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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**

Number of Elements	Combinations
2	3,160
3	82,160
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}
15	6.64×10^{15}
20	3.45×10^{18}
30	8.87×10^{21}
40	1.07×10^{23}

Phase Diagrams in Hyperspace

The number of possible compounds 10^{90} will exceed the number of atoms in the Universe! Or will Complexity intervene?

- For a 4 element Ni-Al based system, with 2 transition elements – 406 combinations

Conceptual Approach

- No one methodology will work in all circumstances
- 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**

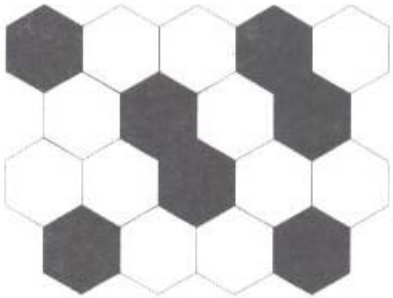
Hierarchical Evaluation

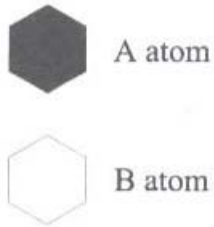
- **Rapid approximant methods**
  - **Less precise but quickly eliminate most likely ‘dead-ends’**
- **Refining Steps**
  - **Higher degree of precision**
  - **Identify critical experiments**
- **Utilize relative strengths of many techniques**
  - **i.e., *ab initio* and Calphad**

Miedema Model

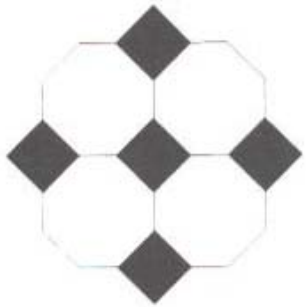
- Developed to predict formation enthalpies of binary compounds
  - Assume metals are in their standard state
  - Macroscopic view of alloying
    - Not an atomistic approach
  - Interfacial energy between the two metals is ~ their liquid heat of formation
  - Formation energy is ~ contact interaction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

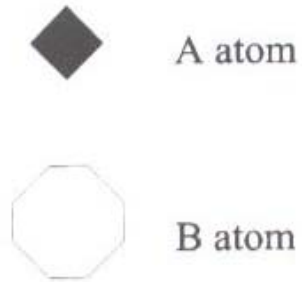
Physical Basis





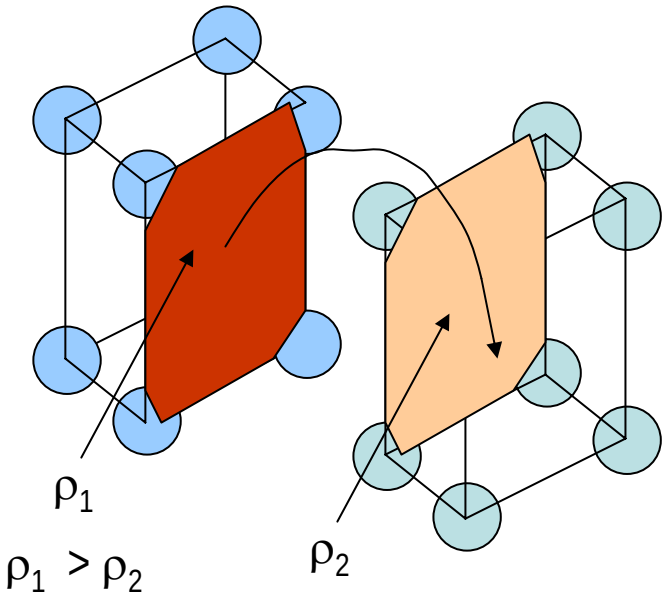
Solid solutions





Intermetallics

Ref: Enthalpies in Alloy, H. Bakker



- **Discontinuity of electron densities**
- **Flow of charge**

Physical Basis

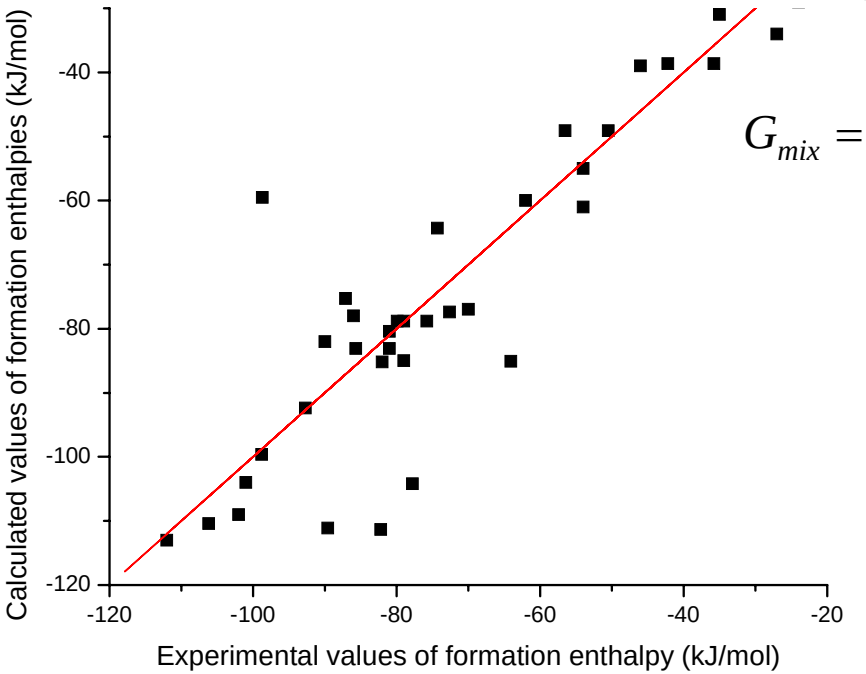
- **Charge flow**
- **Removal of discontinuity in charge density**

$$\propto (\Delta\varphi)^2$$

$$\propto (\Delta\eta_{WS}^{1/3})^2$$

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

Enthalpies of Alloys



The sub-regular formalism

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

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

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

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

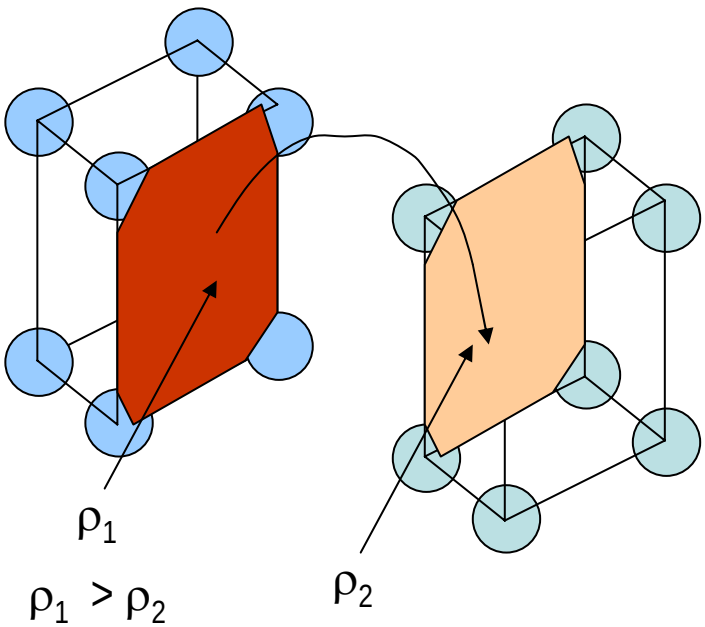
$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}$$

- **Enthalpies of mixing can be calculated by accounting for the concentration dependence – same as sub-regular solution model.**
  - **$f(c) = c_a^s \cdot c_b^s$**

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

Stability

- **Positive contributions to enthalpy destabilizes the system. Presence of stable alloys and intermetallics suggest the existence of negative contributions.**

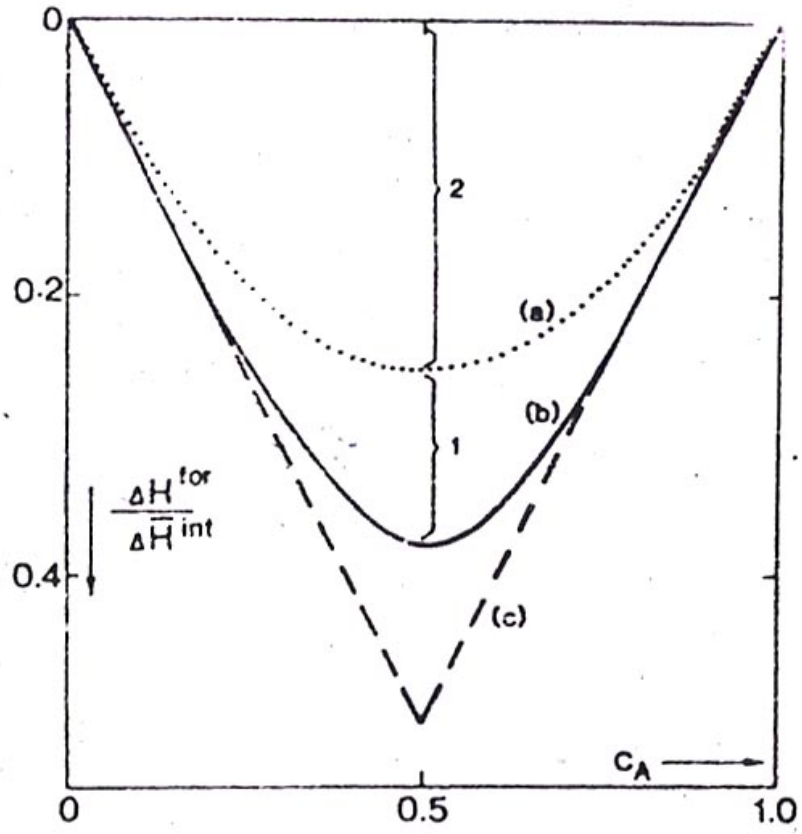


- **Visualized on an atomic scale, the electron transfer along the density gradient corresponds to the negative contribution**

- **Description of ionicity – work function, ϕ**

Concentration Dependence

- **Total contact area between dissimilar atoms is the relevant quantity for calculations**



$$\Delta H = f\Delta H^{o}$$

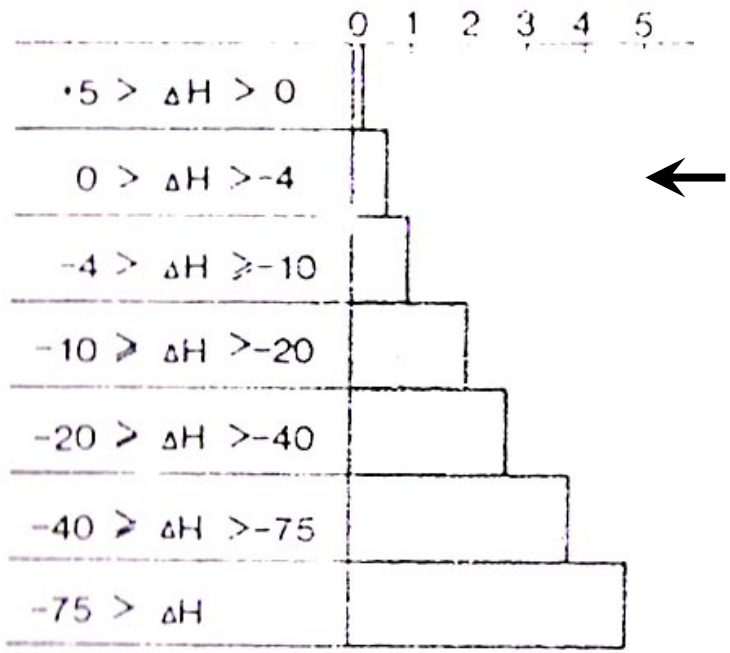
$$c_A^S = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + (1 - c_A) V_B^{2/3}}$$

For statistically ordered alloy

$$f_B^A = c_B^S \left[1 + 8 (c_A^S c_B^S)^2 \right]$$

Transition Metals

- **Almost complete absence of p-type wave function interactions**
- **The proportionality constants are determined as per the relation: Q/P = 9.4**



- **The relation between the average number of stable intermediate phases and enthalpy of formation at equiatomic combinations**

Non-Transition Metals

- **Boom et. al. : Q/P values remains same. But each falls by 30%**

- **Structure plays a key role here. Optimum filling of Brillouin zones minimize the enthalpy**

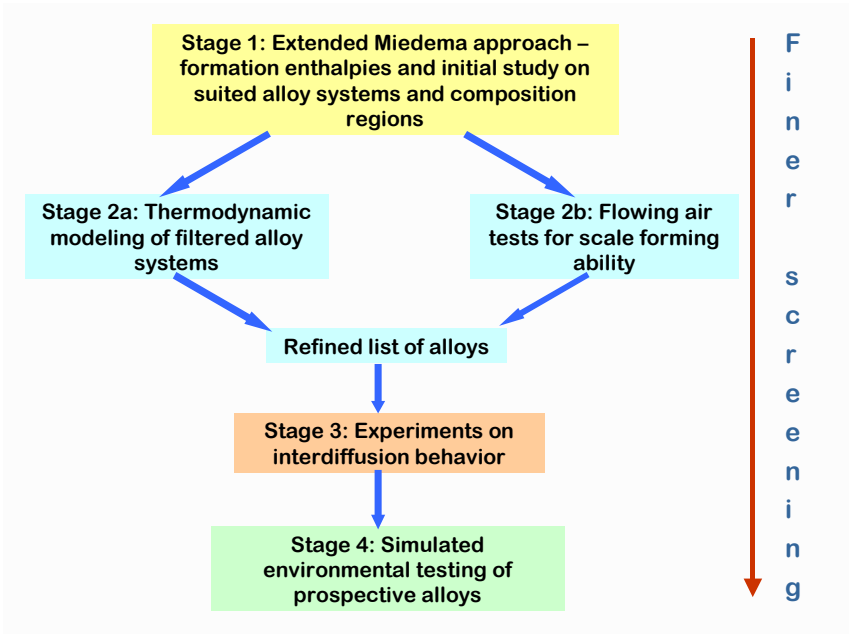
- **Problems arise while dealing with elements like Si and Ge, which are electrical conductors in liquid state, but semiconductors in solid state**

Mixed System

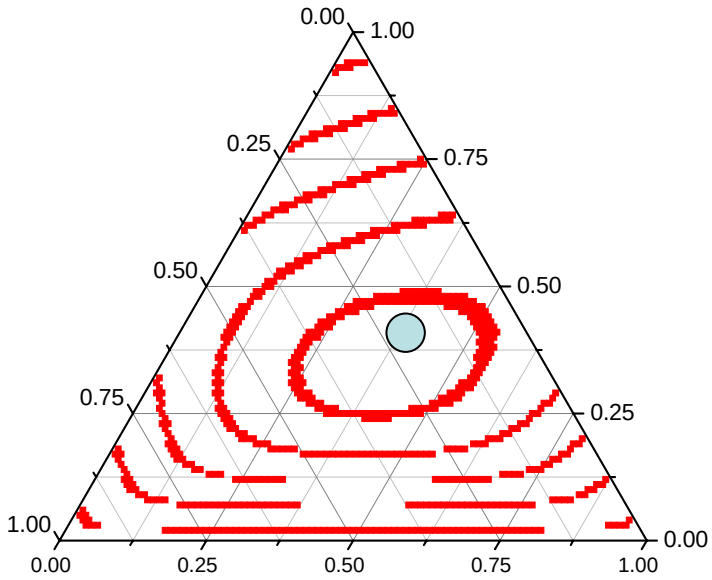
- **We ascribe cohesion and bonding primarily due to interactions of outer or valence electrons.**
- **That being the case, since TM-nonTM alloys bring together different types of wavefunctions, one can expect the scenario to be different than for the case where like wavefunctions overlap**
- **While a good theoretical basis for predicting the outcome of such cases is yet to be established, the following relation seems to give a qualitative agreement with facts**

High Temperature Systems

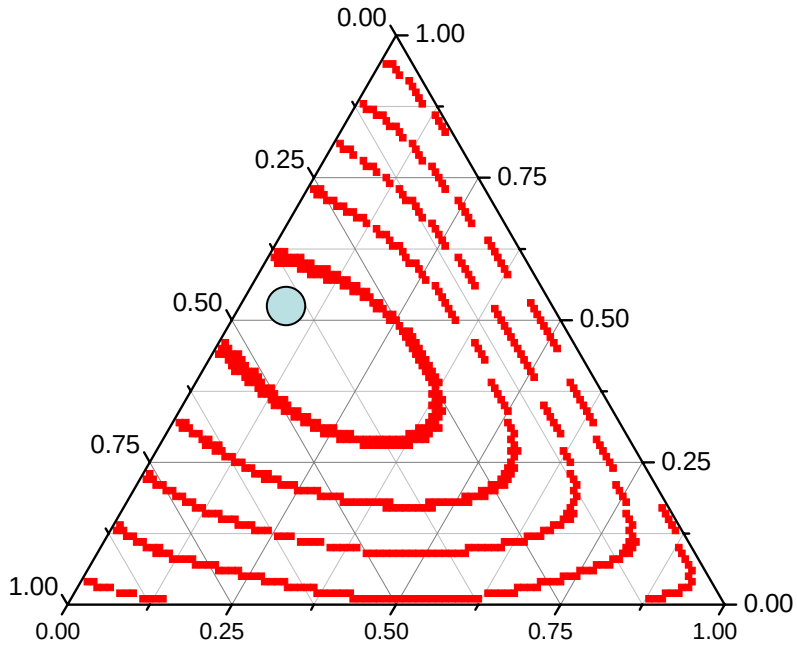
- **Ni-based superalloy**
  - **Well research**
  - **What alloy additions would be good candidate for a Ni-based system?**
    - **Don't dramatically decrease the T_m**
    - **Don't form compounds with Al**
      - **Possibly soluble in NiAl**
      - **Preferably increase stability of NiAl**



Thermodynamic assessments of Ni-Al-X-Y



Ni-Al-Fe



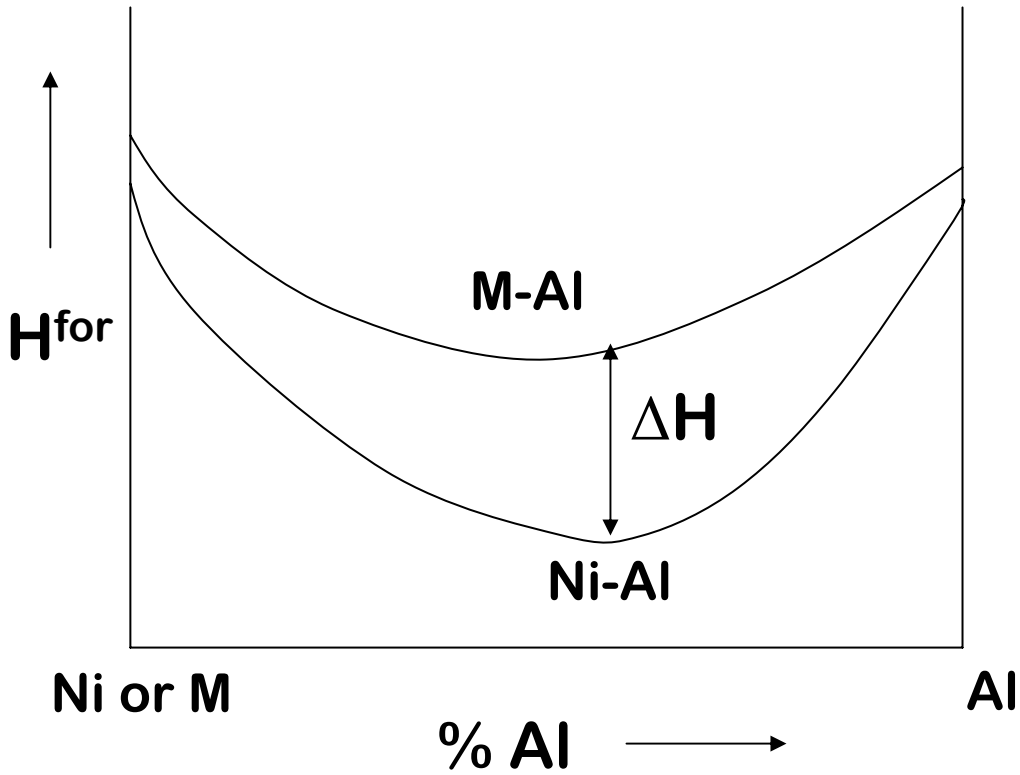
Ni-Al-Cr

Formation enthalpies and melting temperatures

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 -136	Pd -171	Ag -94
La -181	Hf -211	Ta -152	W -96	Re -97	Os xxx	Ir xxx	Pt -171	Au -96

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

Relative stability of aluminides



- Oxidation resistance is provided by NiAl or the Ni_3Al
- Larger enthalpy difference, when Ni-Al curve lies lower indicates greater stability of NiAl or Ni_3Al as compared to M-Al

Relative stability of aluminides + formation enthalpy

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

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 -136	Pd -171	Ag -94
La -181	Hf -211	Ta -152	W -96	Re -97	Os xxx	Ir xxx	Pt -171	Au -96

Initial list according to enthalpy

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

Second list according to T_m

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

Second list according to higher stability of Ni-Al

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

List of elements for bulk alloying

- **Mo, Re**
- **V, Nb, Ru**
- **If the enthalpy criterion is slightly relaxed, then can consider W and Cr**

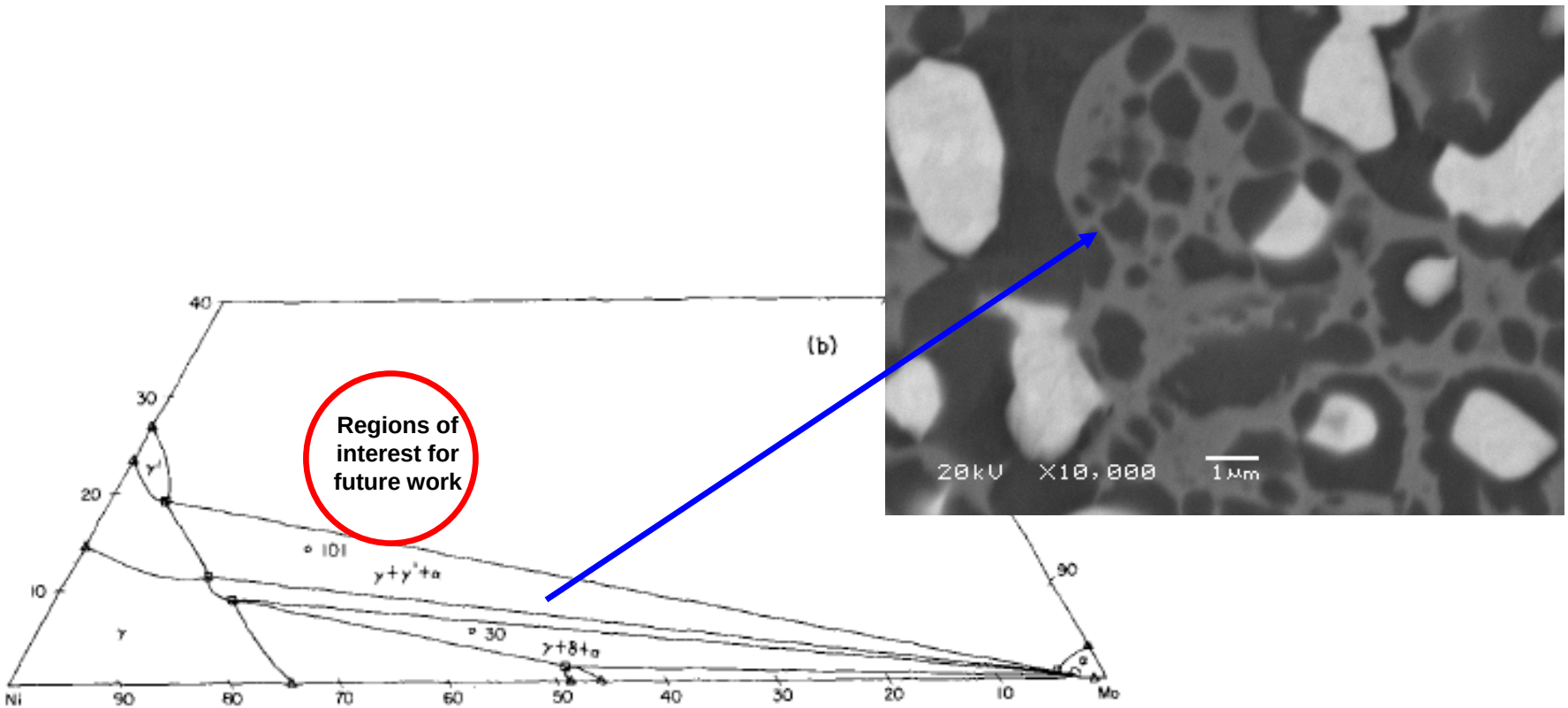
However, this list is just based on thermodynamics; some of these elements may be unsuitable from oxidation point of view

Choice of quaternary additions

- current scheme of things, 4 components is the limit of the Miedema's model
- The Miedema model suggest combination of elements which increase the formation enthalpy when added to Ni-Al, but does not increase the formation enthalpy when alloyed with the refractory metal matrix
    - Prospective compounds are now being check using ab initio
- Should have a enthalpy minima when the 4^{th} element is substituted for Ni
- Possible quaternary additions: Pd, Pt and Rh (these two increase the enthalpy and have the same crystal structure as nickel)

Results

- **Microstructures in Mo-Ni-Al system**



Future work

- Exploration of $Mo_{(ss)}$+$Ni_xAl_yM_z$ alloys
- Thermodynamics: Improvement of the Miedema model + estimates of T_m
- Experimental studies: oxidation behavior, microstructures, DTA and XRD
- Further computational studies: Use of ab initio to study minor element (quarternary) additions

Summary

- **Possible Phase space is too large to consider an Edisonian approach for searching for new alloys**
- **Calphad is effective when thermodynamic parameters are known (i.e., database exists)**
- **Ab initio techniques provide accurate information, but limited to 'hypothetical systems'**
- **Hierarchical approach using more precise methods provides flexibility to quickly search through large regions of phase space to find prospective alloy systems.**