IOWA STATE UNIVERSITY
OF SCIENCE AND TECHNOLOGY

AMES LABORATORY

Computational and Experimental Development of Novel High Temperature Alloys

Matthew J. Kramer, Pratik Ray, Travis Brammer, Mufit Akinc

Ames Laboratory
Department of Materials Science and Engineering
Iowa State University

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The Problem

- **Increasing efficiency require higher operating temperatures, goal ~1300°C is very aggressive**
  - **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 higher T's require more effort**
      - **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**

Extent of the Opportunities

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

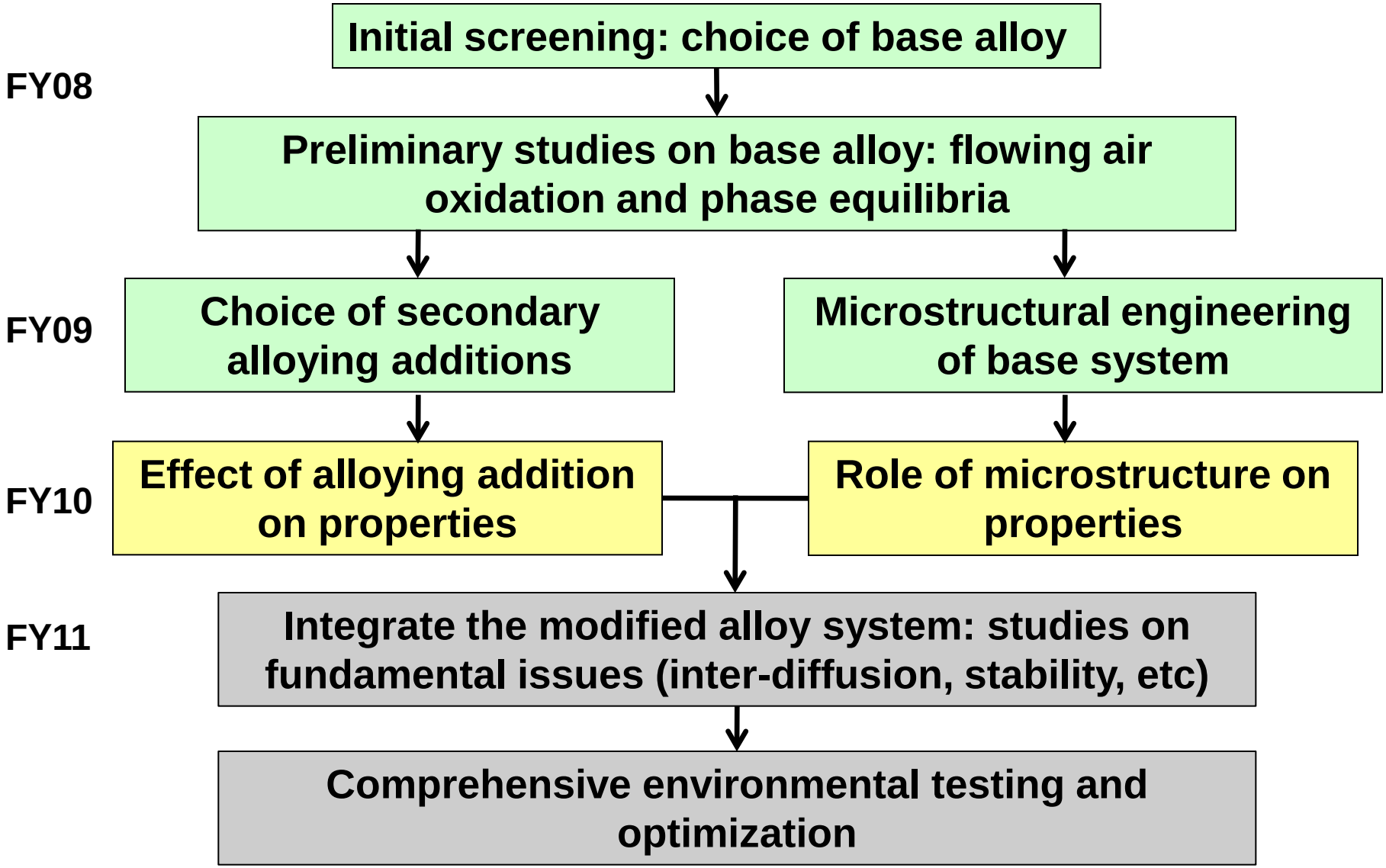
Hierarchical Evaluation

- **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



Milestones

Tasks	FY2009				FY2010				FY 2011				FY 2012				FY2013			
	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4
1. Development of an extended Miedema model and use it for initial screening																				
2a. Thermodynamic modeling of prospective systems																				
2b. Preliminary experiments for scale forming ability																				
3a. Studies on Microstructural evolution and optimization of base-alloy																				
3b. Ab-initio studies on effect of minor alloying elements																				
4a. Oxidation evaluation and alloy optimization																				
4b. Mechanical properties screening																				
5. Environmental testing of selected alloys																				
6. Studies on fracture mechanics and low cycle fatigue behavior																				

Two-Phase Alloy Approach

- **Alloy consists of two part**
  - **Skeleton**
    - **Strength and toughness**
      - **BCC or FCC**
    - **High melting T**
      - **Creep strength**
  - **Flesh**
    - **Reservoir for passivating elements**
      - **Al, Si, Cr**

Screening for High Temperature Systems

- **Alloy architecture based on Ni-based superalloys**
  - **Replace Ni matrix with more refractory metal**
    - **V, Zr, Nb, Mo, Ru, Rh, Hf, Ta, W, Re, Os, Ir, Pt**
  - **Retain NiAl for oxidation stability**
    - **Assume Al-O as a primary passivating phase**
  - **New matrix should not form compounds with Al**
    - **Avoid brittle intermetallics**
- **How to down-select?**
  - **higher T_m is reflected in an increase in enthalpy**

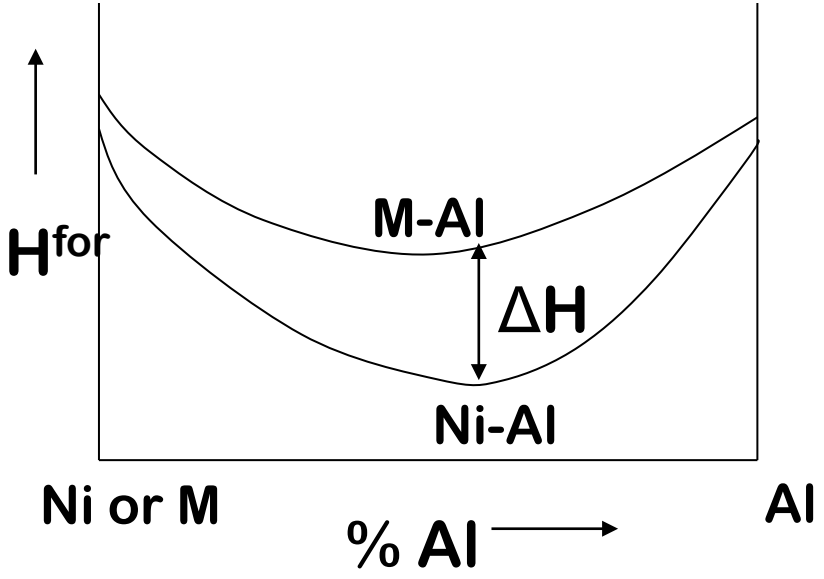
Initial screening of the base alloy

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

Look for a TM whose formation enthalpy is less favorable than Ni-Al

Possible choice of "backbone" metals:

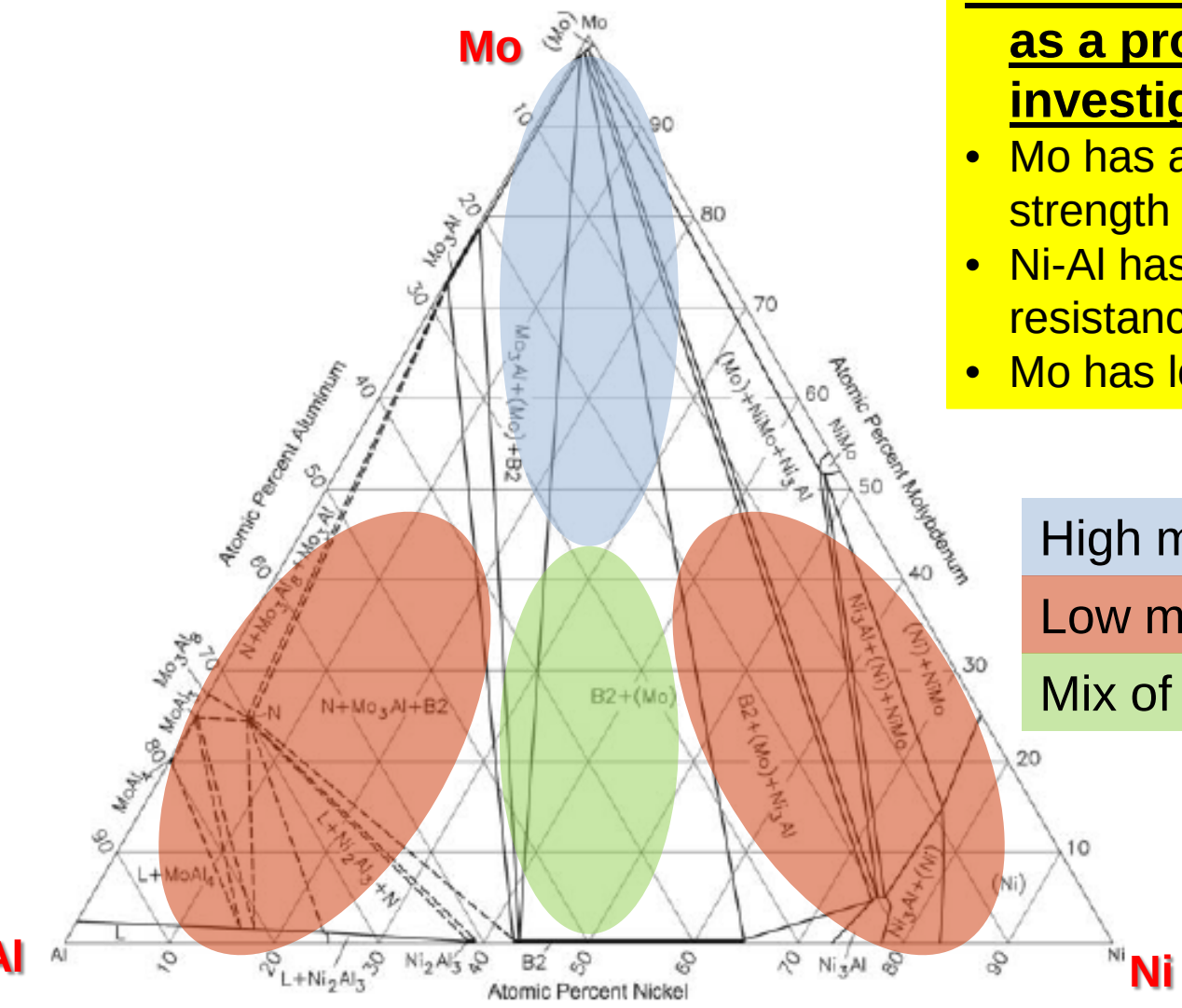
Mo, Nb, W



The Mo-Ni-Al system

FY2009 – identified Mo-Ni-Al as a promising system for investigation

- Mo has a high Tm and high strength
- Ni-Al has good oxidation resistance
- Mo has low solubility for Al or Ni



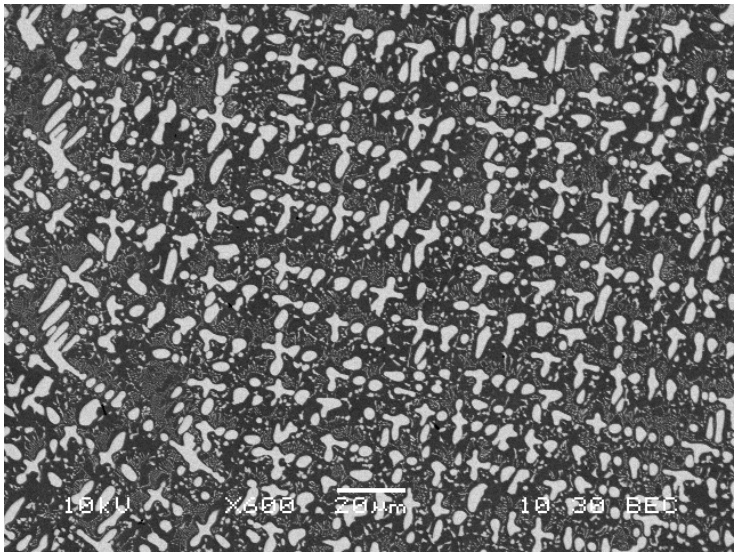
High melting + poor oxidation

Low melting + good oxidation

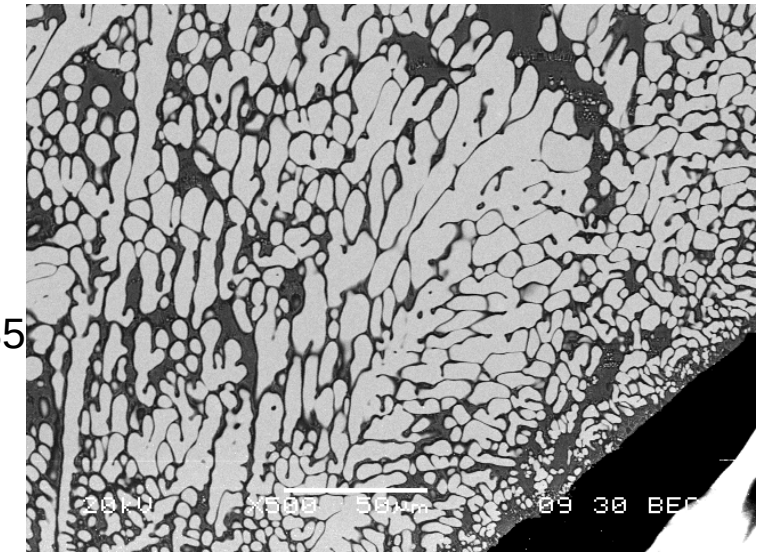
Mix of oxidation and melting

X. Lu, Y. Cui, Z. Jin, Metallurgical and Materials Transactions A, Vol 30, Issue 7 (1999) 1785 - 1795.

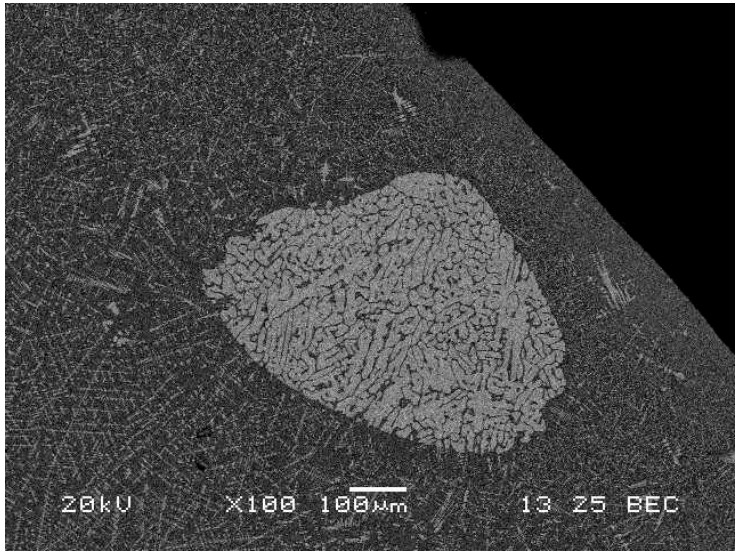
Solidification Microstructures



$Mo_{30}Ni_{35}Al_{35}$



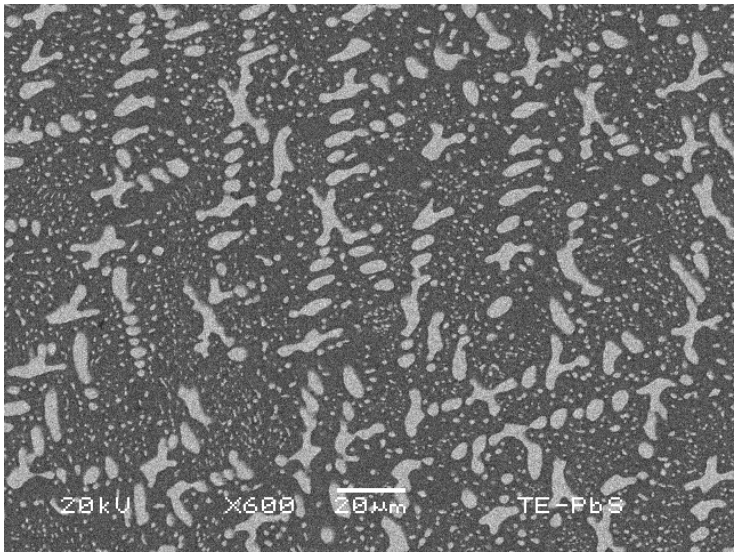
$Mo_{20}Ni_{40}Al_{40}$



Inhomogeneous microstructures obtained via arc-melting / drop casting

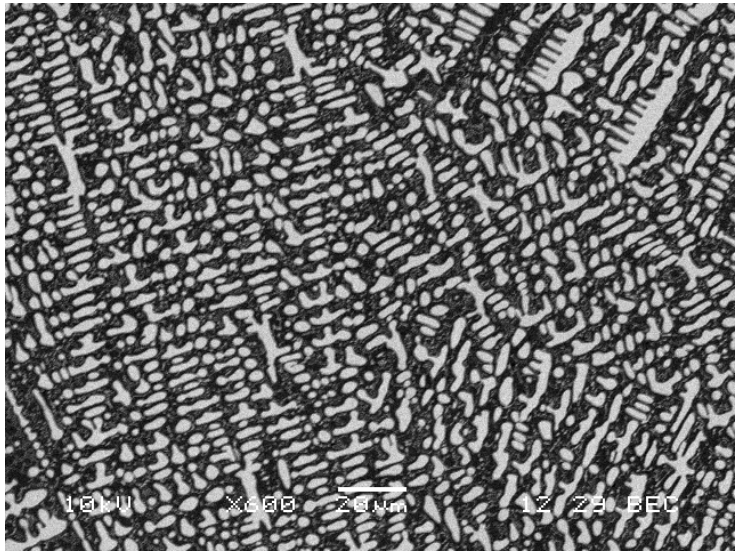
Solidification microstructures

Mo-20



Mo-25

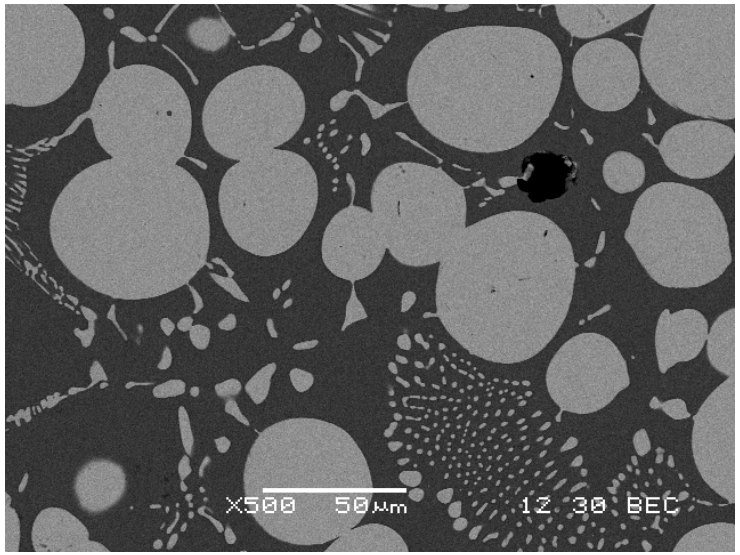
Mo-40

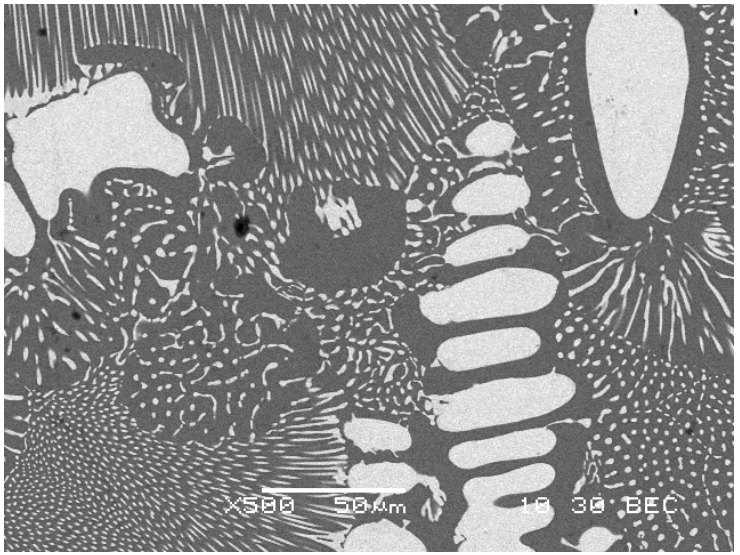


- Pelletized from elemental powders
- Arc-melted and drop cast

Sintered microstructures

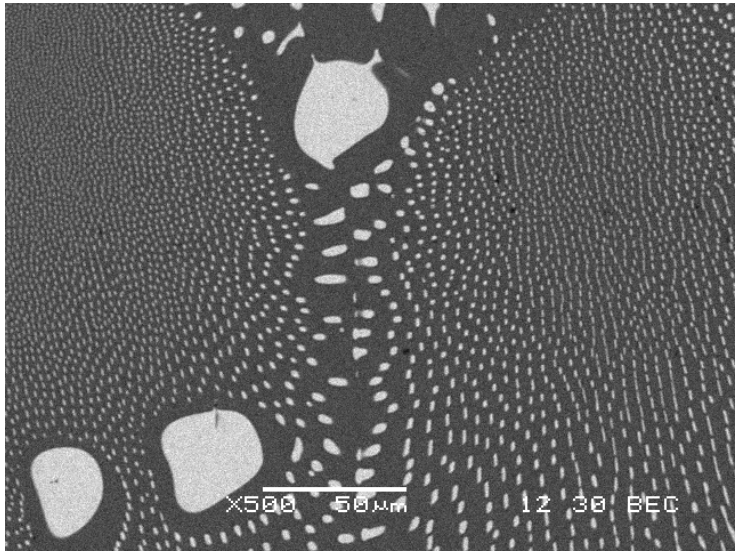
Mo-35





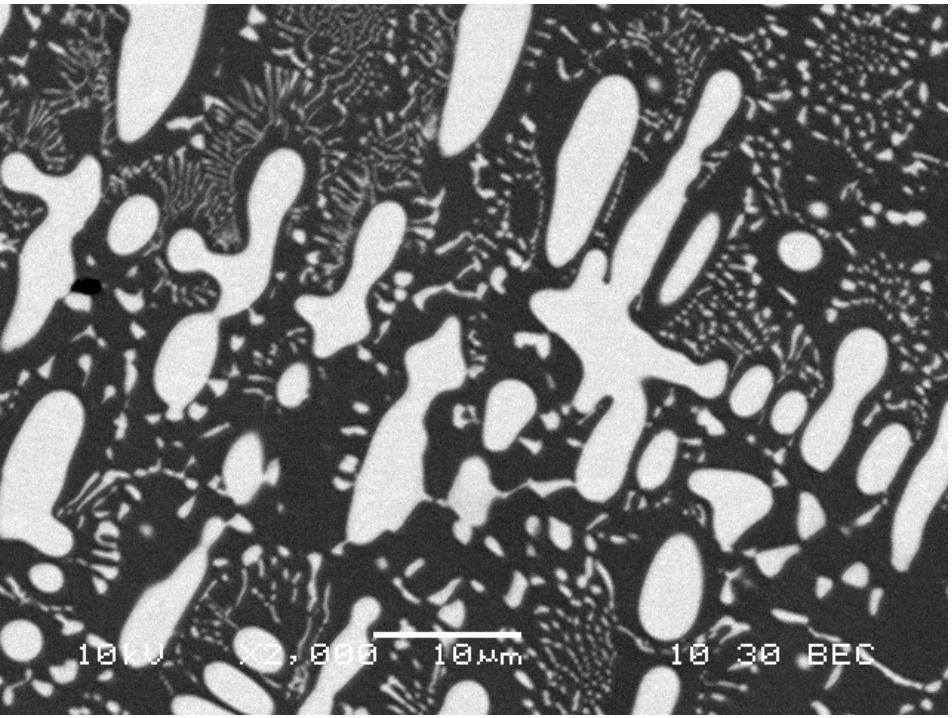
Mo-25

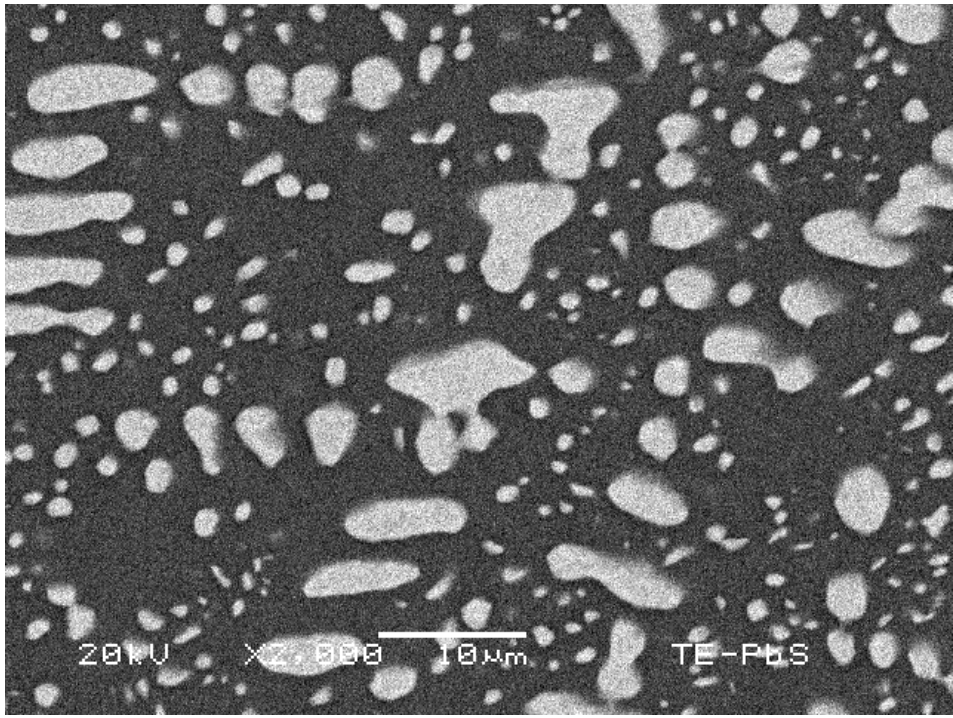
Mo-20



Dry-pressed pellets sintered at 1750°C for 1 hour

Microstructural stability



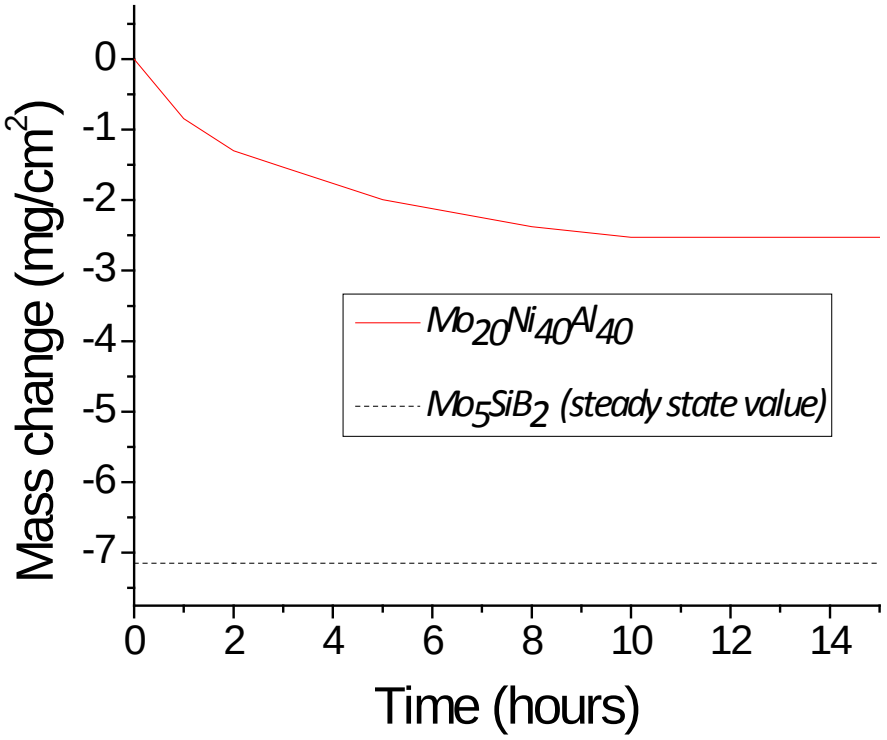


Before annealing

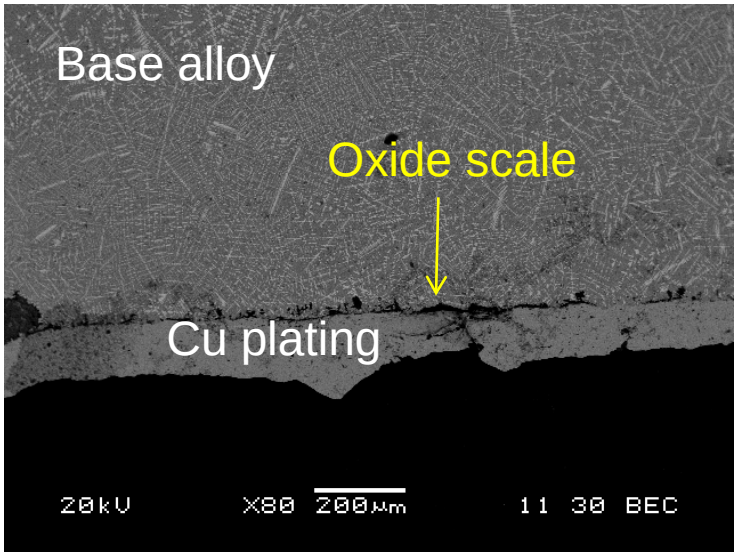
After annealing

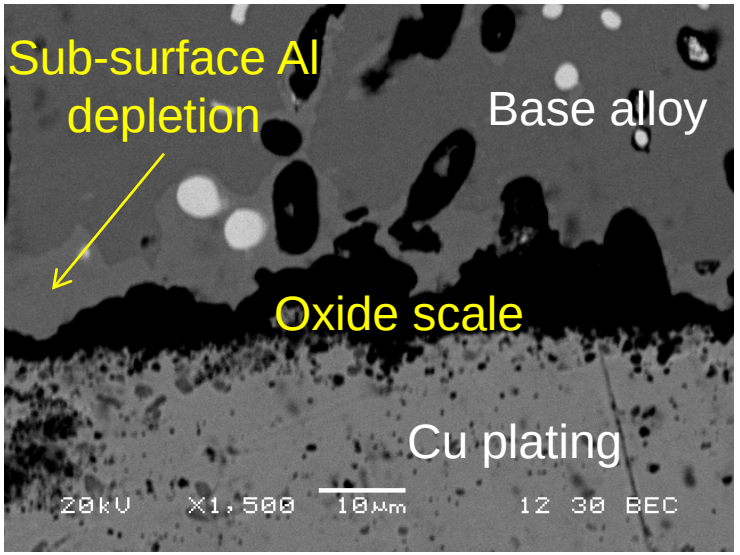
Temperature – 1500° C
Time – 6 hours

Oxidation of an as-cast alloy

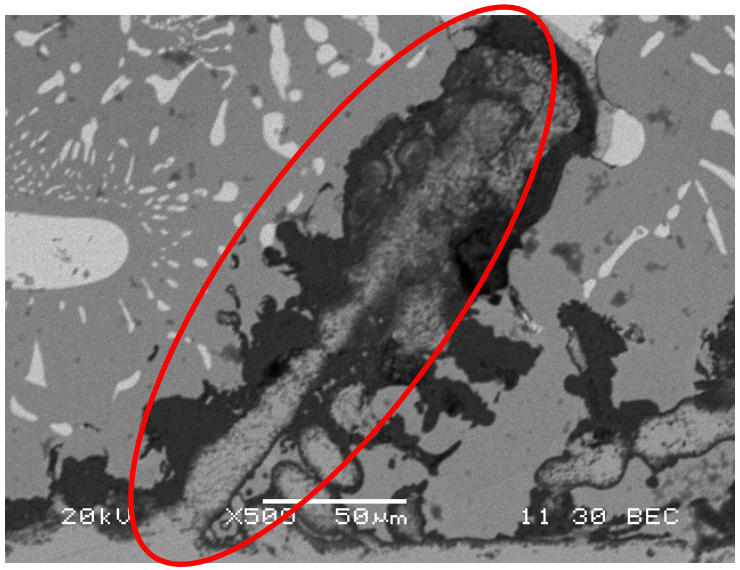


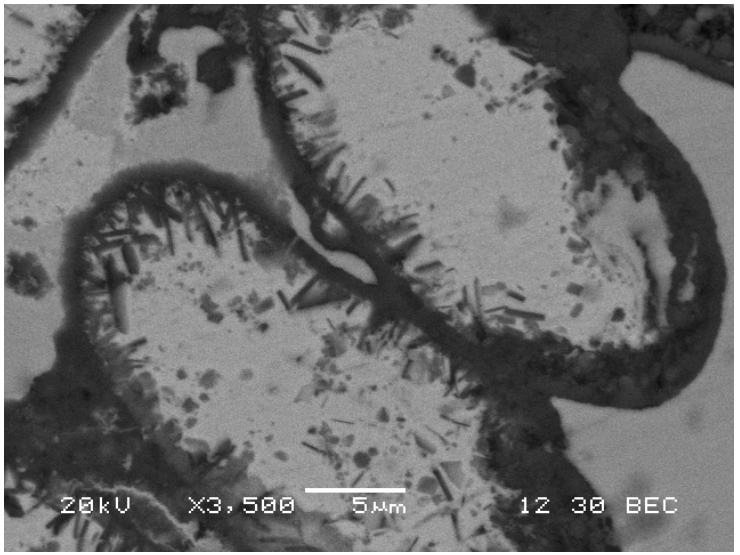
Interrupted flowing air oxidation of an arc-melted and drop cast alloy ($Mo_{20}Ni_{40}Al_{40}$) at 1200°C

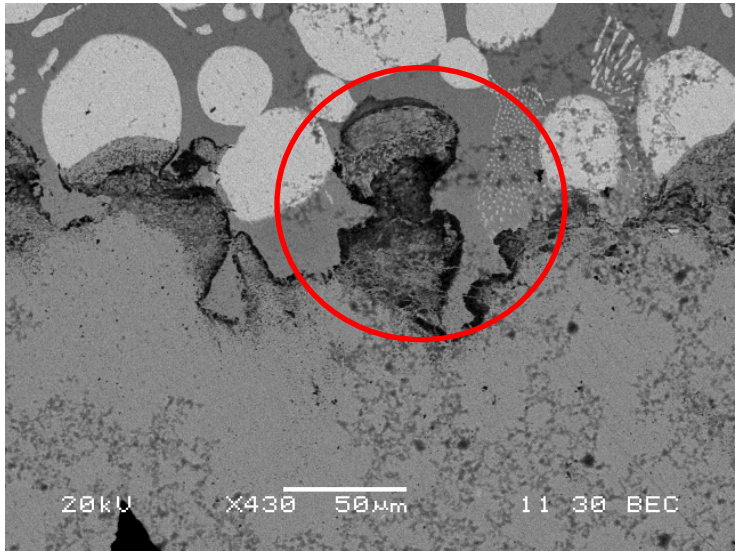




Oxidation pathways







Maximum breakaway oxidation length observed so far is of the order of 150-200 microns

Oxidation pathways

$$Mo + \frac{3}{2}O_2 \rightarrow MoO_3(g)$$

$$Ni + \frac{1}{2}O_2 \rightarrow NiO$$

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$$

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4$$

$$3NiO + 2Al \rightarrow 3Ni + Al_2O_3$$

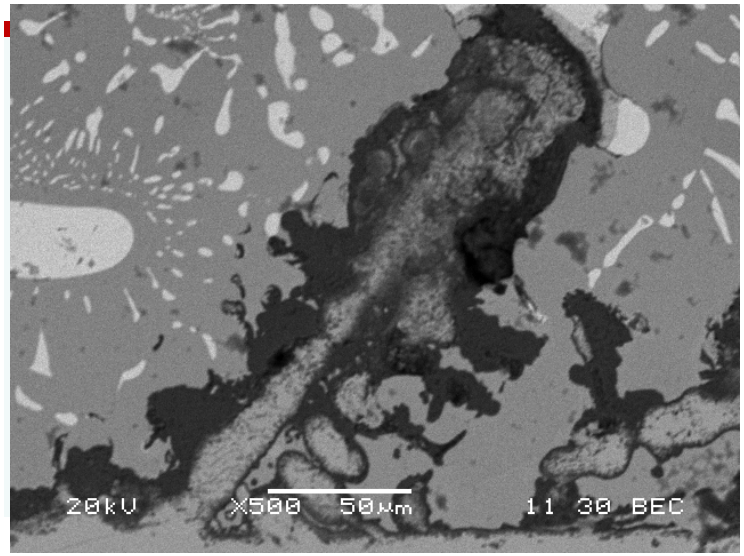
Mass loss at rapid rate

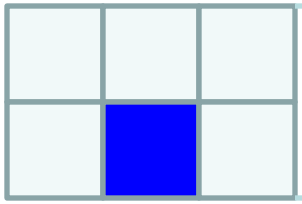
Slow mass gain

Hypothetically, the major factor behind possible failure of these alloys would be the presence of interconnected Mo grains

Effect of Mo phase fraction

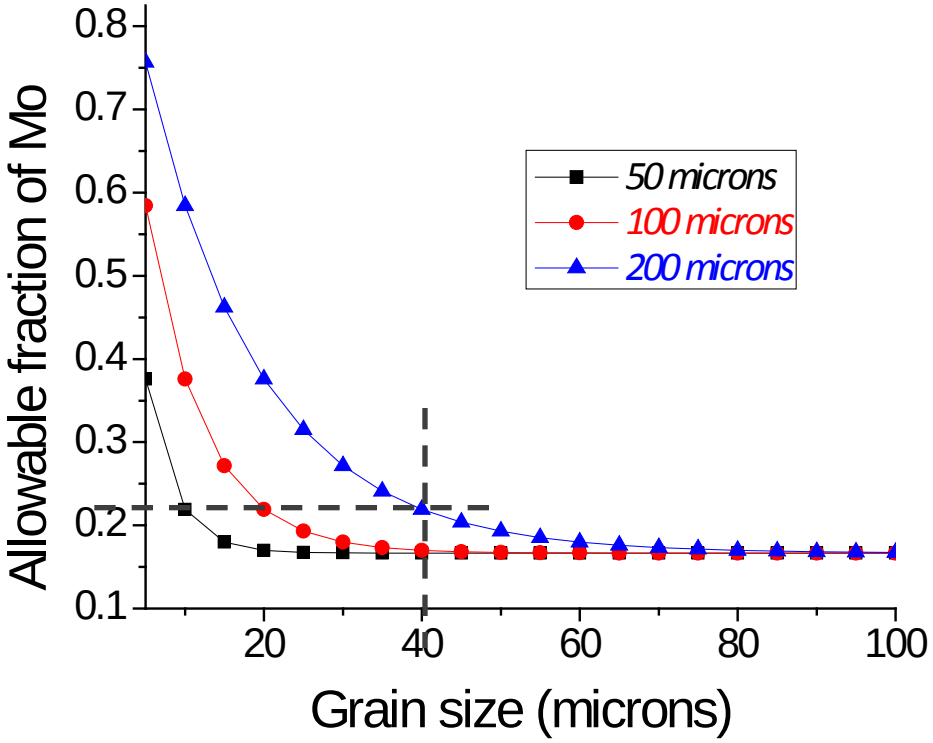
1200 C 24 hrs





Repeat this block *k* times

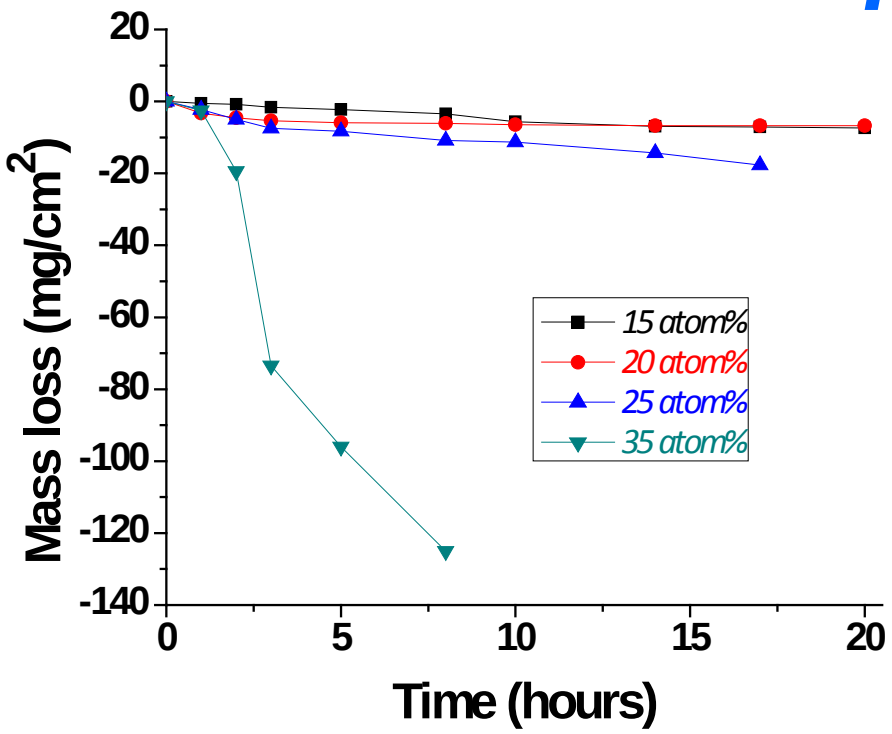
$k = l/d_g$

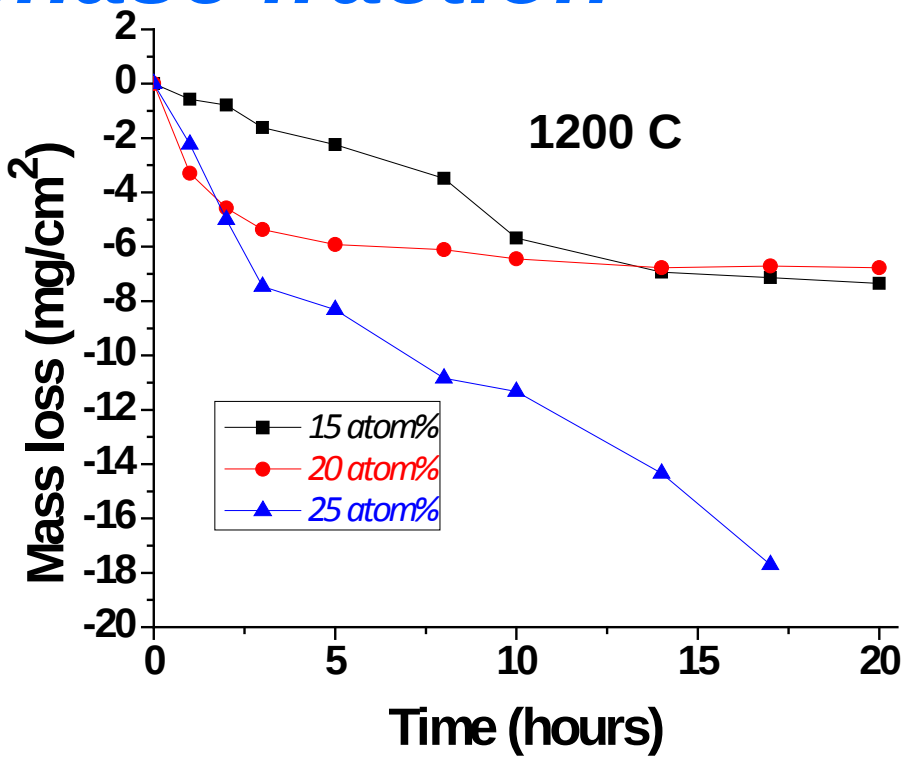


$$(P_m)^k = \phi$$

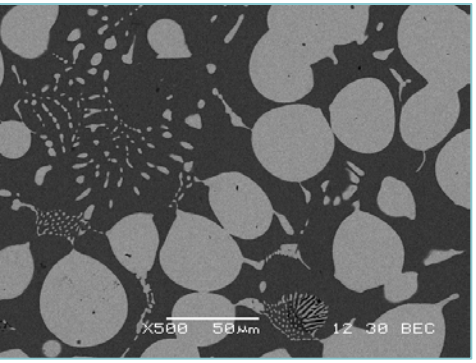
$$P_m = f(V_{Mo})$$

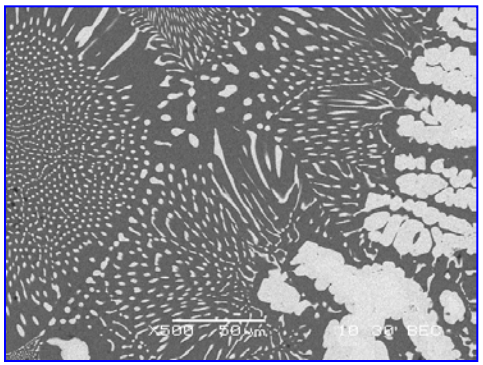
Effect of Mo phase fraction

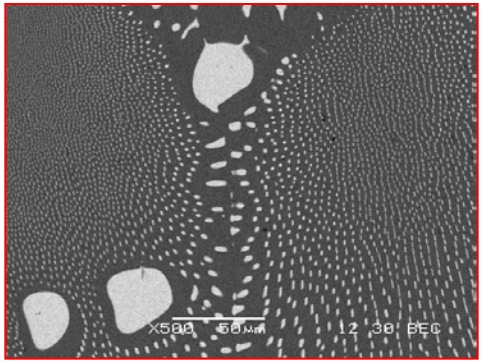


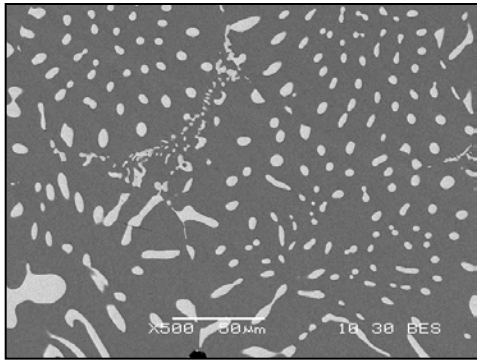


Decreasing Mo content

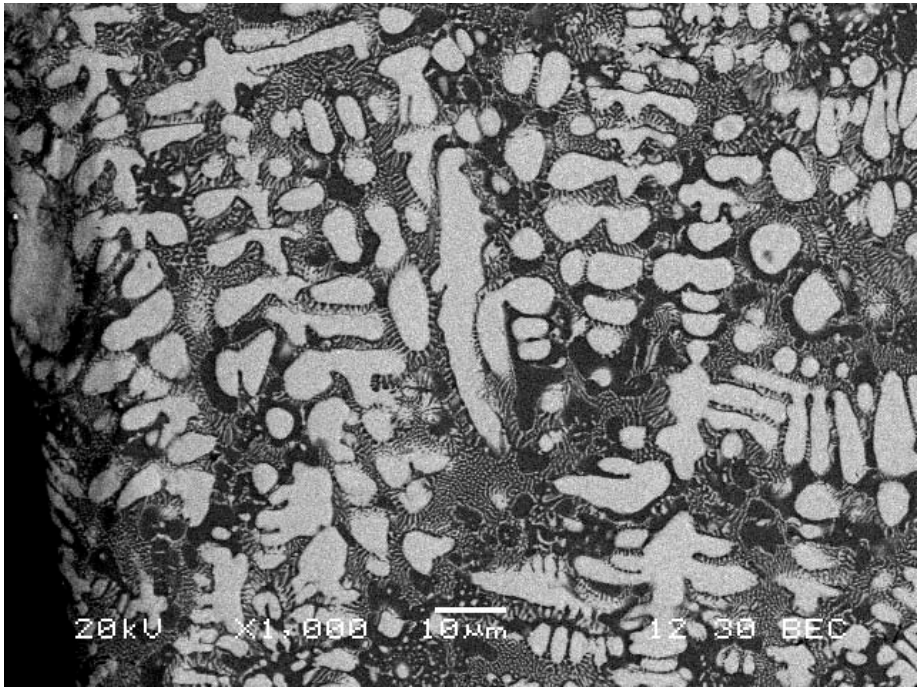


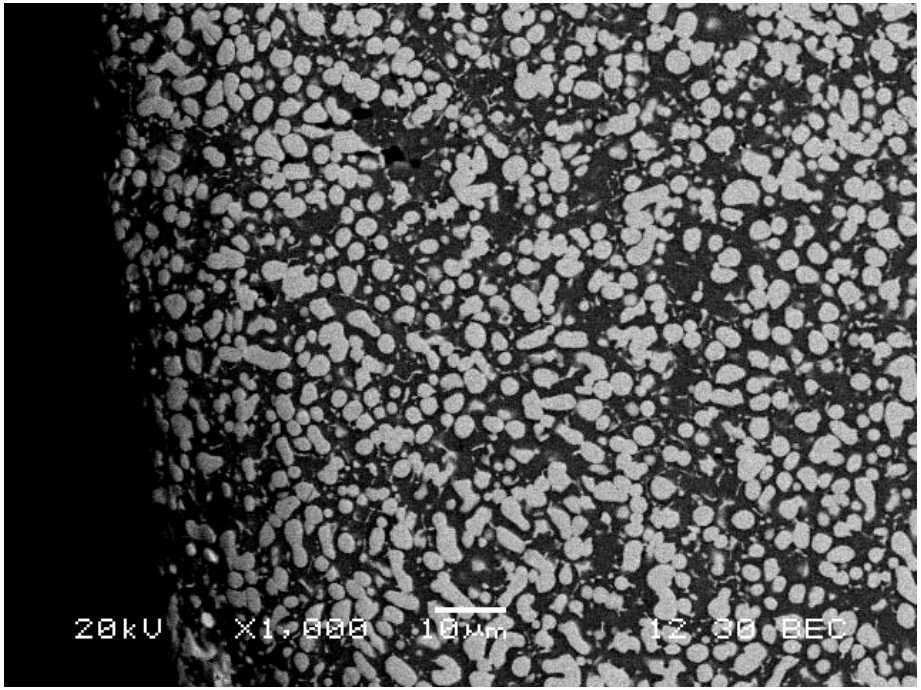






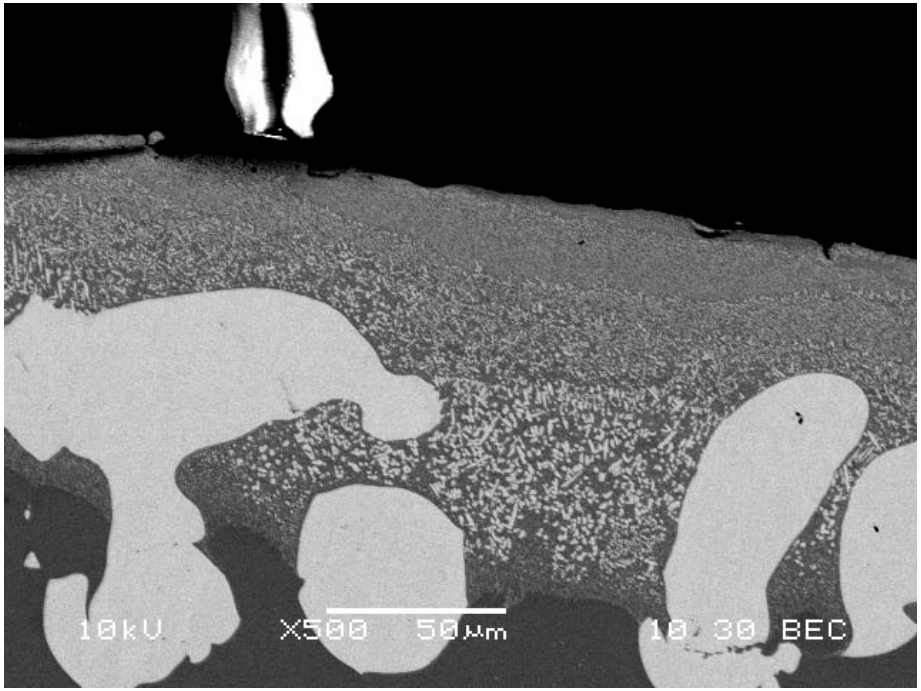
Laser re-melted microstructures

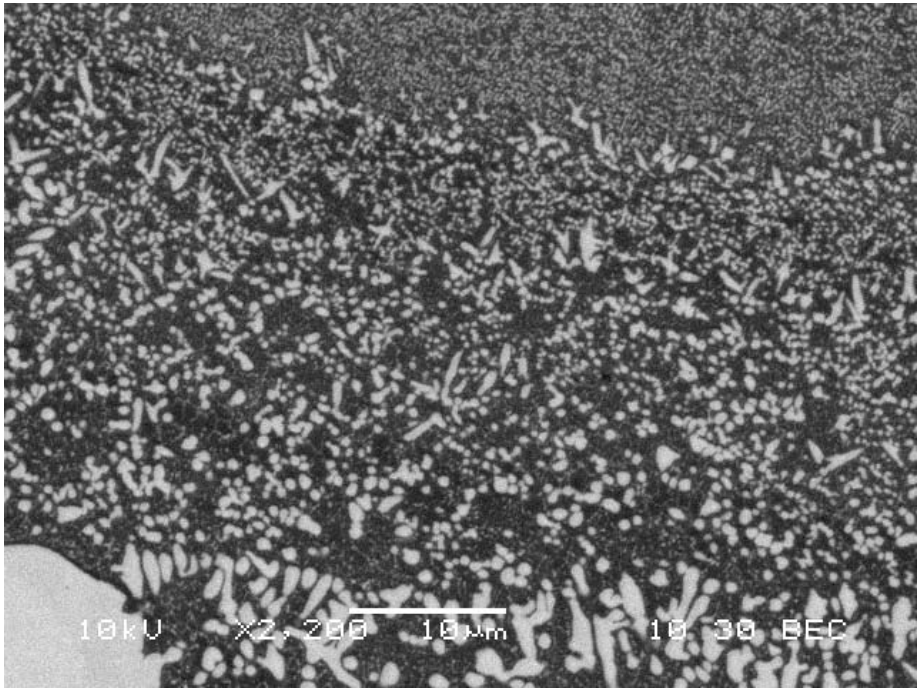




Under appropriate conditions, using a laser beam can break down the Mo dendrites and yield relatively fine nodular structure. Possibly good for oxidation resistance.

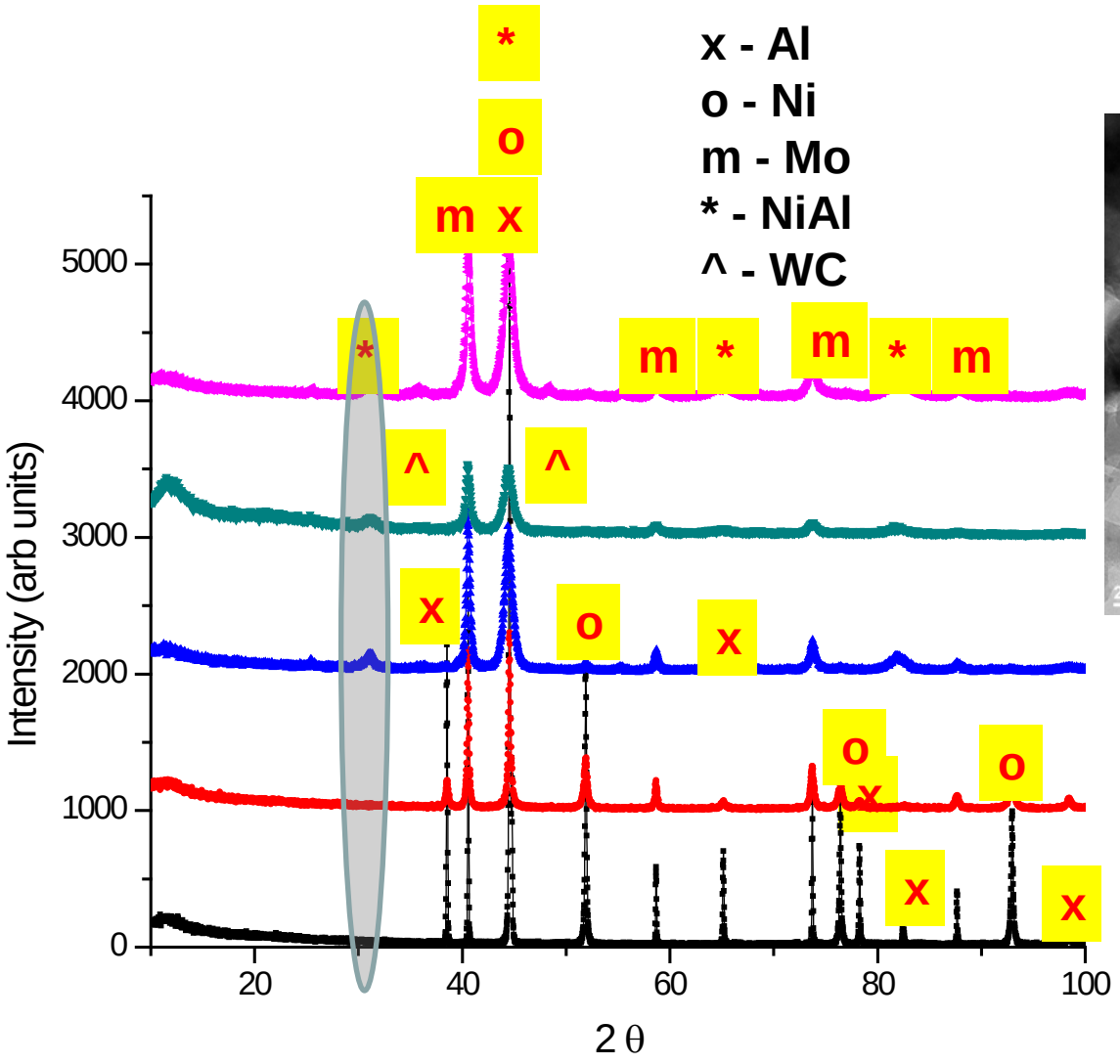
Laser re-melted microstructures

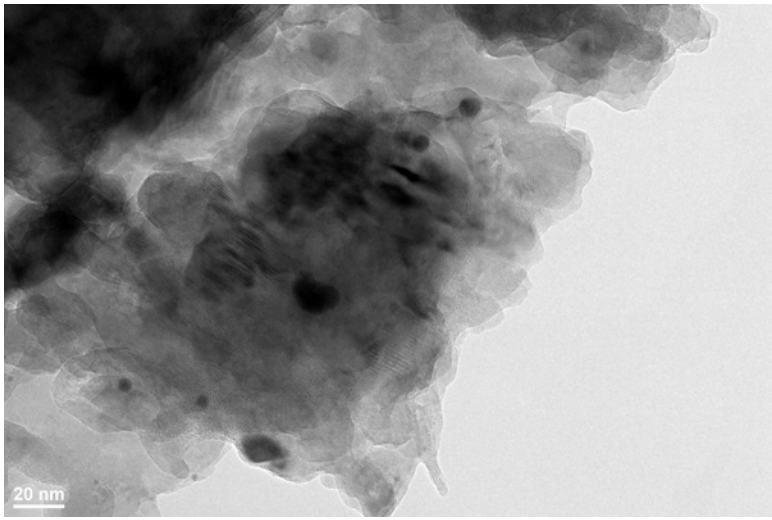




A pulsed laser and a higher power density can result in even finer microstructures

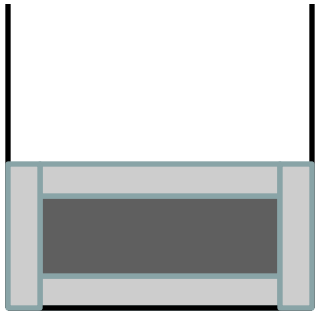
High Energy ball-milling



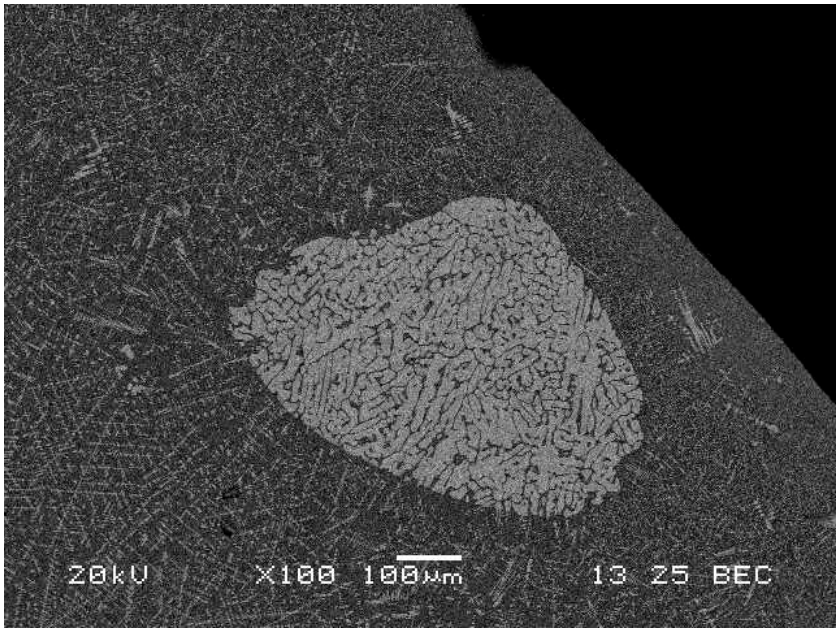


Grain sizes of the order of 25 nm (from TEM)

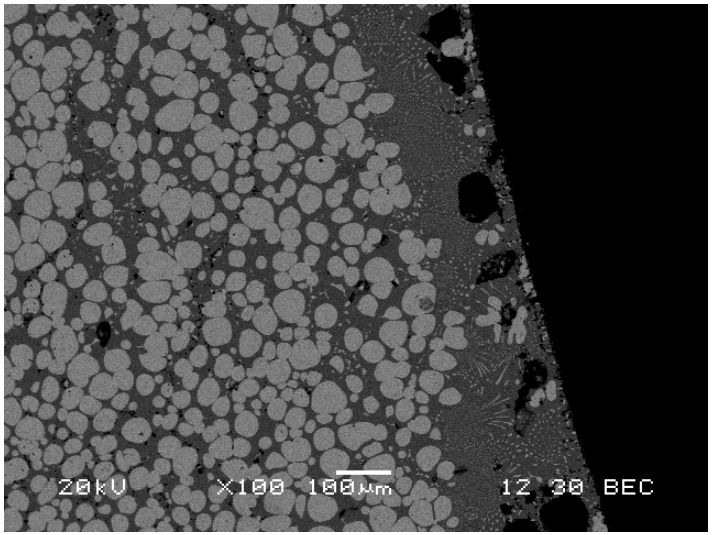
Developing core-shell structures

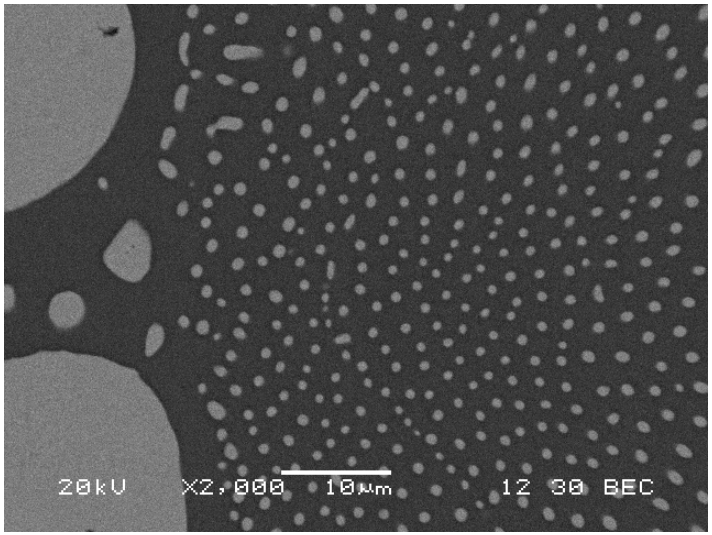


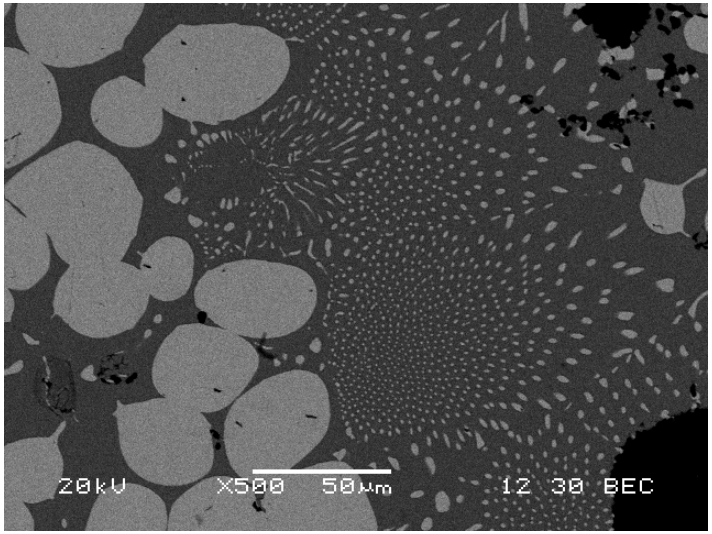
Back to basics –
Mo for mechanical properties, NiAl for oxidation
"Failures are the pillars of success"
Putting Mo clustering to good use …

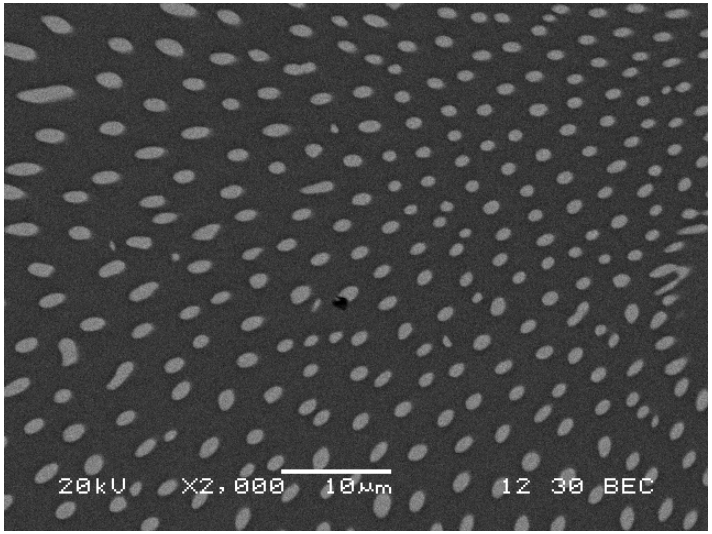


Developing core-shell structures







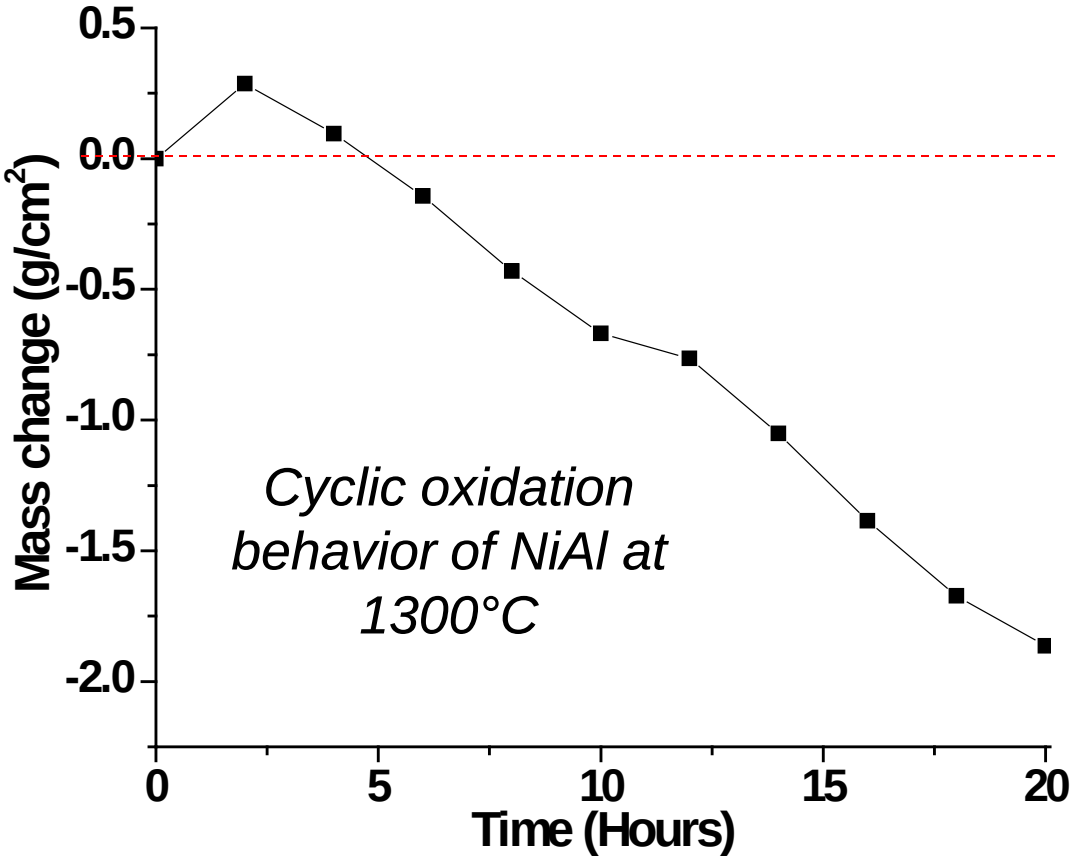


Part II: additions to oxidation resistant phase

Need to Increase Operating T on the Oxidatively Stable Phase

The highest oxidation temperature was 1200°C, although the target temperature is 1300°C.

Key impediment: Spallation of the oxide scale



Part II

- **Use the Miedema model 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!**

Ternary adddition to NiAl

- **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 -220	Pt -171	Au -96

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

List of favorable elements

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

Finer screening

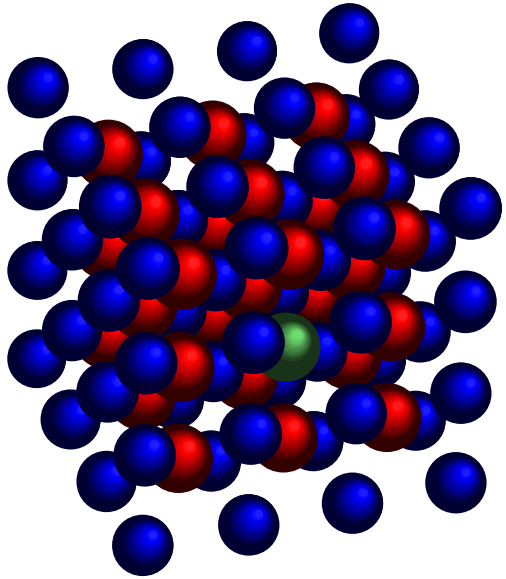
- Eliminate alloying additions that stabilize the liquid
- Eliminate alloying additions that tend to form porous non-volatilizing oxides (e.g. Nb)

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

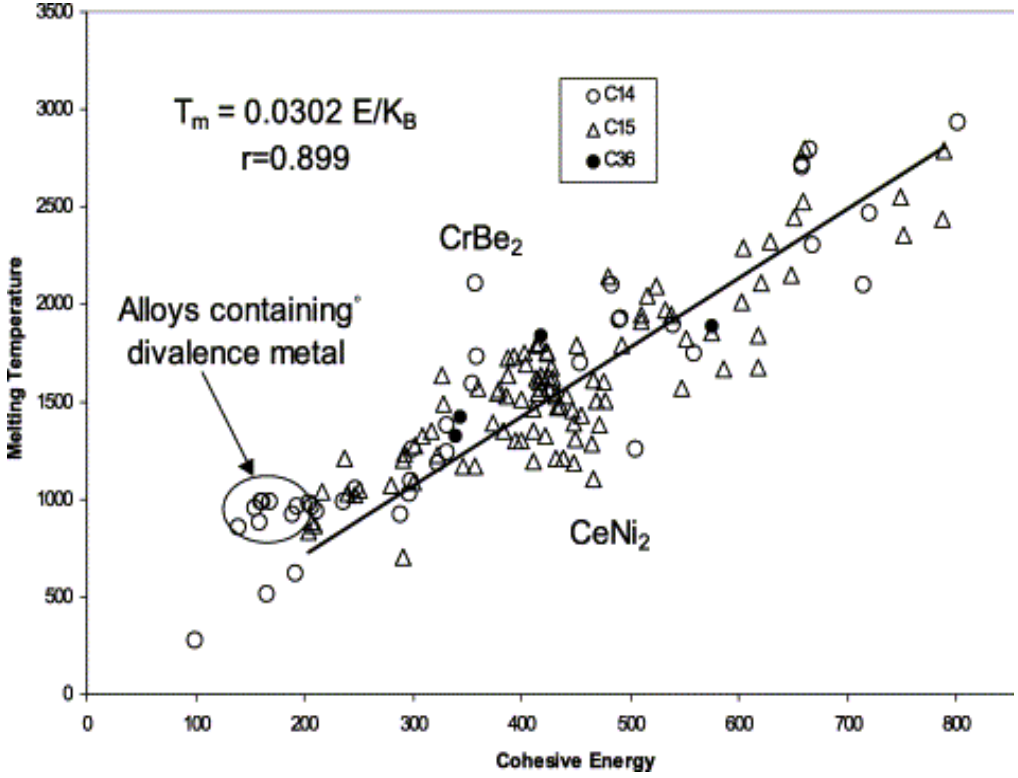
- ***Ab-initio*** **studies using VASP with GGA potentials, NiAl (B2)**
- **54 atom unit cell used for all the calculations**
- **Calculations carried out by substituting ternary alloying element for Ni and Al**
  - **Substitute 1, 2, 4 or 6**
    - **Test both Ni and Al sites**
  - **Y, Hf, Zr, Rh,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

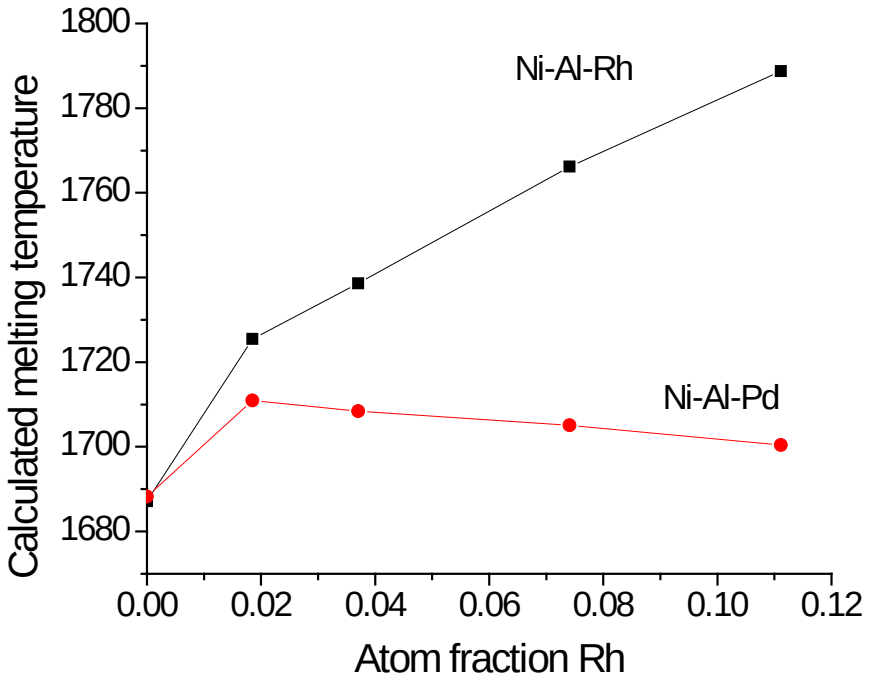


3x3x3 unit super-cell

Estimates of melting

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





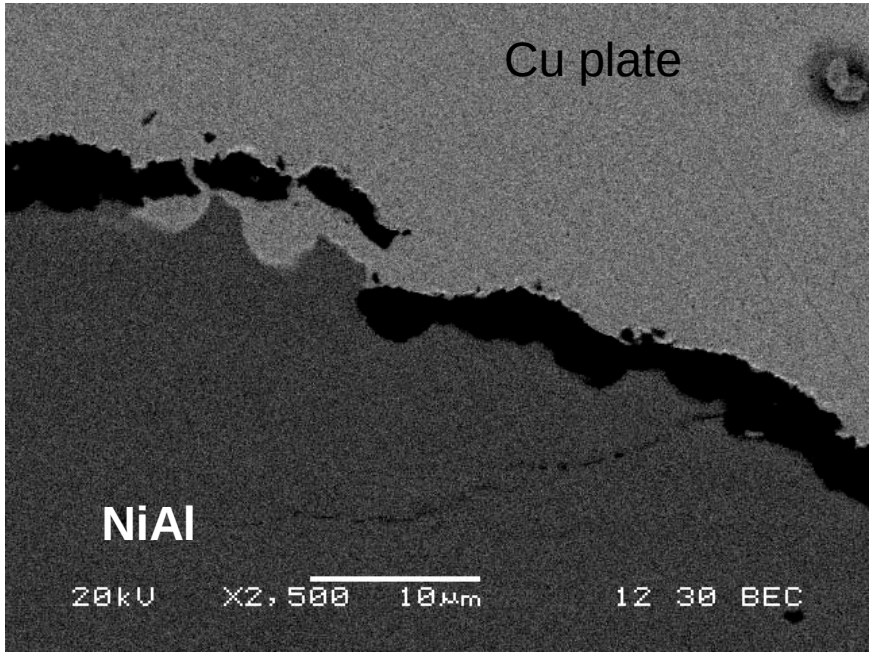
Ternary addition should increase T_m!

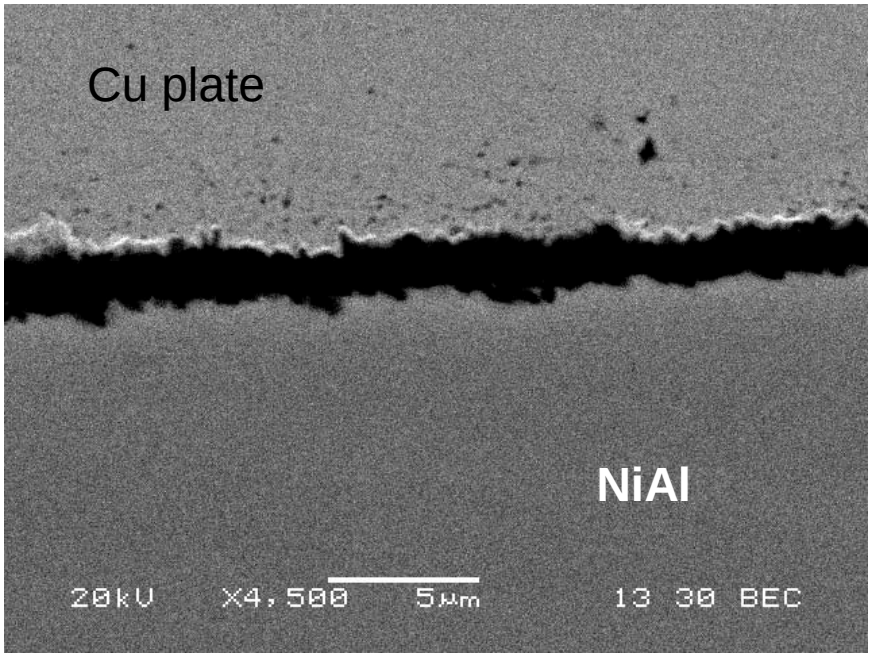
Reference: Li et. al., J Phys Chem Sol 64(2003) 201

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

Effect of alloying additions

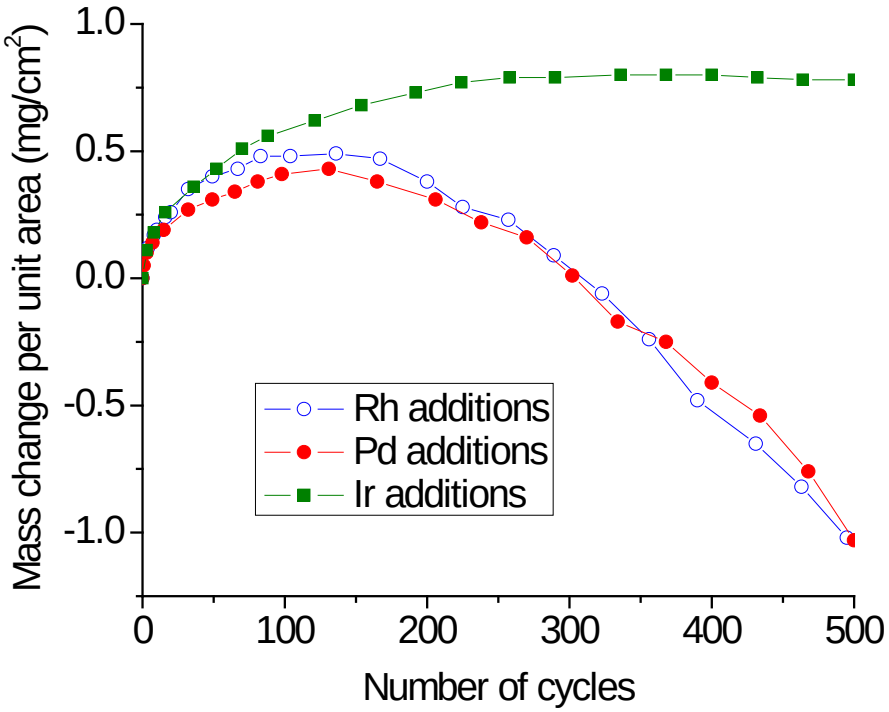




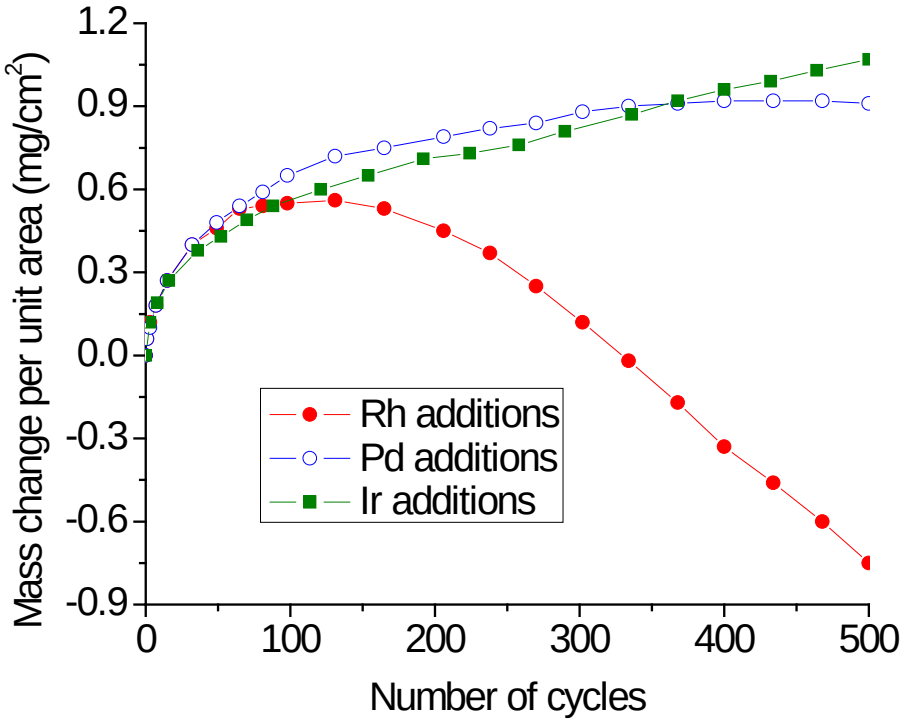
NiAl without any addition (1150C, 25hrs)

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

Cyclic oxidation behavior



1 cycle =
1 h @ 1150°C + 0.5 h @ ambient



- Ir is good
- Rh can be good too

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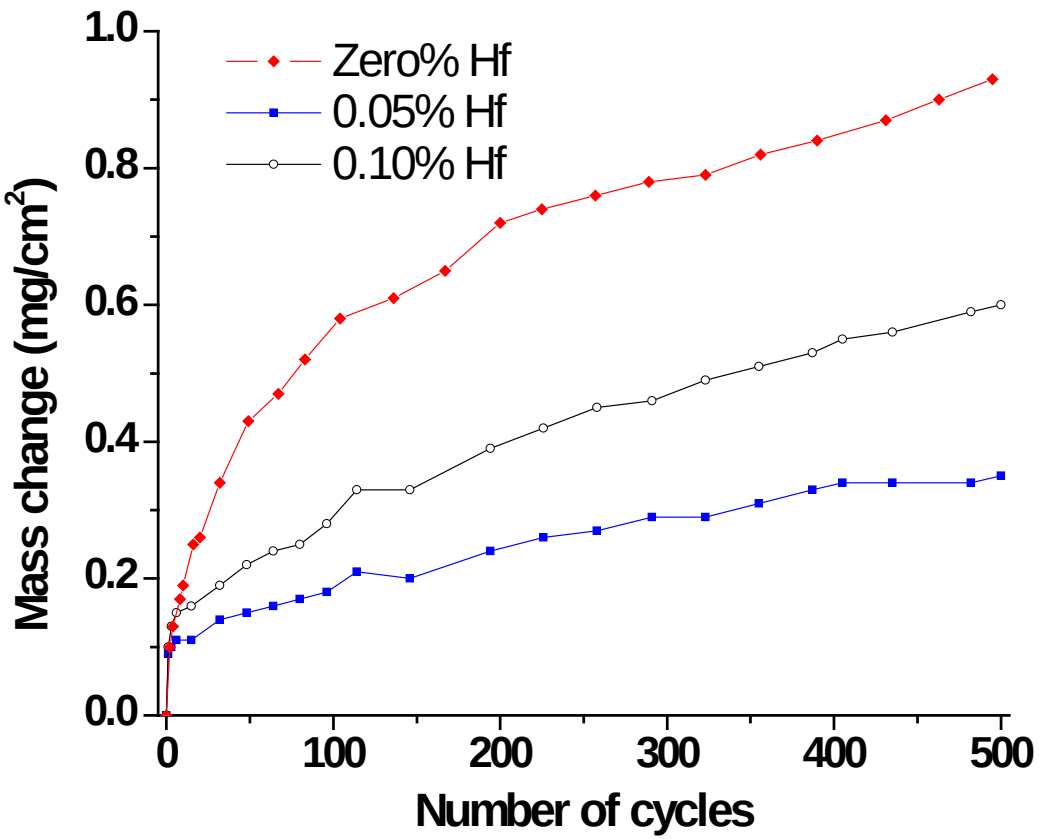
Oxidation behavior with Hf

$Ni_{44}Al_{50}Rh_6$ – cyclic oxidation @ 1150°C



Hf helps at 1150°C !!

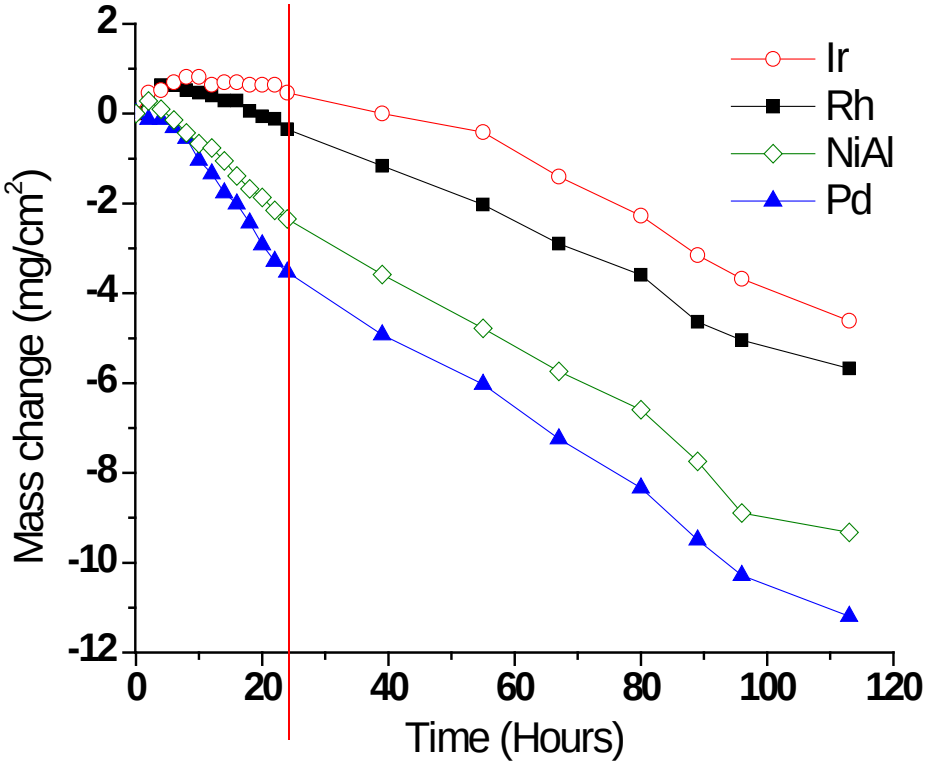
Isothermal oxidation @ 1300°C for 24 hours for $Ni_{44}Al_{50}Rh_6$ + Hf

% Hf addition	Mass change
0.00	-1.08
0.05	0.46
0.10	0.47
0.25	0.48
0.50	0.54

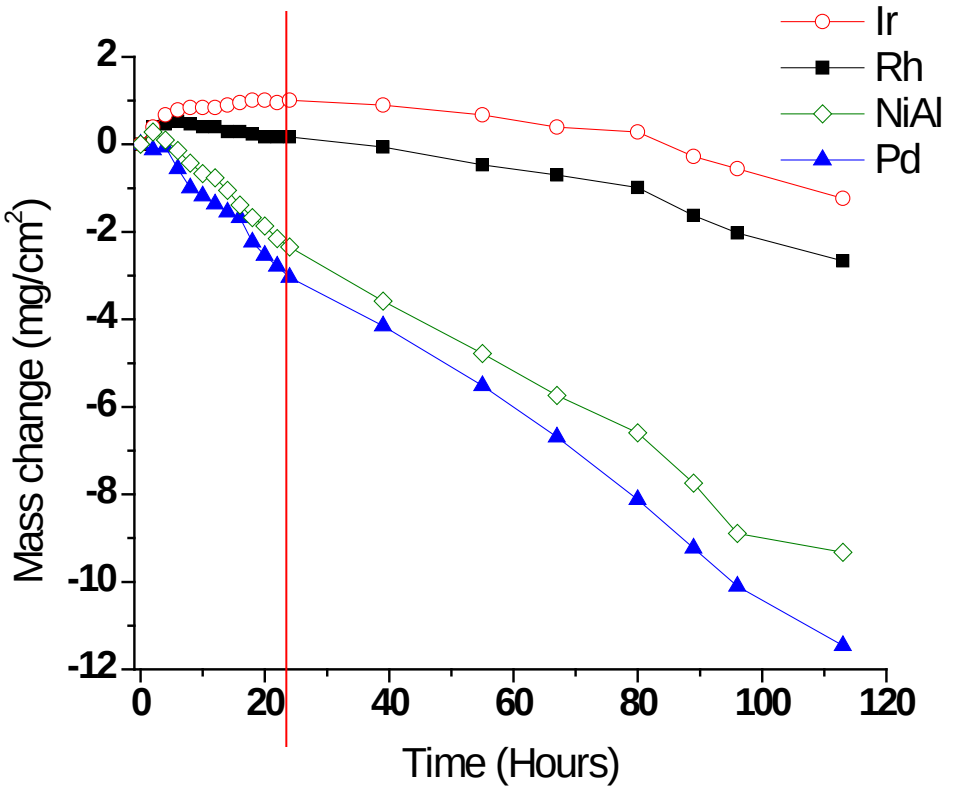
Hf is beneficial for Rh additions as well, but does not help much beyond a certain extent

Cyclic oxidation at 1300°C

$Ni_{44}Al_{50}X_6$



$Ni_{41}Al_{50}X_9$



Summary

Started from scratch and down-selected a base alloy system using semi-empirical approaches

Base Alloy Development

1. Arc-melting
2. Liquid phase sintering
3. Laser re-melting
4. High energy ball milling
5. Induction melting

Studied the oxidation behavior and found a strong microstructure / alloy chemistry dependency

Oxidatively Stable Phase

1. TM additions prefer Ni site
2. Few additions yield single phase
3. Ir and Rh help cyclic oxidation
4. Ir looks promising at 1300° C

The way ahead is to combine both the base alloy and the modified Ni-Al, although both these areas in themselves are still open areas of research

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- **Sumohan Misra**
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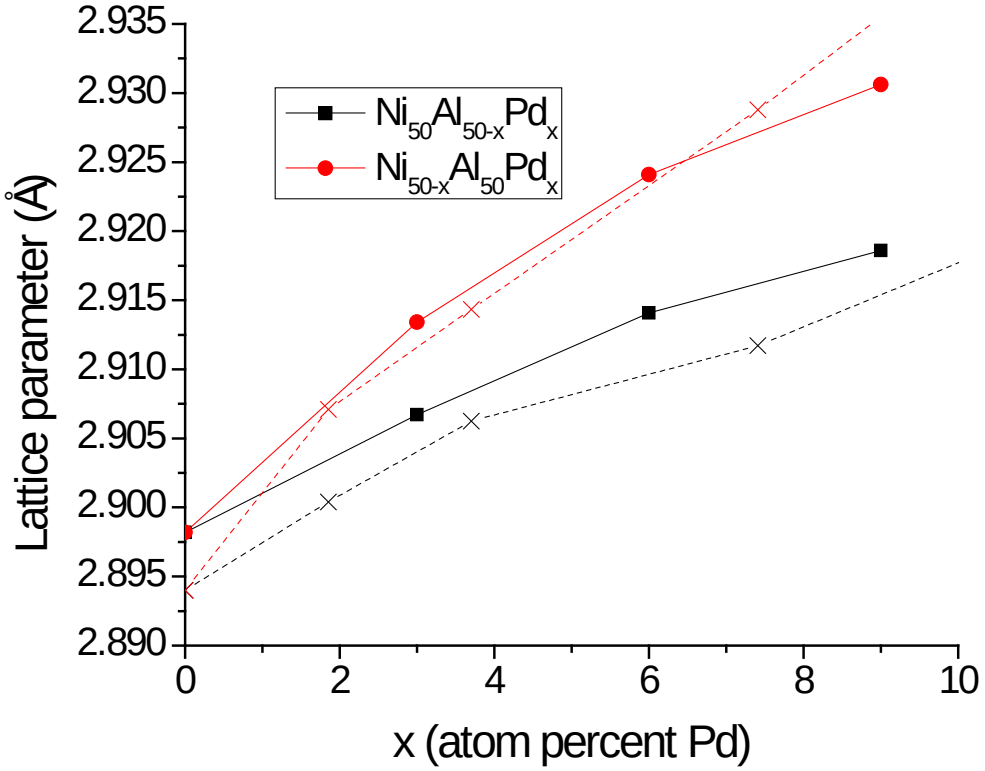
- **Kevin Severs**
  - **Sample preparation**
- **This work was supported by DOE-FE (ARM program) through Ames Laboratory contract number DE-AC02-07CH11358**

X-Ray diffraction



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

single crystal XRD

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