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AMES LABORATORY

Computational and Experimental Development of Novel High Temperature Alloys

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The Problem

- Increasing efficiency require higher operating temperatures
  - Loss in creep strength
  - Dramatic Increase in oxidation rates
- Coal combustion environment
  - Highly Variable
    - H_2O, HS, NO_x etc.
    - Particulate erosion
- Cost of materials
  - Balance of down-time vs lifetime
    - i.e., are Ni-based alloys worth the cost?
- Are there better materials systems?
- Are there more effective ways of tweaking existing systems

Options

- Large region of the potential phase space unexplored
  - Edisonian approach is not an option
  - Computational Thermodynamics
    - Extrapolation of known thermodynamic data
      - Can easily handle multidimensional phase space
      - Large lead time for database development
  - *Ab initio*
    - Precise formation enthalpies
      - At 0 K
      - No entropic information
    - Density of States
      - What phases could form
    - Need to know what compounds are of interest!
- Approximate methods
  - Miedema

Conceptual Approach

- No one methodology will work in all circumstances
  - Utilize less rigorous computational methods as an initial screening tool
  - More accurate methods as phase space is refined
- Respect the researcher's intuition and experience
- Utilized the existing knowledge base
- Critical metrics (experiments) are required for validation

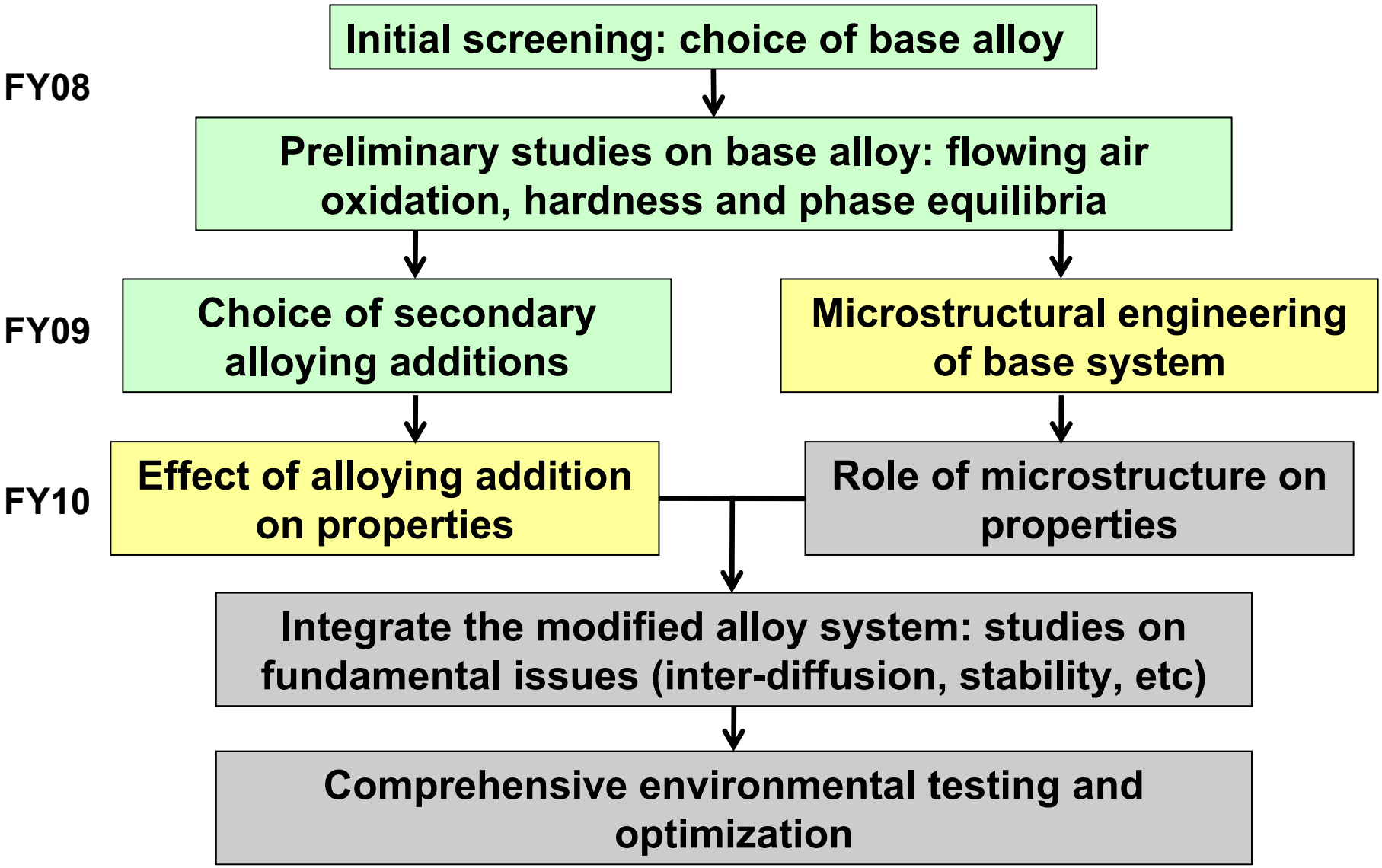
Hierarchical Evaluation

- Rapid Screening of potential systems
  - High melting temperature
    - i.e., high formation enthalpies
  - Elements comprising the major weight fraction should be low cost
  - Matrix should be a refractory metal with BCC or FCC
    - Strength and ductility
  - Contain a ‘reservoir’ for passivating components
    - Al, Cr, Si

Hierarchical Evaluation

- Rapid approximant methods
  - Less precise but quickly eliminate most likely ‘dead-ends’
- Refining Steps
  - Higher degree of precision
  - Identify critical experiments
- Utilize relative strengths of many techniques
  - i.e., *ab initio* and Calphad

Project layout



Initial screening of Alloy systems – the two-phase base alloy system

The need for speed

Number of elements	Possible combinations
2	3160
3	82160
4	1.58×10^{6}
5	2.40×10^{7}
6	3.00×10^{8}
7	3.18×10^{9}
8	2.90×10^{10}
9	2.32×10^{11}
10	1.65×10^{12}

- **Say, for a 4 element Ni-Al based system, with 2 elements from TM block – 406 combinations**
- **5 elements – 3654 combinations**
- **6 elements – 23751**
- **Within these, there are compositional variations**

Exploring a vast phase space using an Edisonian approach is not efficient

Miedema Model

- Developed to predict formation enthalpies of binary compounds
  - Assume metals are in their standard state
  - Macroscopic view of alloying
    - Not an atomistic approach
  - Interfacial energy between the two metals is ~ their liquid heat of formation
  - Formation energy is ~ contact interaction between the two metals
- Can this be extended to ternary and higher systems

The ternary Miedema

The total formation enthalpy:

$$\Delta H = \phi_1 \Delta H_{AB}(\alpha) + \phi_2 \Delta H_{BC}(\beta) + \phi_3 \Delta H_{CA}(\gamma)$$

Enthalpy of the binary systems computed using Miedema's model

$$\sum_{i=1}^{3} \phi_i = 1$$

$$\phi_1 \alpha + \phi_3 (1-\gamma) = x_A$$

$$\phi_2 \beta + \phi_1 (1-\alpha) = x_B$$

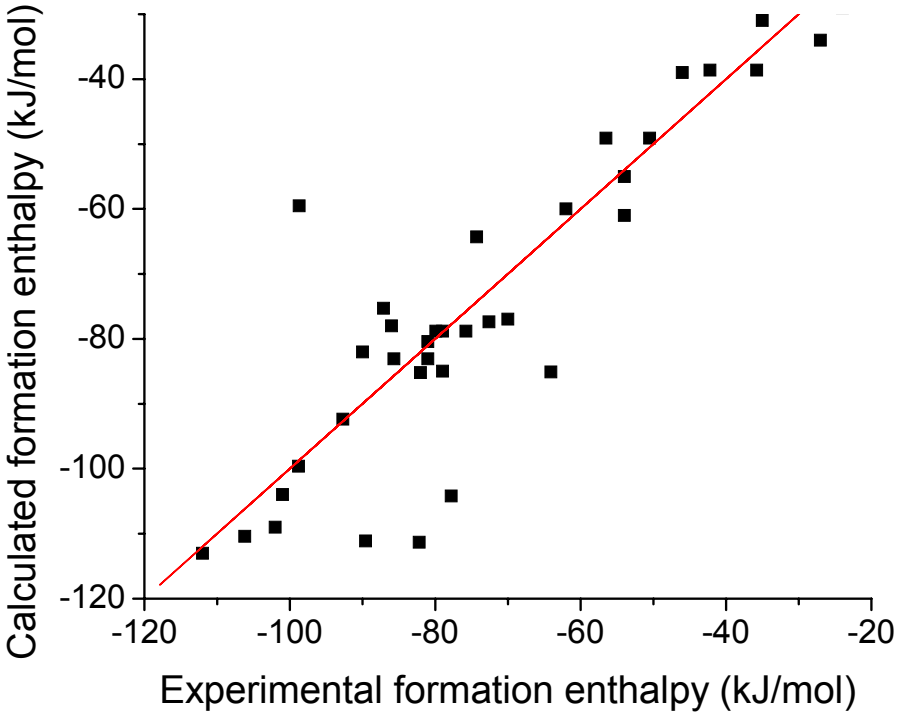
$$\phi_3 \gamma + \phi_2 (1-\beta) = x_C$$

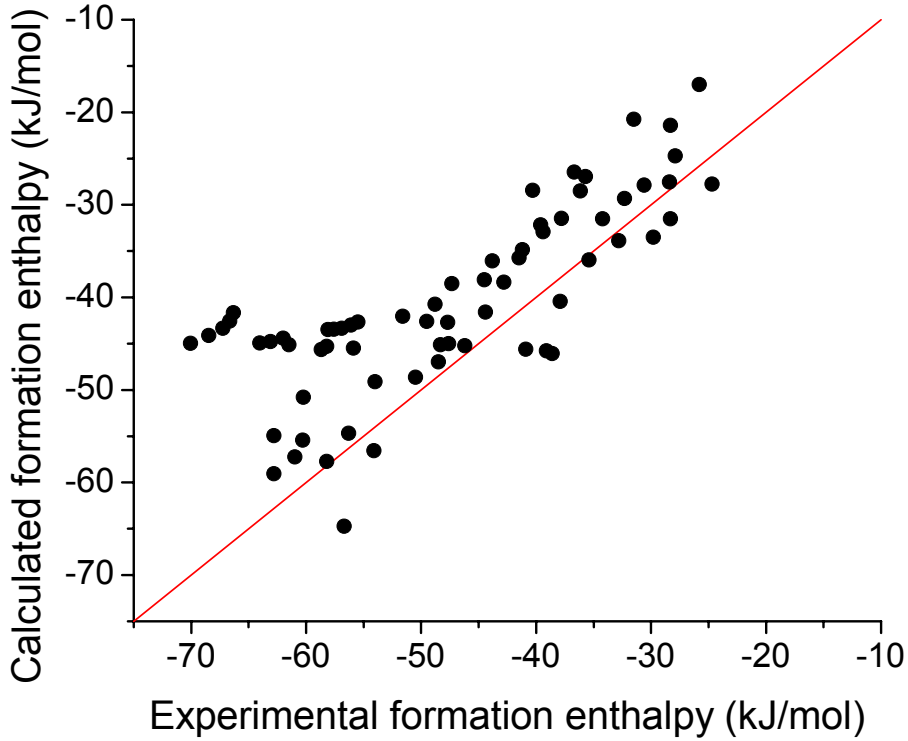
Constraints arising due to mass balance

Parameters optimized such that the formation enthalpy is minimized. The final enthalpy is the one that is calculated with the optimized parameters.

The ternary Miedema

A comparison of experimentally observed formation enthalpy of TM-Al vs Al-Ni-X alloys





The binary Miedema

The extended Miedema

Experimental values from R. Hu, P. Nash, Journal of Materials Science 41 (2006) 631-641.

Screening for High Temperature Systems

- **Conceptual Framework**
  - **Strength and Toughness**
    - **Matrix needs to be high symmetry**
    - **Avoid brittle intermetallics**
  - **Oxidation stability**
    - **Need source of Al, Cr etc., depending on application**
  - **High melting T**
- **Alloy architecture based on Ni-based superalloys**
  - **Replace Ni matrix with more refractory metal**
  - **Retain NiAl for oxidation stability**
  - **New matrix should not form compounds with Al**
  - **higher T_m is reflected in an increase in enthalpy**

Relative stability & melting

3	4	5	6	7	8	9	10	11
Sc 0.3	Ti 0.2	V -8	Cr -33	Mn -4	Fe -16	Co -5	Ni xxx	Cu -36
Y 0.22	Zr 0.7	Nb -6	Mo -24	Tc xxx	Ru -3	Rh 0.3	Pd 0.7	Ag -41
La 0.16	Hf 0.5	Ta -5	W -28	Re -19	Os xxx	Ir xxx	Pt 0.7	Au -17

ΔH (NiAl) – ΔH(TMAl)

← More negative is better!

But not enough also need a high melting T →

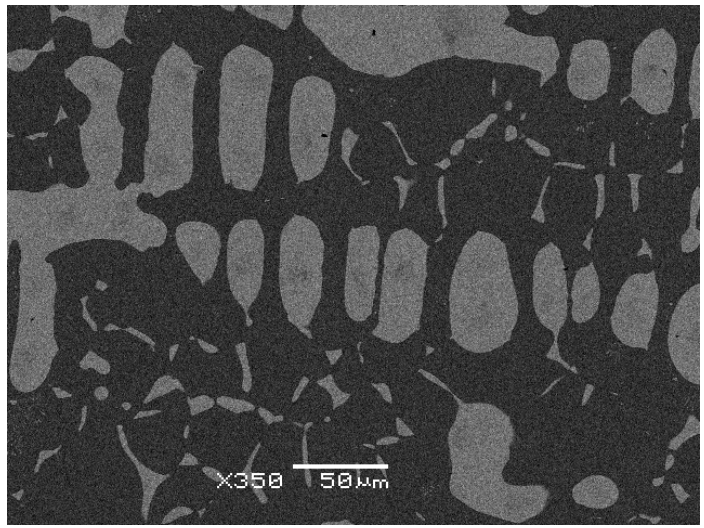
3	4	5	6	7	8	9	10	11
Sc 1539	Ti 1670	V 1902	Cr 1857	Mn 1244	Fe 1540	Co 1495	Ni 1453	Cu 1083
Y 1526	Zr 1852	Nb 2467	Mo 2617	Tc 2200	Ru 2250	Rh 1963	Pd 1552	Ag 961
La 920	Hf 2227	Ta 3014	W 3407	Re 3180	Os 3027	Ir 2443	Pt 1772	Au 1065

Initial screening: base alloy

Possible choice of "backbone" metal

Sc, Ti, V, Mn, Fe, Co, Y, Zr, Nb, Mo, Ru, Rh, Re, Pd, Pt, La, Hf

Alloy system = NiAl (oxidation resistant phase) + backbone phase (metal rich solid solution)



Cast ingot of a Mo-Ni-Al:

Mo dendrites (bright) show very little ss w/ Ni or Al

Mo appears to be the best choice for the backbone metal based on strength, ductility, T_m and cost.

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Secondary screening of Alloy systems: additions to oxidation resistant phase

Secondary screening

- **Use the Miedema model results to find elements that increase the formation enthalpy (makes it more negative) when added to Ni-Al, but does not increase the formation enthalpy when alloyed with the refractory metal matrix**

- **Find the enthalpy minima when the 4th element is substituted for Ni (Mo-Al-Ni-X)**

- **Possible quaternary additions: Pd, Pt, Rh (these increase the enthalpy and have the same crystal structure as nickel)**
- **Augment semi-empirical with more accurate *ab initio***
  - **Need for more precise enthalpies**
  - **Specific limits of solid solutions**
  - **Don't need a database!**

Secondary screening

- **Choice of alloying additions to NiAl – enthalpy criterion**

3	4	5	6	7	8	9	10	11
Sc -195	Ti -179	V -128	Cr -96	Mn -120	Fe -101	Co -109	Ni xxx	Cu -95
Y -187	Zr -232	Nb -152	Mo -100	Tc xxx	Ru -113	Rh -146	Pd -171	Ag -94
La -181	Hf -211	Ta -152	W -96	Re -97	Os xxx	Ir xxx	Pt -171	Au -96

Red colors indicate elements most likely to alloy w/ Ni-Al and not Mo

Secondary screening

List of favorable elements

Sc, **Ti**, **Y, Zr**, La, **Hf, Pd, Pt, Rh**, Nb, Ta

Finer screening

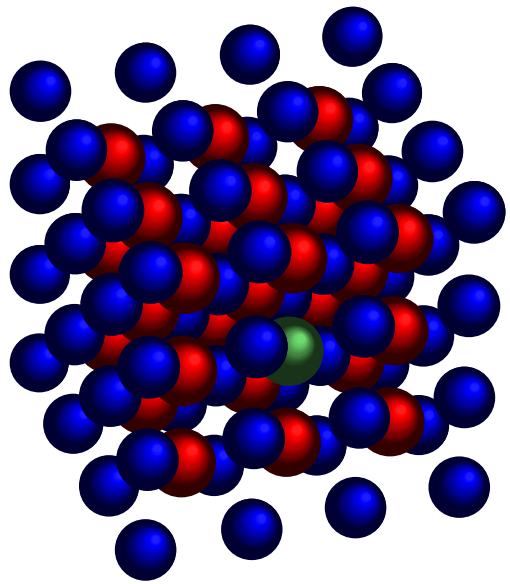
- Eliminate alloying additions that stabilize the liquid
- Eliminate alloying additions that tend to form porous non-volatilizing oxides (e.g. Nb)

Effect of alloying additions

- ***Ab-initio*** **calculations and site preference**
- **Thermal stability – ultra high temp DTA**
- **Oxidation resistance as a function of temperature (flowing air and cyclic tests)**
- **Studies on the oxide scale**
- **Mechanical strength**

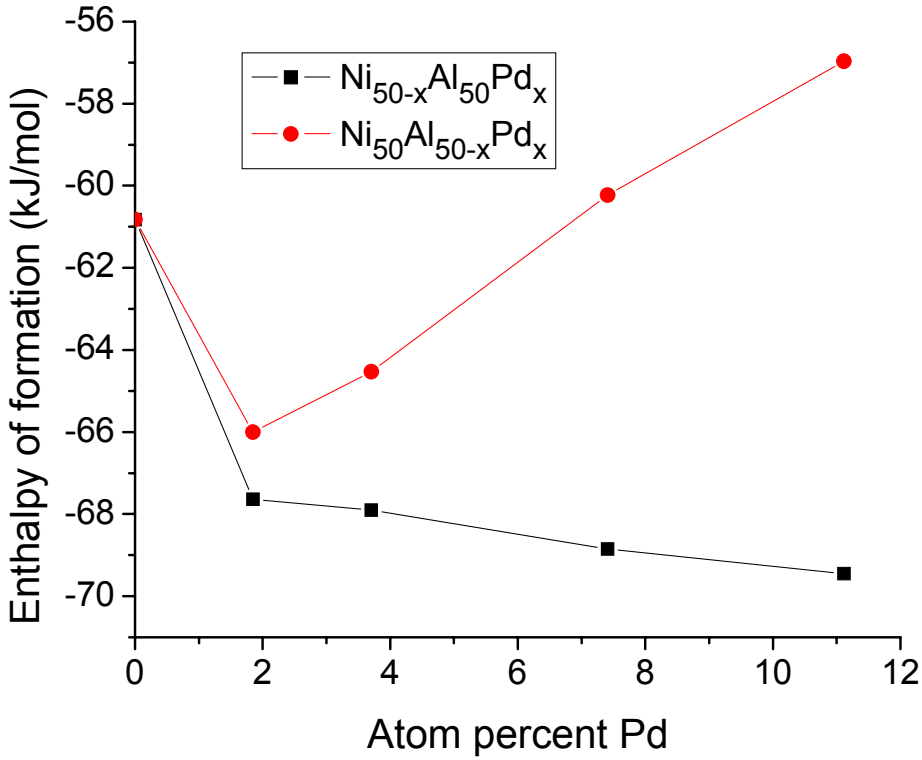
Final Computational Screen

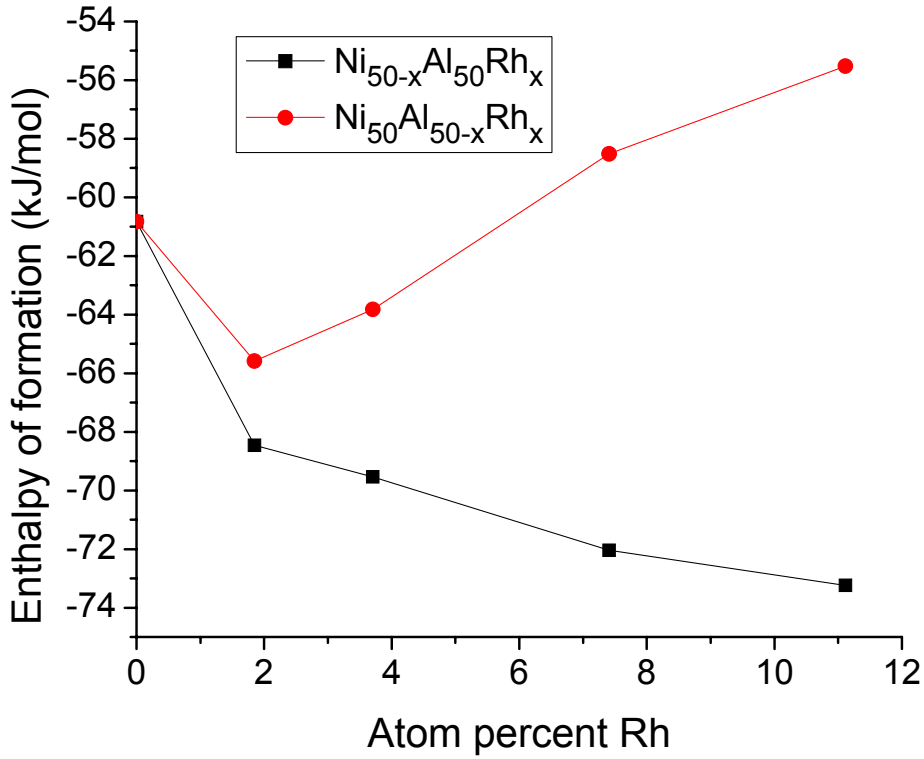
- ***Ab-initio*** **studies using VASP with GGA potentials, NiAl (B2)**
- **54 atom unit cell used for all the calculations**
- **Calculations carried out by substituting ternary alloying element for Ni and Al**
  - **Substitute 1, 2, 4 or 6**
    - **Test both Ni and Al sites**
  - **Y, Hf, Zr, Rh, Pd, Ru, Ti, Pt, Nb, Ru, Sc**



3x3x3 unit super-cell

Site Preference

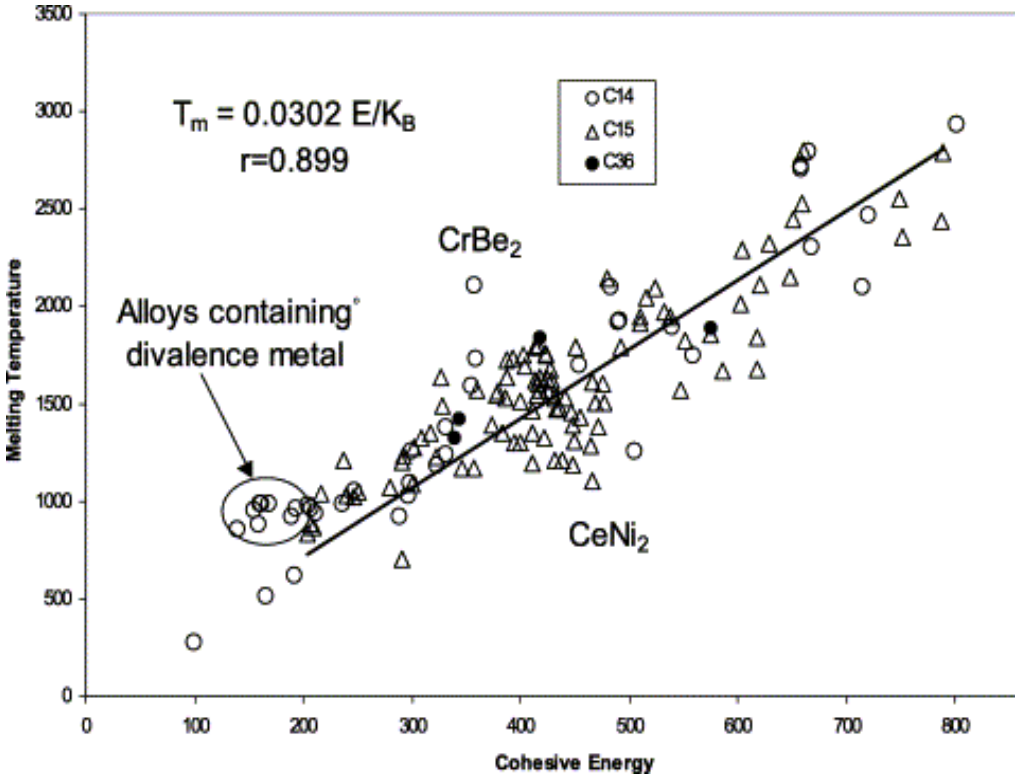


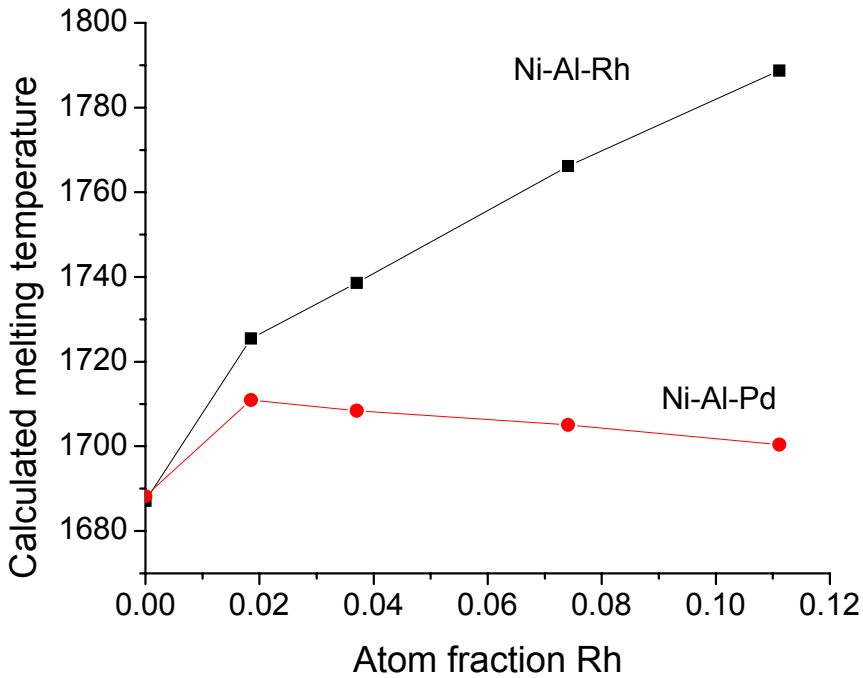


- **Thermodynamically, the Ni site is preferred!**
- **Substitution in Ni site results in a drop in formation enthalpy**
  - **Guide for Experiments!**

Estimates of melting

- **Rose-Ferrante relation for melting – based on the universal binding curve**





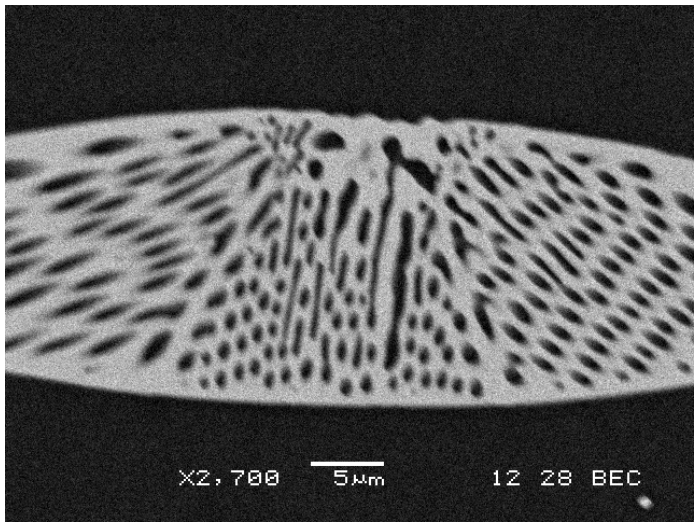
Ternary addition should increase T_m!

Reference: Li et. al., J Phys Chem Sol 64(2003) 201

Experimental Validation

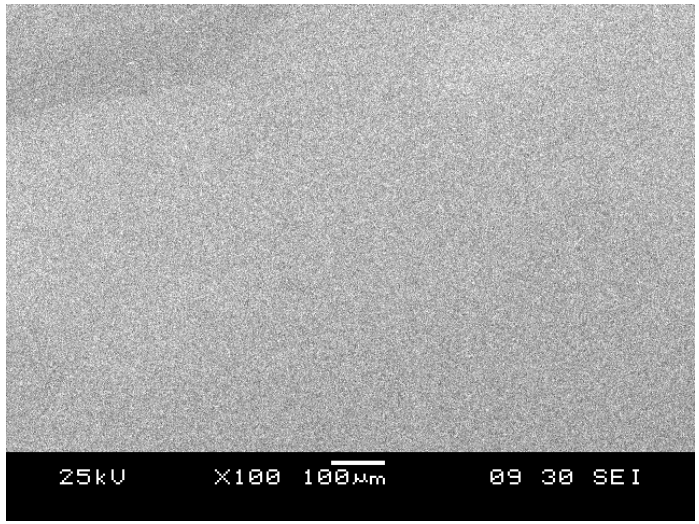
- Tested NiAl+TM, both Ni and Al sites
  - TM = Zr, Y, Hf, Rh and Pd
- Arc-melted in a 2-stage process
- Drop-cast to obtain cylindrical samples
- Annealed at 1300°C for 6 hrs
- Characterization – SEM, XRD
  - Single phase?
- Further testing, Rh and Pd
  - flowing air oxidation
    hardness

What worked & what didn't

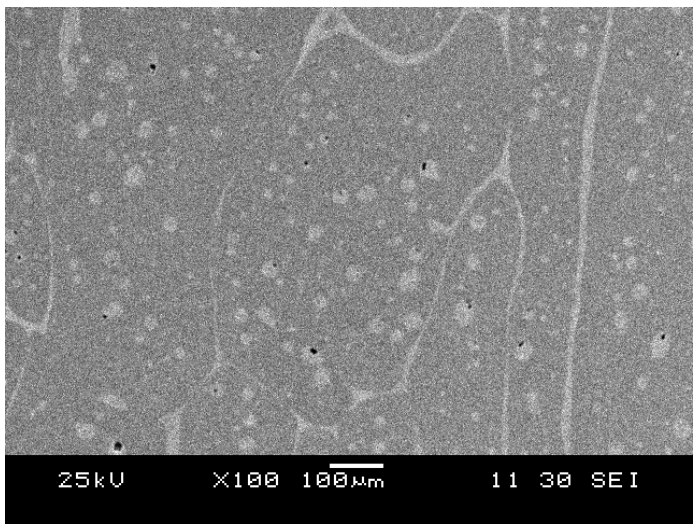


Ni-Al-Hf ←

Ni-Al-Pd →

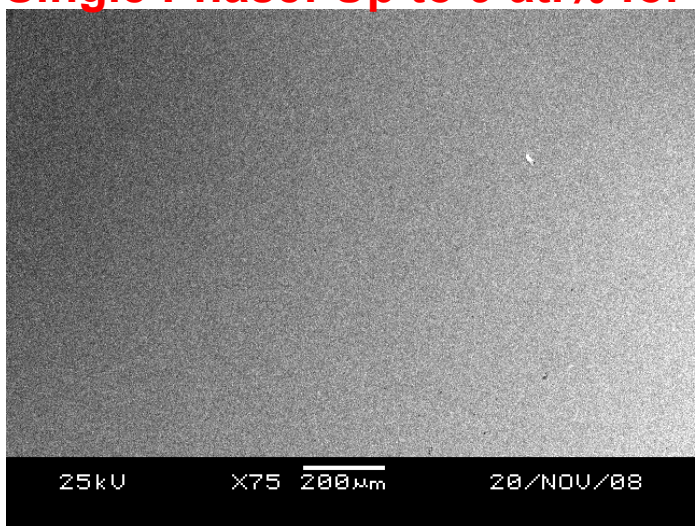


Single Phase! Up to 9 at.% for Ni

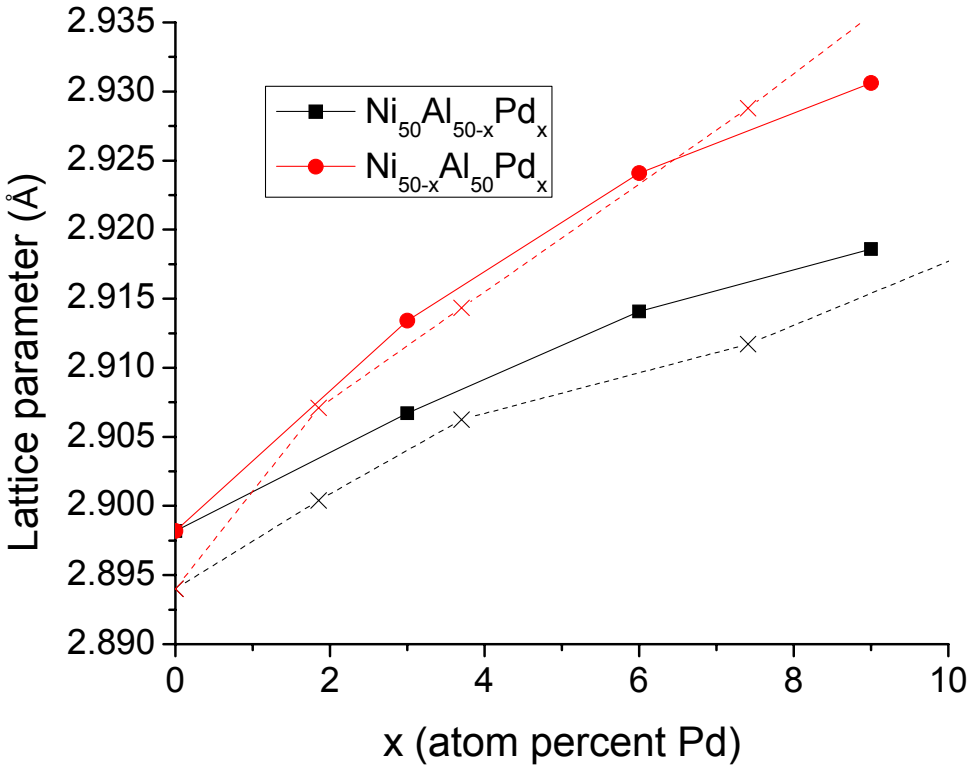


Ni-Al-Zr ←

Ni-Al-Rh →



X-Ray diffraction

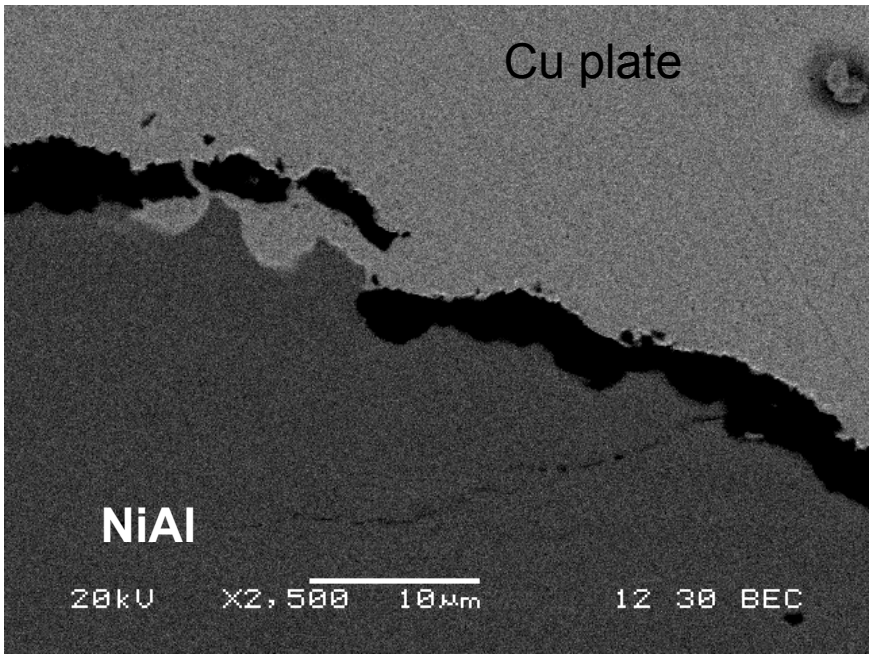


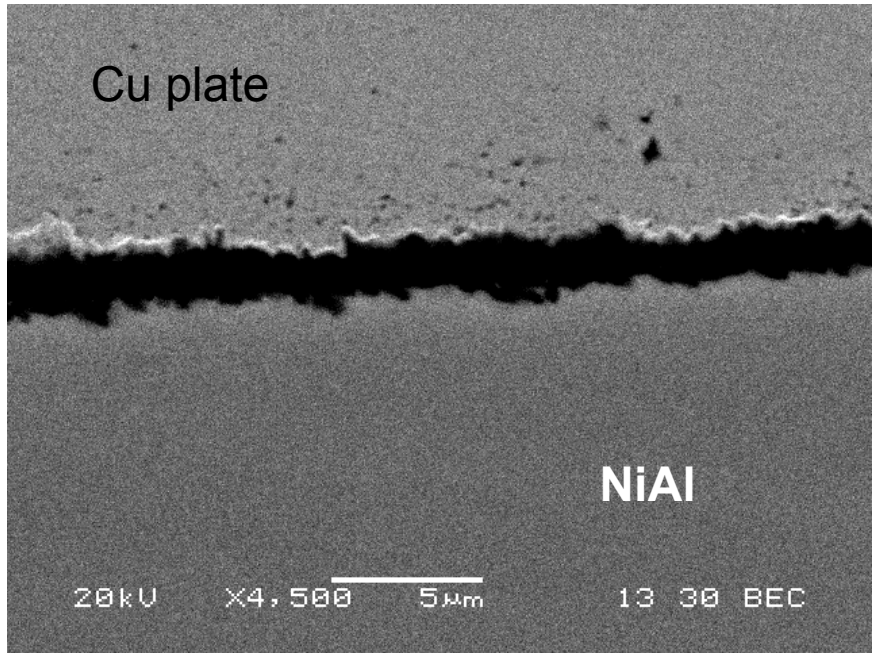
- **Linear increase in lattice parameter**
- **2nd phase formation when Pd/Rh is substituted for Al**
- ***ab initio calculated lattices (dashed)***

<u>single crystal XRD</u>

- **Confirms Pd/Rh substitutes Ni**
- **Occupancies in good agreement with target compositions for single phase alloys**

Effect of alloying additions

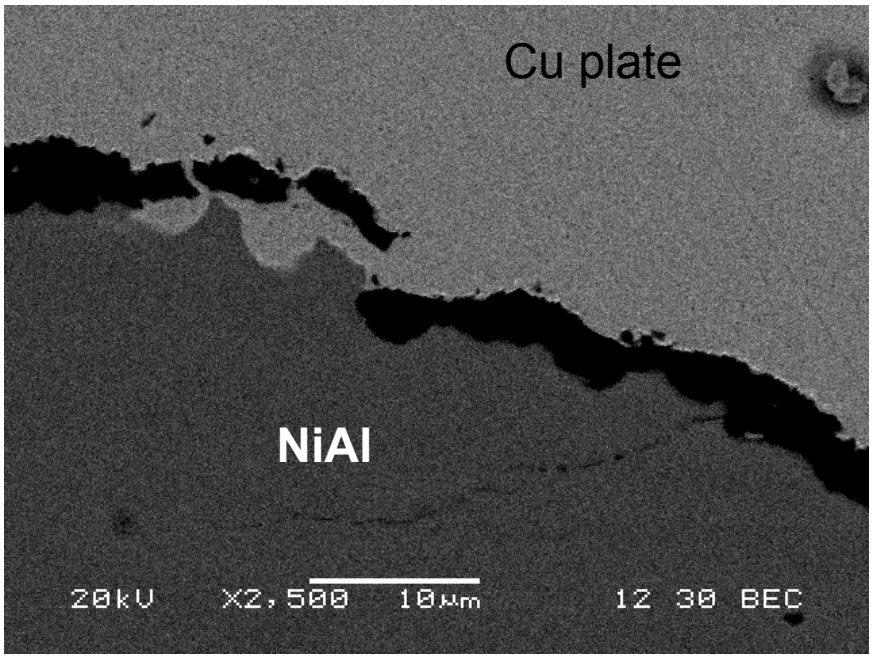


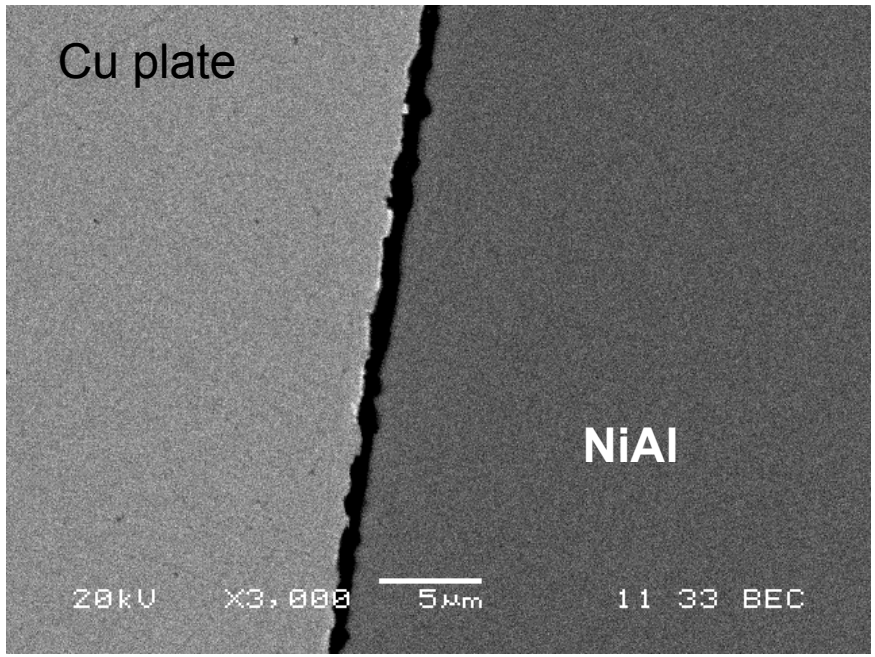


NiAl without any addition (1150C, 25hrs)

$Ni_{41}Al_{50}Rh_9$ (1150C, 25hrs)

Effect of alloying additions





NiAl without any addition (1150C, 25hrs)

$Ni_{41}Al_{50}Pd_9$ (1150C, 25hrs)

Preliminary oxidation studies: Pd and Rh improve oxidation resistance for NiAl

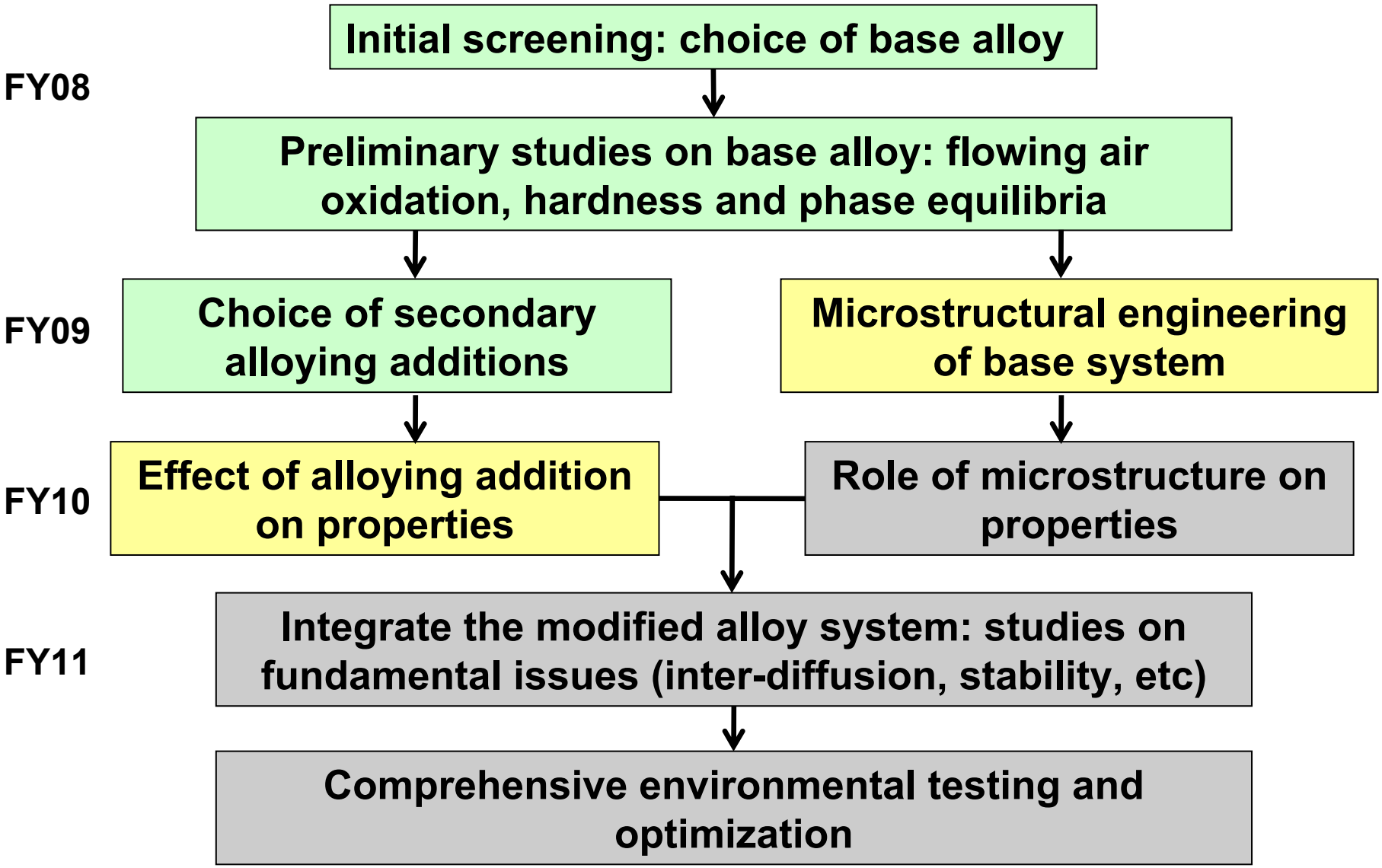
Summary

- **Hierarchical scheme works!**
  - **Estimated formation enthalpies on >10^2 ternary compounds, Miedema**
  - **Reduced that to 11 for *ab initio***
- **Identified base alloy: Mo-Ni-Al**
  - **High Temperature backbone w/ source for oxidatively stable elements**
  - **Need for microstructure control**
- **Identified quaternary additions to further stabilize Mo-NiAl**
  - **Pd and Rh best candidates**
  - **Possible alloy additions were well identified by computational tools**
    - **But did require experimental validation (Zr and Hf didn't work)**
- **Rh expected to have a beneficial effect on melting temperatures**
  - **Requires experimental validation**

Key tasks over next year

- Thermal stability of Ni-Al-TM alloys
  - Validate estimates on T_m
- Oxidation studies up to 1300°C
  - Ternary compound first
- Mechanical behavior of Ni-Al-X alloys
  - Brittleness of NiAl a concern
- Microstructure tailoring of Mo-Ni-Al-X alloys
  - Directional Solidification studies

Project layout



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Acknowledgements

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  - **Ab initio calculations**
- **Sumohan Misra**
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- **Travis Brammer**
  - **Sample preparation**
- **This work was supported by DOE-FE (ARM program) through Ames Laboratory contract number DE-AC02-07CH11358**

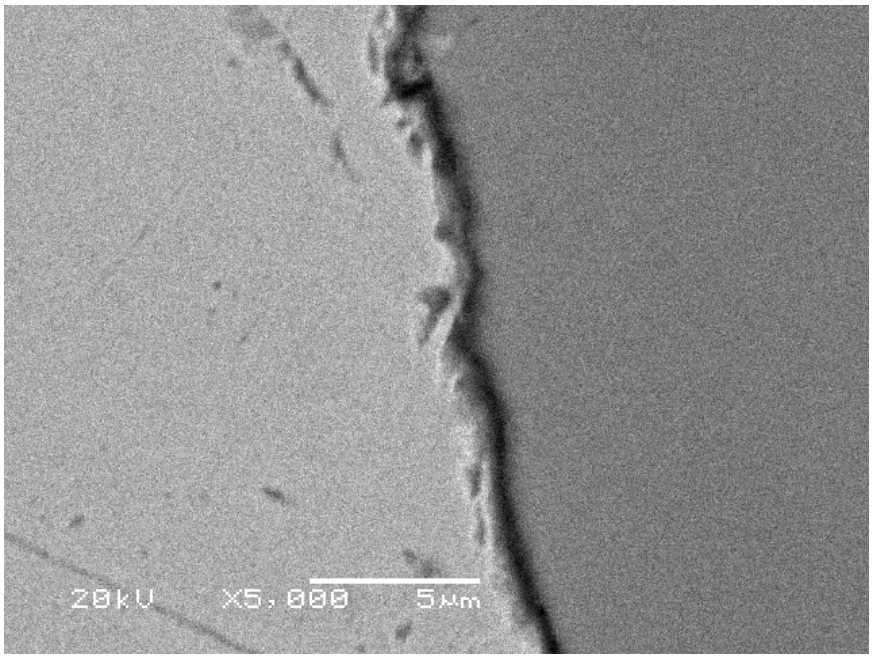
Putting it Together

- **Basic concept: align the Mo dendrites so as to have minimal surface area exposed**
- **Initial proof of concept studies being carried out by pulsed laser melting**
- **Still remains a processing challenge**

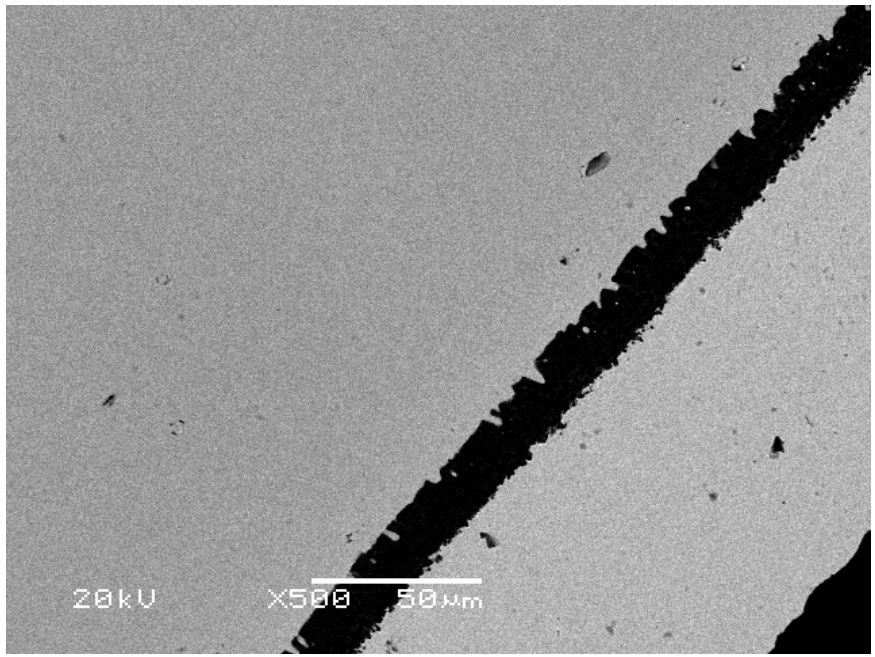
Effect of alloying additions

- Flowing air tests at 1300°C
- Massive scale spallation in NiAl
- Spallation observed in Rh containing alloys to a lesser extent

Effect of alloying additions



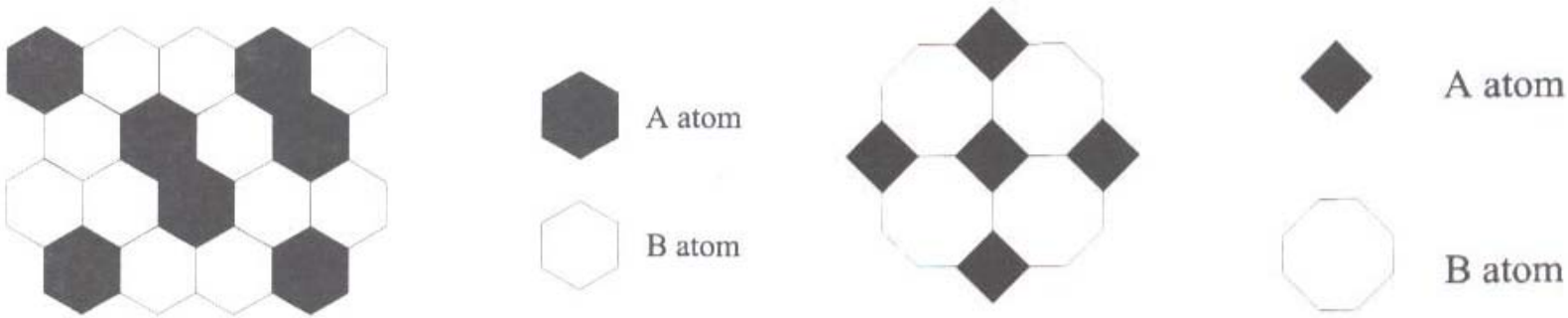
NiAl without any addition
(1300C, 100hrs)



$Ni_{41}Al_{50}Rh_9$
(1300C, 100hrs)

Miedema model for binary alloys

The "macroscopic atom" picture



Solid solutions

Intermetallics

Ref: Enthalpies in Alloy, H. Bakker

- Flow of charge $\propto (\Delta\varphi)^2$
- Removal of discontinuity in charge density $\propto (\Delta\eta_{WS}^{1/3})^2$

$$\Delta H_{AB}^{i/c} = \frac{V_A^{2/3}}{\left(\eta_{WS}^{1/3}\right)_{av}} \left\{ -P(\Delta\varphi)^2 + Q\left(\Delta\eta_{WS}^{1/3}\right)^2 \right\}$$

Miedema model for binary alloys

The sub-regular formalism

$$G_{mix} = \sum_i x_i G_i + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \left(\Omega_{ij}^i x_i + \Omega_{ij}^j x_j \right)$$

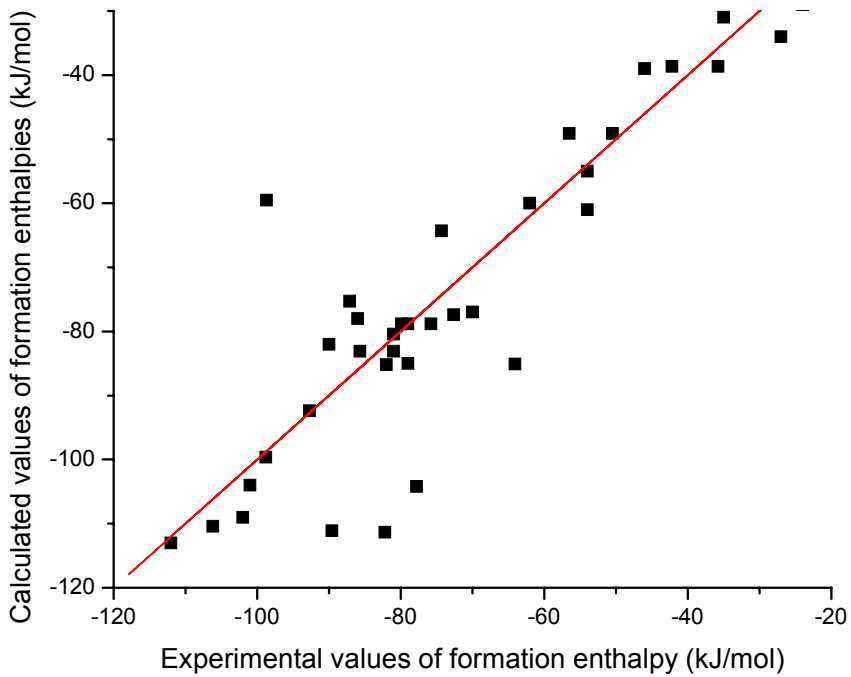
$$\Delta H_{AB}^{i/c} = \frac{V_A^{2/3}}{\left(\eta_{WS}^{1/3}\right)_{av}} - P(\Delta\varphi)^2 + Q\left(\Delta n_{WS}^{1/3}\right)^2$$

$$\Delta H = c_A c_B \left(f_B^A \Delta H_{AB}^{i/c} + f_A^B \Delta H_{BA}^{i/c} \right)$$

$$f_B^A = c_B^s [1 + \gamma (c_A^s c_B^s)^2]$$

$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}$$

Ref: Miedema et. al., Physica 100(1980)1-28



Volume and structural corrections

Volume change during alloying

$$\Delta V_i = \frac{1.5 c_j^s V_i^{2/3} (\phi_i^* - \phi_j^*)}{2(n_{ws}^{-1/3})_{av}} (n_{ws,i}^{-1} - n_{ws.j}^{-1})$$

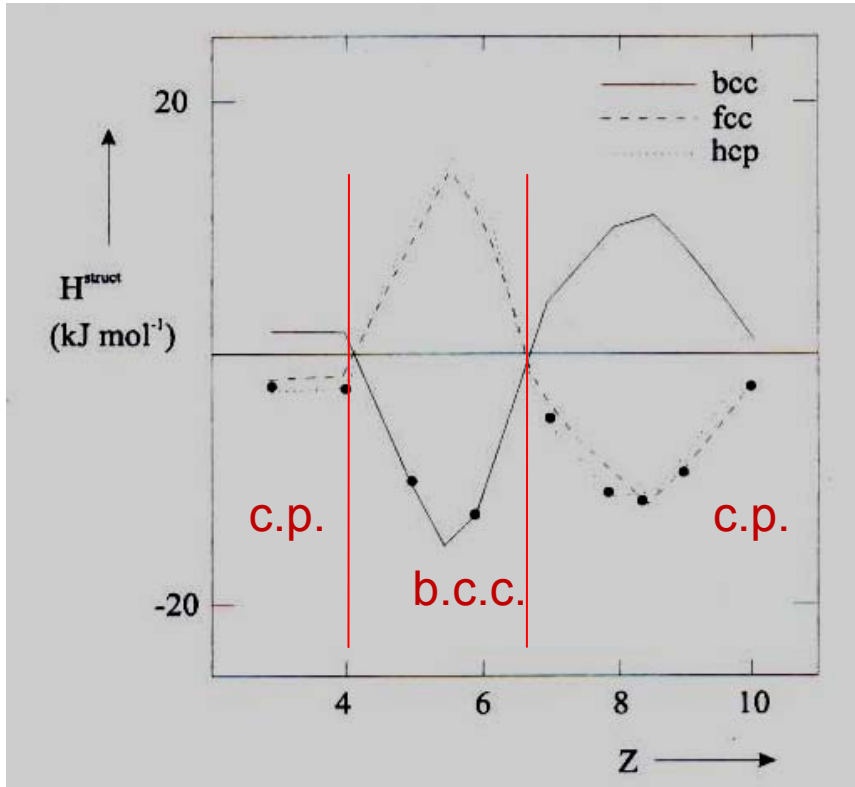
$$V_i^* = V_i + \Delta V_i$$

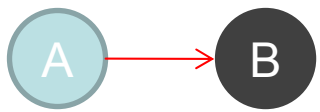
(*Ref: Miedema and Niessen, Physica 114B (1982) 367.*)

Structural contributions

$$H_{AinB}^{struct} = (Z_A - Z_B) \frac{\partial E^{struct}(B)}{\partial Z} + (E_B^{struct} - E_A^{struct})$$

(*Ref: Enthalpies in Alloy, H. Bakker*)





Lose structural enthalpy of A

Gain structural enthalpy of B

Significance of structural and volume contributions

- Structural contributions
  - The structural term is not symmetrical. Hence is more acute when H^{struct}_{AinB} and H^{struct}_{BinA} have vastly different values.
  - Eg. Hf-Ni system. (H^{struct}_{NiinHf} = 36kJ/mol; H^{struct}_{HfinNi} = -47kJ/mol)
- Volume contributions
  - Arises in order to accommodate the increase in charge at the W-S boundary $\left(\left|\Delta Z\right| / n_{WS}\right)$
  - Volume change is proportional to
  - Has a minor contribution in case of transition metal alloys, but has a significant effect in case of main group elements

Dependence on accuracy of binary systems

Deviation of calculated enthalpy from experimentally observed values

Method	Mean	Median	Standard deviation
Al-Ni	0.9781	0.15974	4.31164
Al-Hf	-19.09031	-19.01878	6.43103
Hf-Ni	1.12844	0.54827	3.51746
Al-Y	10.42351	17.00984	13.39821
Ni-Y	-9.31121	-9.40568	6.14083
Al-Ni-Y	-0.91962	0.36871	6.01413
Al-Ni-Hf	-2.4572	-2.5608	1.80778