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

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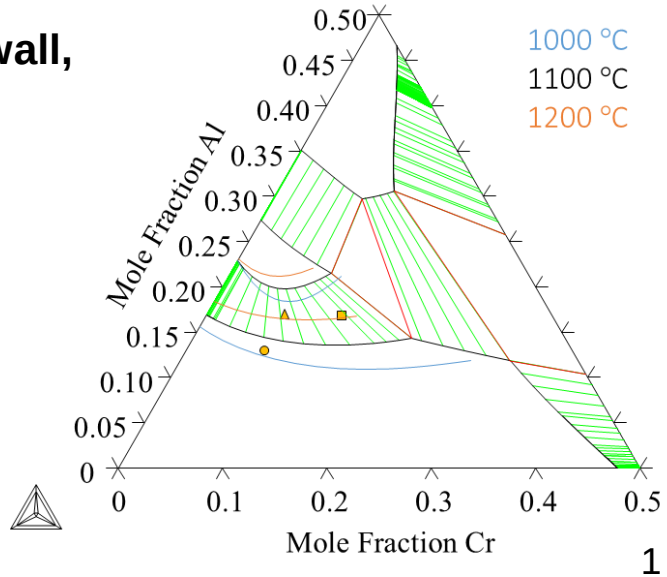
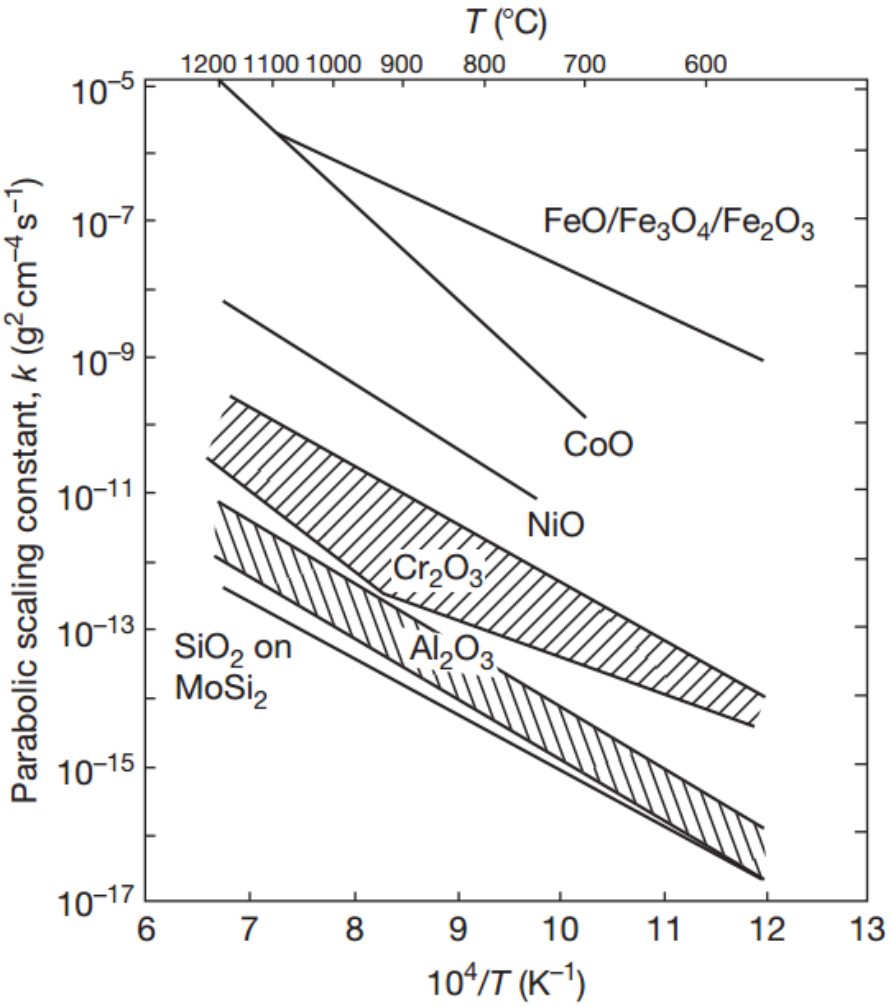


Outline

- 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

Alumina Scale Formation on Alloys



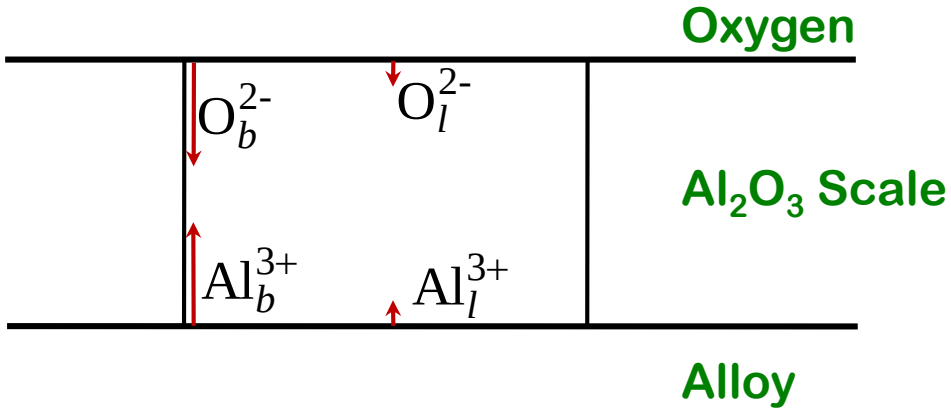
Extrinsic Al_2O_3 scale growth desired for the protection against high temperature corrosion

Gleeson, B. (2010). In *Shreir's Corrosion* (pp. 180–194). Elsevier.

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

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

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



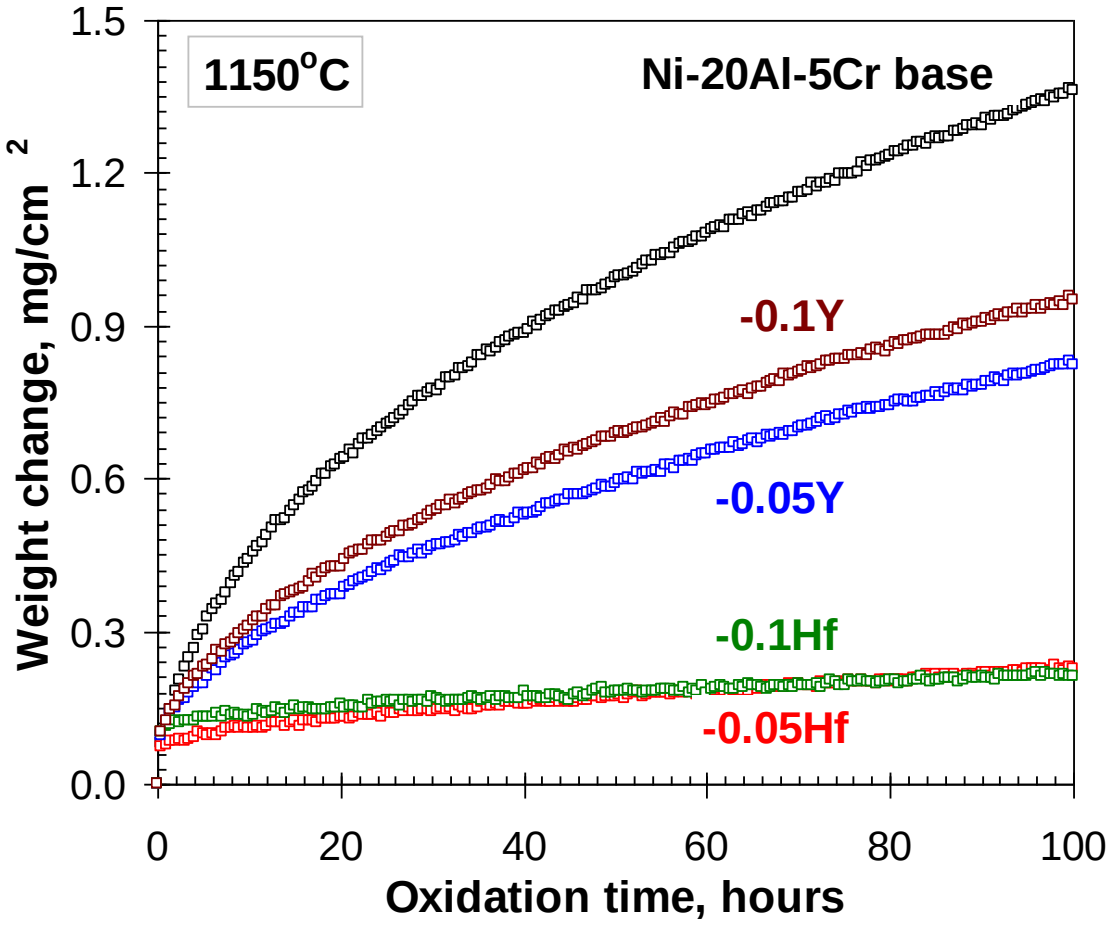
Comparisons	Effects on			Inference
	k_p	Grain size	Outward transport	
Fe, Ni-based with RE *vs.* Without	Down 2×	Down 1.5-2×	Down 4×	RE reduces D_b^{Al} by 4×, has little effect on D_b^{O}

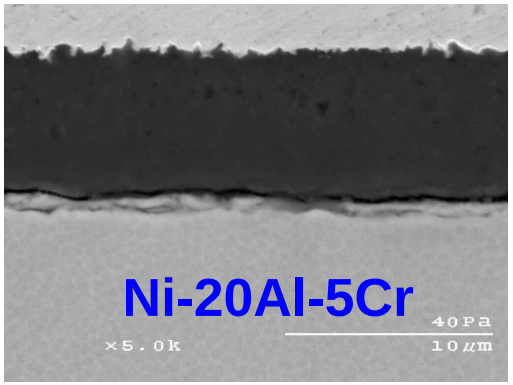
RE = Hf, Y, Zr, La, …

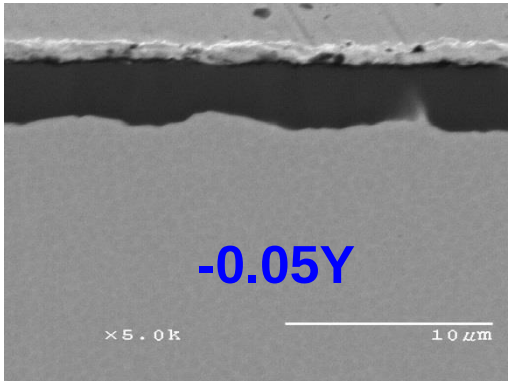
Isothermal Oxidation Kinetics at 1150°C

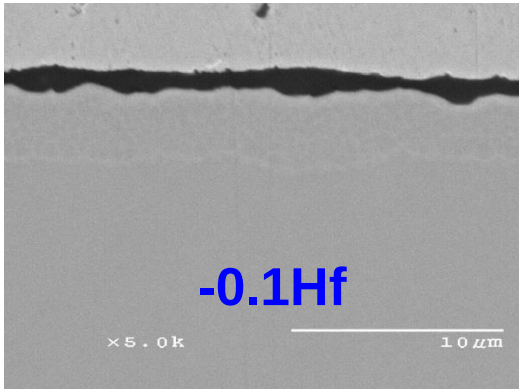
Single Doped : Hf vs. Y

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

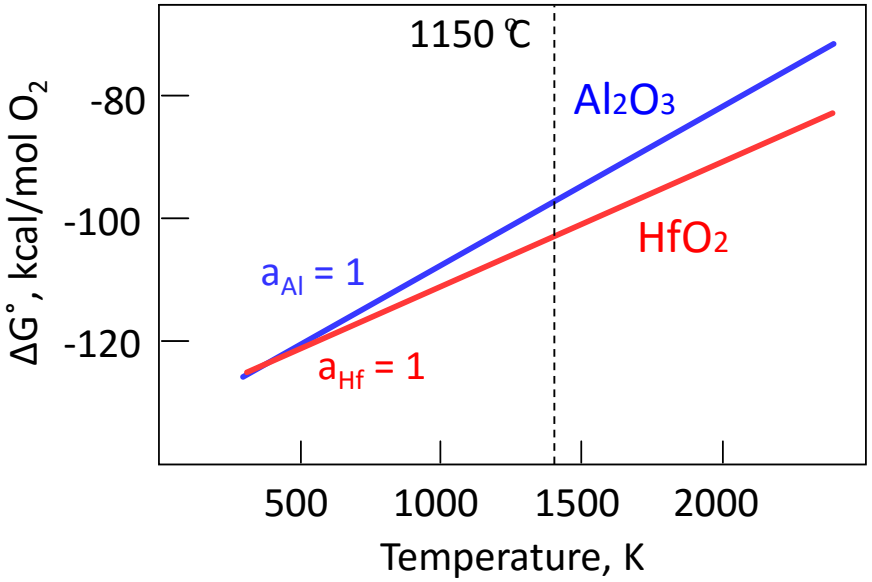








Thermodynamic considerations of oxidation



$$3Hf + 2Al_2O_3 \rightarrow 3HfO_2 + 4Al$$

$$\Delta G^{o} = -RT \times \ln K_{eq} \quad \text{and} \quad K = \frac{a_{Al}^{4}}{a_{Hf}^{3}}$$

In order to suppress HfO_2:

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)

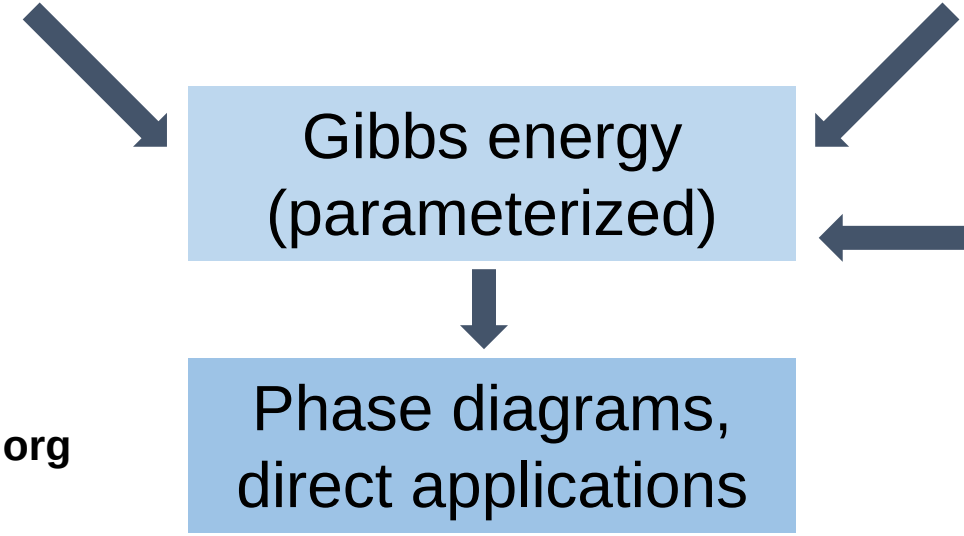
Modeling Approach - CALPHAD

Fewer data points supplemented by **first-principles calculations**

Experimental data plenty, hard to predict using first-principles

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

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



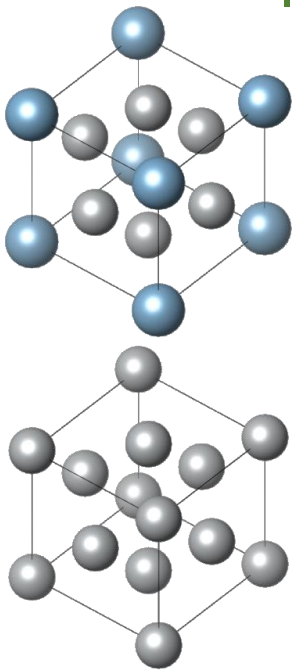
http://www.calphad.org

Pure elements → Binary → Ternary → Multi-component

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

Ni-Al	**Ni-Cr**	**Ni-Co**	**Ni-Si**	**Ni-Hf**	**Ni-Y**	**Al-Cr**
Al-Co	**Al-Si**	**Al-Hf**	**Al-Y**	**Cr-Co**	**Cr-Si**	**Cr-Hf**
Cr-Y	**Co-Si**	**Co-Hf**	**Co-Y**	**Si-Hf**	**Si-Y**	**Hf-Y**

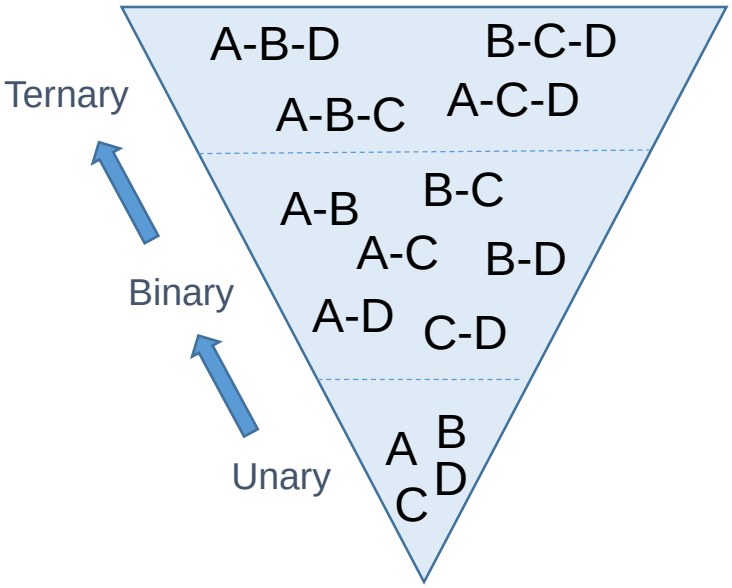
Ni-containing ternary systems

Ni-Al-Cr	**Ni-Al-Co**	**Ni-Al-Si**	**Ni-Al-Hf**	**Ni-Al-Y**
Ni-Cr-Co	**Ni-Cr-Si**	**Ni-Cr-Hf**	**Ni-Cr-Y**	
Ni-Co-Si	**Ni-Co-Hf**	**Ni-Co-Y**		
Ni-Si-Hf	Ni-Si-Y			
Ni-Hf-Y				

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**



Challenge

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

ESPEI

***E**xtensible, **S**elf-optimizing **P**hase **E**quilibrium **I**nfrastructure*

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

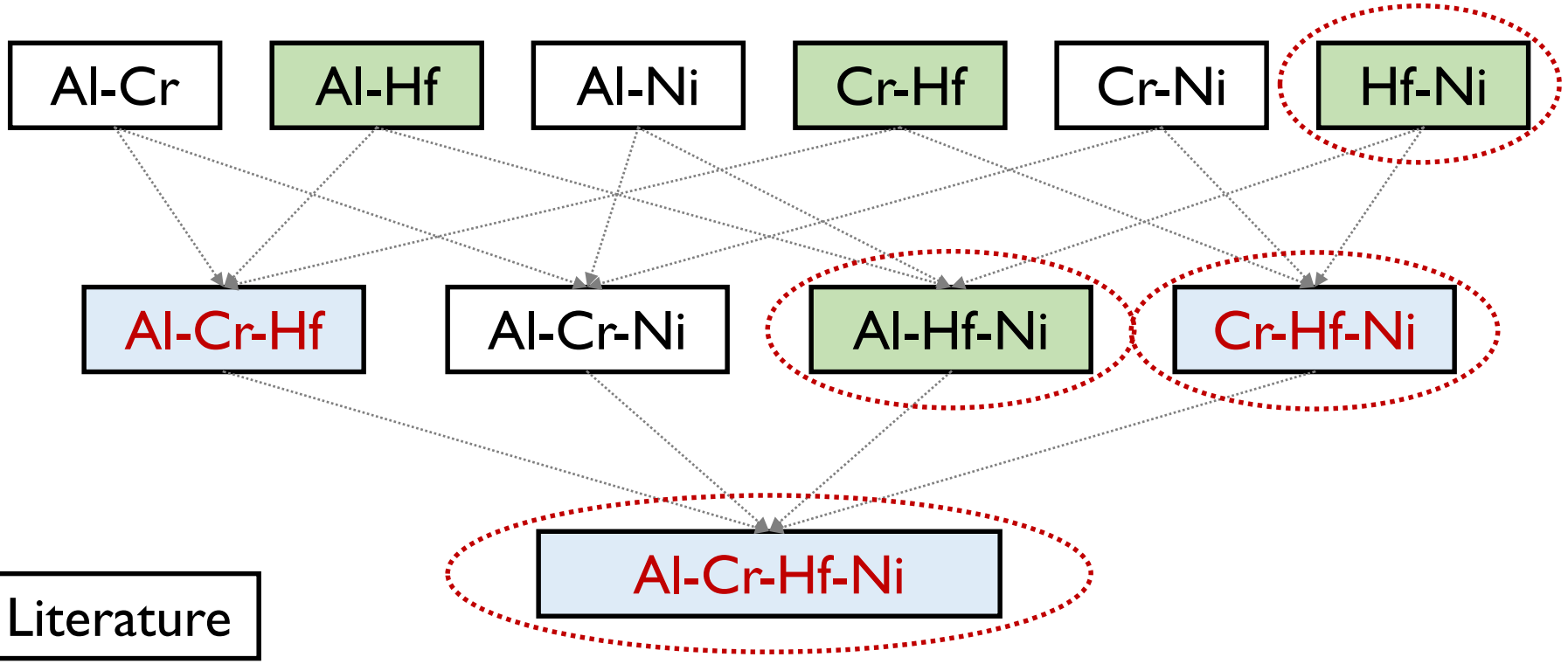
Partly financed by DOE

- 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

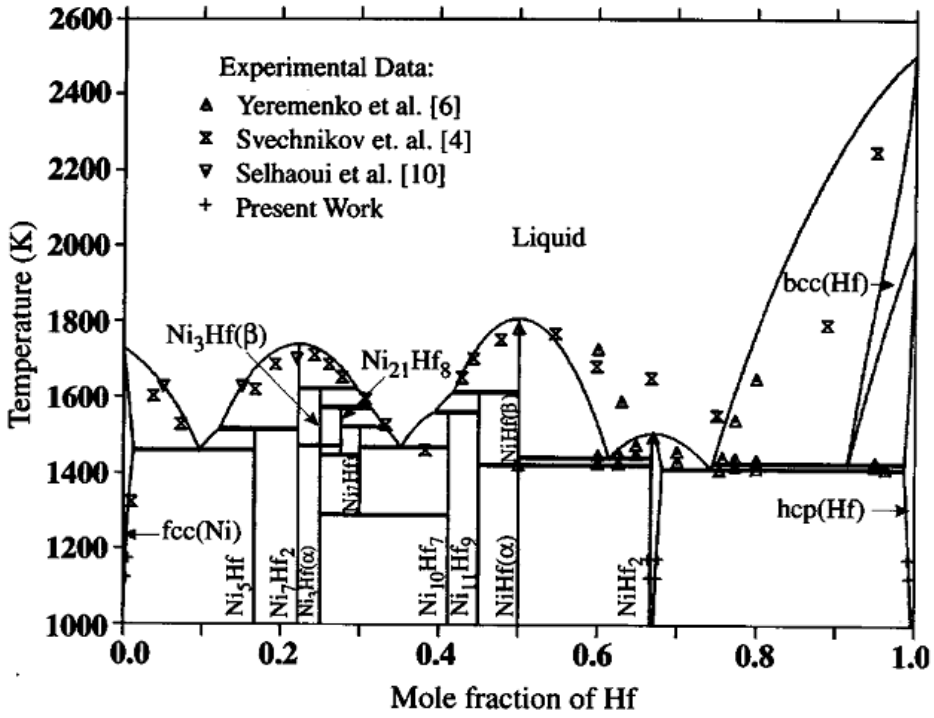


Ni-Hf thermodynamic re-modeling

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

Ni-Hf DFT calculations

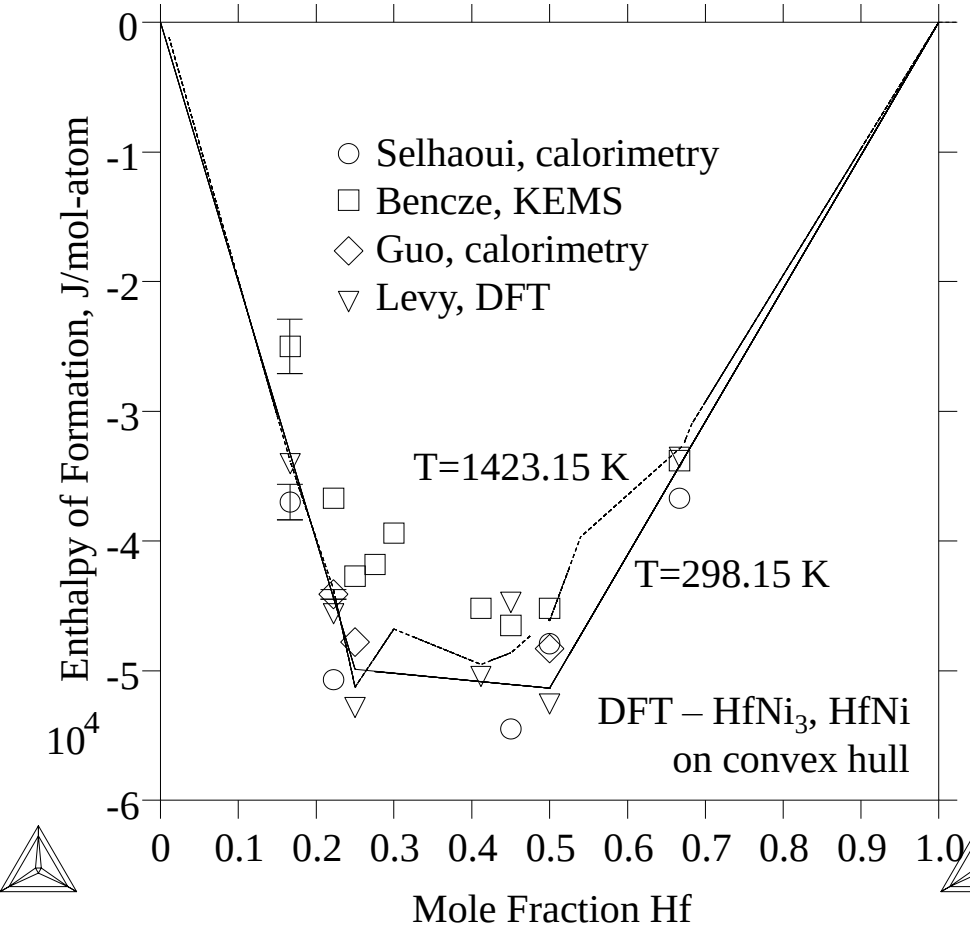
Ni	Ni_5Hf	Ni_7Hf_2	Ni_3Hf-L12	α-Ni_3Hf	$Ni_{21}Hf_8$
Ni_7H_3	$Ni_{10}Hf_7$	X_1Hf_1-B33	NiHf-B2	X_1Hf_2-C16	BCC_A2
Hf					

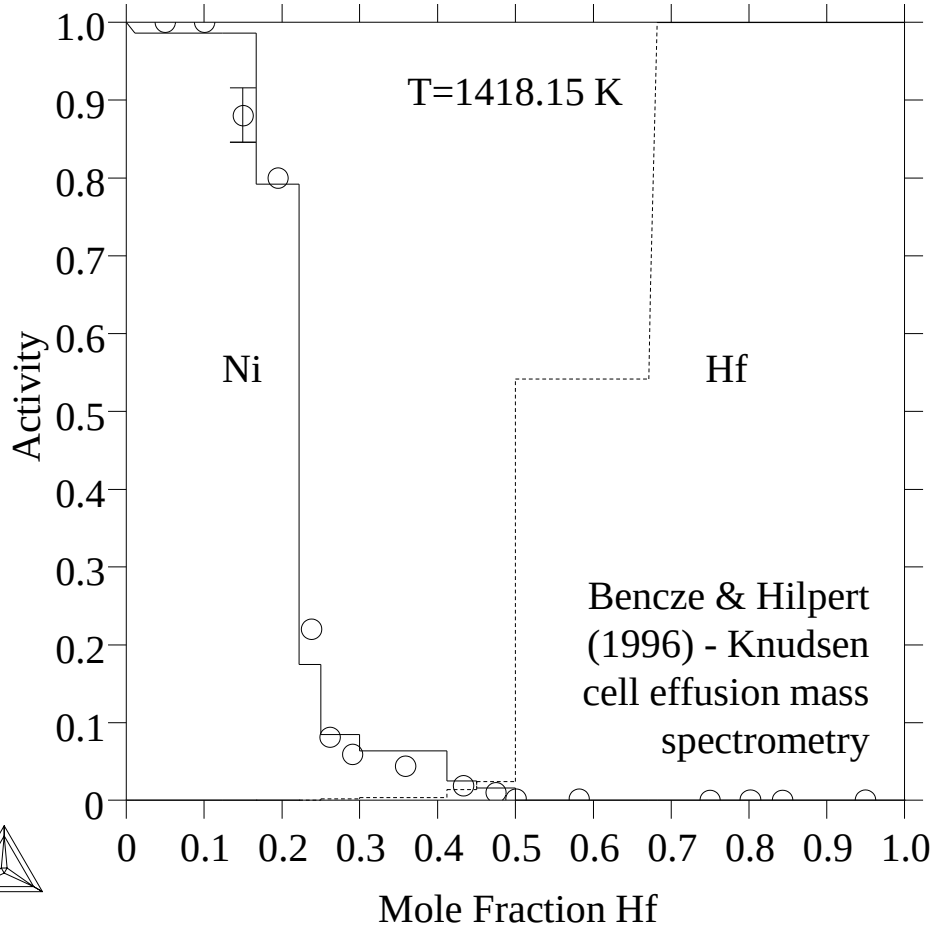


Finite Temperature DFT
0K DFT
No DFT

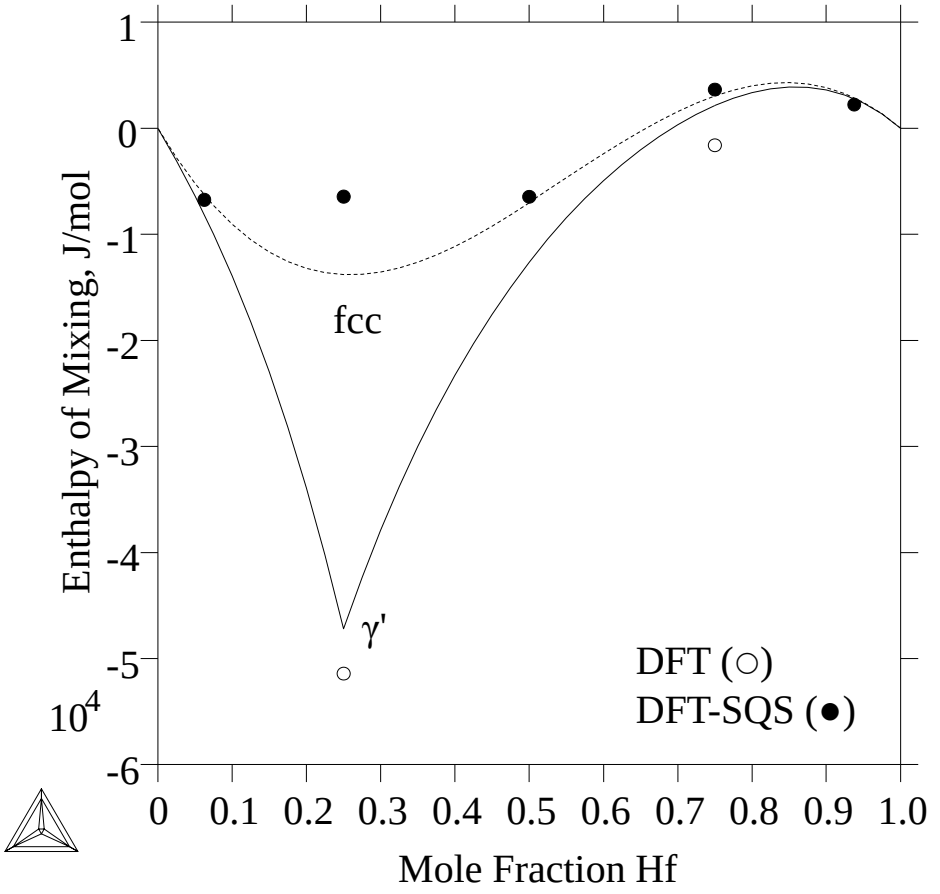
Previous modeling from Tao Wang et al. (2001) Z. Metallkd. 92 (2001) 5

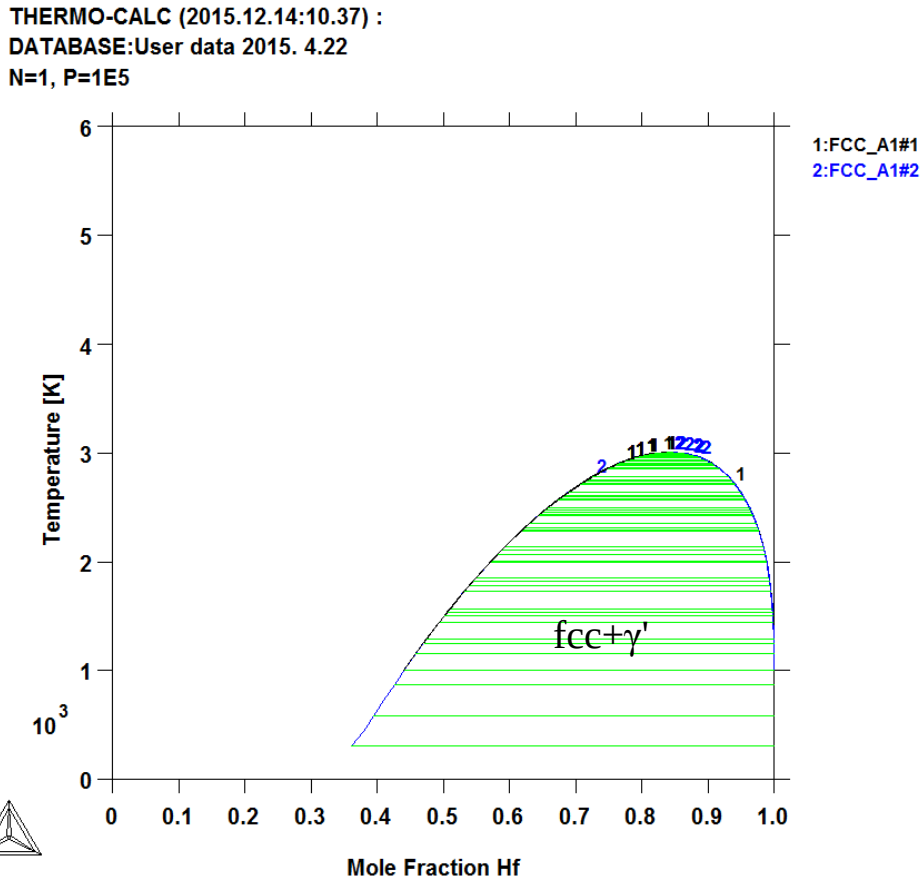
Ni-Hf: thermodynamics



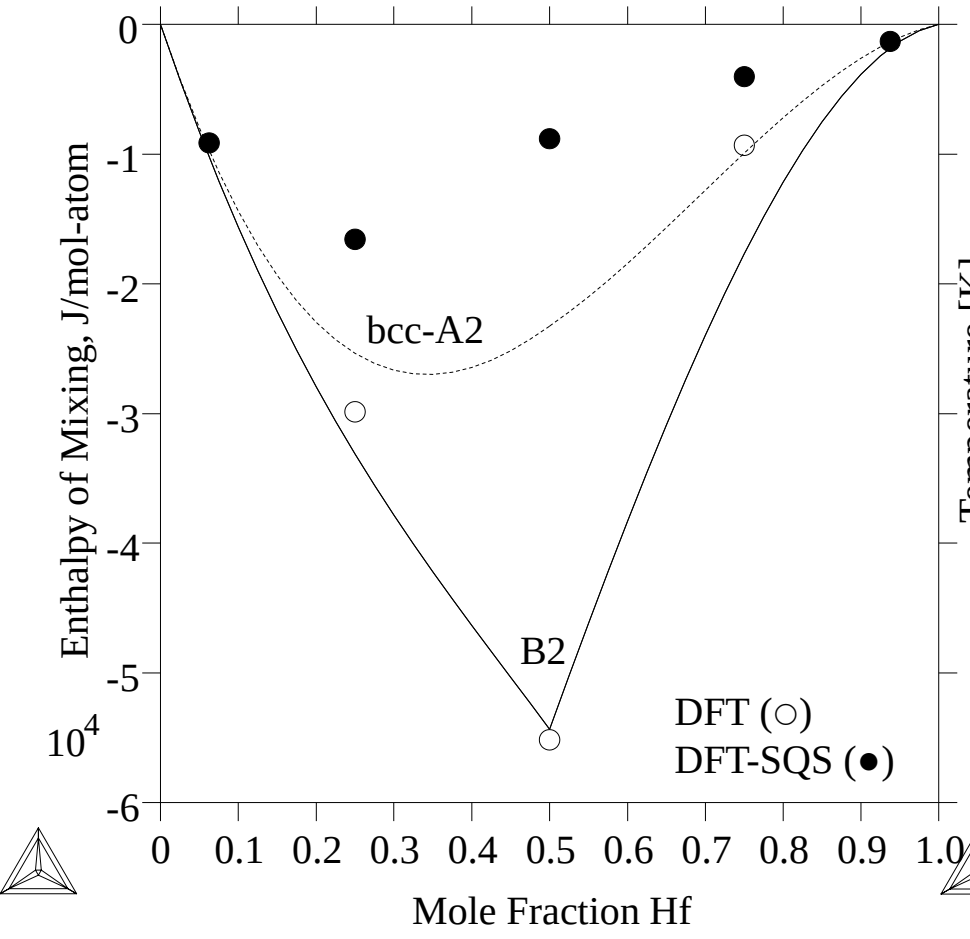


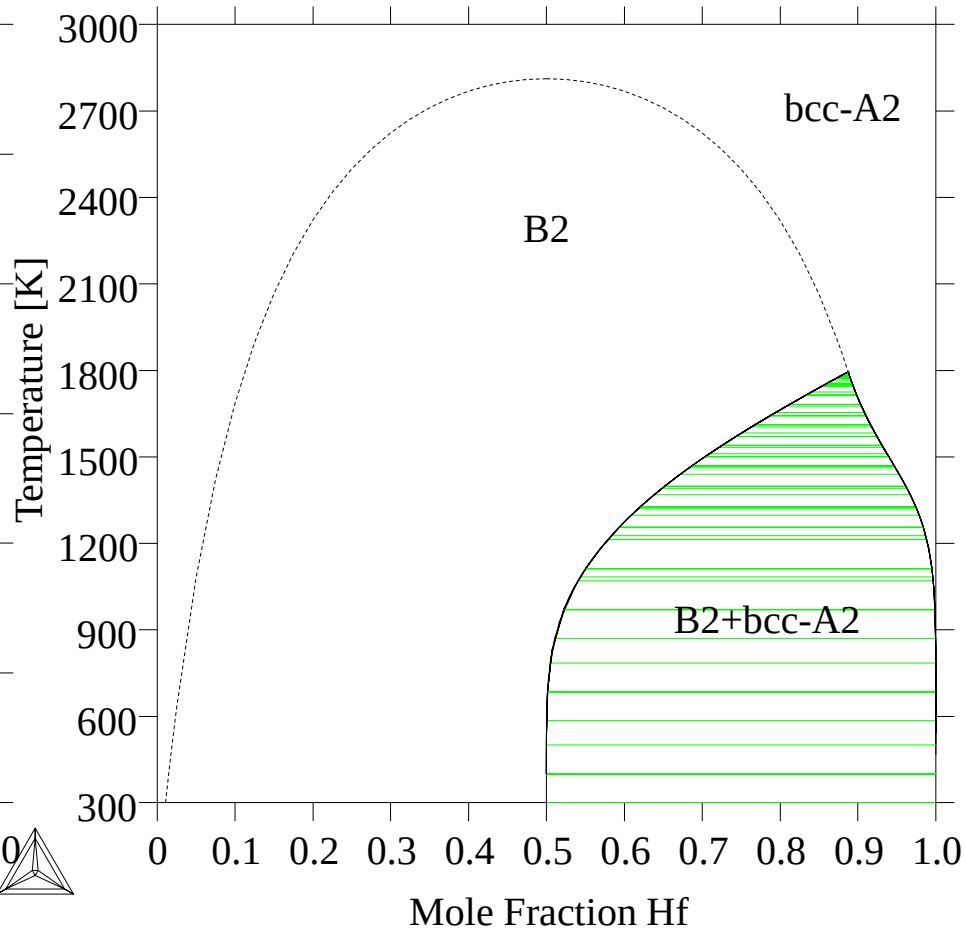
Ni-Hf: fcc phase



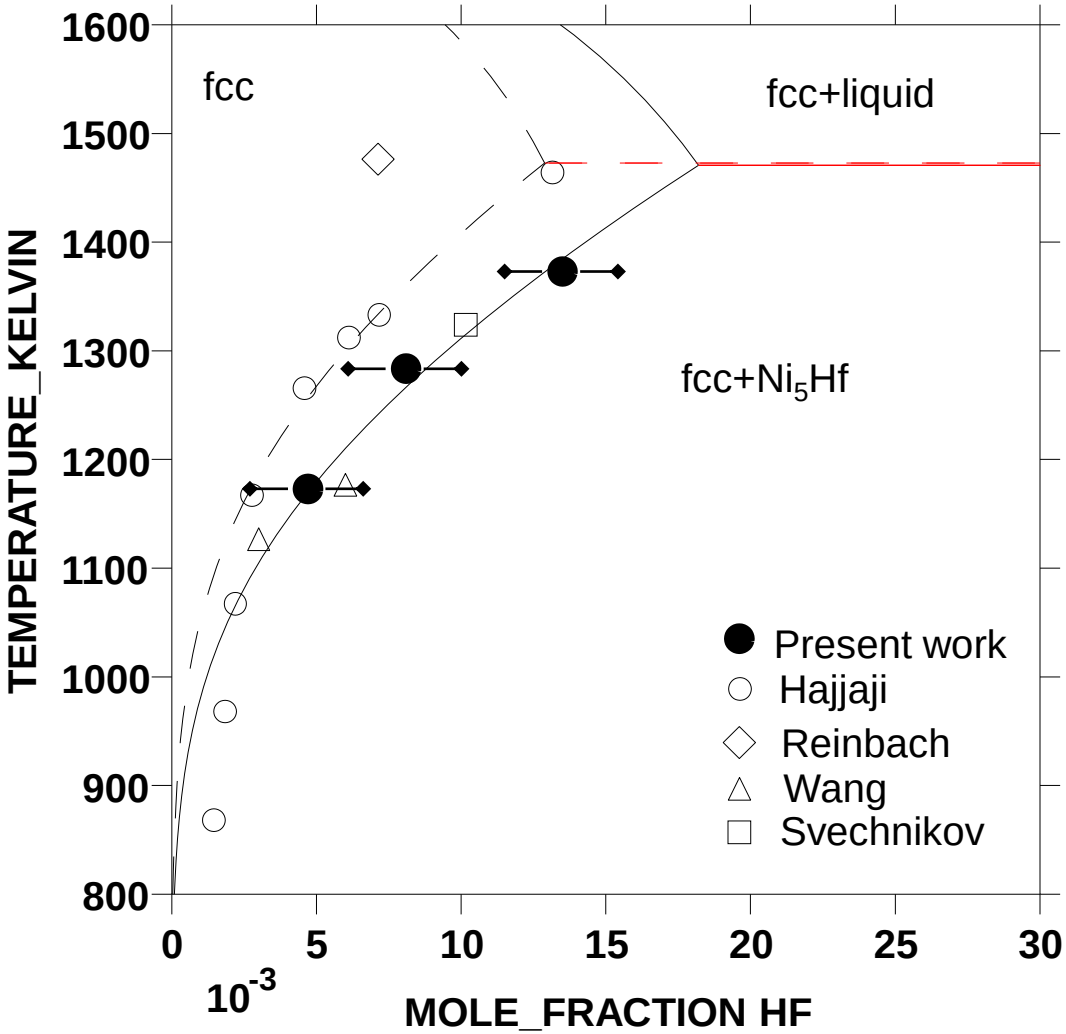


Ni-Hf: bcc phase





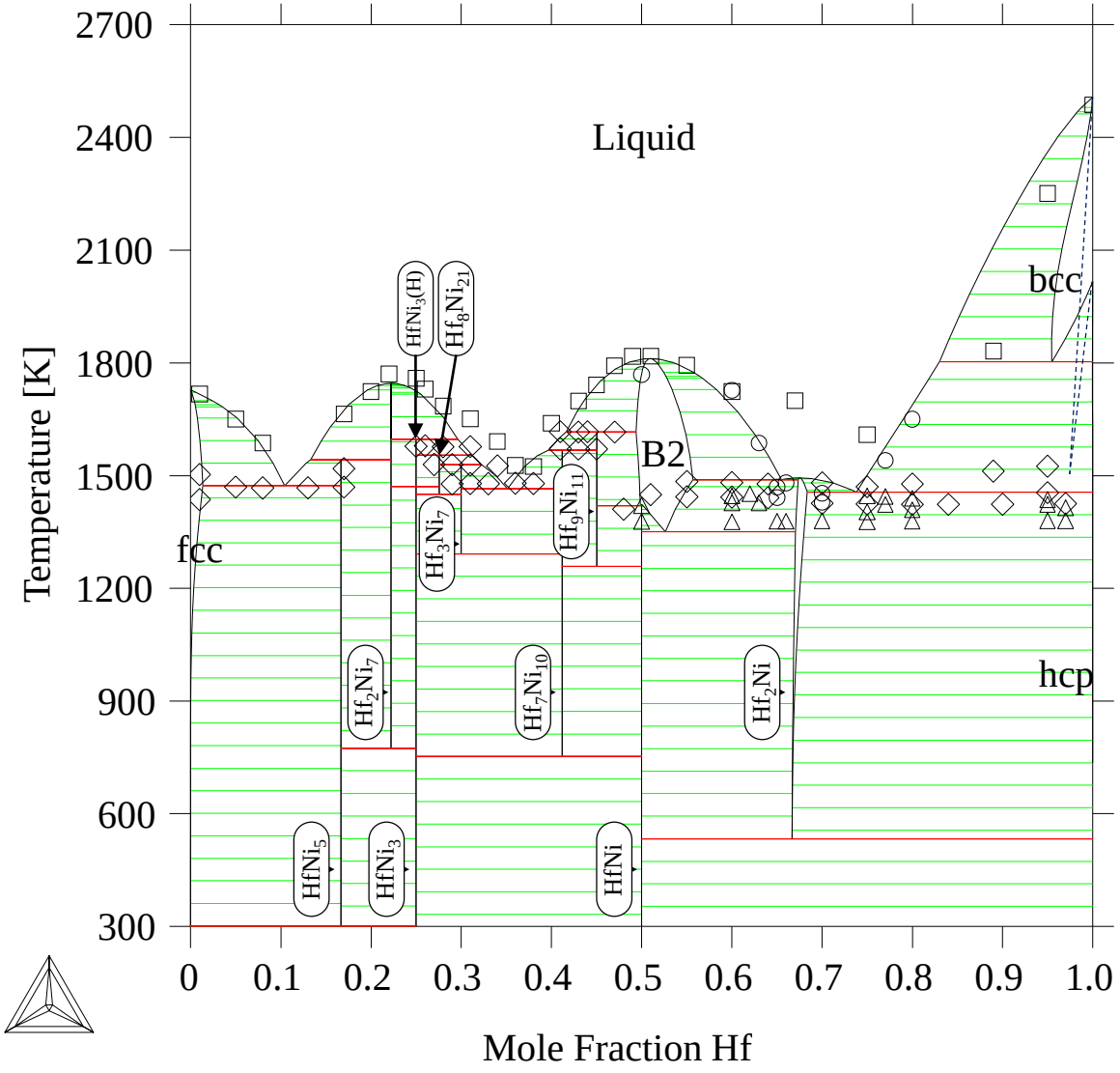
Calculated Hf solubility in fcc Ni



Previous modeling in the literature

Current modeling

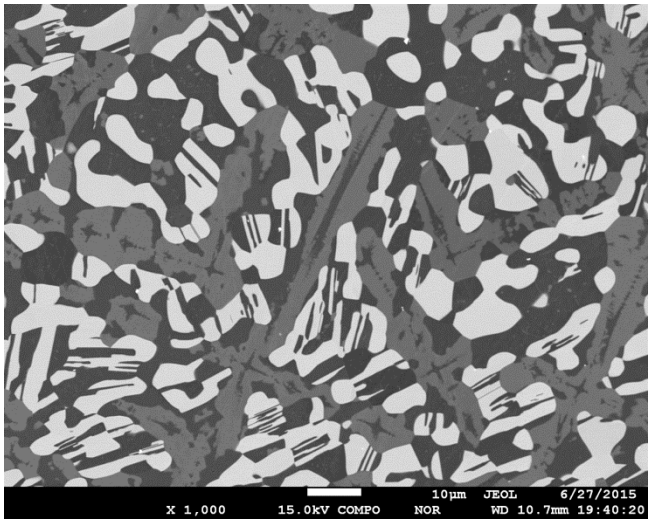
Calculated Ni-Hf phase diagram

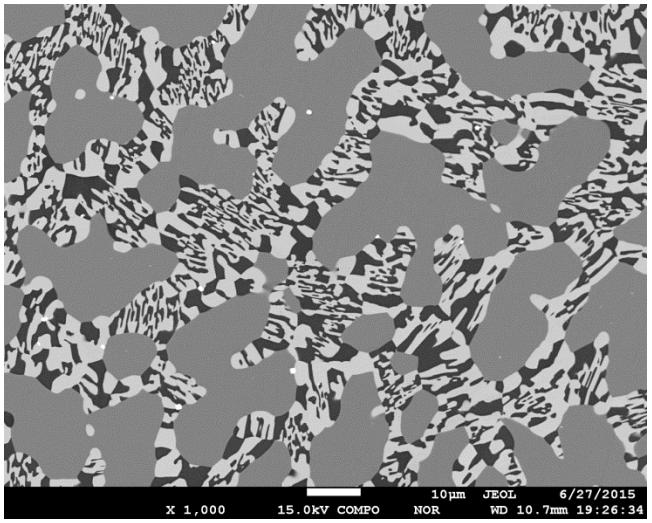


New cast alloys - Ternaries

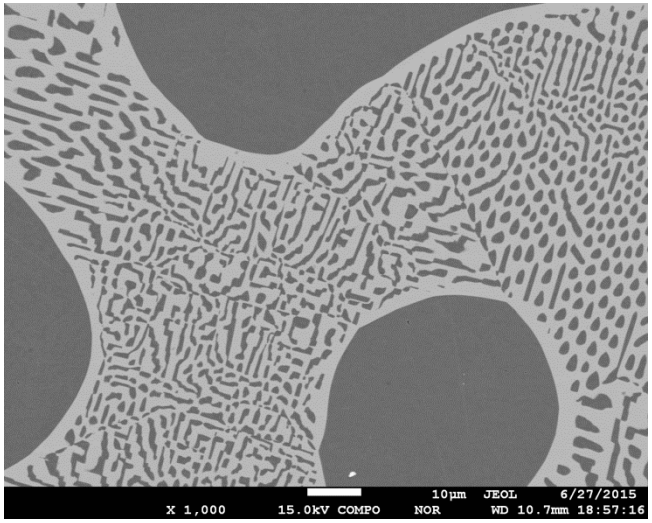
Micrographs, 1100 °C

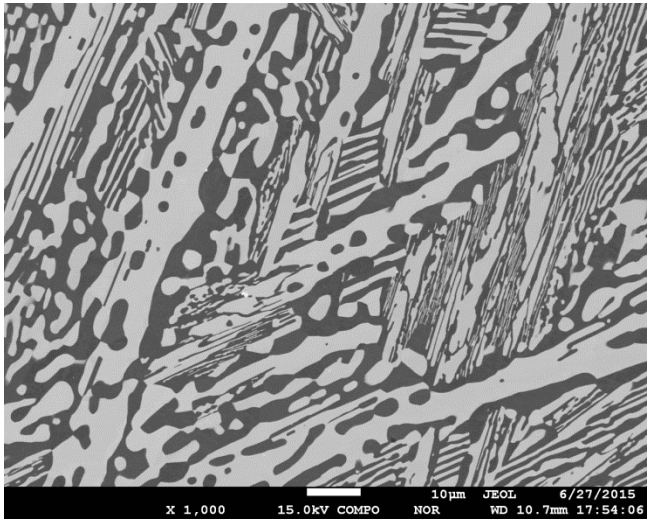
Al-Hf-Ni



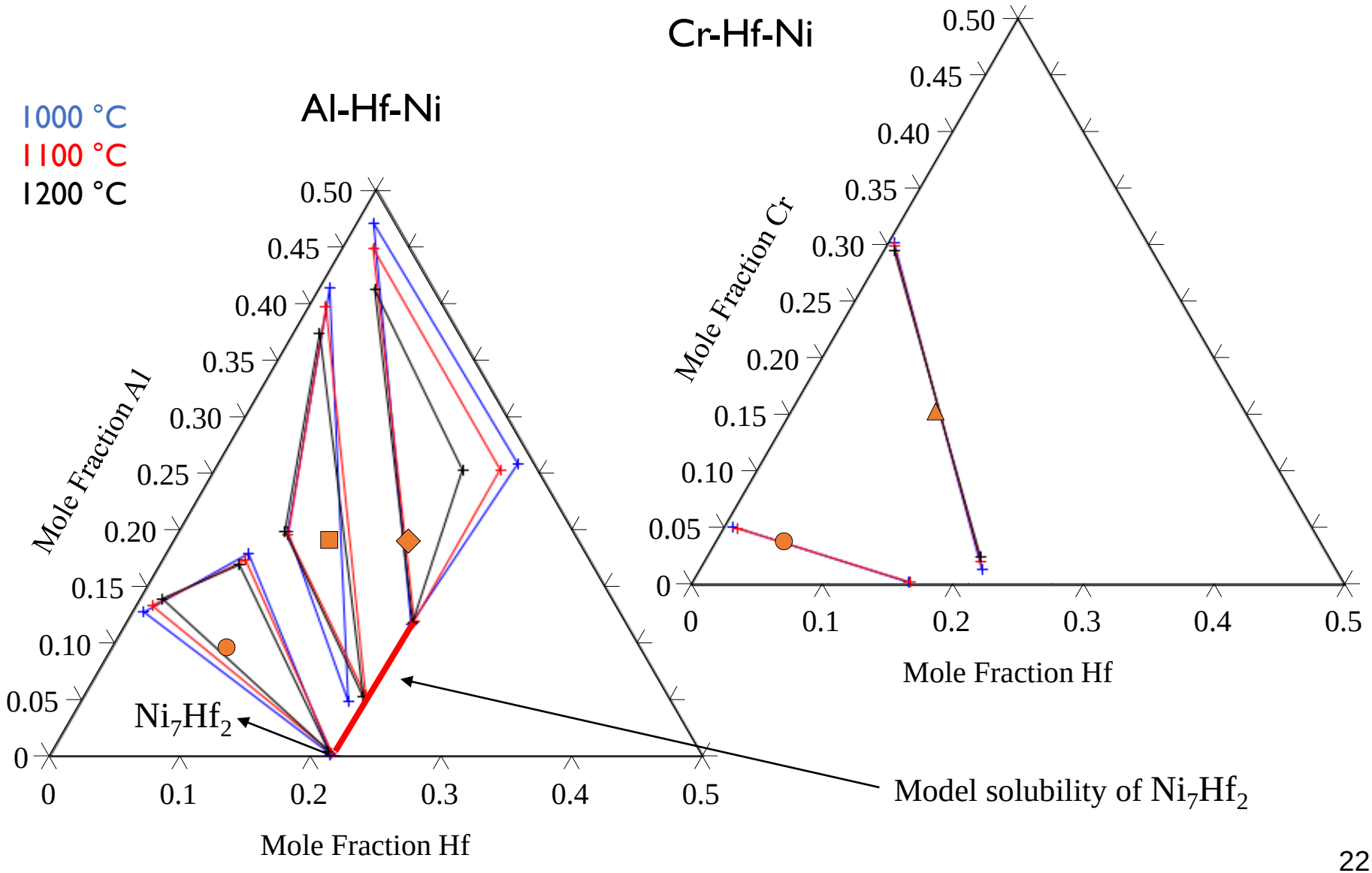


Cr-Hf-Ni



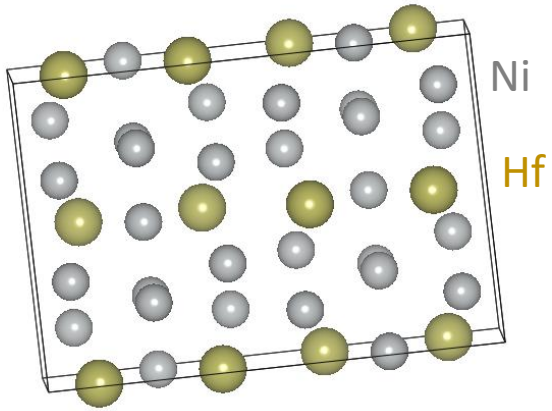


New cast alloys - Ternaries



Ni_7Hf_2 new sublattice model to include Al solubility

Compound	Prototype Structure	Space Group
Ni_7Hf_2	Zr_2Ni_7	C2/m



No	Atom	Multiplicity	Wyckoff
1	Ni	8	j
2	Ni	8	j
3	Ni	8	j
4	Hf	4	i
5	Ni	4	i
6	Hf	4	i

New Sublattice Model

$(Hf,Ni)_2(Al,Ni)_7$

↑

Al,Ni Interaction parameter from experiments

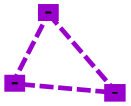
Assumption: all Al goes into the Ni site

DFT endmembers:

$(Hf)_2(Ni)_7$, $(Hf)_2(Al)_7$,$(Ni)_2(Ni)_7$, $(Ni)_2(Al)_7$

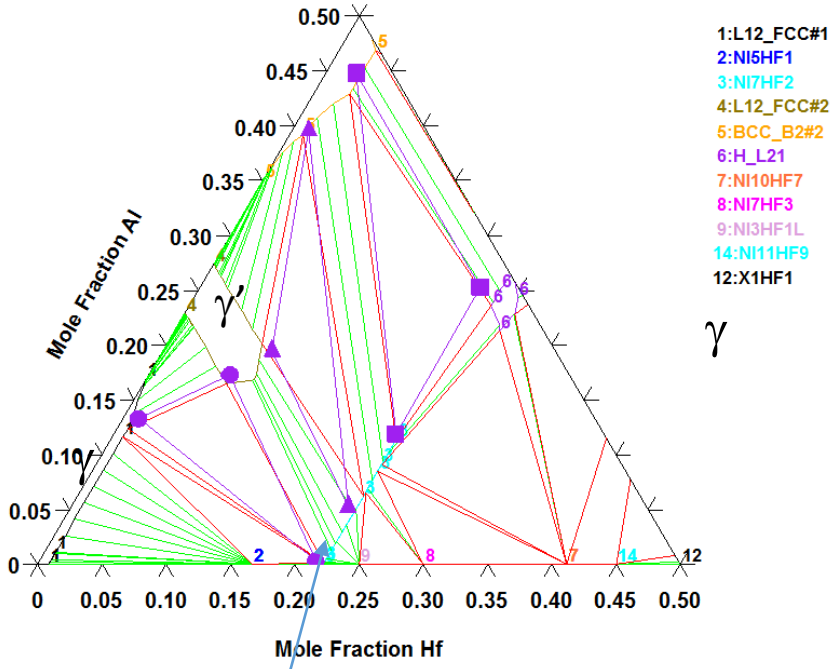
Calculated Al solubility in Ni_7Hf_2

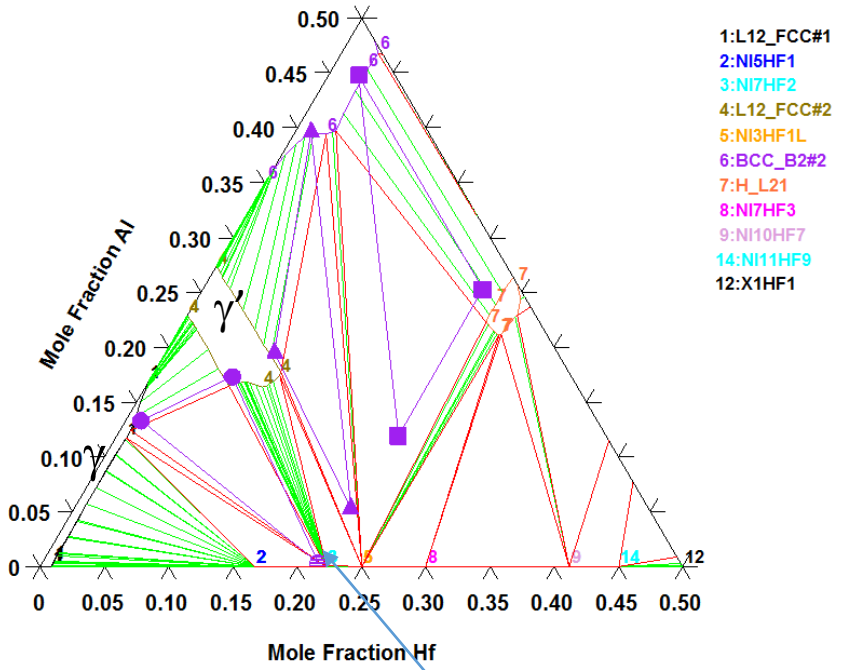
Considering Al solubility in Hf_2Ni_7



Experimental tie-triangle

Not considering



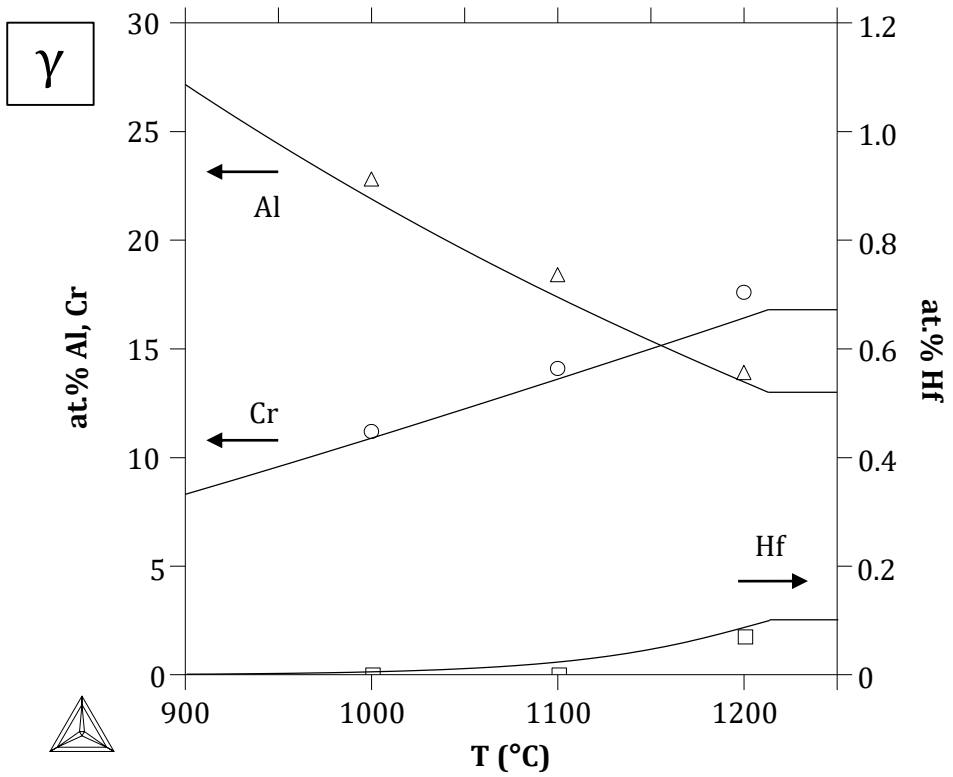


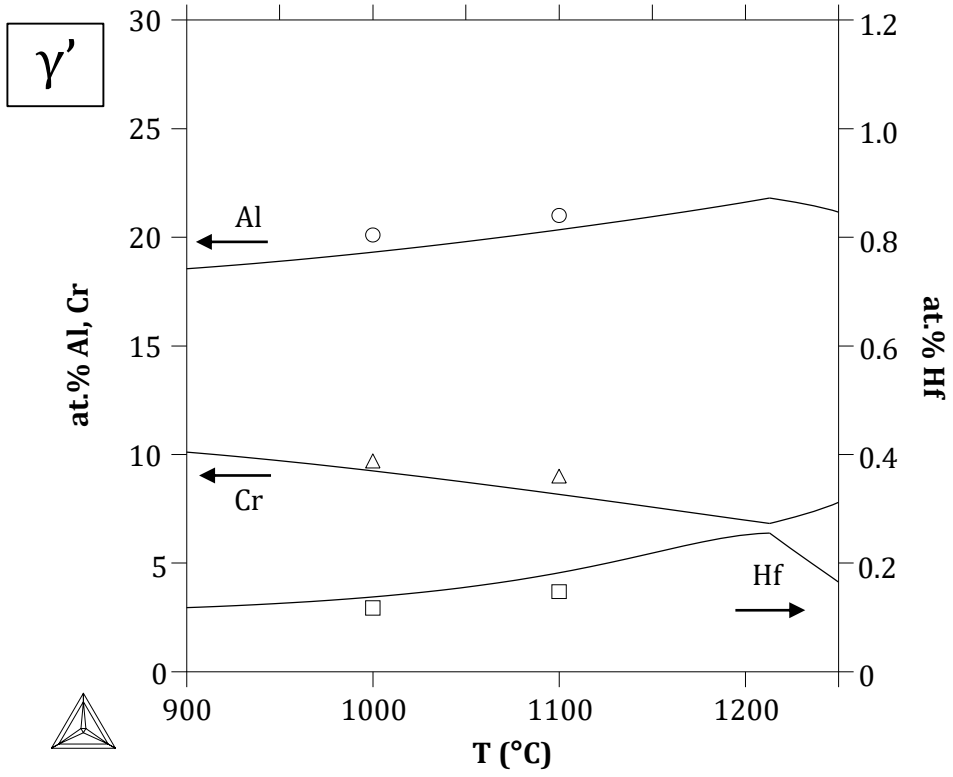
Ni_7Hf_2

T=1100℃

Ni_7Hf_2

Phase compositions in NiCrAl-Hf alloys



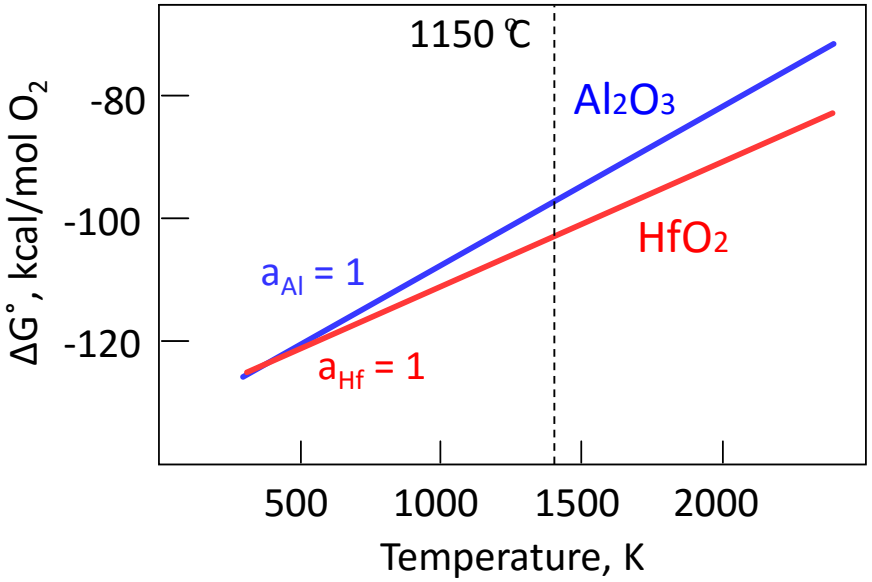


○ □ △ Experiments

——— Current thermodynamic modeling

II. Prediction of Hf tolerance in NiCrAl bond coat alloys

Thermodynamic considerations of oxidation



$$3Hf + 2Al_2O_3 \rightarrow 3HfO_2 + 4Al$$

$$\Delta G^{o} = -RT \times \ln K_{eq} \quad \text{and} \quad K = \frac{a_{Al}^{4}}{a_{Hf}^{3}}$$

In order to suppress HfO_2:

must have $K < K_{eq}$

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

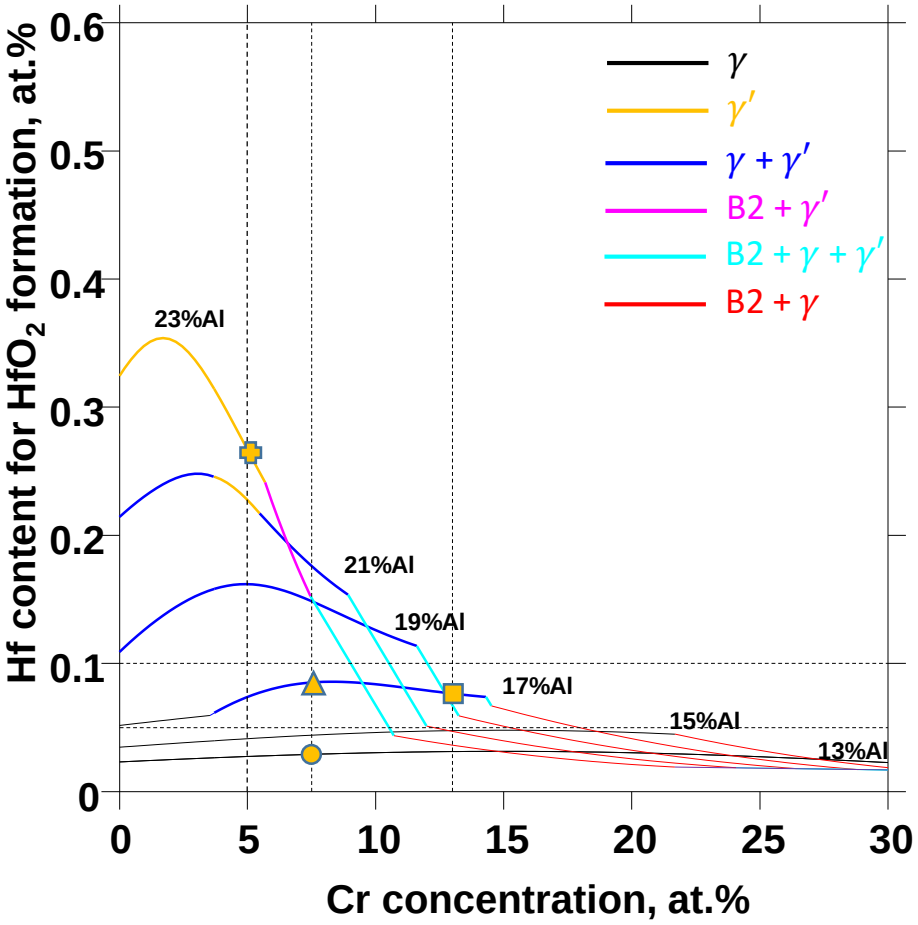
Control the Hf activity a_{Hf} in the alloys is key!

Oxidation of NiCrAl-Hf alloys

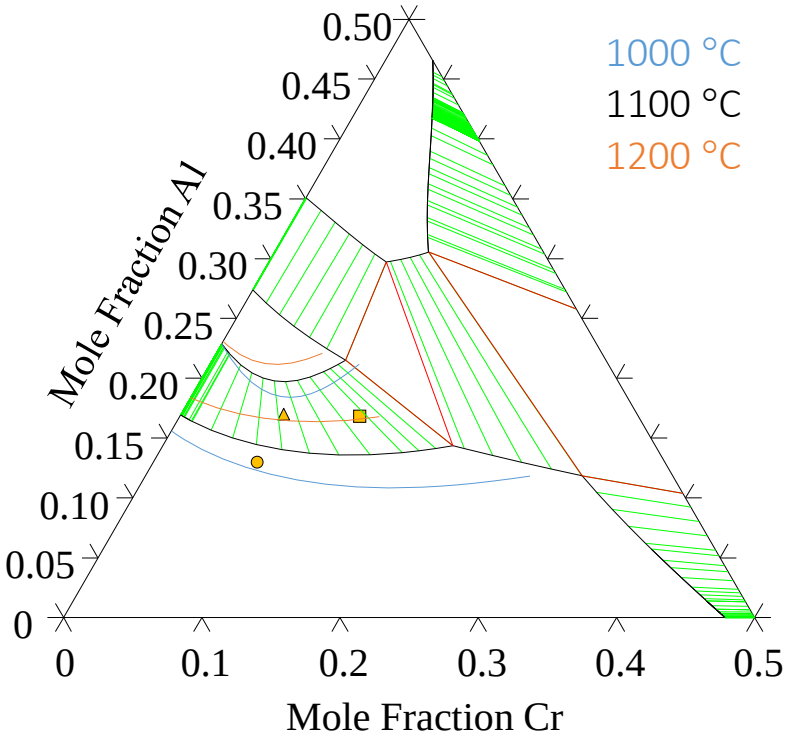
Three Ni-Al-Cr + 0.1 at. % Hf alloys

	HQ7	HQ8	HQ9
1000 °C	γ-γ'	γ-γ'	γ-γ'
1100 °C	γ	γ-γ'	γ-γ'
1200 °C	γ	γ	γ

Predicted HfO_2 formation "boundary" at 1000 °C

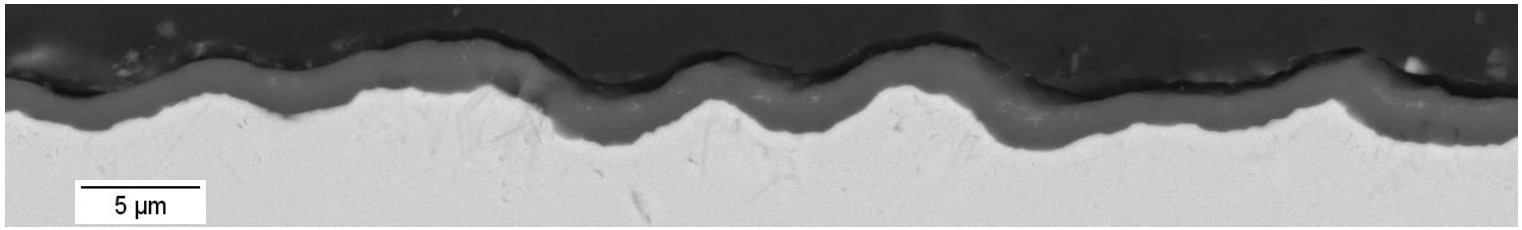


Calculated Al-Cr-Ni isothermal section

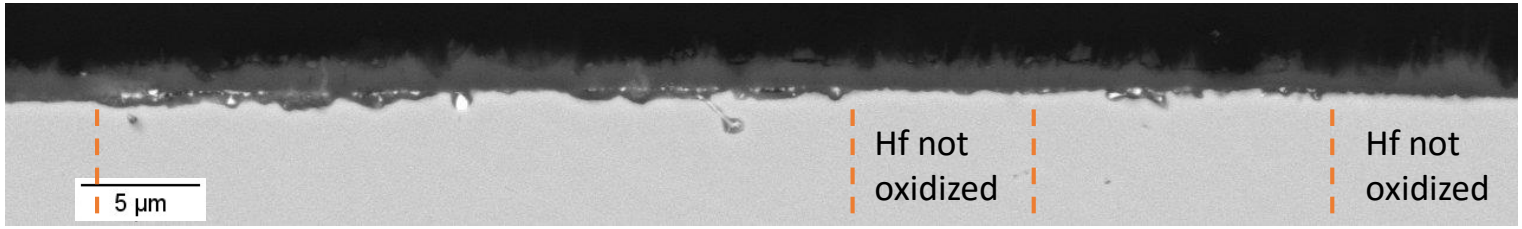


Determination of whether Hf oxidized or not

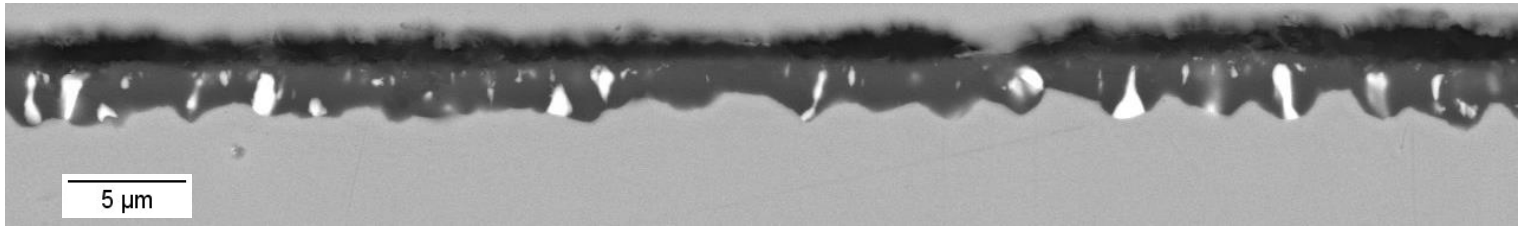
- No Hf oxidation (traces present in middle of scale probably left from transient stage)



- Localized Hf oxidation (this is a subjective call)



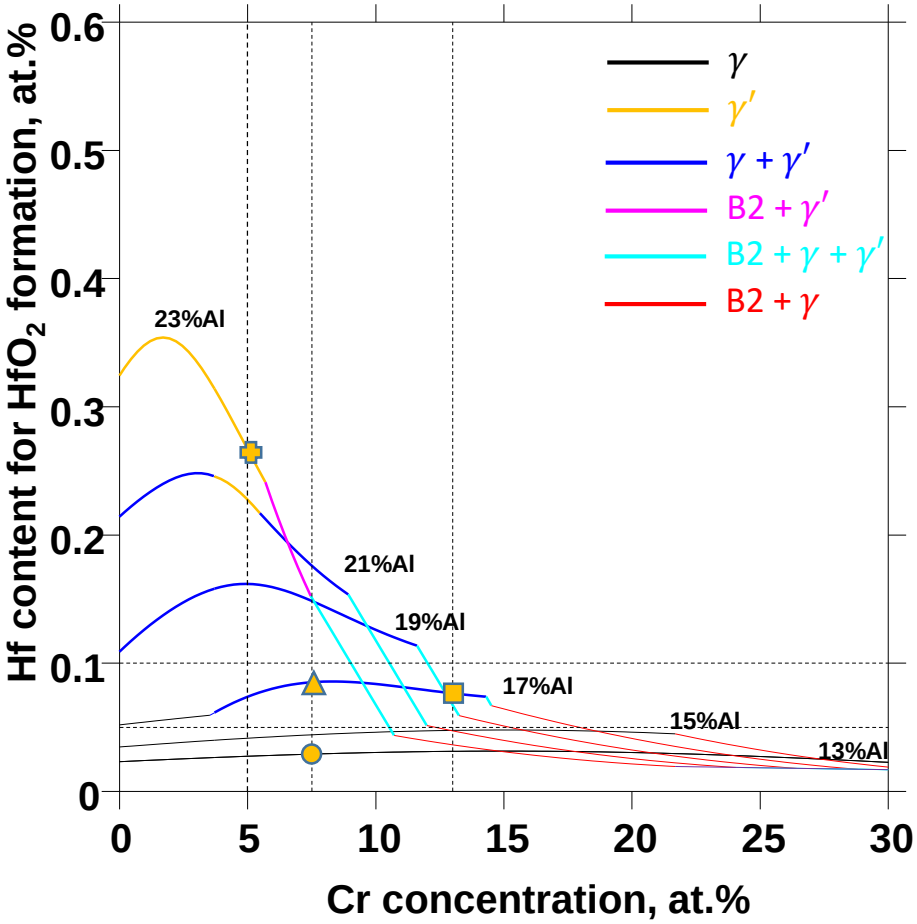
- Hf oxidation



Oxidation of NiCrAl-Hf alloys

Note: all three alloys contained 0.1 at. % Hf

Predicted HfO_2 formation "boundary" at 1200 °C

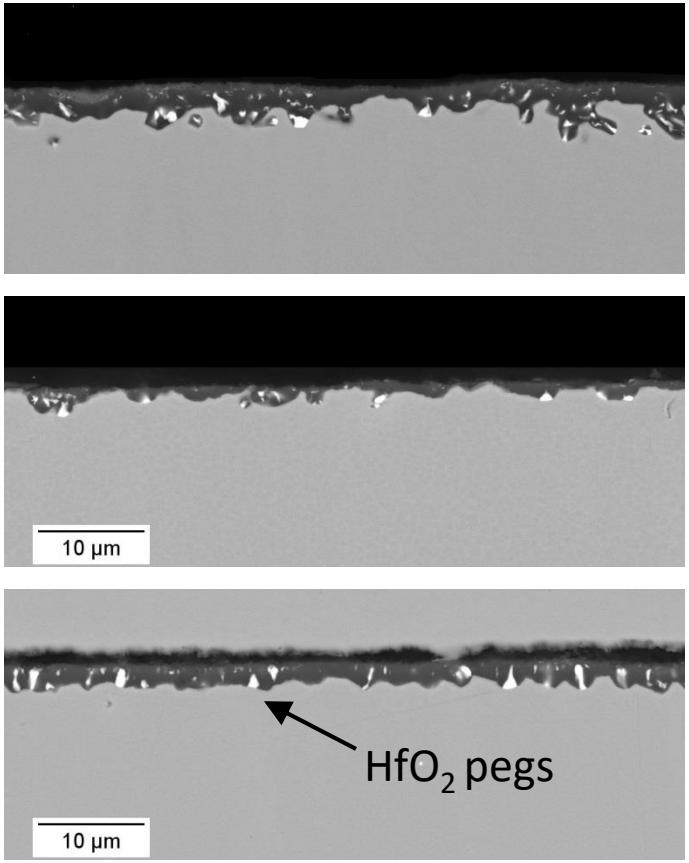


7.5Cr-13Al

7.5Cr-17Al

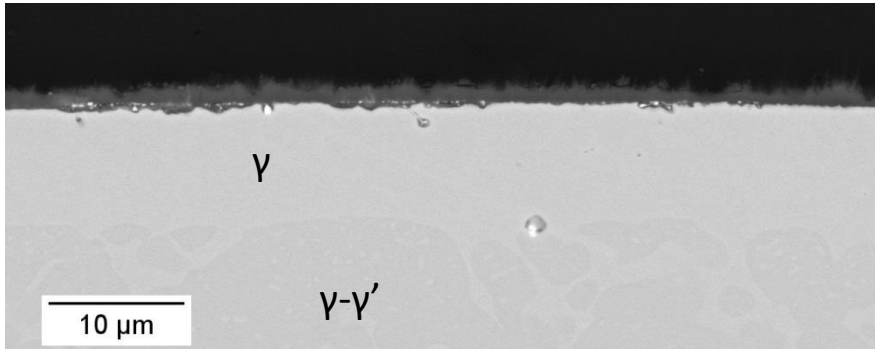
13Cr-17Al

1200 °C

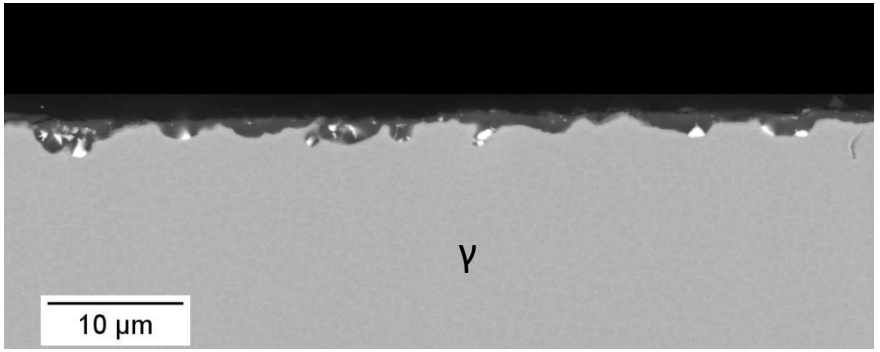


- Effect of **temperature**: tolerance reduced (larger driving force for HfO_2 formation) with increasing temperature

alloy HQ8 1100 °C

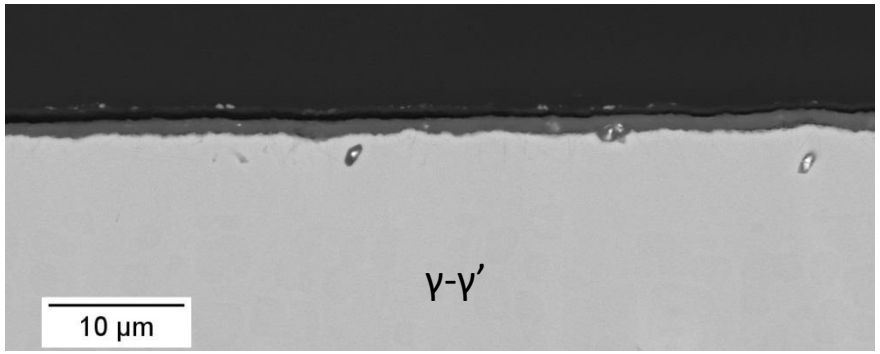


1200 °C

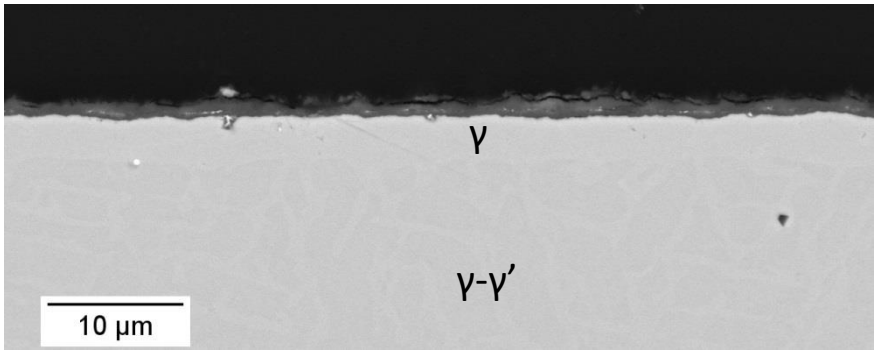


less zones with no oxidation

alloy HQ9 1000 °C



1100 °C

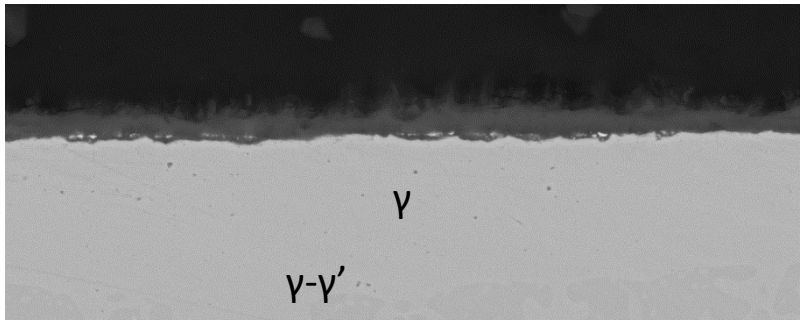


less zones with no oxidation

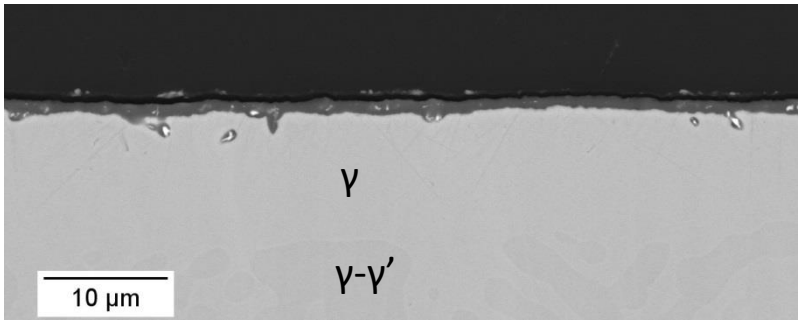
- Effect of **Hf** (more Hf promotes HfO2 formation)

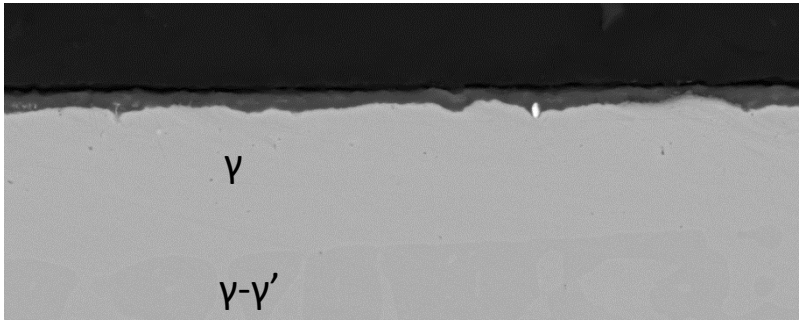
HQ10: Ni-8Cr-17Al-**0.05Hf**

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

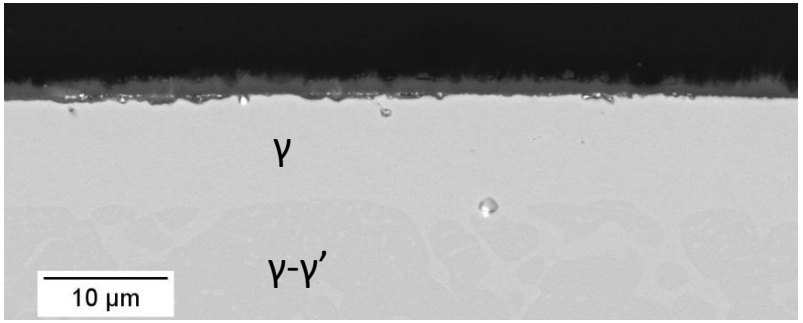


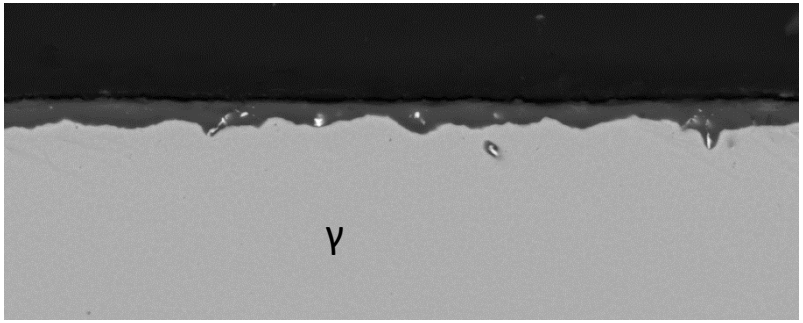
1000 °C



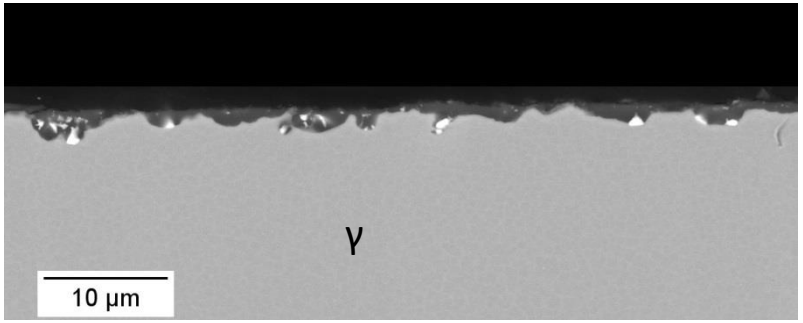


1100 °C





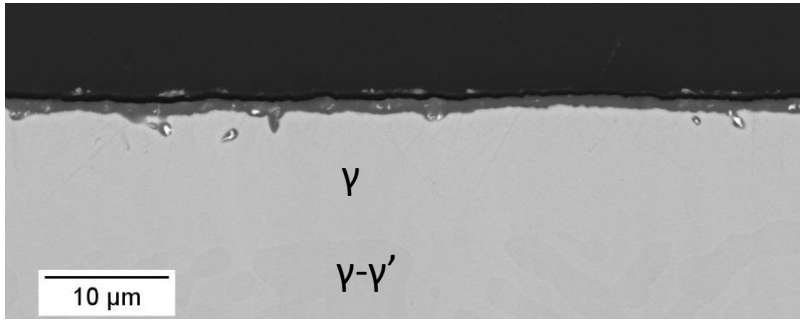
1200 °C



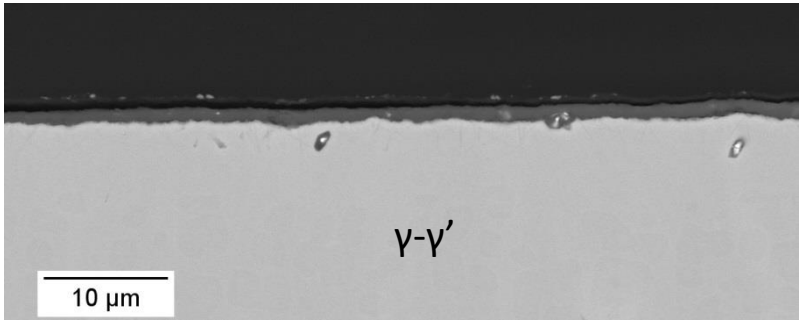
- Effect of **Cr** (prediction: Hf tolerance decreases when Cr increases)

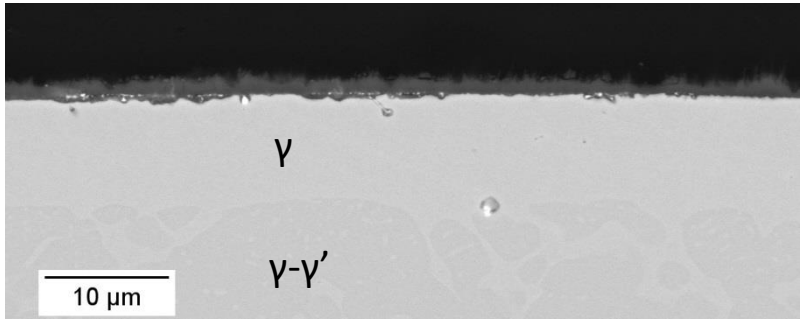
HQ8: Ni-**8Cr**-17Al-0.1Hf

HQ9: Ni-**13Cr**-17Al-0.1Hf

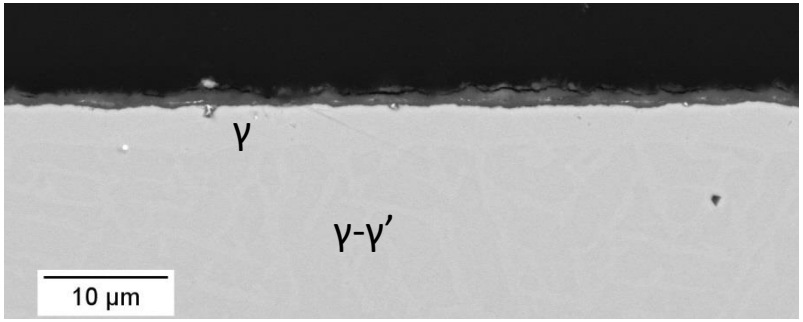


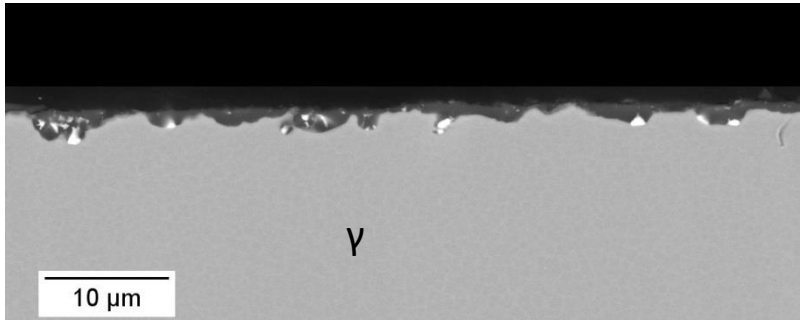
1000 °C



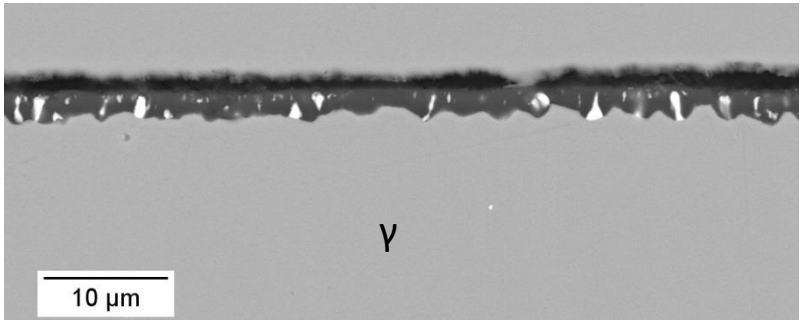


1100 °C





1200 °C



III. Preliminary results on the effect of Y

Ternary Assessments of Y-containing systems in Literature

Base	Al-Co-Cr	Al-Co-Ni	Al-Cr-Ni	Co-Cr-Ni		
X_1-X_2-Y	Al-Co-Y	Al-Cr-Y	Al-Ni-Y	Co-Cr-Y	Co-Ni-Y	Cr-Ni-Y
X_1-X_2-Hf	Al-Co-Hf	Al-Cr-Hf	Al-Ni-Hf	Co-Cr-Hf	Co-Ni-Hf	Cr-Ni-Hf
X_1-X_2-Si	Al-Co-Si	Al-Cr-Si	Al-Ni-Si	Co-Cr-Si	Co-Ni-Si	Cr-Ni-Si
X_1-Hf-Y	Al-Hf-Y	Co-Hf-Y	Cr-Hf-Y	Ni-Hf-Y		
X_1-Hf-Si	Al-Hf-Si	Co-Hf-Si	Cr-Hf-Si	Ni-Hf-Si		
X_1-Si-Y	Al-Si-Y	Co-Si-Y	Cr-Si-Y	Ni-Si-Y		
Additions	Hf-Si-Y					

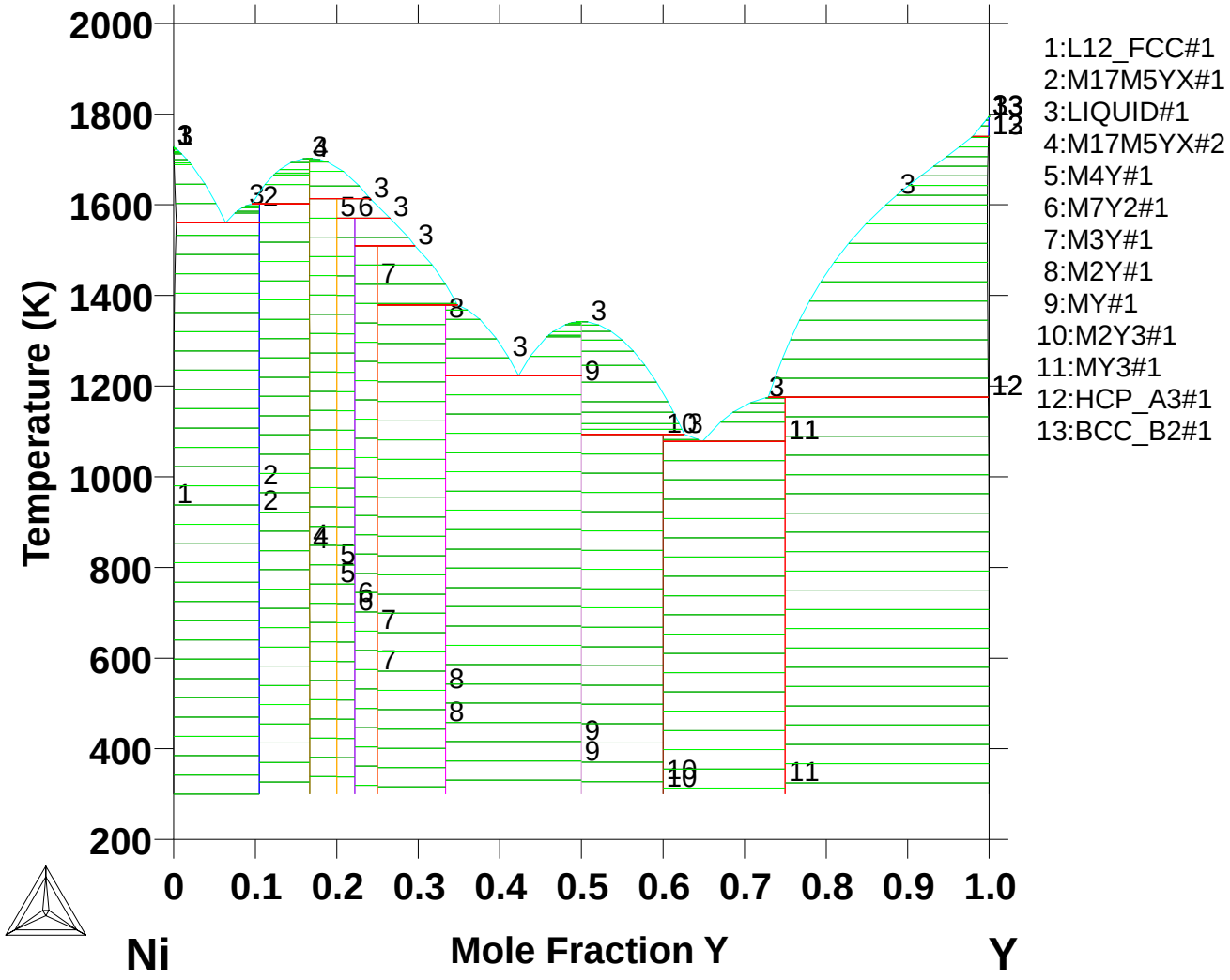
Assessment available

Good from binaries

Assessment not found

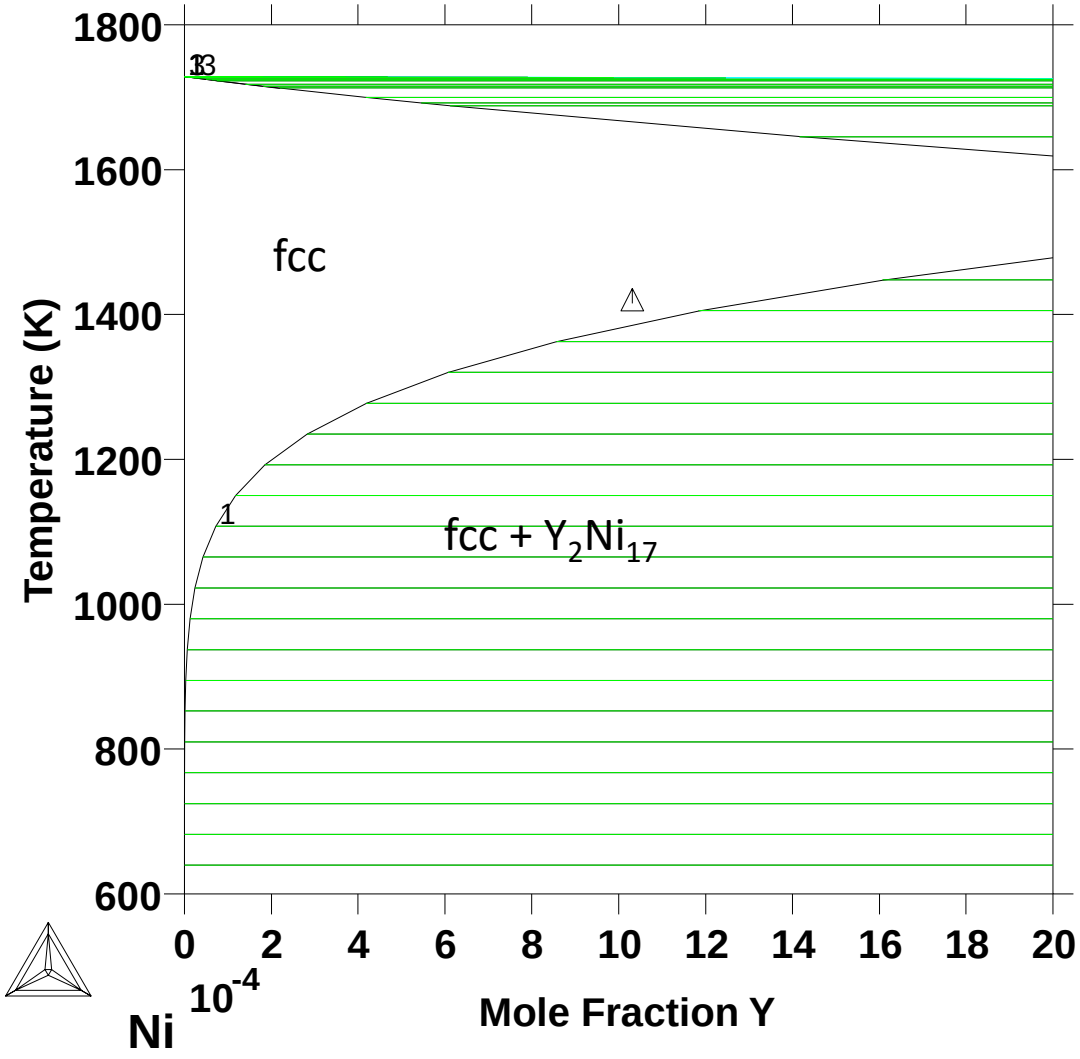
Assessment under investigation

Ni-Y



Du, Z., & Lü, D. (2005). Thermodynamic modeling of the **Co–Ni–Y** system. *Intermetallics*, *13*(6), 586–595.

Y Solubility in Ni



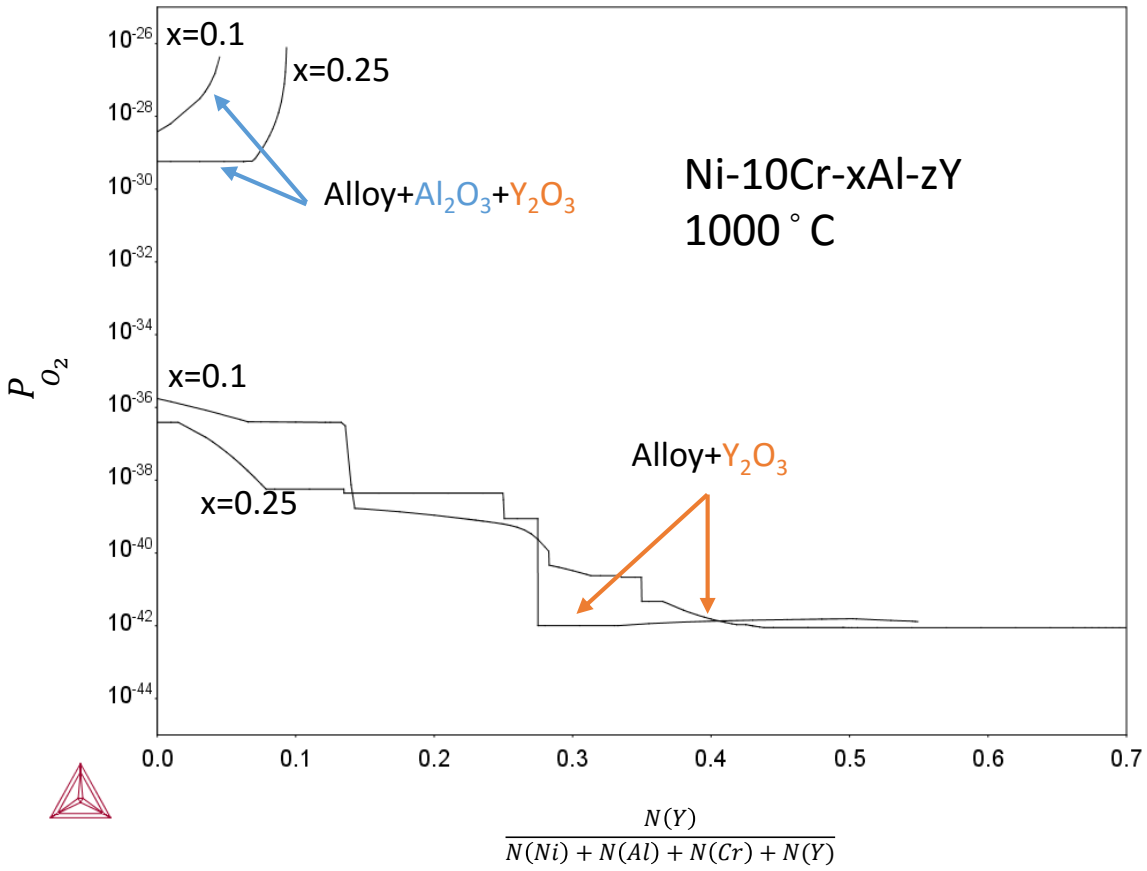
Interactions in the fcc phase from Huang et al. (2015).

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

Huang, J., Yang, B., Chen, H., & Wang, H. (2015). *Journal of Phase Equilibria and Diffusion*, *36*(4), 357–365.

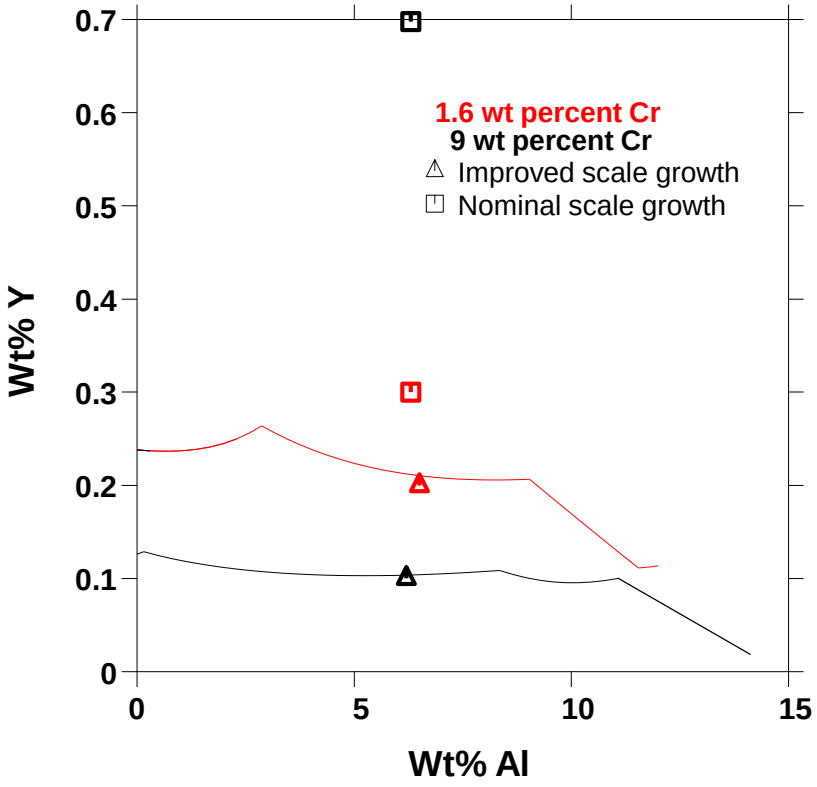
Beaudry, B. J., Haefling, J. F., & Daane, A. H. (1960). *Acta Crystallographica*, *13*(9), 743–744.

Stability of Y_2O_3

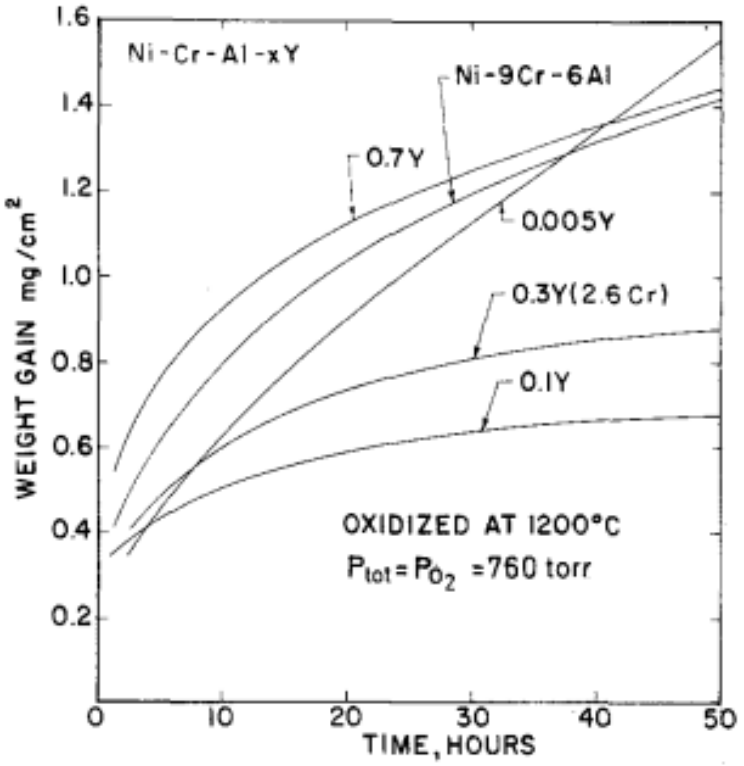


Hf tolerance concept not present: Y_2O_3 always more stable at low P_{O2}

Oxidation of Ni-Al-Cr-Y Alloys at 1200 °C: possible correlation between oxide scale formation and yitrides formation



Yittrides tolerance curves



Kvernes, I. A. (1973). *Oxidation of Metals*, *6*(1), 45–64.

Future Works in Phase II

- Continue to investigate the Y and Si effects on oxide scale formation in Phase II
- Study the *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

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- Project manager: Jason Hissam
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Thank you for your attention.

Any questions?