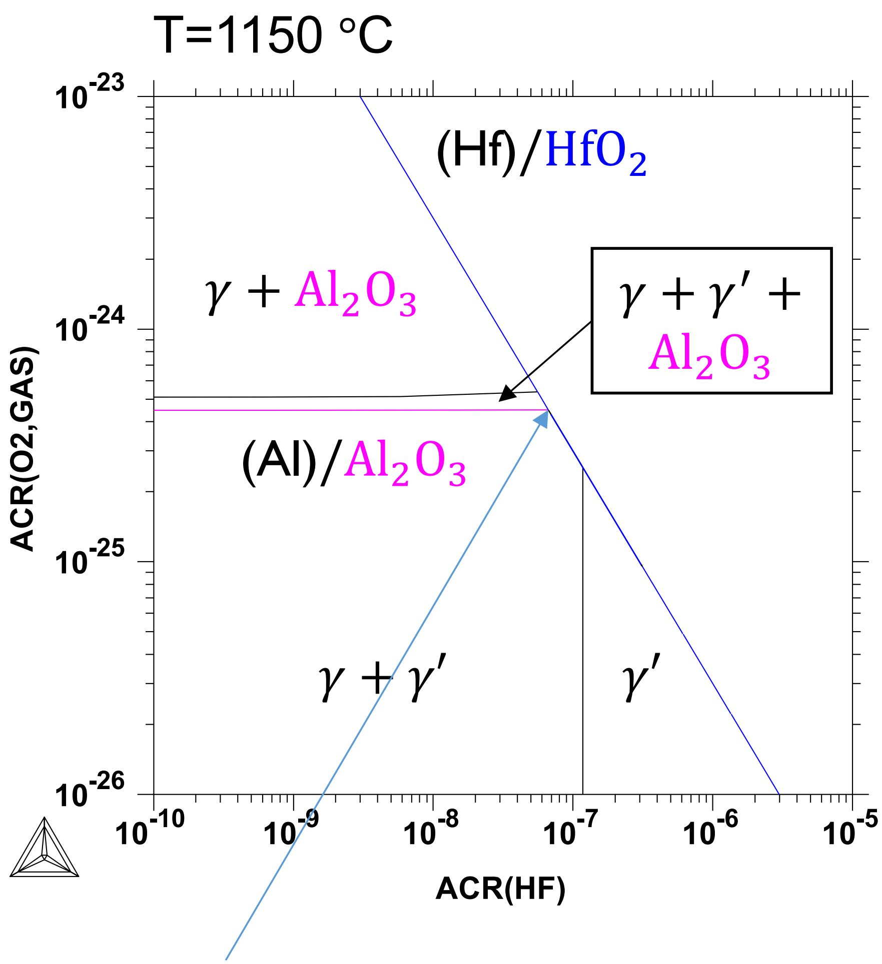
In single phase

$$\frac{\partial \mu_{Hf}}{\partial N_{Al}} > 0$$

In two-phase region: average of two phases



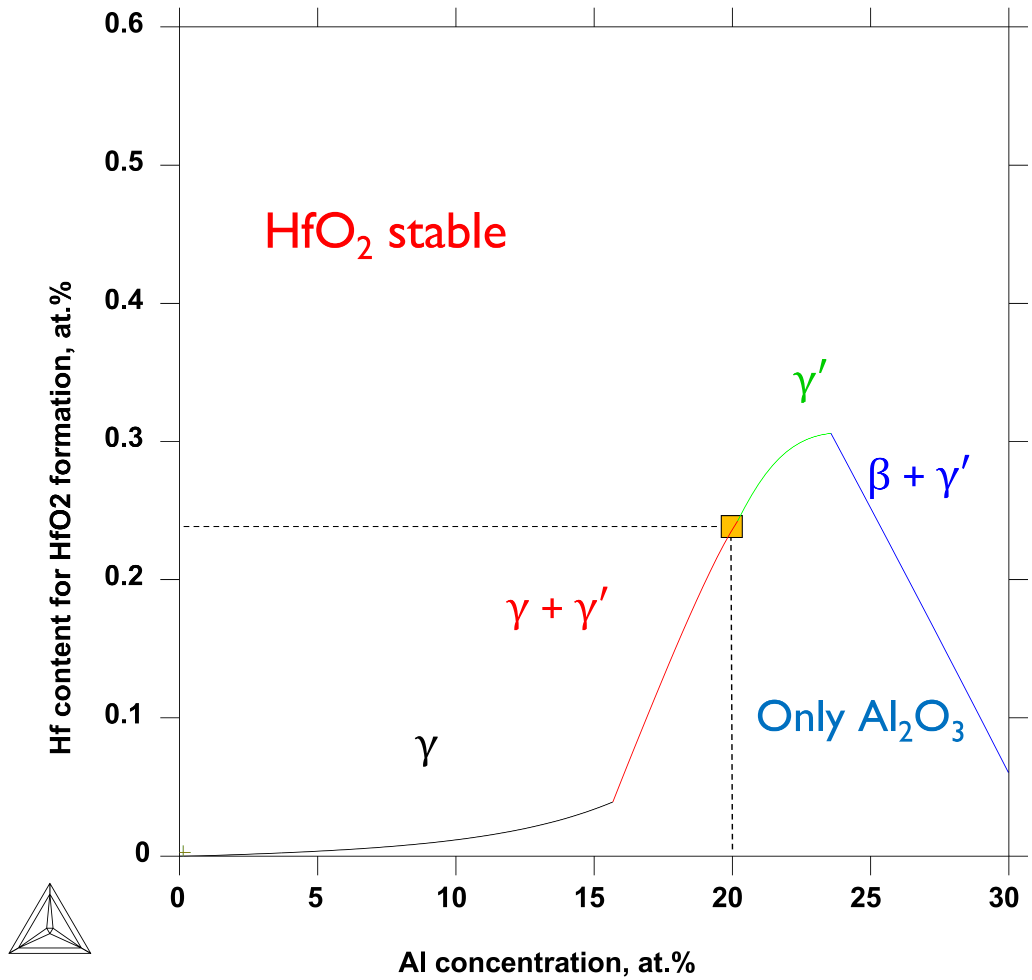
Defining Hf tolerance



$$a_{\mathrm{Hf}}^{\max} = 6.7 \cdot 10^{-8}$$

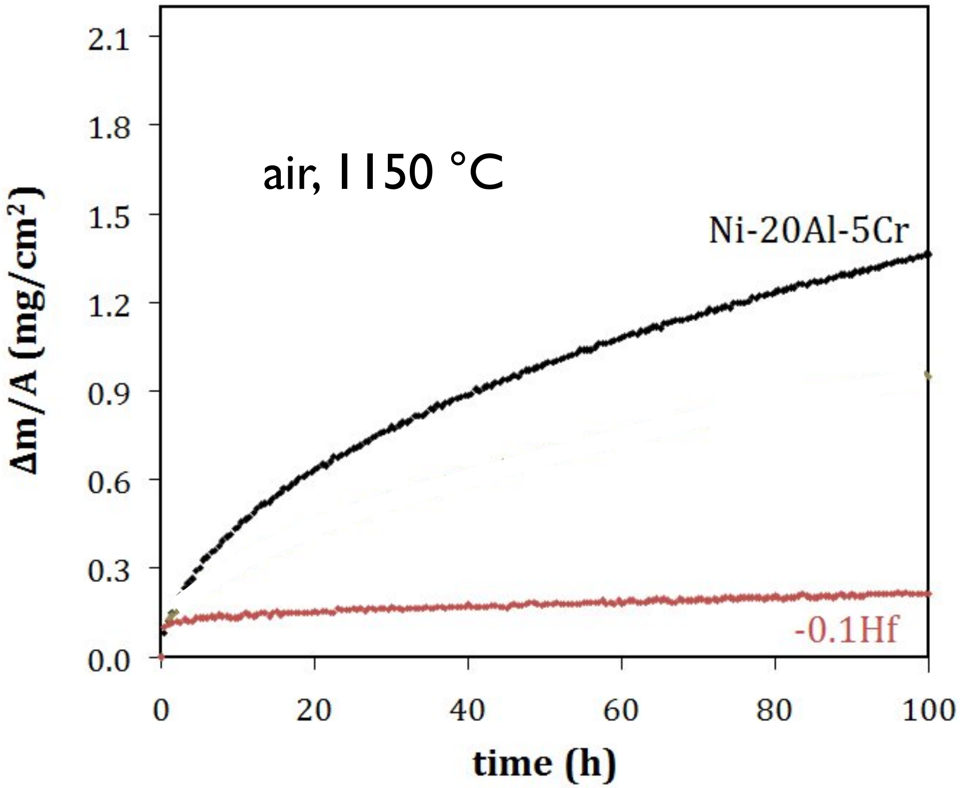
$$x_{\mathrm{Hf}}^{\max} = 0.24\ \mathrm{at\%}$$

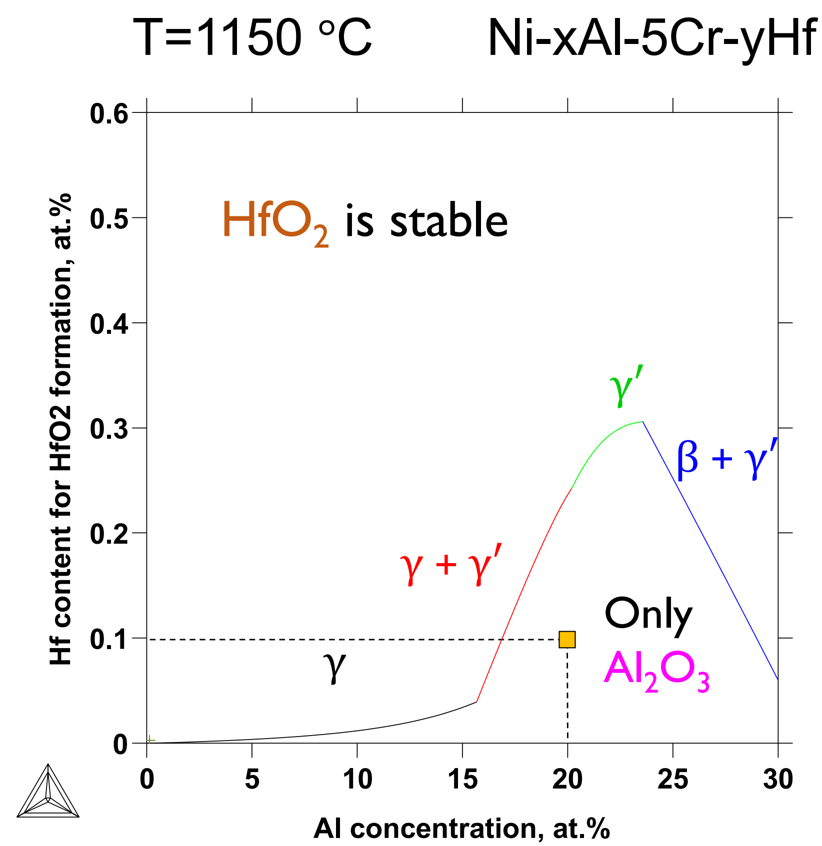
Hf Tolerance: Engineering in Composition Space

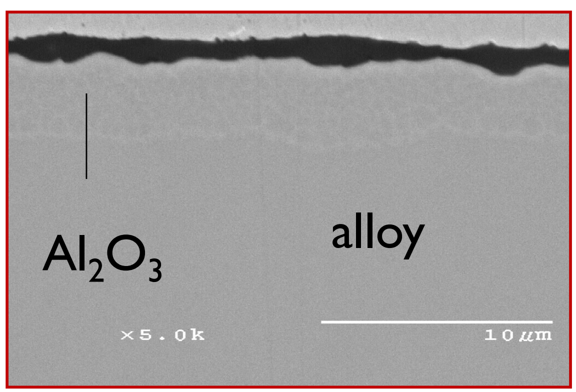


T=1150 °C
Ni-xAl-5Cr-yHf

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

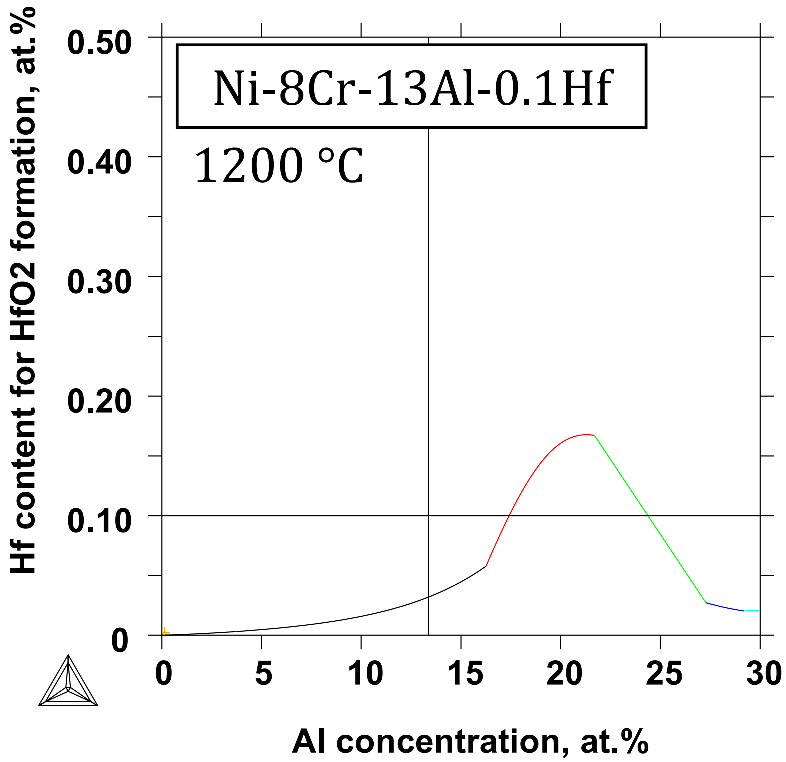


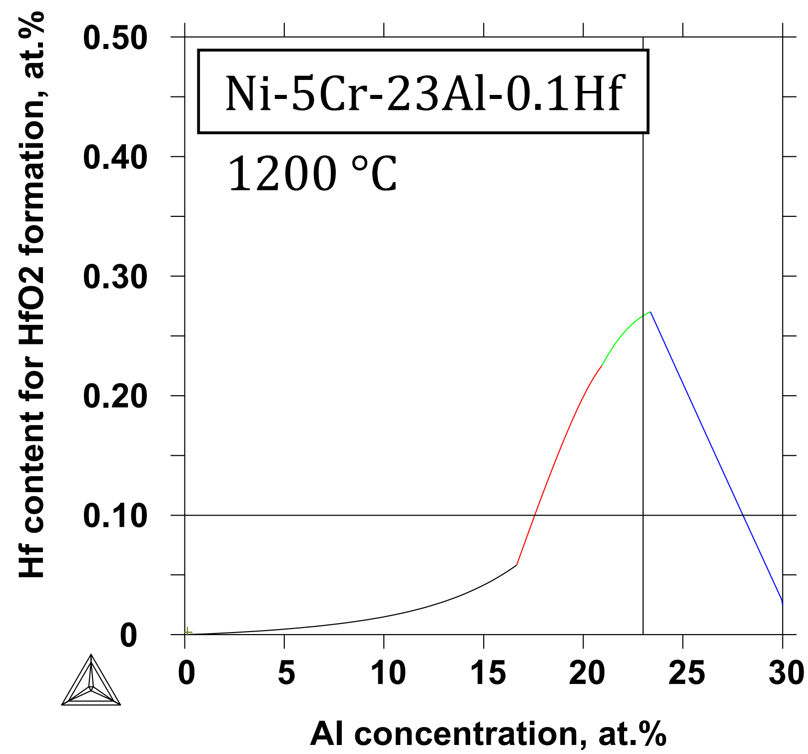


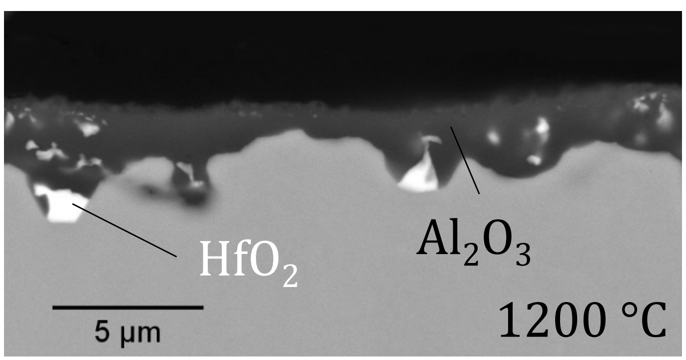


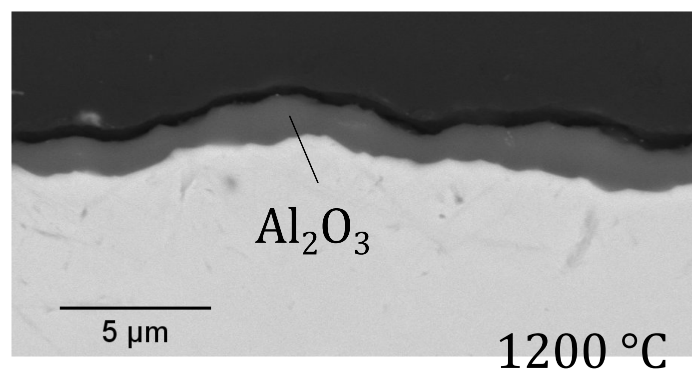
Gleeson, University of Pittsburgh

Experimental Results









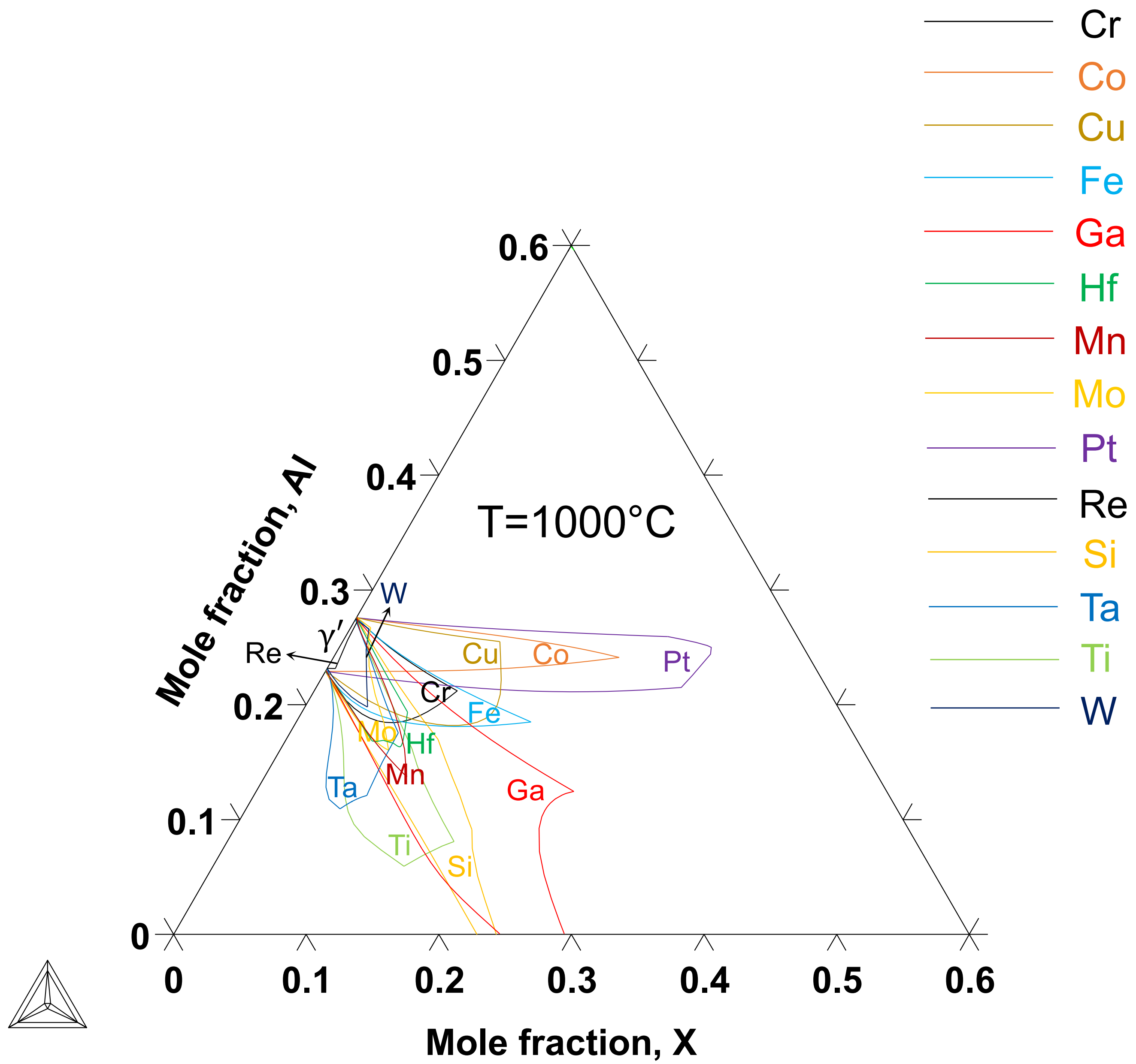
Gheno, Zhou, Ross, et al. (2017). *Oxidation of Metals*.

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.

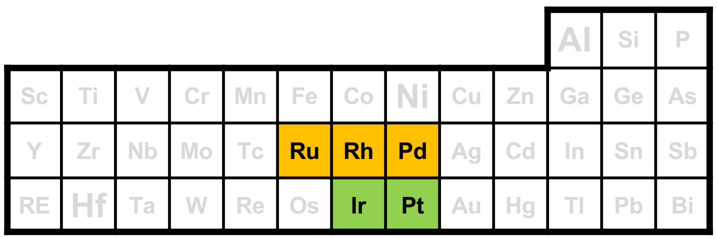
- **Hf-X chemical interaction**: In the Al-Hf-Ni-X systems, elements can be added which decrease the Hf activity in γ and γ'.
  - Effect of X on activity of Hf can be found by determining the enthalpy of mixing between Hf and X.

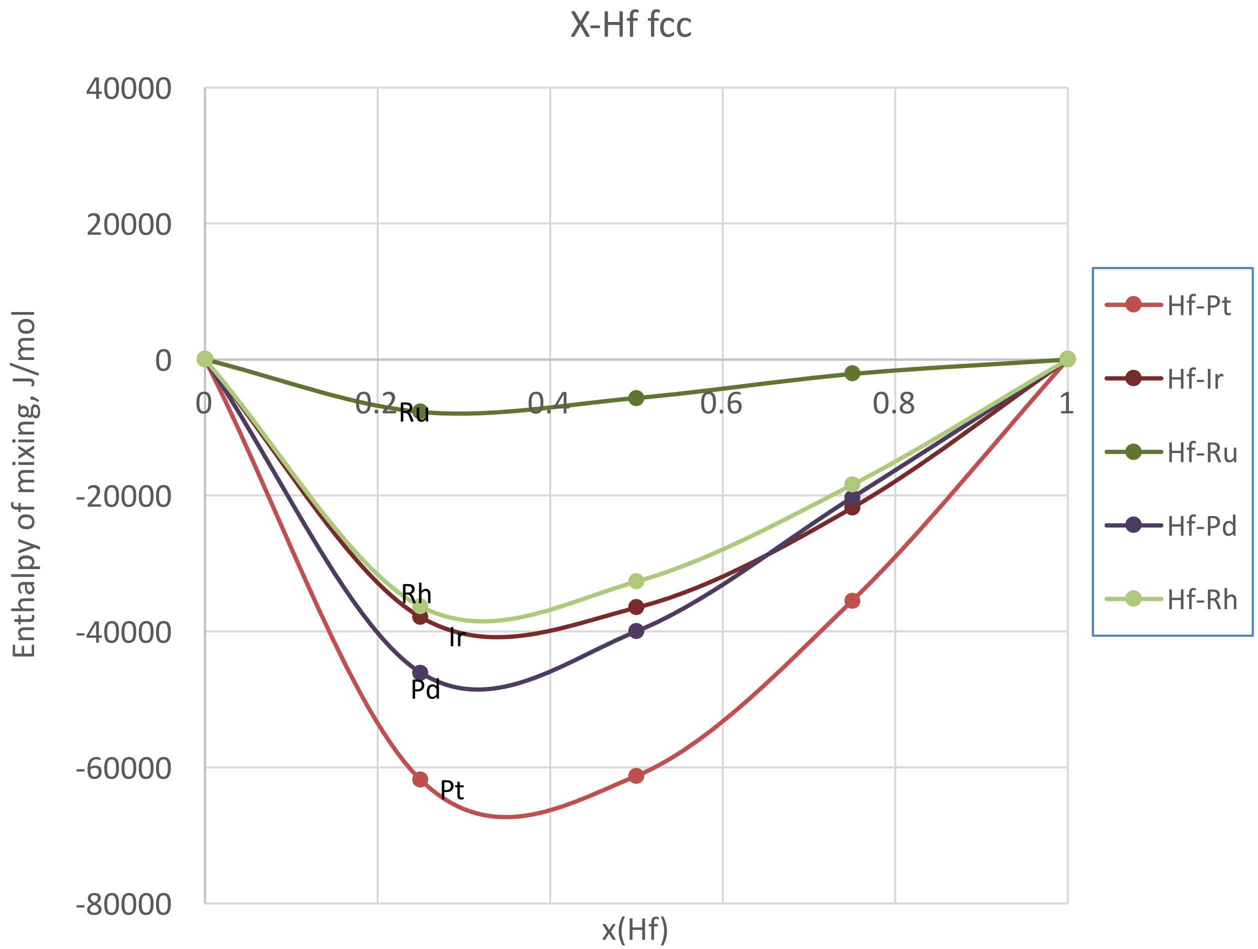
Alloying Effects on γ' Phase Stability in Ni-Al-X

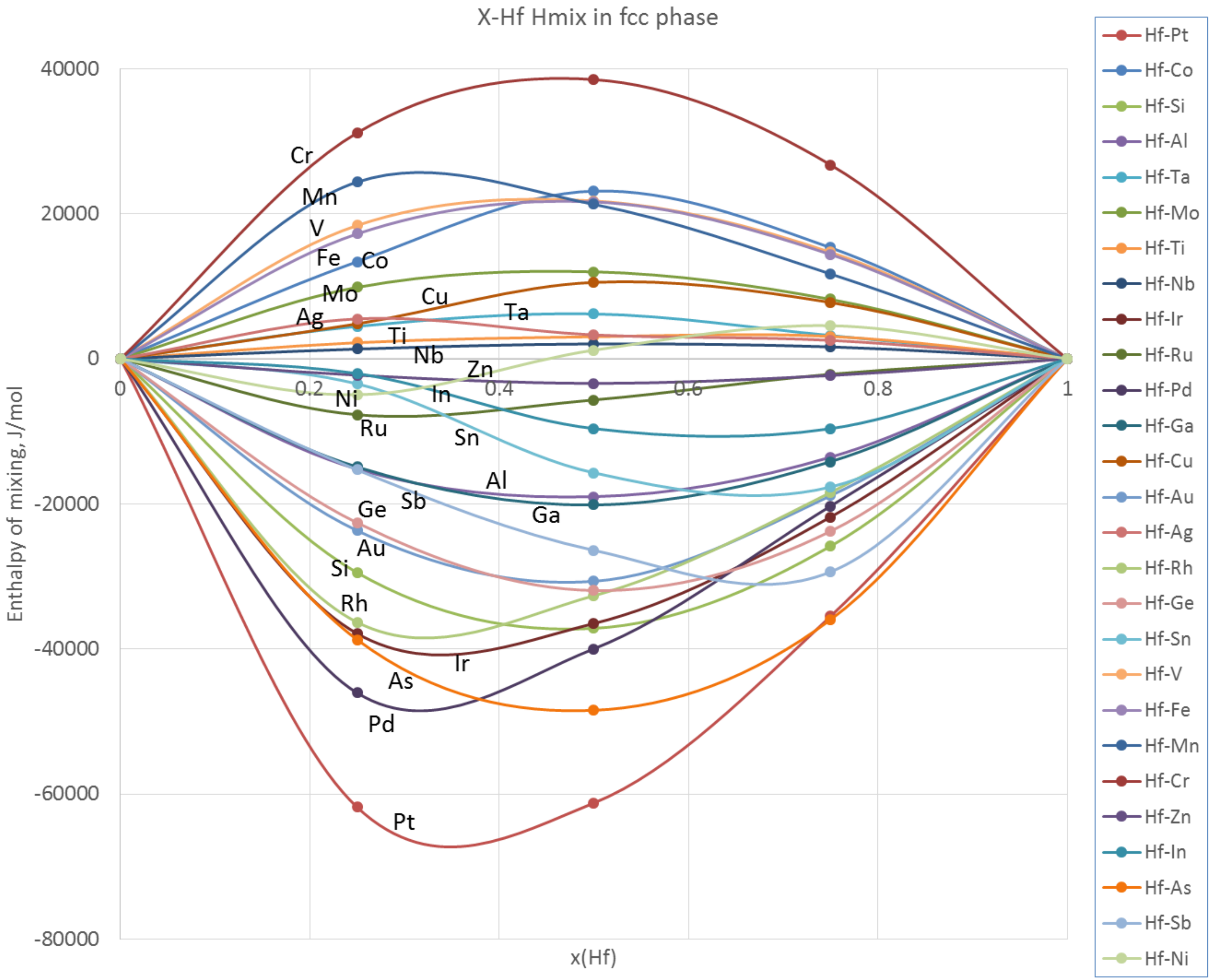


Acta Metall. Vol. 32. No. 2, pp. 289-298, 1984

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

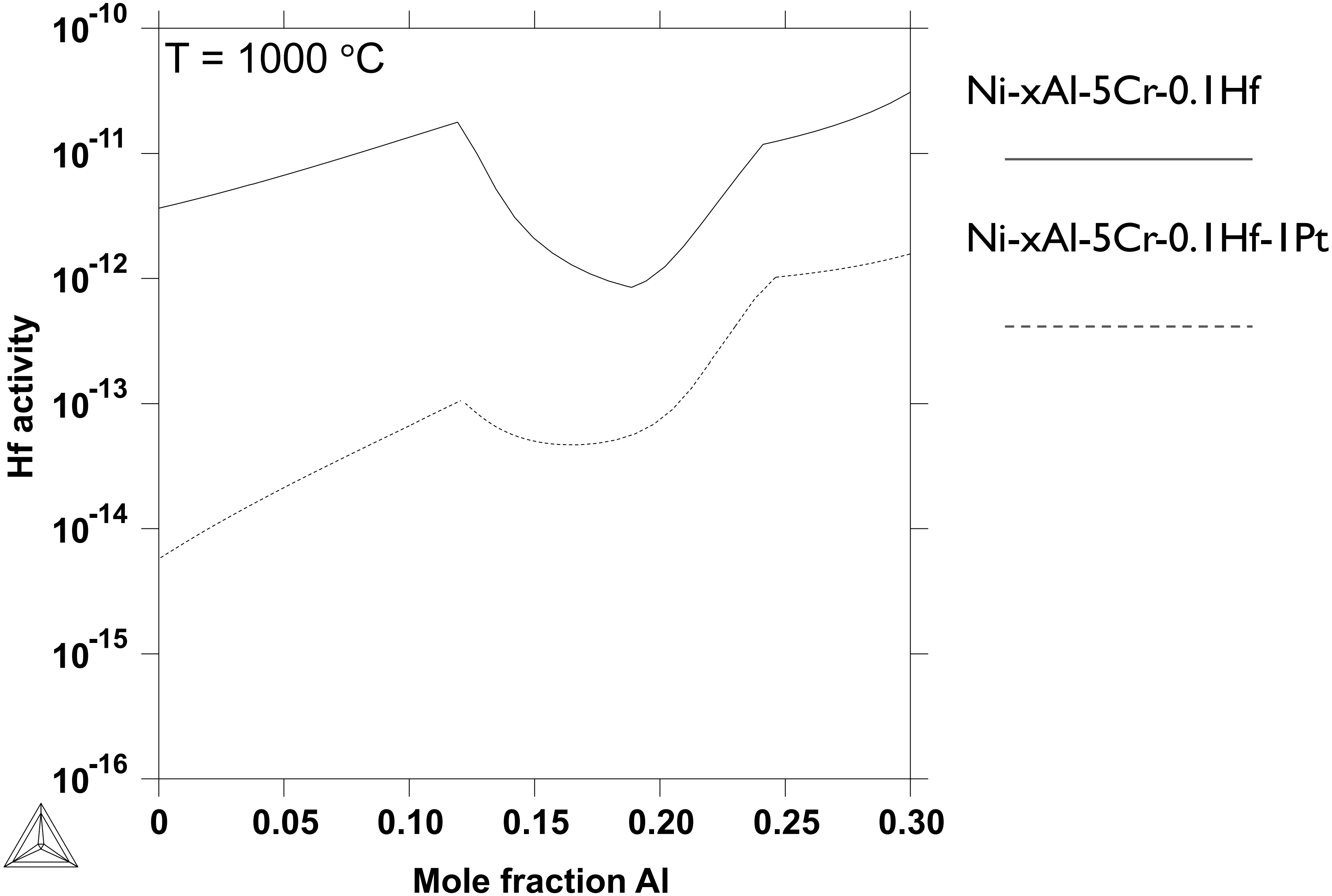




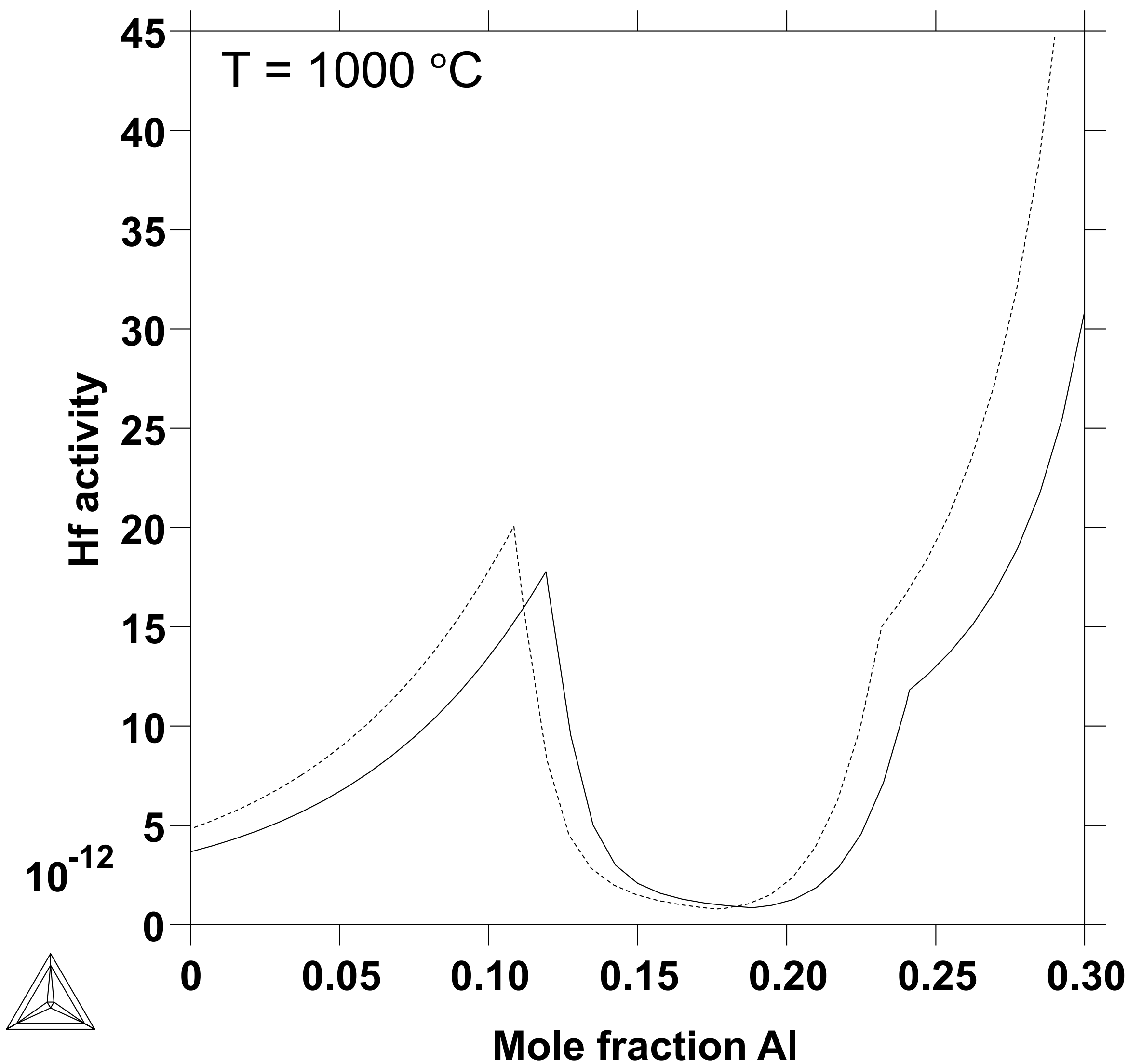


X-Hf Hmix in fcc phase
40000
20000
0
-20000
-40000
-60000
-80000
0
0.2
0.4
0.6
0.8
1
Enthalpy of mixing, J/mol
x(Hf)
Cr
Mn
V
Fe
Co
Mo
Cu
Ag
Ta
Ti
Nb
Zn
Ni
In
Ru
Sn
Al
Sb
Ge
Ga
Au
Si
Rh
Ir
As
Pd
Pt
Hf-Pt
Hf-Co
Hf-Si
Hf-Al
Hf-Ta
Hf-Mo
Hf-Ti
Hf-Nb
Hf-Ir
Hf-Ru
Hf-Pd
Hf-Ga
Hf-Cu
Hf-Au
Hf-Ag
Hf-Rh
Hf-Ge
Hf-Sn
Hf-V
Hf-Fe
Hf-Mn
Hf-Cr
Hf-Zn
Hf-In
Hf-As
Hf-Sb
Hf-Ni

Calculated Effect of Pt on Hf Activity



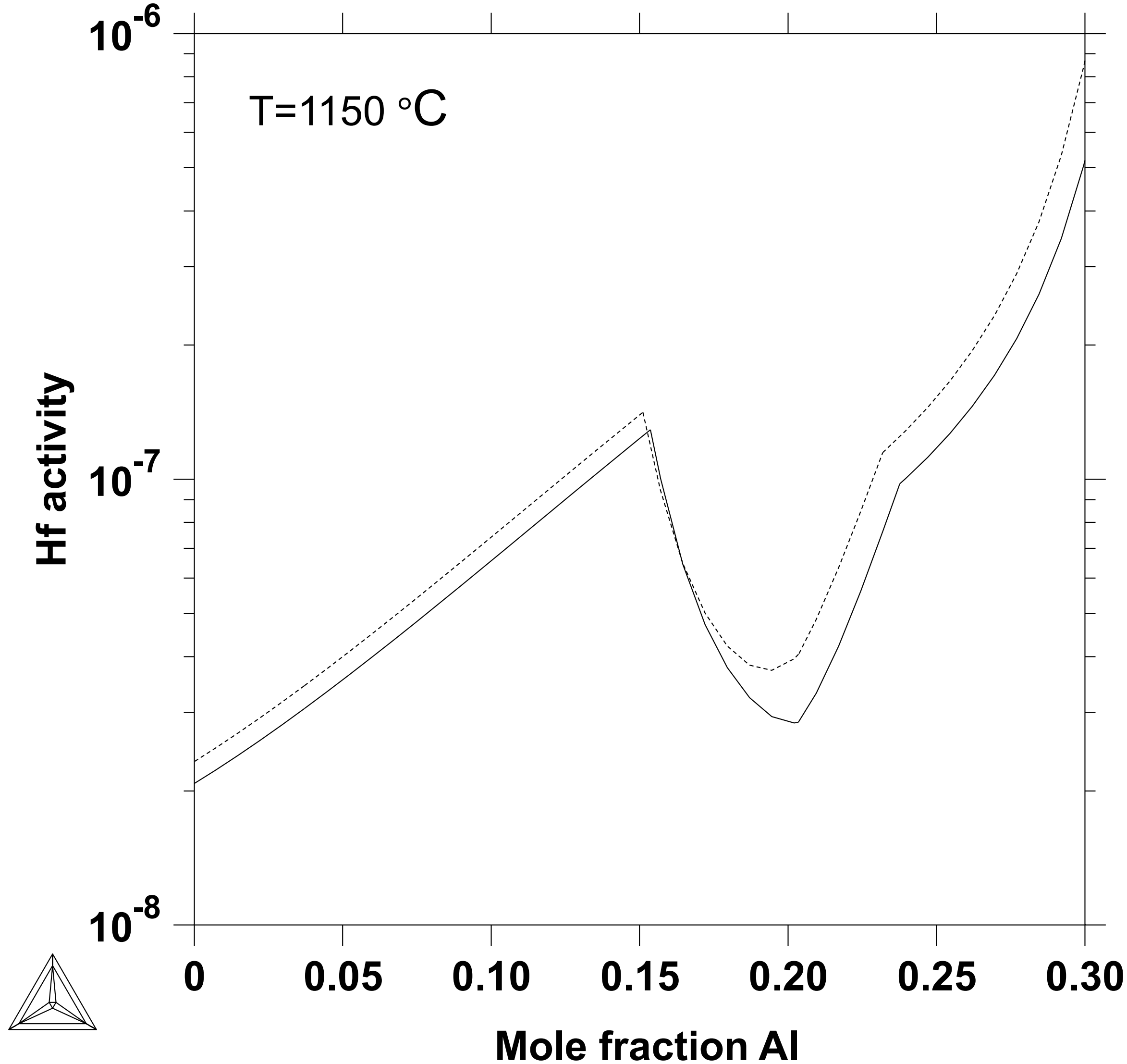
Calculated Effect of Si on Hf Activity



Ni-xAl-5Cr-0.1Hf

Ni-xAl-5Cr-0.1Hf-1Si

Calculated Effect of Cr on Hf Activity

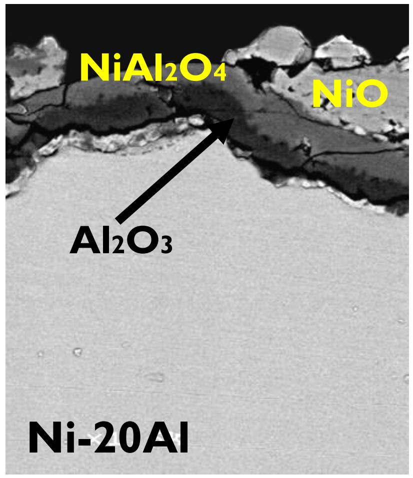


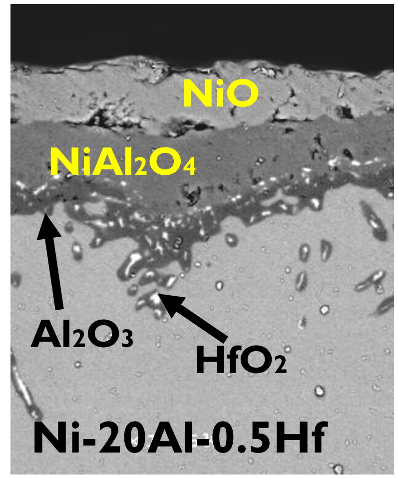
Ni-xAl-5Cr-0.1Hf

Ni-xAl-6Cr-0.1Hf

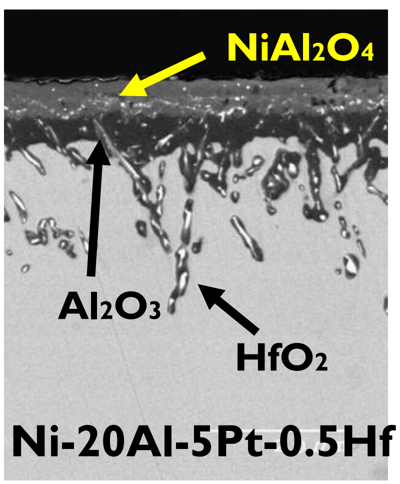
Cross-Sectional Images of Ni-20at.%Al-Pt-Hf γ/γ' Alloys

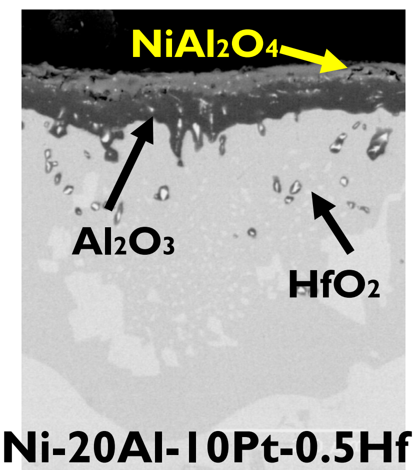
After 500 Oxidation Cycles at 1150°C in Air

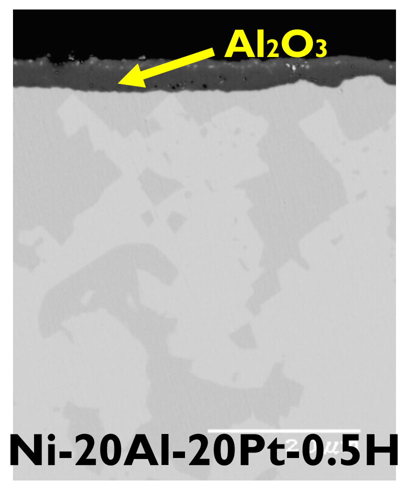




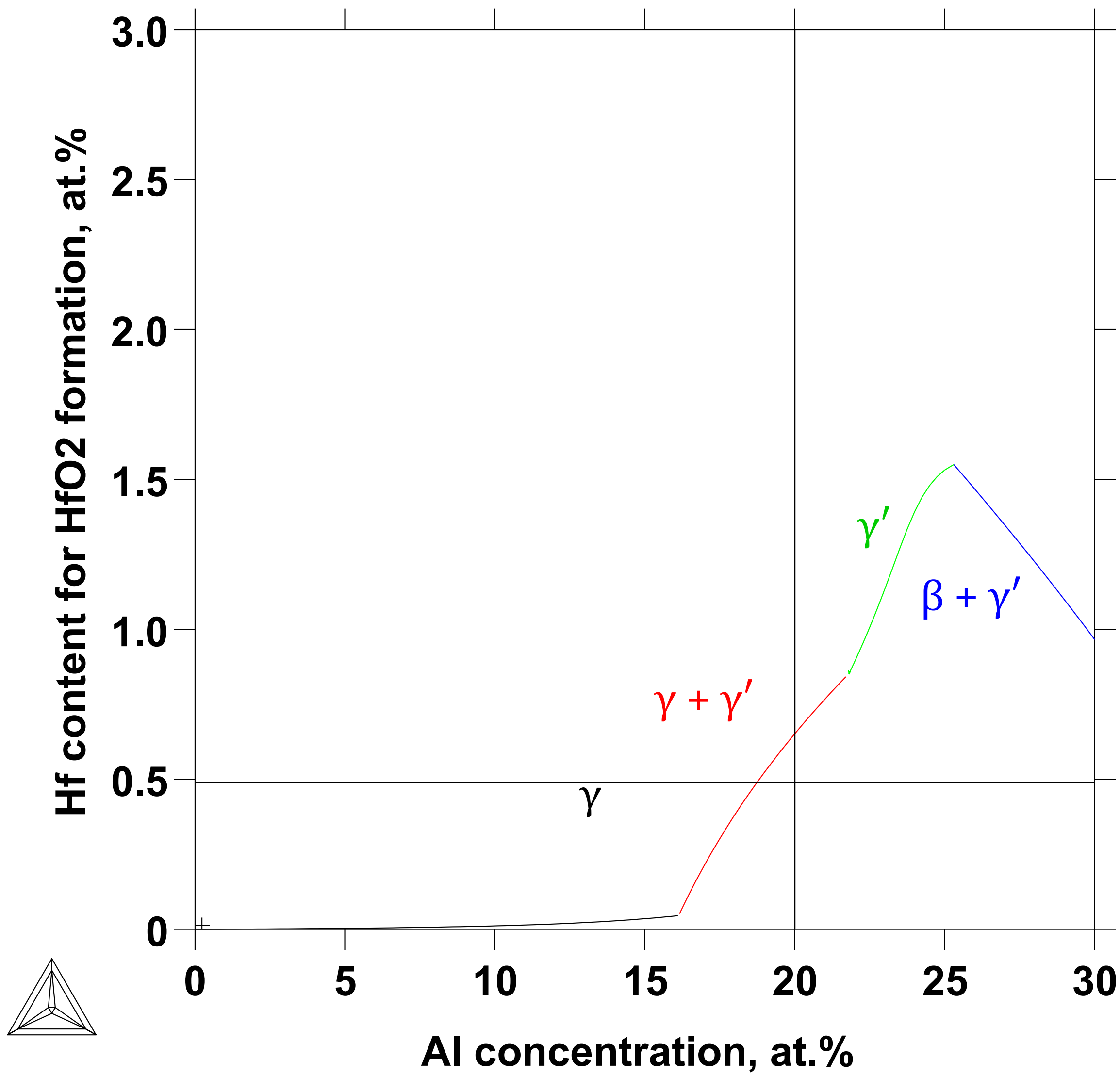
10μm

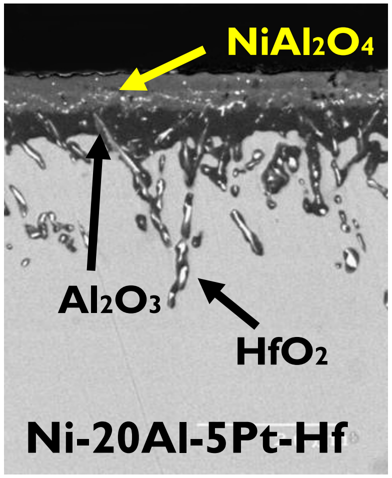




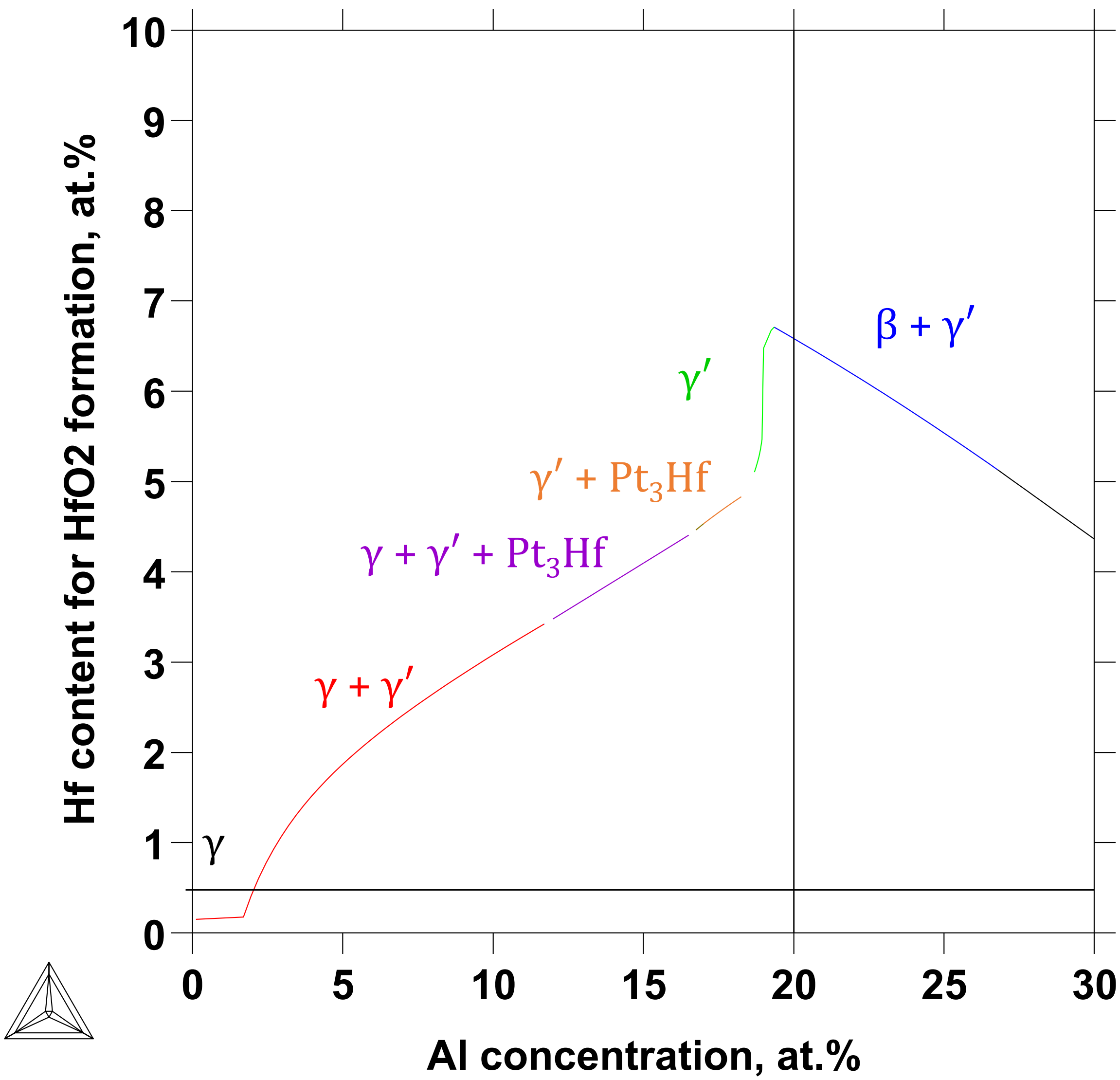


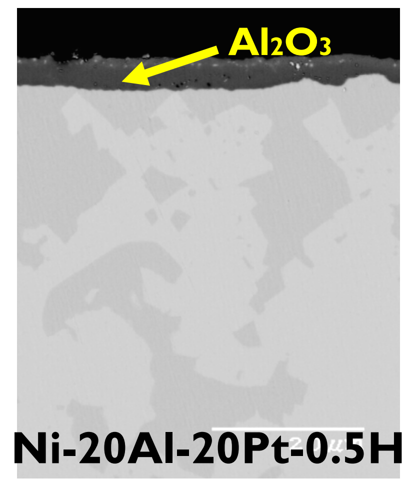
Hf Tolerance: Ni-20Al-5Pt-0.5Hf





Hf Tolerance: Ni-20Al-20Pt-0.5Hf



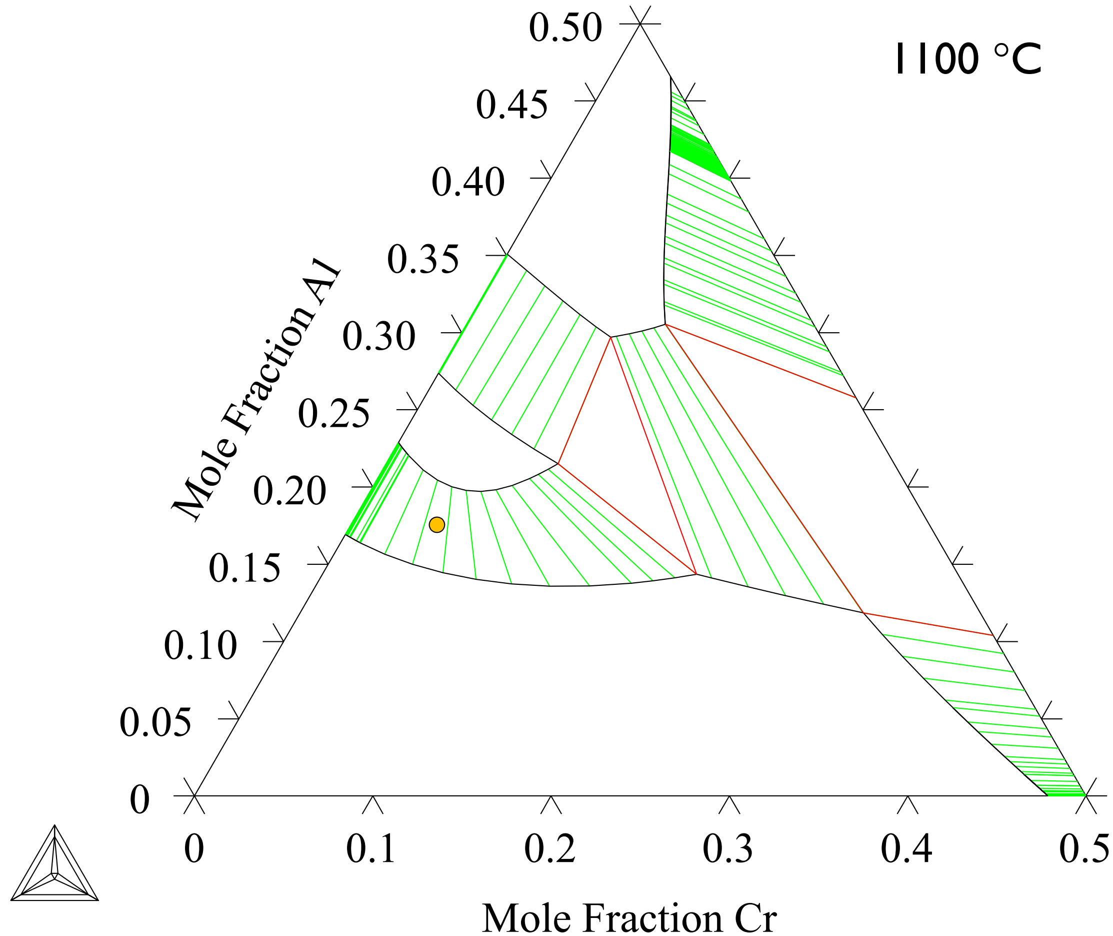


Provided by Dr. Brian Gleeson at the University of Pittsburg

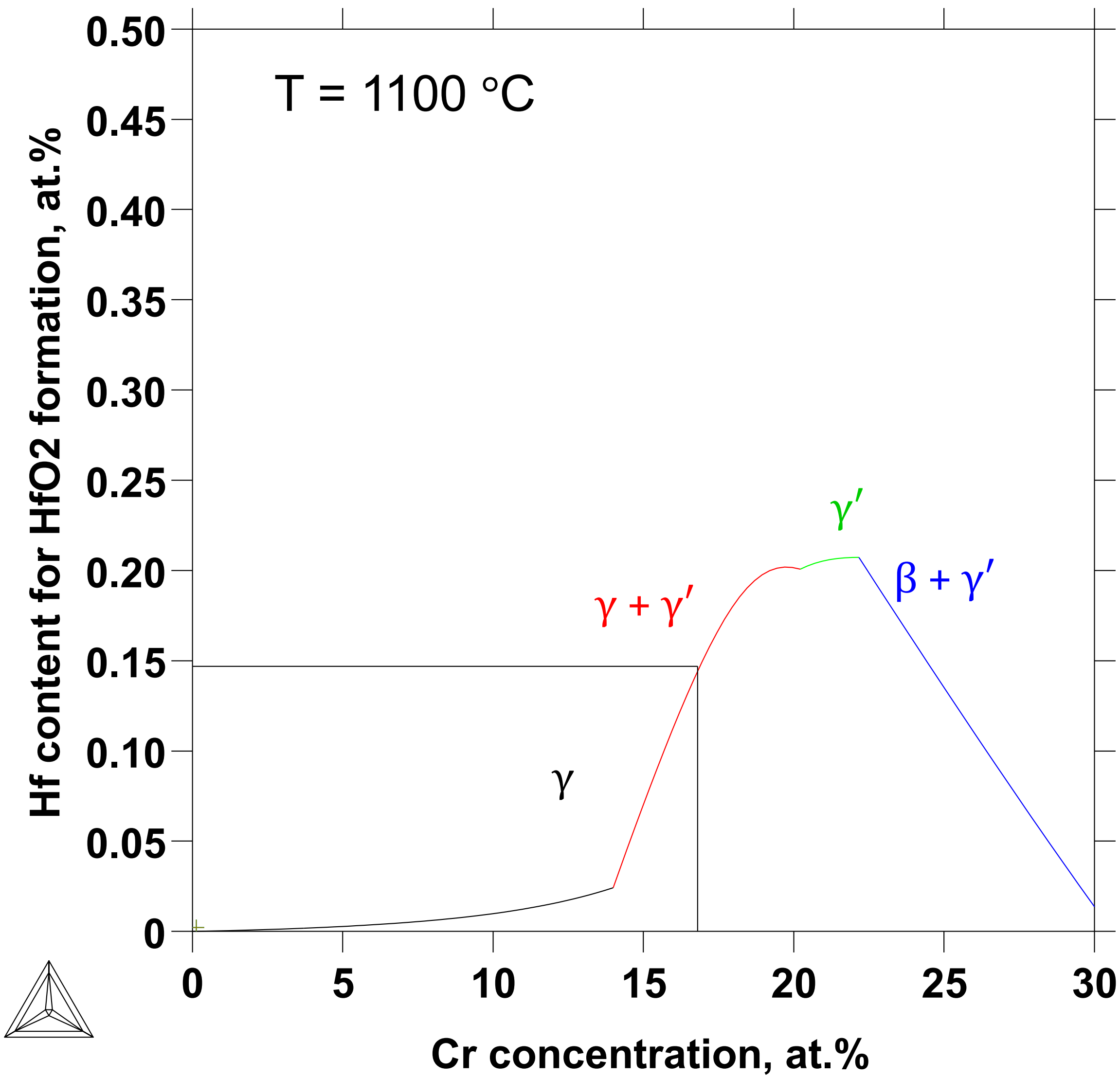
Engineering a RE-doped Alloy/Coating : Choosing a Base Composition

Parameters:
$f^{\gamma'} = 0.57$
$\chi_{Al} = 17\ at\%$
$\chi_{Cr} = 8\ at\%$

Alloy:
Ni-17Al-8Cr



Engineering a RE-doped Alloy/Coating: Doping with Hf



Parameters:

$f^{\gamma'} = 0.57$

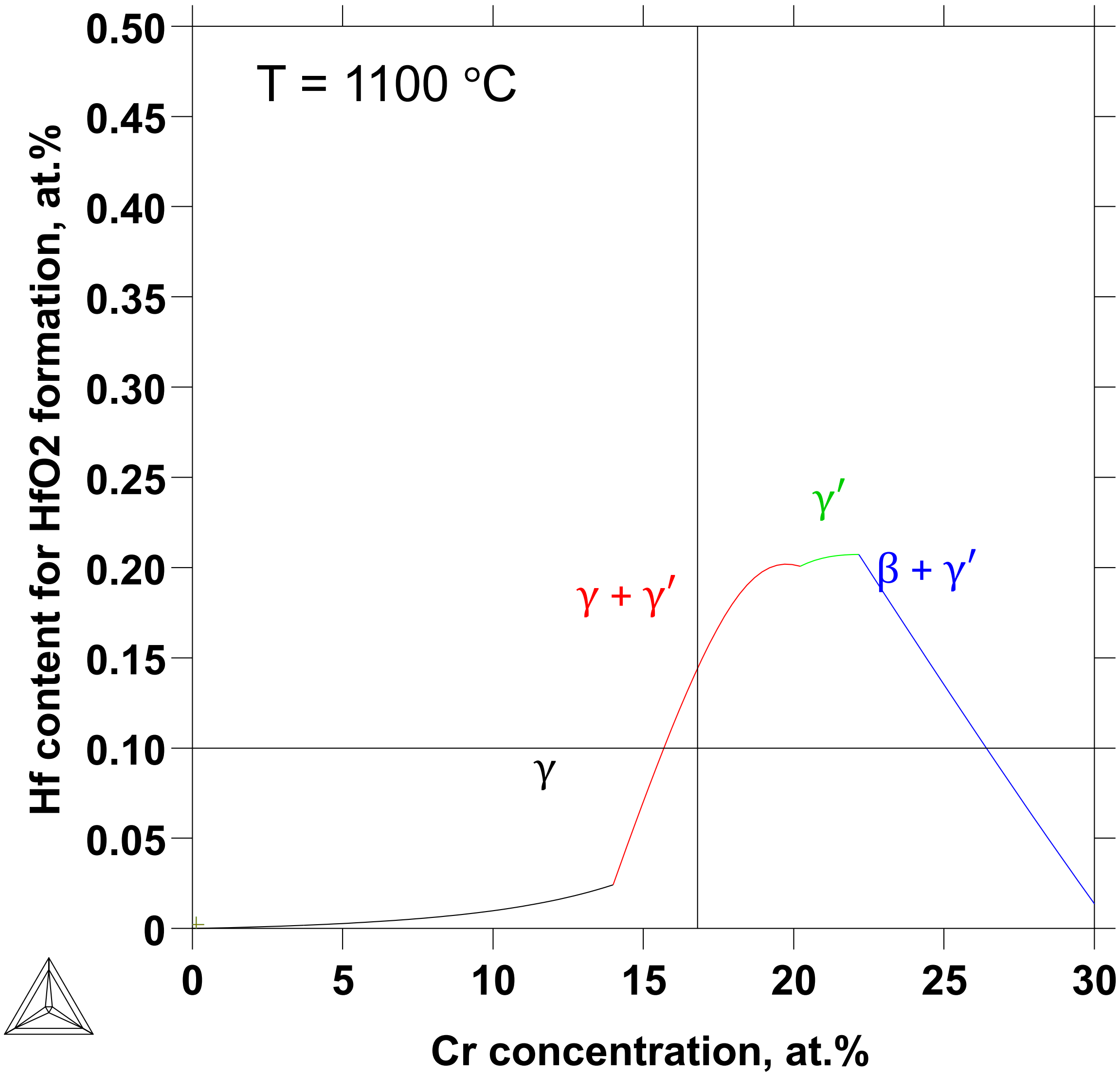
$\chi_{Al} = 17\ at\%$

$\chi_{Cr} = 8\ at\%$

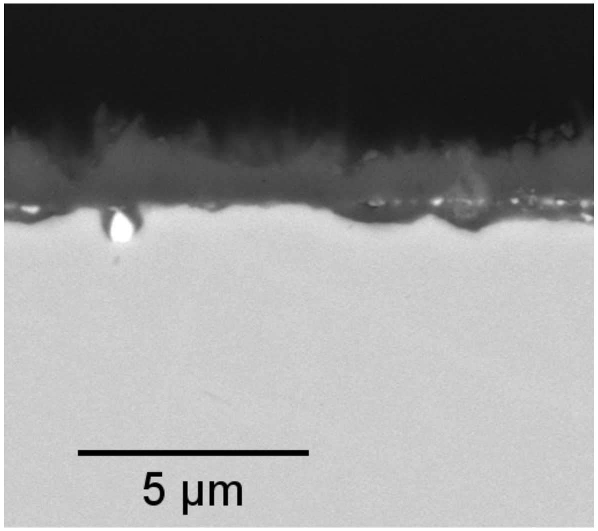
Alloy:

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

Experimental Results for Hf Doped Alloy



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



Gheno, Zhou, Ross, et al. (2017). *Oxidation of Metals*.

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Summary

- The γ' phase in Ni-superalloys produces an appreciable decrease in Hf activity compared to the γ phase, resulting in a high solubility of Hf in γ'.
- The Hf tolerance, a thermodynamic criterion for Hf over-doping, was established in terms of the relative stabilities of HfO_2 and Al_2O_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_2O_3 scale growth.