Computational and Experimental Development of Novel High Temperature Alloys from Theory to Practice

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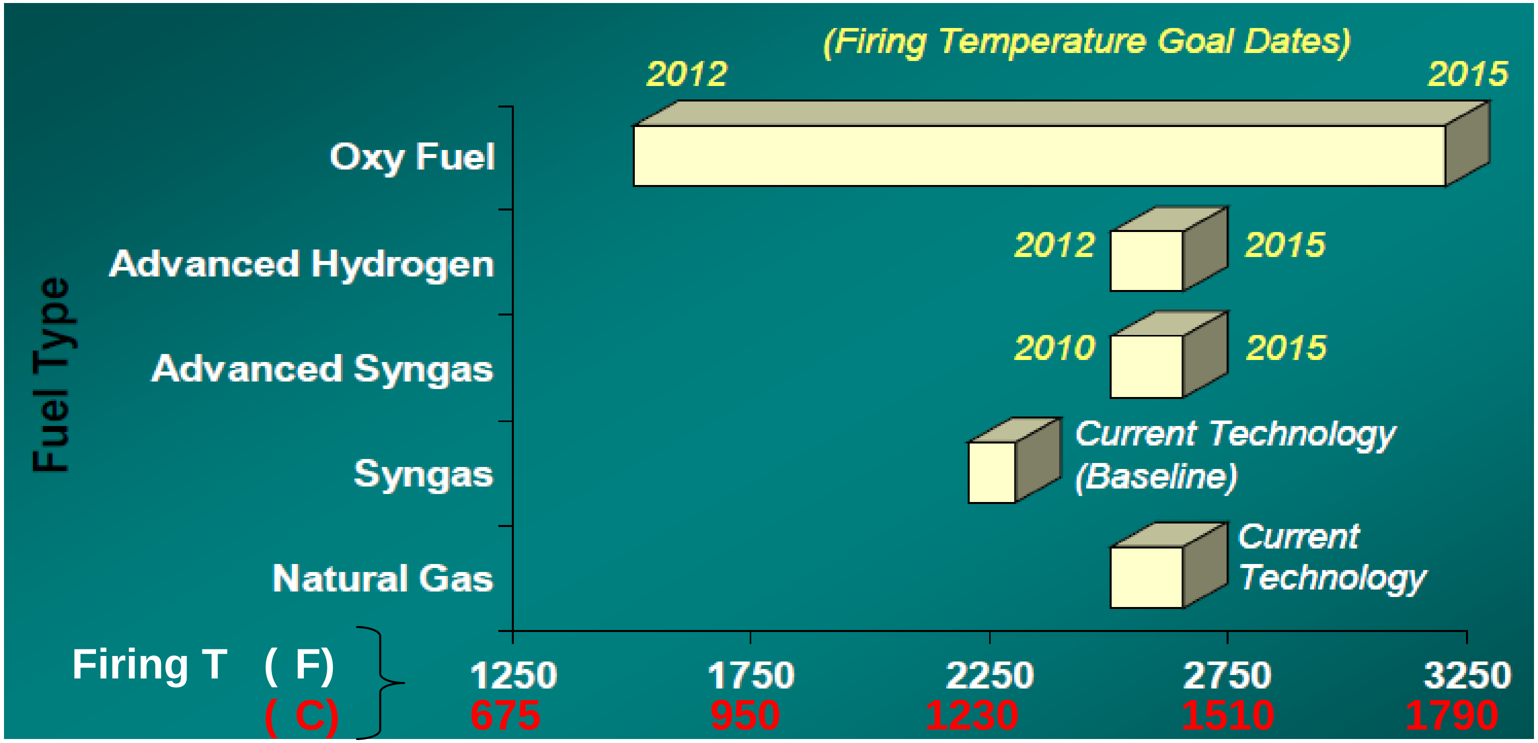
The Ames Laboratory
Creating Materials & Energy Solutions
U.S. Department of Energy

U.S. Department of Energy

Iowa State University

The Problem

Advanced Turbine Systems



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

- Rapid Screening of potential systems
- High melting temperature
- Matrix should be a refractory metal with BCC or FCC
- Contain a 'reservoir' for passivating components
  - Al, Cr, Si

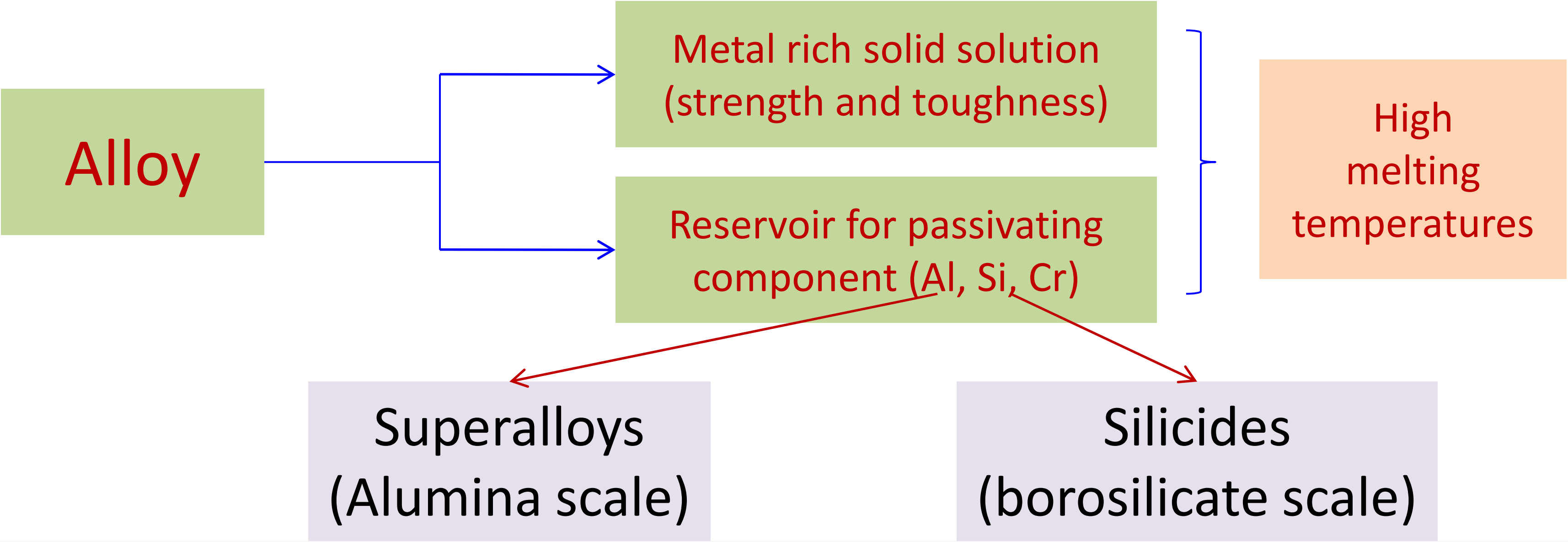
Number of elements	Possible combinations
2	3160
3	82160
4	1.58×10^{6}
5	2.40×10^{7}
6	3.00×10^{8}
7	3.18×10^{9}
8	2.90×10^{10}
9	2.32×10^{11}
10	1.65×10^{12}

Ray, P.K., M. Akinc, and M.J. Kramer, *J of Alloys and Comp, 2010.* ***489(2): p. 357-361.***

The need for rapid and effective hierarchical screening!!

Materials Metrics Considerations

- Key requirements
  - High melting temperatures
  - Adequate strength and toughness
  - Good oxidation resistance



Alloy

Metal rich solid solution (strength and toughness)

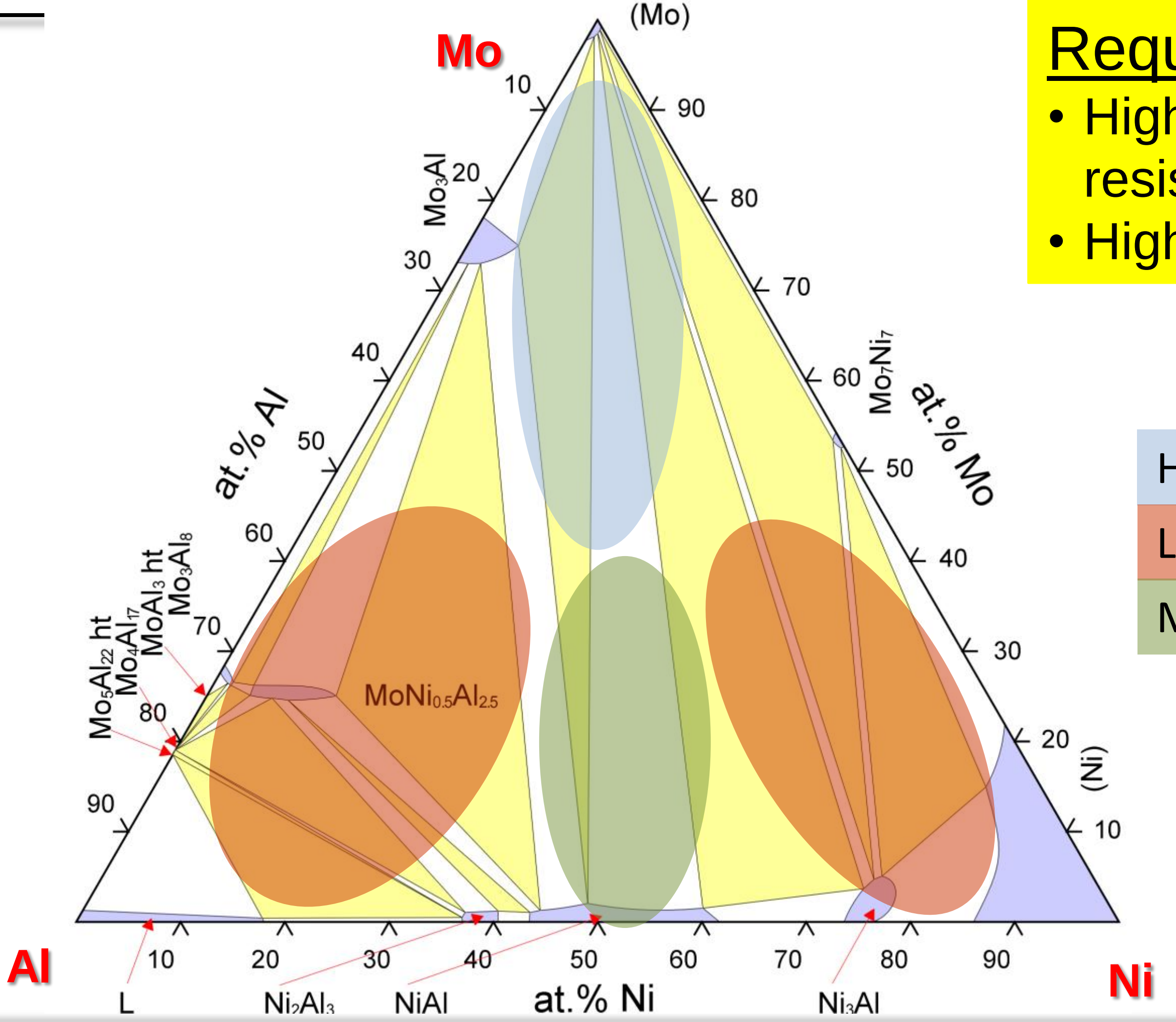
Reservoir for passivating component (Al, Si, Cr)

High melting temperatures

Superalloys (Alumina scale)

Silicides (borosilicate scale)

Alloy Design



http://www1.asminternational.org/asmenterprise/apd/

Requisites

- High temperature oxidation resistance
- High thermal stability

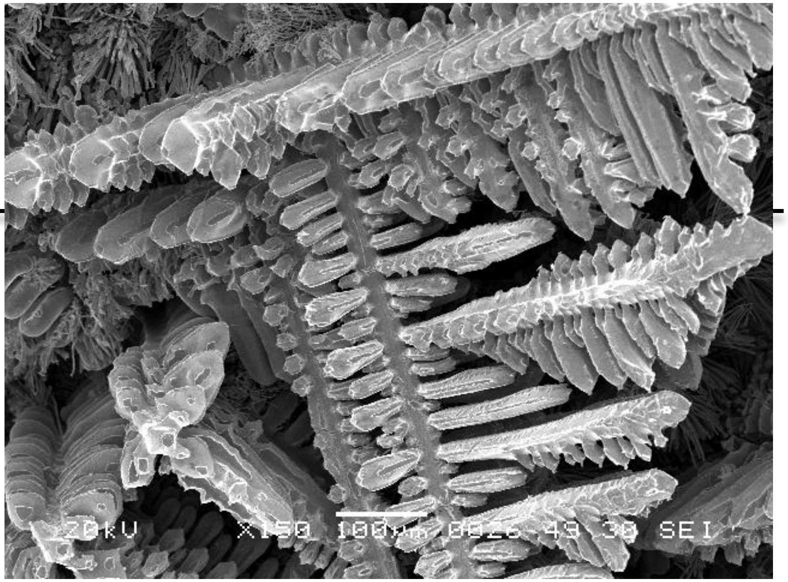
High melting + poor oxidation

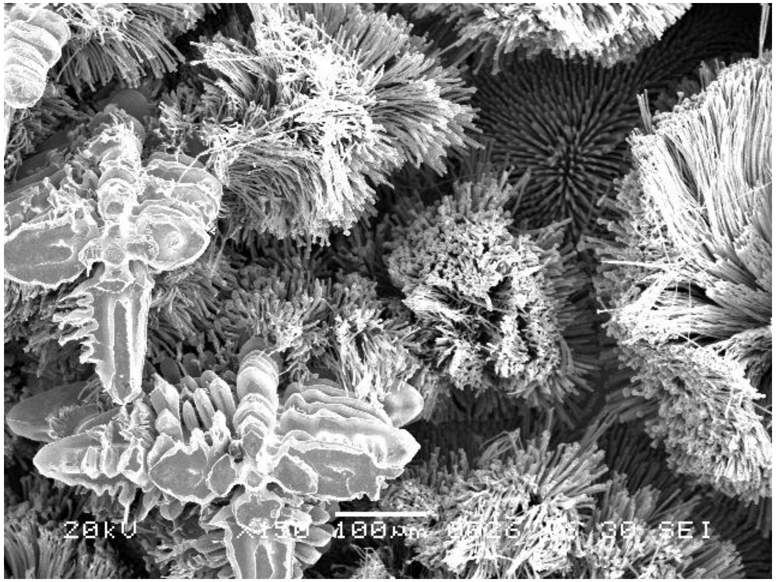
Low melting + good oxidation

Mix of oxidation and melting

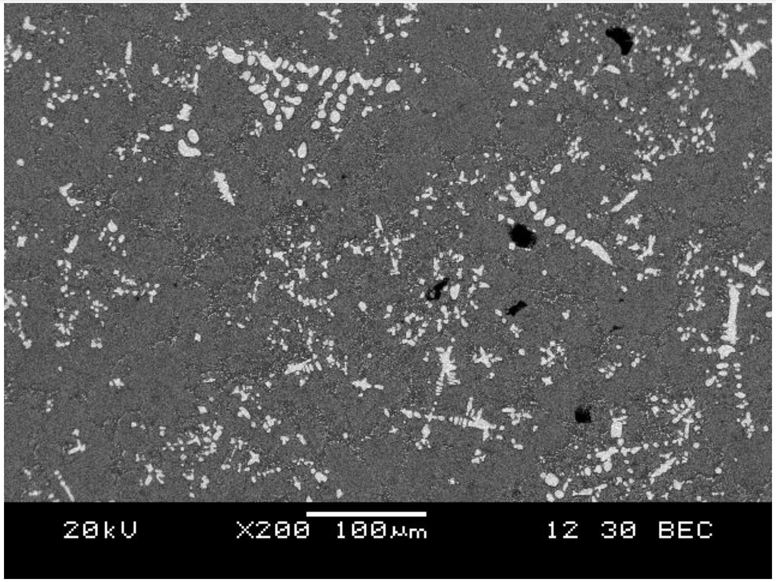
Tasks

- Base Alloy synthesis
  - Sintered
  - Cast
  - Directional Solidification
- Mechanical Testing
  - Fracture toughness
    - Jamie Kruzic, OSU
- Base Alloy oxidation characterization
  - Role of Mo content and morphology
  - Model for estimating catastrophic failure
- Development of coating alloys
  - Optimization of processing
  - Improved Ni-Al stability
    - Replacements for Platinum Group metals

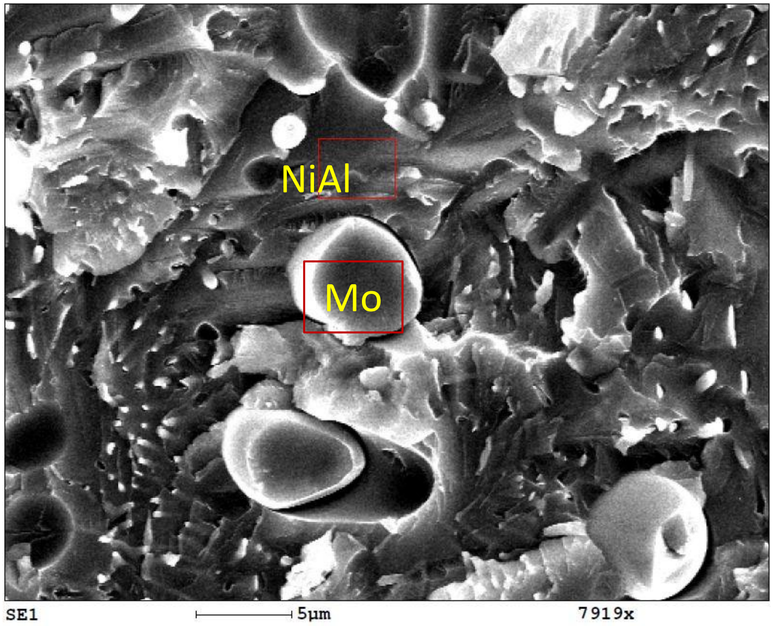




Fracture toughness



- Drop-cast 15 atom% Mo alloy
- Fracture toughness ~ 9.4 MPa.m$^{1/2}$
- Fracture toughness of NiAl ~ 5 MPa.m$^{1/2}$
- Fracture toughness of Mo-Si-B alloys ~ 12 MPa m$^{1/2}$
- DS eutectic Mo-Ni-Al alloy has shown ~10^{7} decrease in creep rate

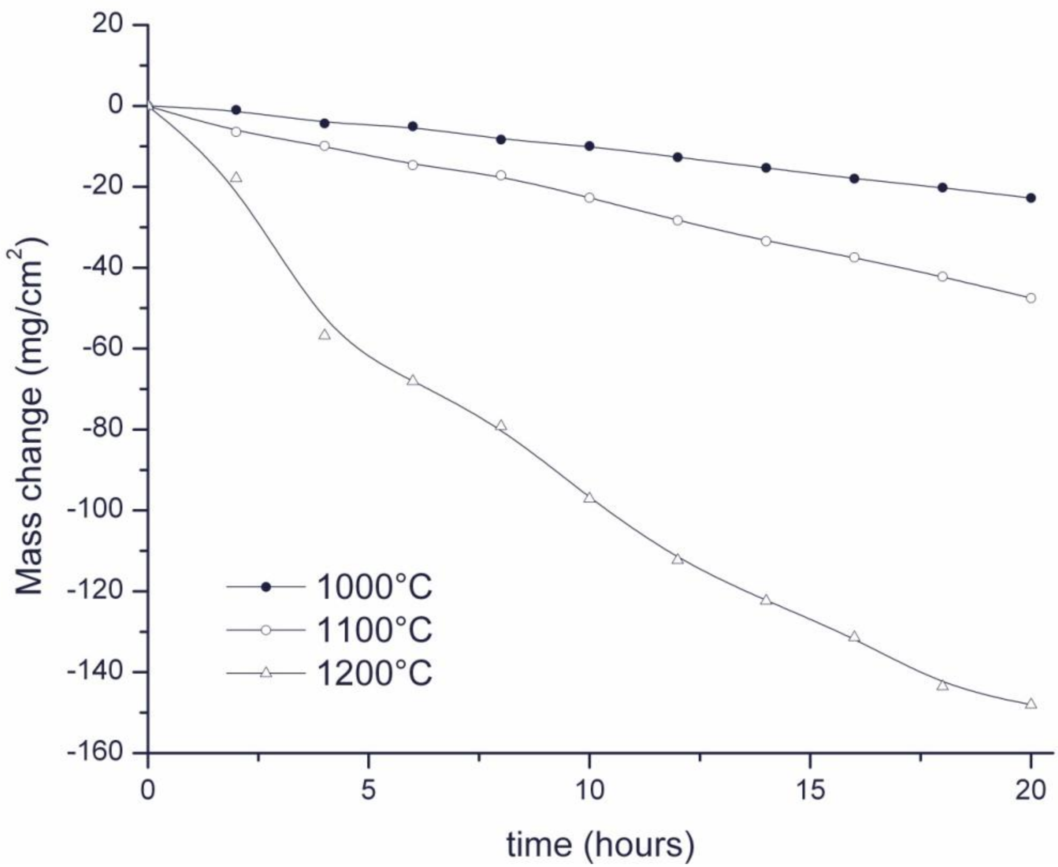


Mo dendrites pull out, indicating its effect on the toughening mechanism in this alloy.

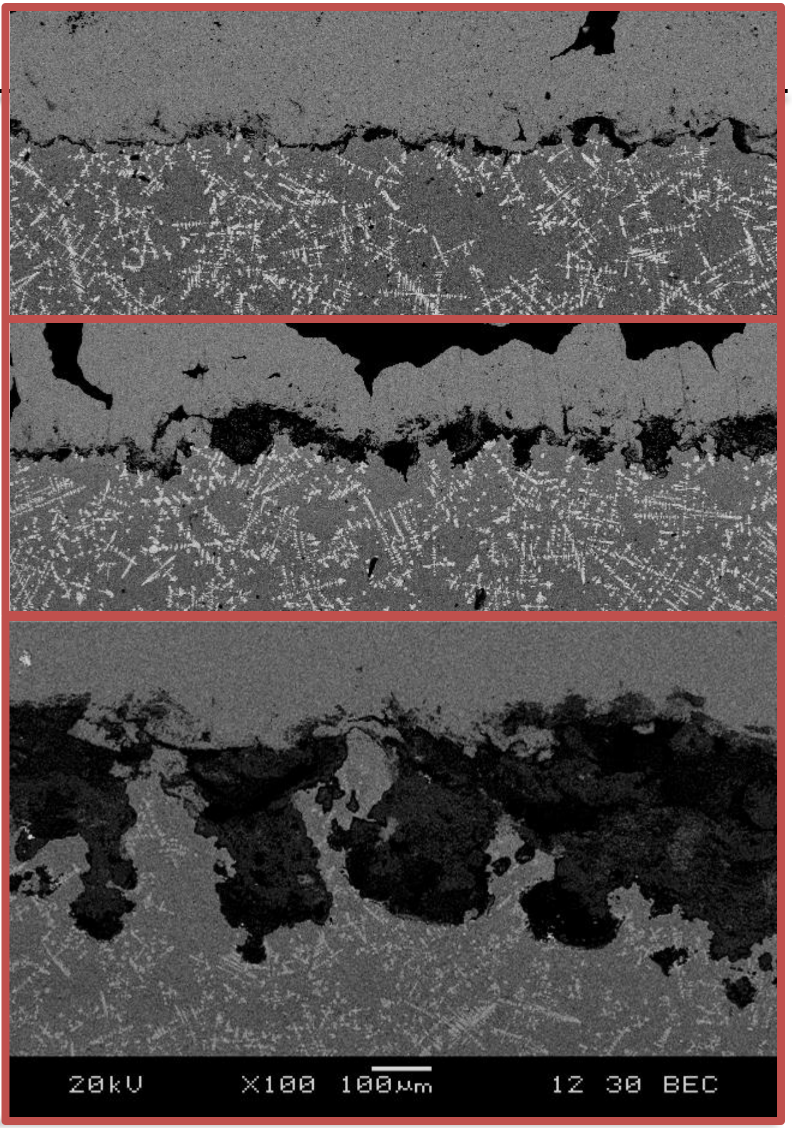
The challenge: Optimize the microstructure of the base alloy in order to optimize the strength and toughness of the alloy.

M. Dudova et. al. Scripta Materialia 65 (2011) 699–702

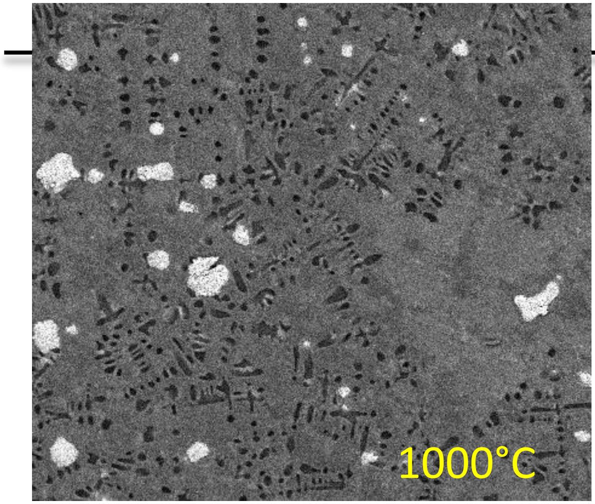
Effect of Temperature on Oxidation

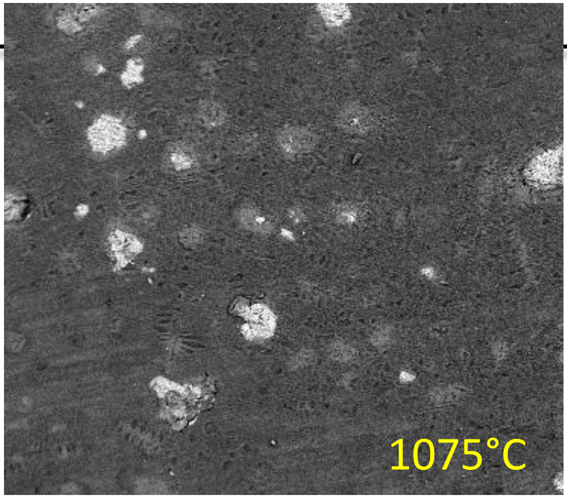


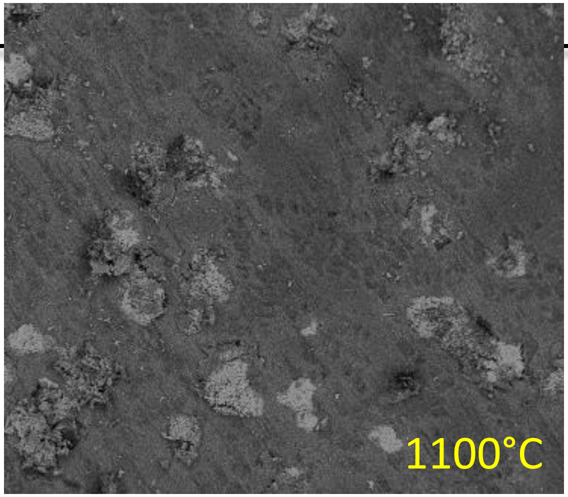
Base alloy shows dramatic loss of oxidation resistance above 1100°C.



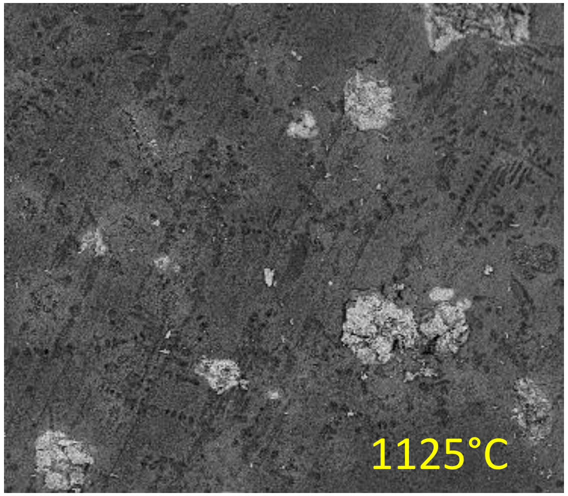
Early stages of oxidation (30 min)

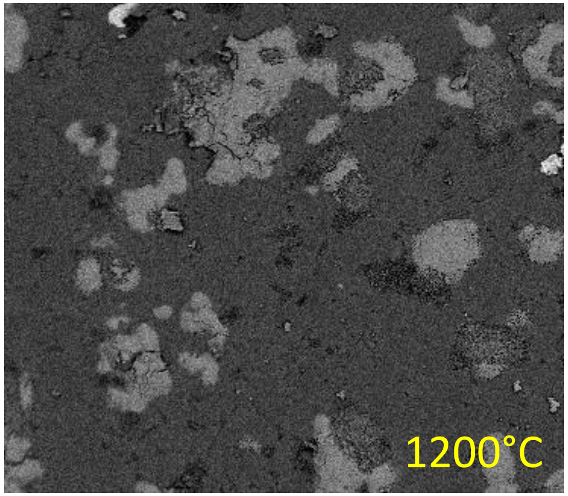






X250 100µm



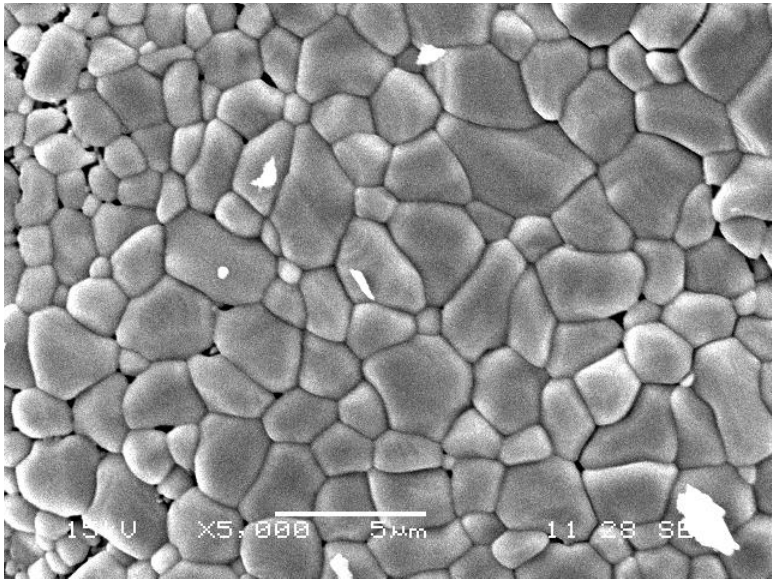


- Size of $NiMoO_4$ increases with temperature.
- This is accelerated from 1100°C onwards.

	1000°C	1075°C	1100°C	1125°C	1200°C
Al_2O_3	Yes	Yes	Yes	Low	Low
$NiMoO_4$	Yes	Yes	Yes	Yes	Yes
$NiAl_2O_4$	Yes	Yes	Yes	Yes	Yes
NiO	No	No	No	No	Yes

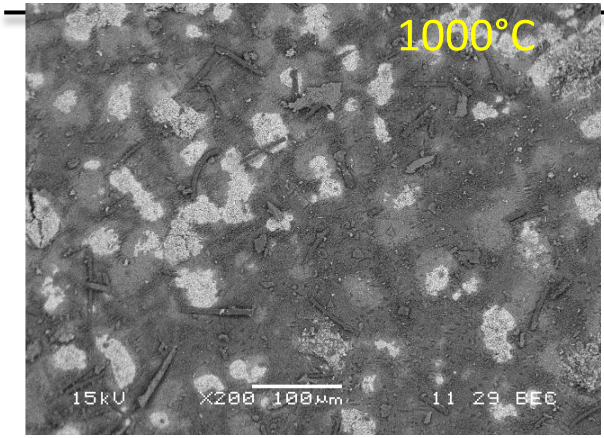
- $NiMoO_4$ and $NiAl_2O_4$ are present at all temperatures from 1000°C to 1200°C
- NiO is absent until 1200°C
- Al_2O_3 is present throughout the entire temperature range, but in small amounts above 1125°C

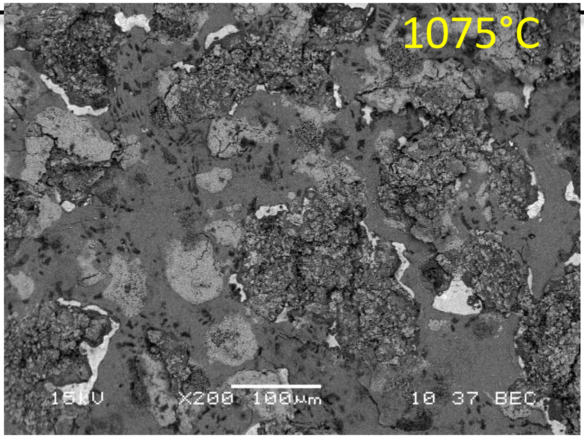
Higher temperatures show low amounts of alumina on the surface, but NiO can be observed. This is contrary to the oxidation of pure Ni-Al alloys.

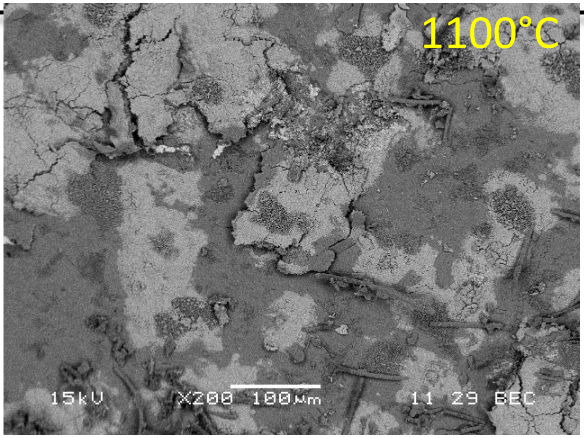


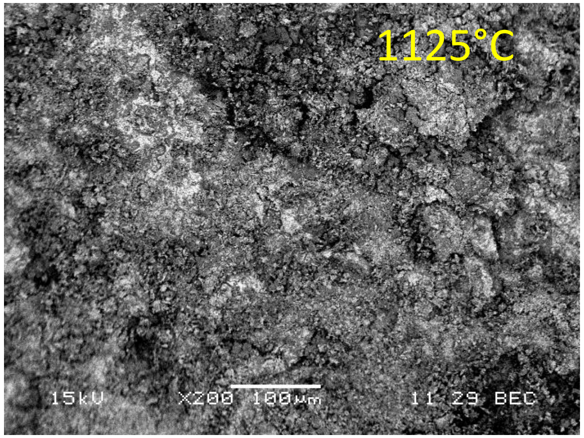
SE image of NiO in the alloy oxidized at 1200°C

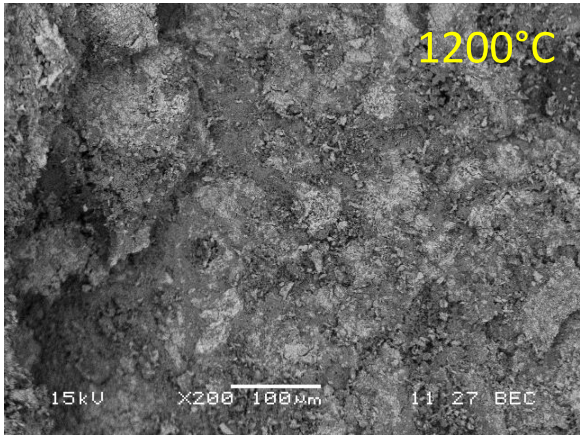
Long term oxidation (10 hours)











EDS indicates the presence of large regions of $NiMoO_4$ in the top micrographsbut not in the bottom micrographs.

The bottom images show copious quantities of NiO which are present in the others in small amounts

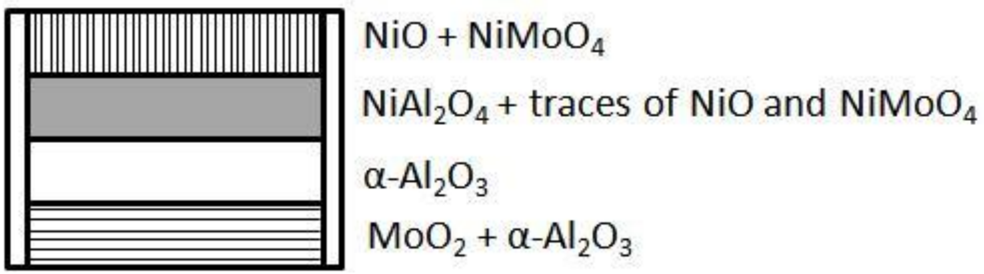
Summarizing Ni-Al-Mo Oxidation

	1000°C	1075°C	1100°C	1125°C	1200°C
Alumina	Stays over time	Decreases over time	Significant decrease	Almost absent	Absent @ end
$NiMoO_4$	Grows over time	Grows over time	Grows over time	Absent @ end	Absent @ end
$NiAl_2O_4$	Present throughout	Present throughout	Present throughout	Present throughout	Present throughout
NiO	Absent throughout	Present @ the end	Present @ the end	Present @ the end	Present* throughout

* Amount of NiO after 10 hrs at 1200°C seems less (visually) than the amount present after oxidation for 10 hrs at 1125°C

Multilayered scale formation: Summary

- Spallation will affect the outer part of the scale rather than the inner part
- Presence of $NiAl_2O_4$ in both regions indicate it to be an interim phase. Furthermore, it is known that $NiAl_2O_4$ is formed by sintering of NiO (outermost layer) and Al_2O_3 (adjacent layer)
- Subscale and the layer adjacent to subscale (and $NiAl_2O_4$) seen to be α-Al_2O_3 from XRD and SEM images



Phase transformation in $NiMoO_4$

Heating $\alpha \longrightarrow \beta$ @ 602 °C

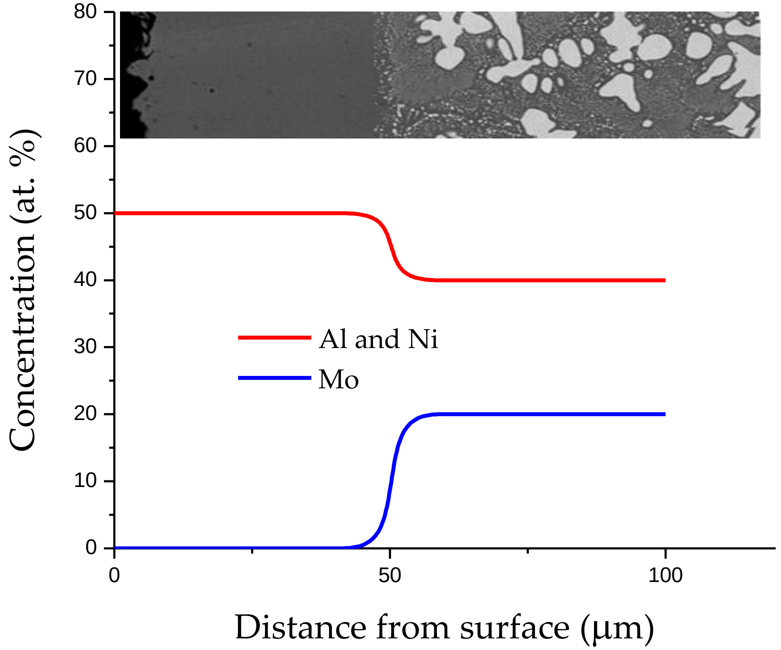
Cooling $\beta \longrightarrow \alpha$ @ 250 °C

Volume change associated with transformation on cooling ~ 20%

Massive volume change is responsible for spallation – hence its only the layers containing $NiMoO_4$ that will spall off

Improving the Oxidation of the Base Alloy

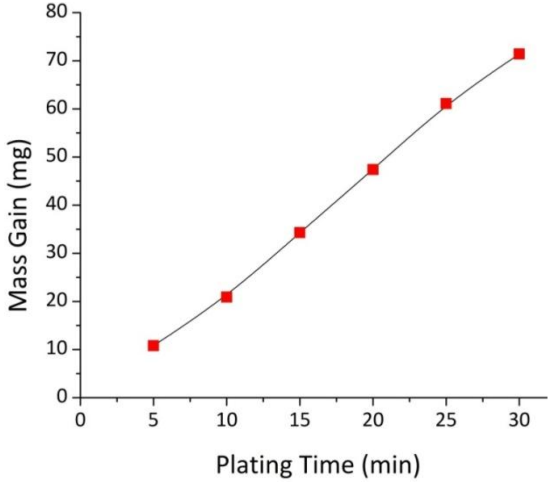
- Complicated, multi-phase oxdiation of (Mo)+NiAl alloys limits this alloys use in high temperature environments
- To control the oxidation process a coating can be implemented to limit the exposure of the base alloy to the oxidizing environment
- Inherent oxidation resistance of the base alloy is good enough to provide protection from catastrophic failure



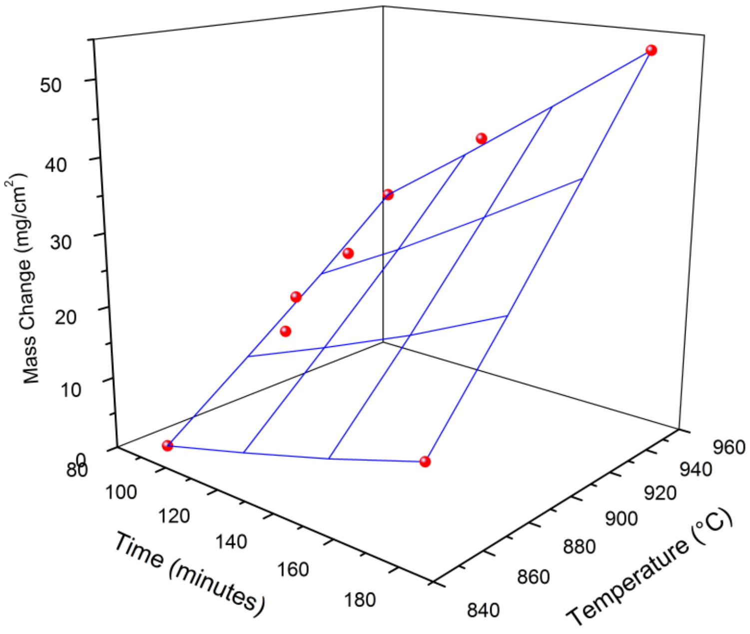
"Core-Shell" Idea

By using β-NiAl as a coating, on top of the MoNiAl alloy, chemical gradients are decreased, which can prolong the life of the coating

Pack Cementation Process



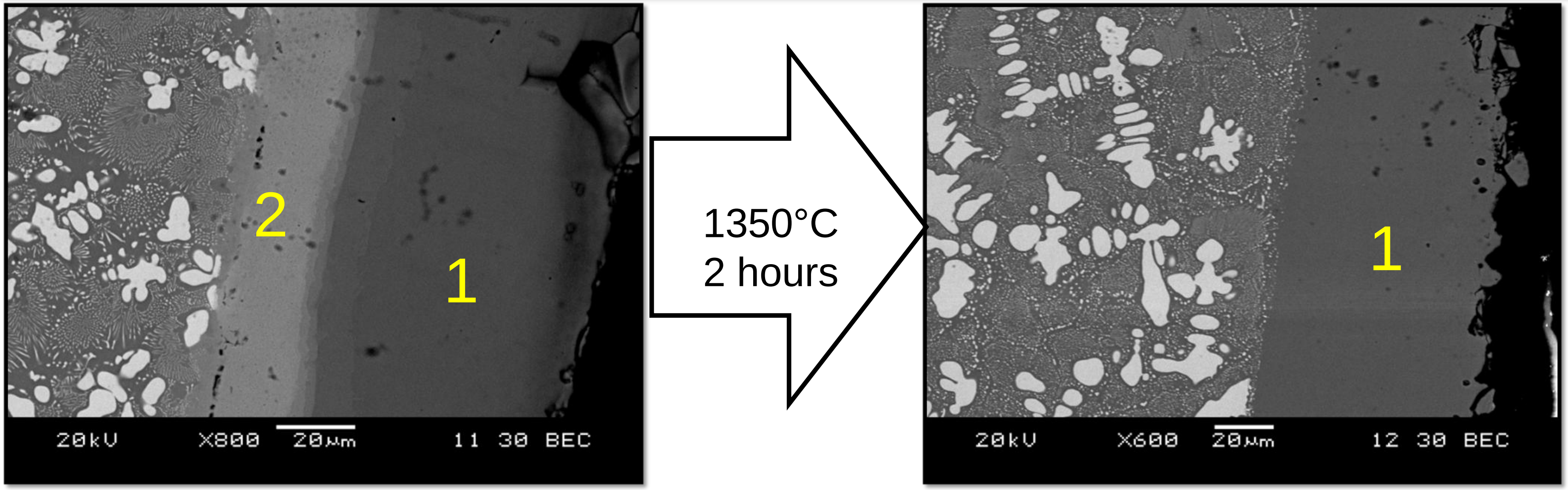
By utilizing a constant current plating method using a 90+% efficient plating solution, control of Ni deposition is straightforward



Ni Plating Solution	
Nickel Sulfate	175 g/L
Nickel Chloride	85 g/L
Boric Acid	20 g/L

Pack Composition, wt.%	
Aluminum	15%
Ammonium Chloride	4%
Alumina	81%

Coating Formation

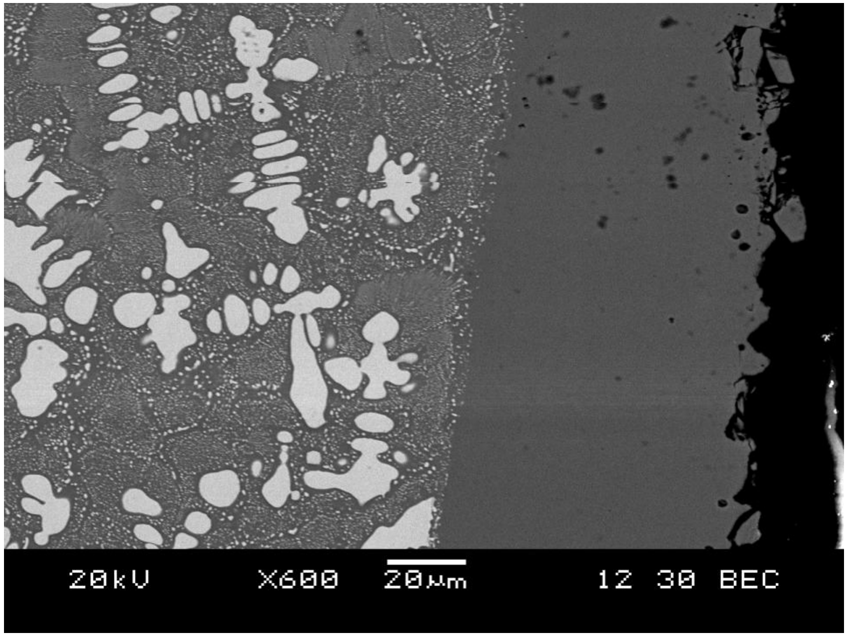


Area	Al(at.%)	Ni(at.%)
1	60.8	38.9
2	5.2	94.8

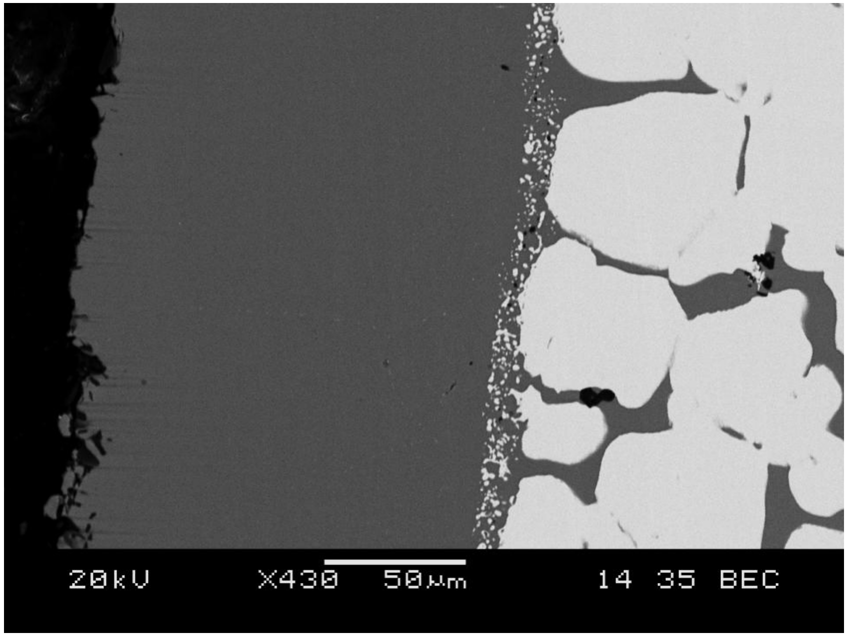
Area	Al(at.%)	Ni(at.%)
1	46.7	53.3

Anneal at 1350°C is required to homogenize the coating

Processing Flexibility



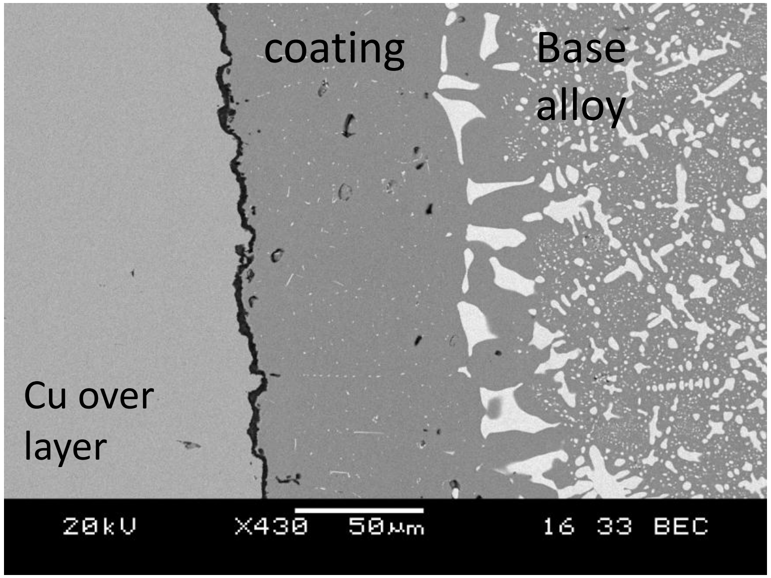
20% Mo



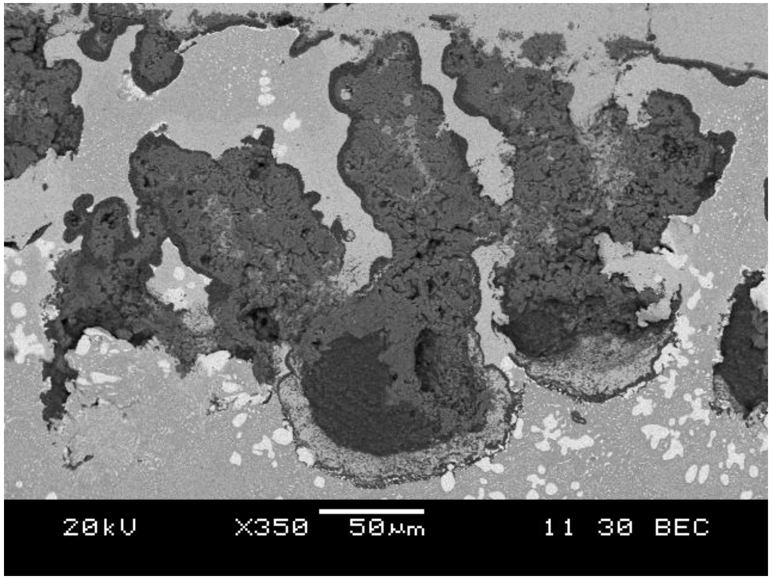
75% Mo

- The coating can be synthesized, independent of the bulk alloy composition
- Oxidation performance of the coating needs to be evaluated

Oxidation Stability



100 hours at 1200°C

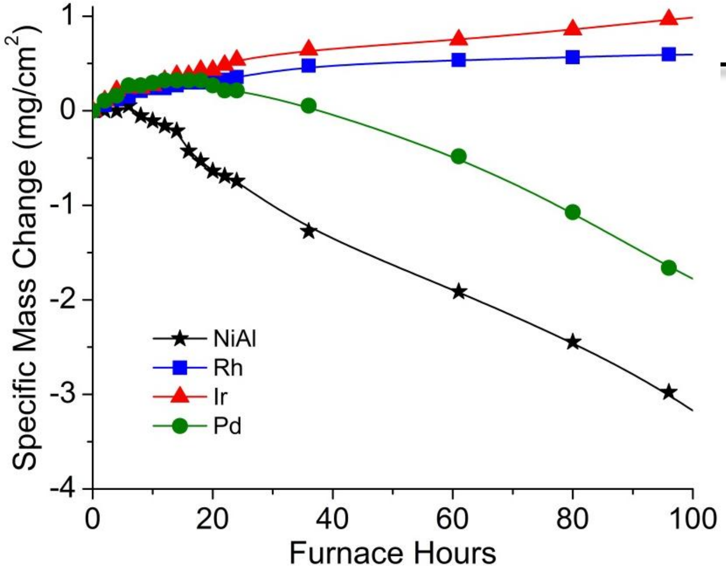


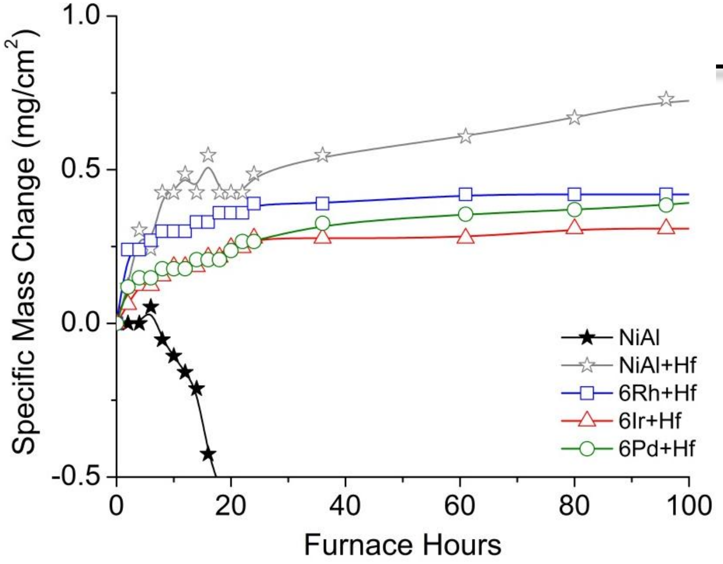
20 hours at 1200°C uncoated

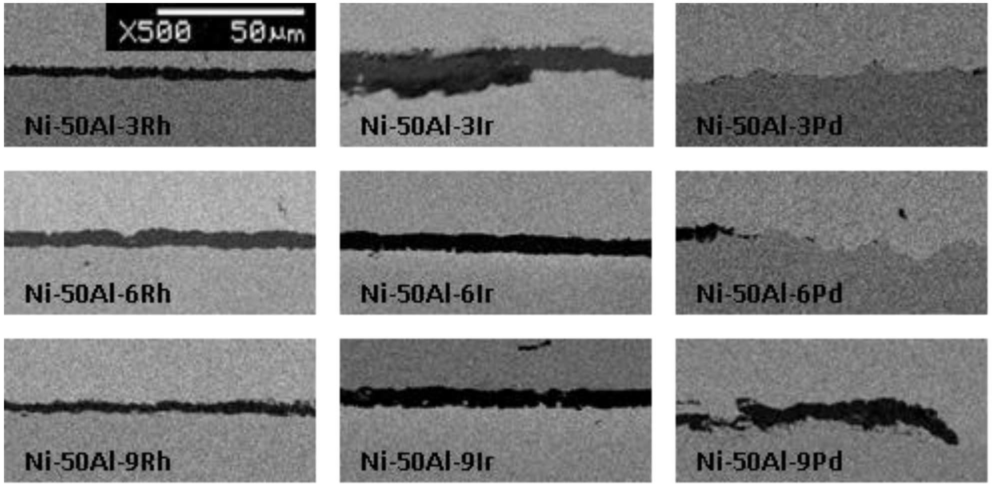
The coated 20-Mo samples show a dramatic improvement in the oxidation resistance.

Coated sample showed weight change of -1.8mg/cm^2

Need for Higher T Range

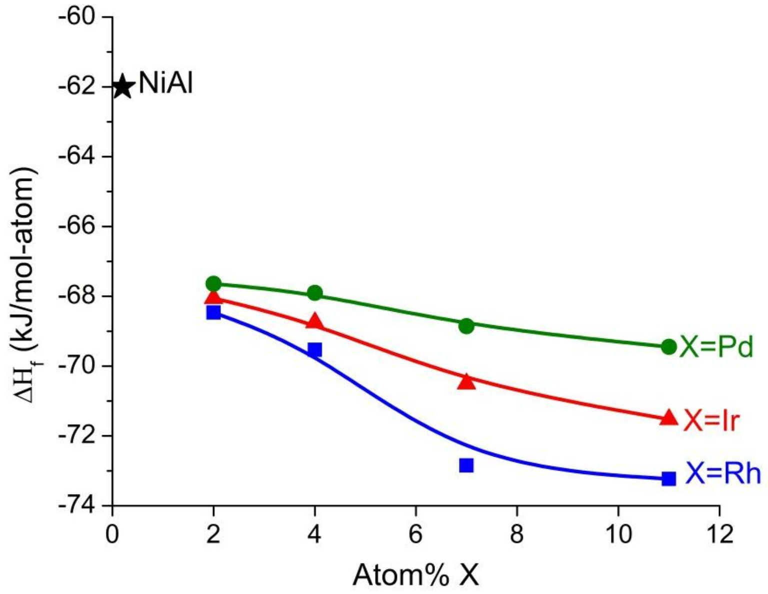


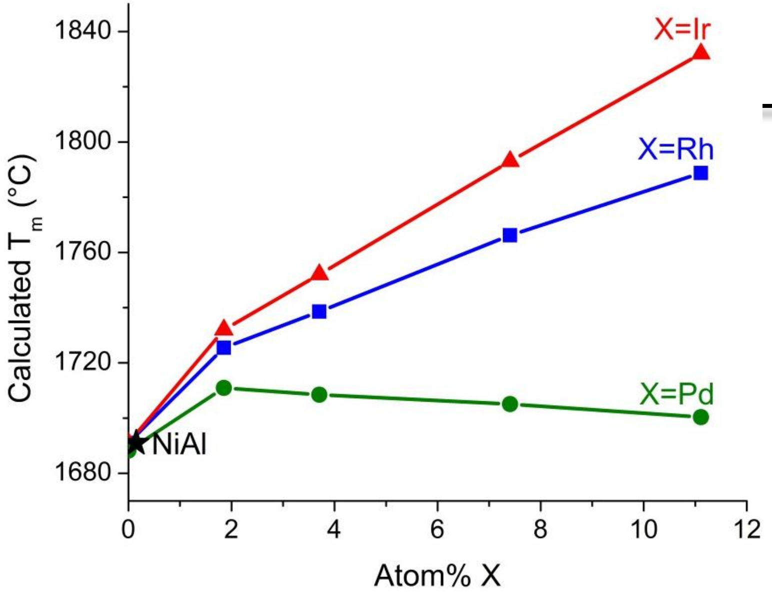




- Addition of PGM elements helps in avoiding spallation.
- Hf addition further reduces the growth rate of the oxide scale.

Thermal Stability





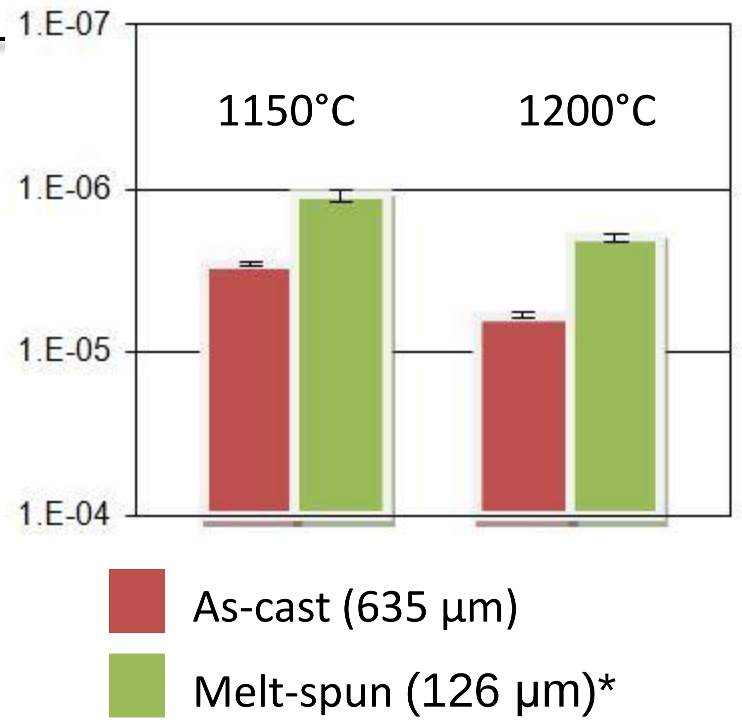
$$T_m = 0.032\, E^c / k_B$$

From Debye's theory of solids, derived by Smith, Rose and Ferrante, *Appl. Phys. Lett (1984)*

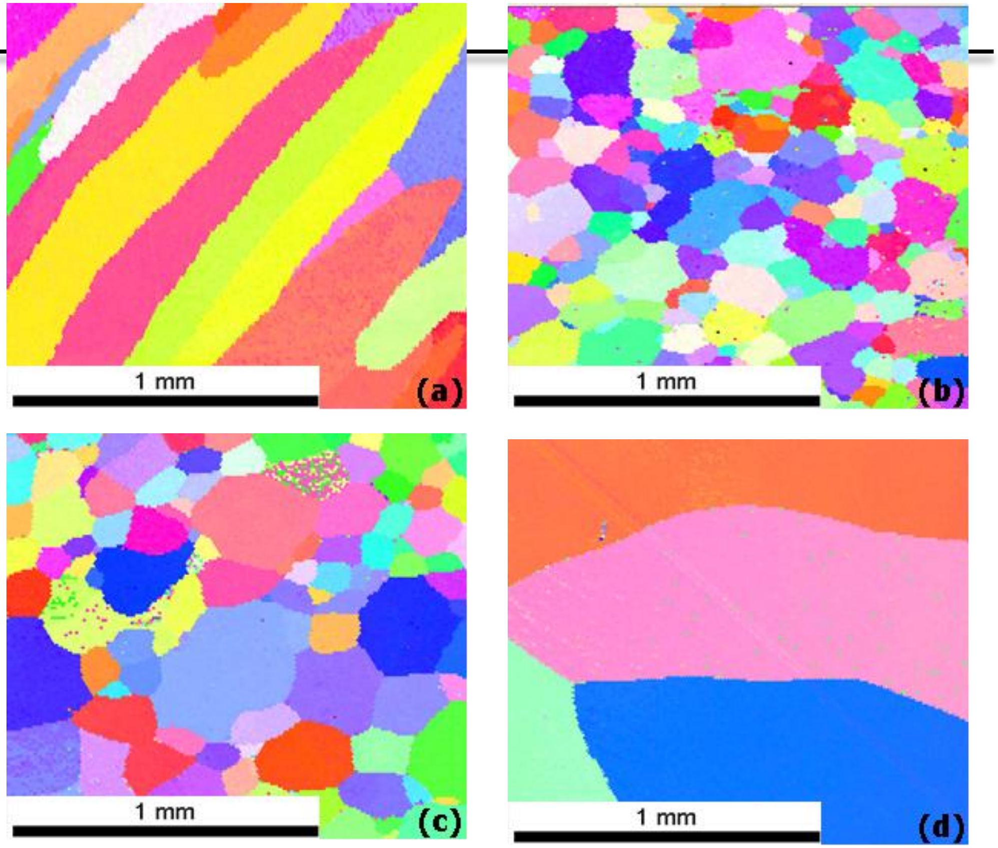
$$E^c = x_1 E_1{}^c + x_2 E_2{}^c + x_3 E_3{}^c - \Delta H_f$$

Metal	Cohesive E (kJ/mol)
Al	327
Ni	428
Rh	554
Ir	670
Pd	376

Effect of Processing and Alloy Additions



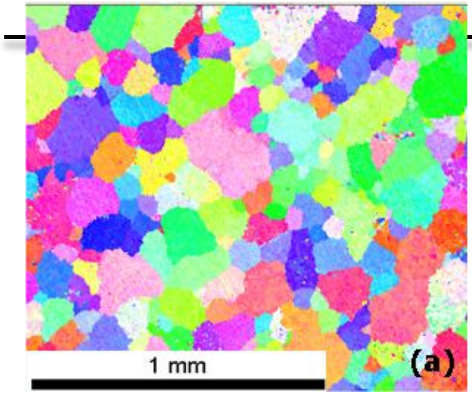
* *After annealing for 6 hours at 1350°C*



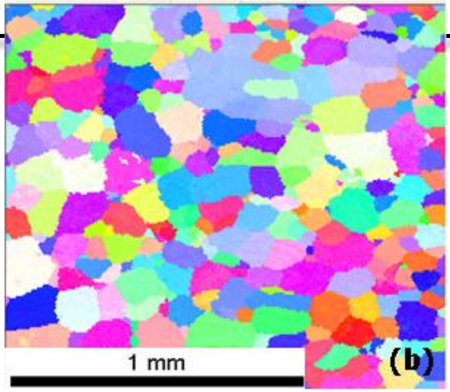
Grain size of (a) NiAl, (b) 3% Ir, (c) 3% Rh and (d) 3% Pd in as-cast conditions.

Alloy	NiAl	9% Ir	9% Ir + Hf
K (μm^2/hr)	10,528	6,198	327

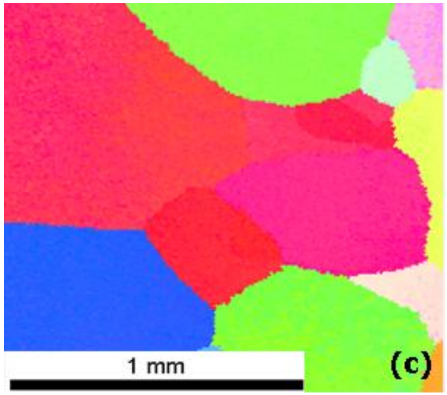
Grain Size Control



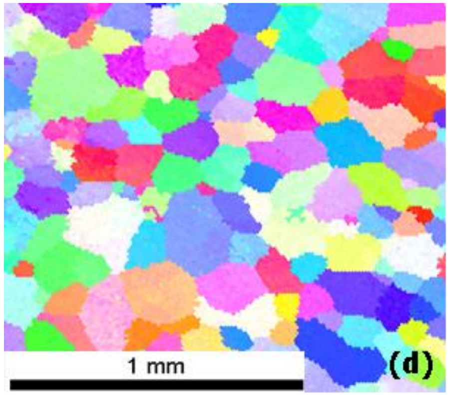
9% Ir, 6hrs @ 1300°C



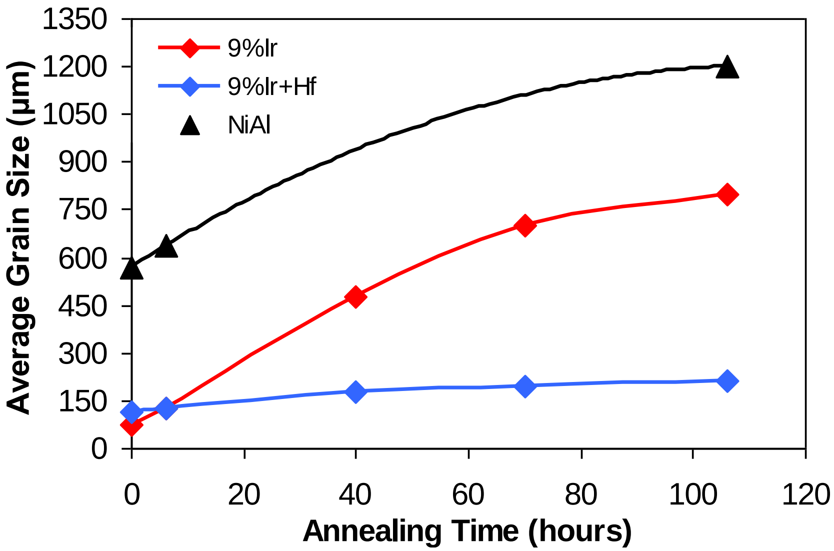
9% Ir + Hf, 6hrs @ 1300°C

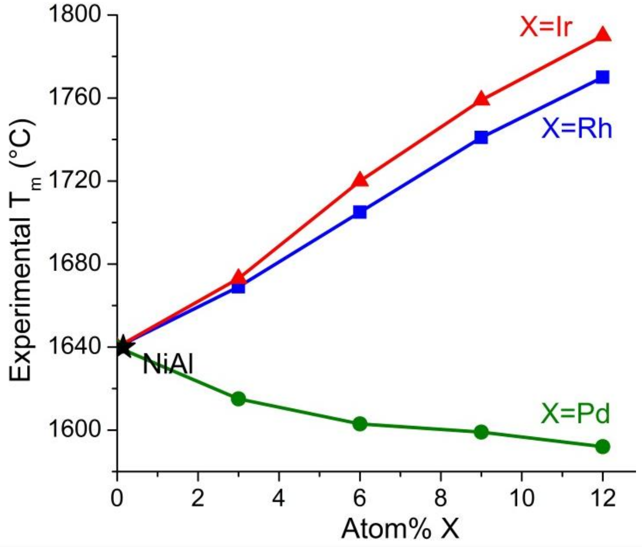


9% Ir, 106hrs @ 1300°C



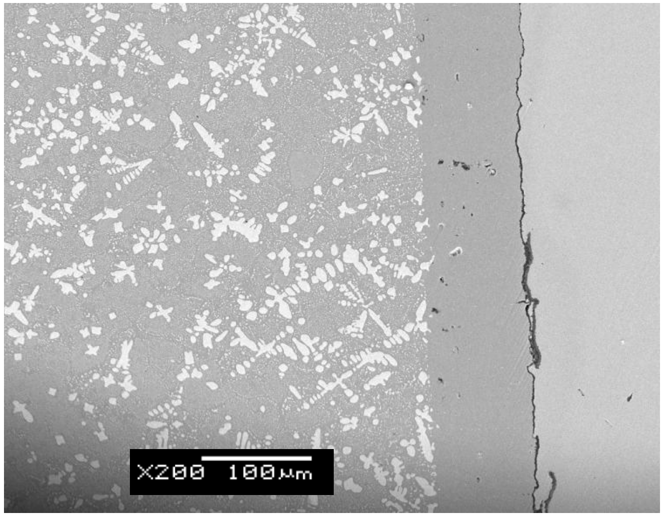
9% Ir + Hf, 106hrs @ 1300°C



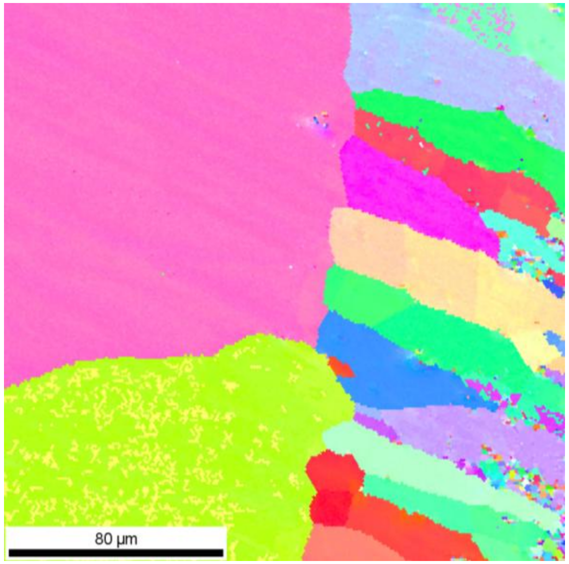


Putting it Together

- Grains produced by coating are columnar
- Exposed grain size is approximately 20µm



SEM of NiAl coating

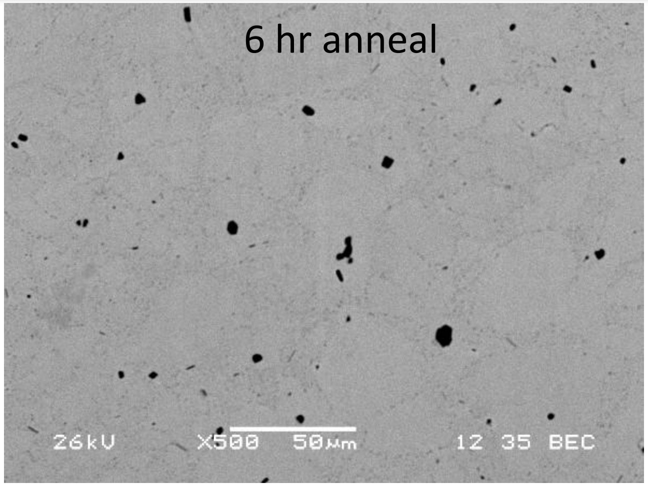


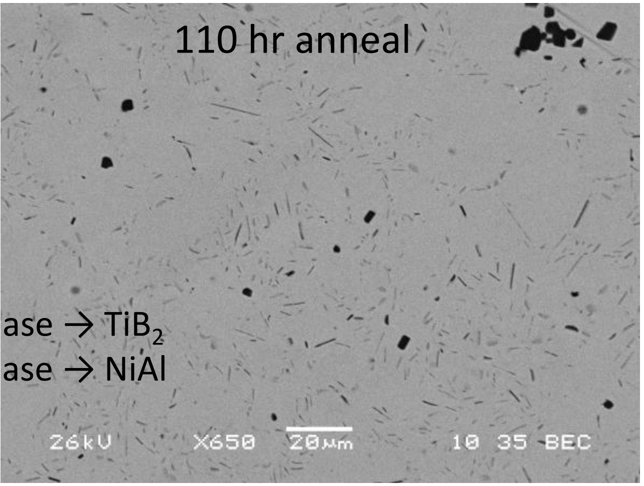
OIM of NiAl coating

Coherent but not epitaxial interface between the base alloy and coating.

Alternatives to PGM

- Rather than use expensive elements to control the grain size of NiAl
  - Thermodynamic assessment of elements with low heats of mixing with Ni and Al were evaluated
    - TiB_2 was chosen
- Long term annealing at 1300°C shows little change in the morphology of the NiAl and TiB_2 particles
  - Concern about effect on oxidation

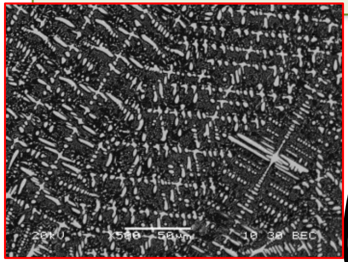

6 hr anneal


110 hr anneal

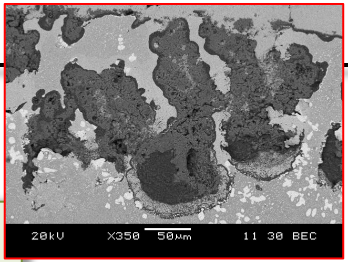
Dark Phase → TiB_2
Light Phase → NiAl

Summary

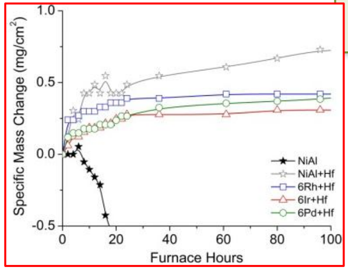
Base alloy selection



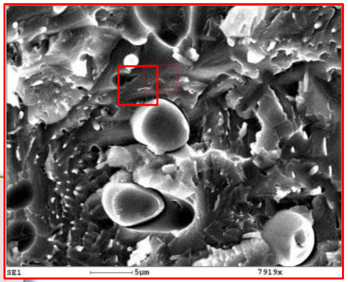
Oxidation mechanisms in the base alloy



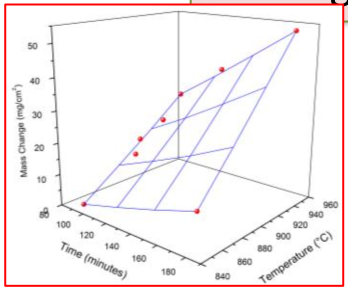
Development of coating materials



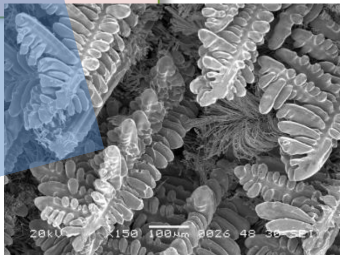
Preliminary mechanical testing



Development of coating methods



Microstructure optimization

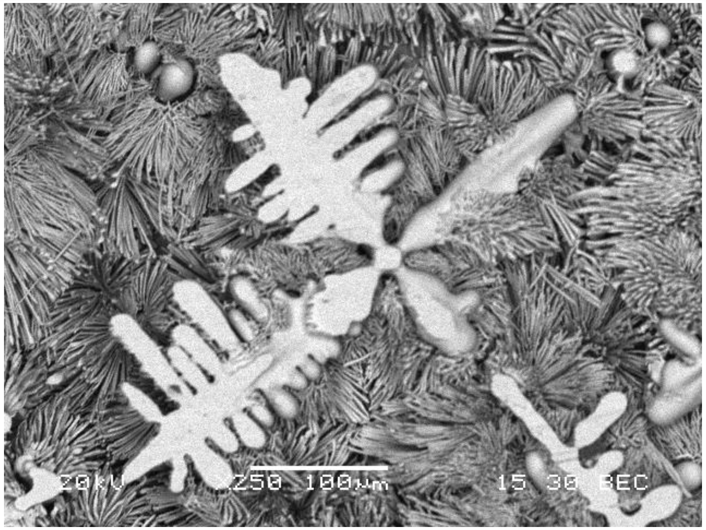


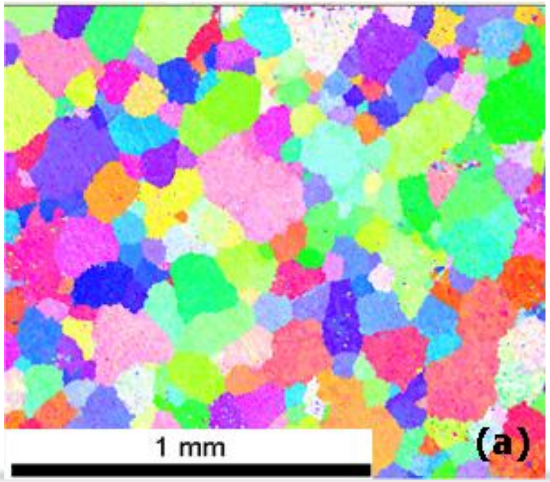
Assess future research needs

Computational assessments for alloy modifications

Research Plans (FY2012 – FY2013)

- Hyper-eutectic structure of the (Mo)-NiAl alloy shows promise for optimization of mechanical properties through directional solidification
- Work to determine the optimal parameters for increasing fracture toughness and strength
    - Composition
    - Solidification rate
- Grain size of NiAl was determined to be an important parameter for oxidation performance
    - Determine methods of refining grain size and controlling grain growth to maintain optimal grain size





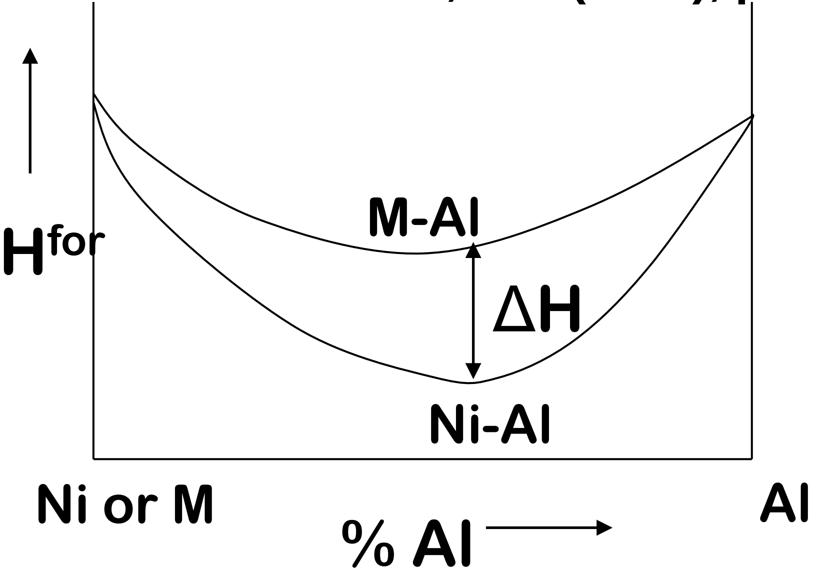
System selection

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**

Empirical Method used to down select possible ternary alloy with promising formation enthalpies in the M-Al-X

JOM, V62 (2010), p25

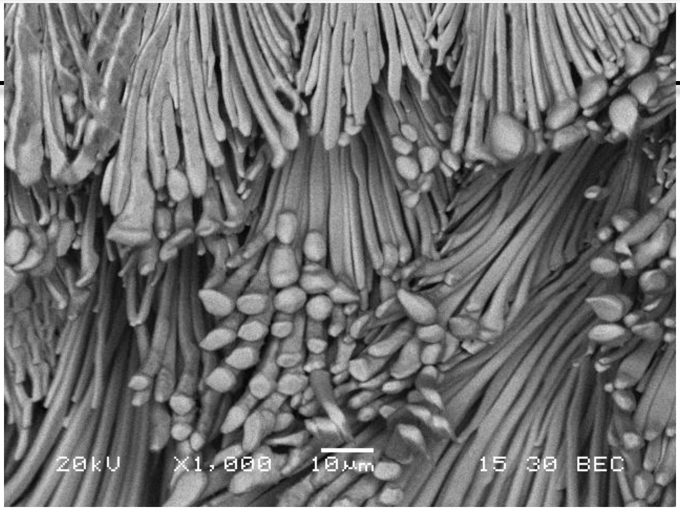
Formation enthalpy for Al-X should < M-Al, potentially forming M-skeleton and a flesh of M-Al as a reservoir for forming a passivating scale.



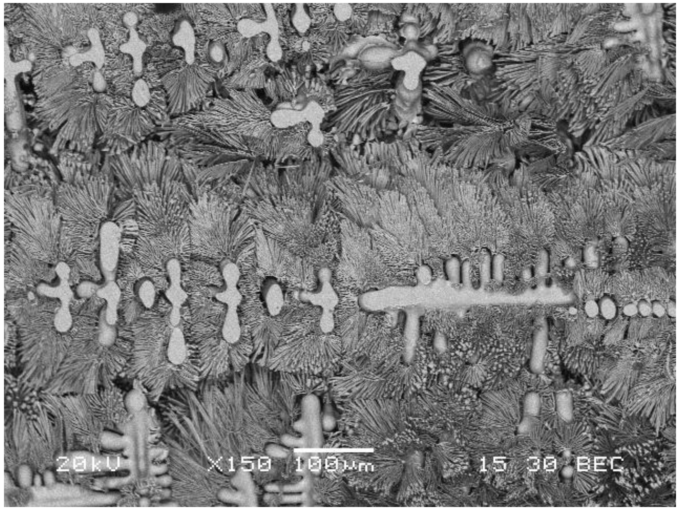
Potential "backbone" metals can not be scarce!

Mo, Nb, W

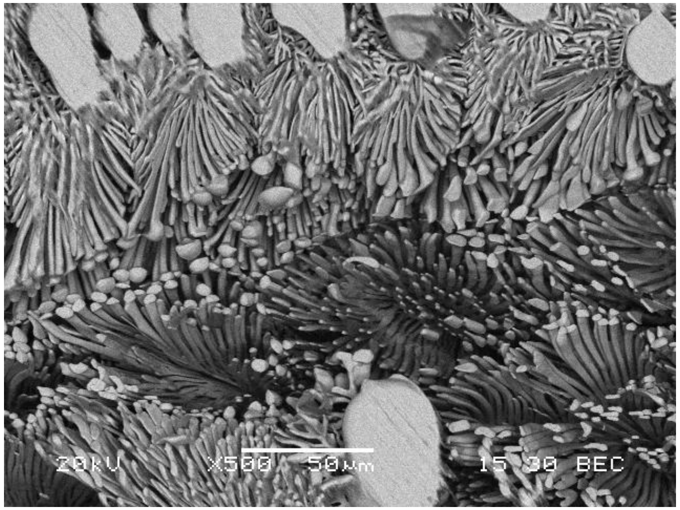
Directional solidification



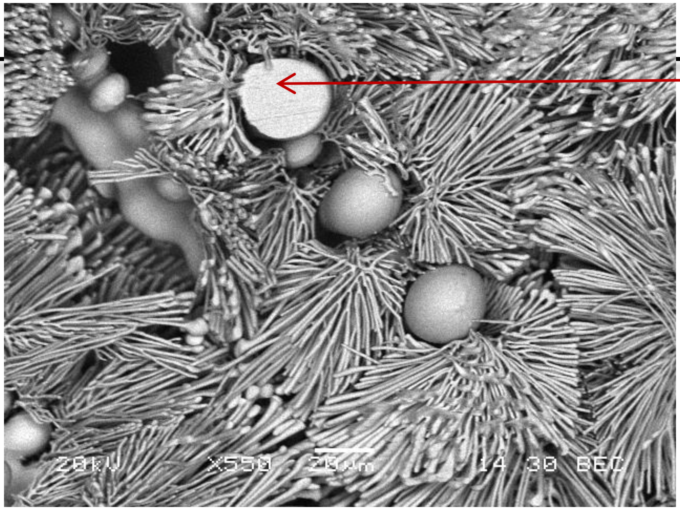
Eutectics may, or may not have an orientation change across the grain boundary

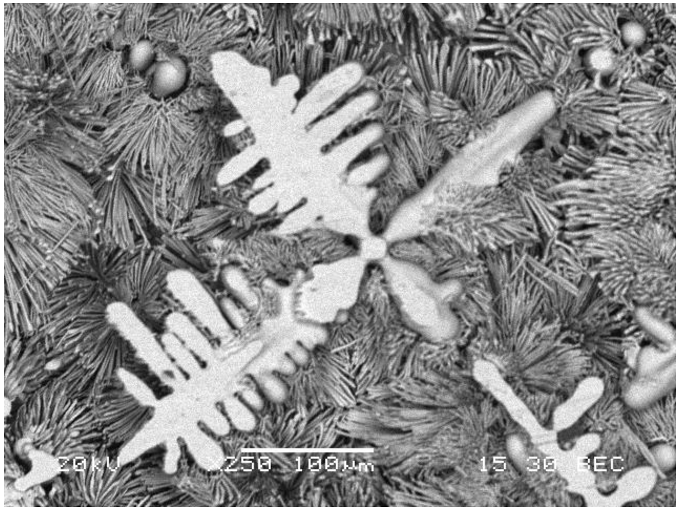


bottom → top

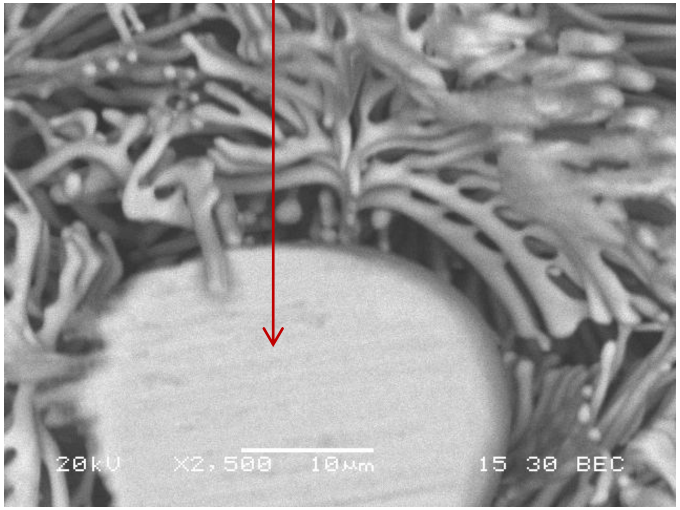


Directional solidification



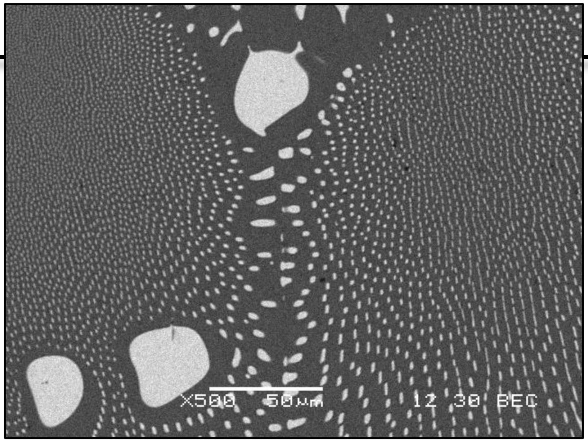


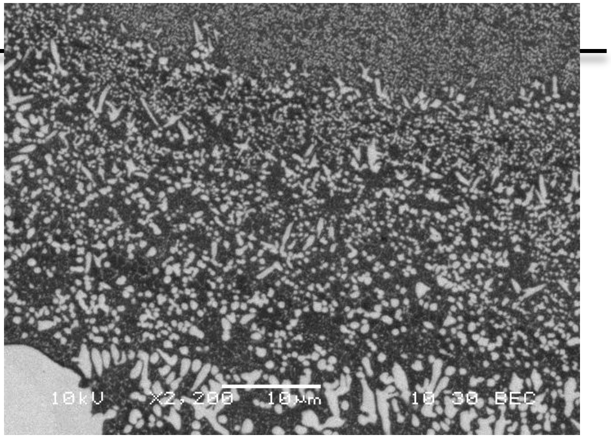
Truncated dendrite arms (sawed off while sectioning)

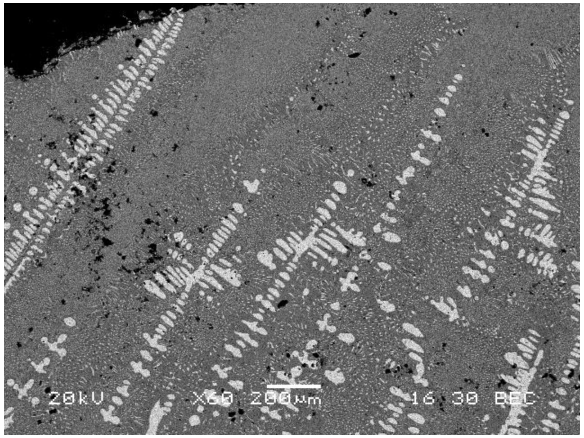


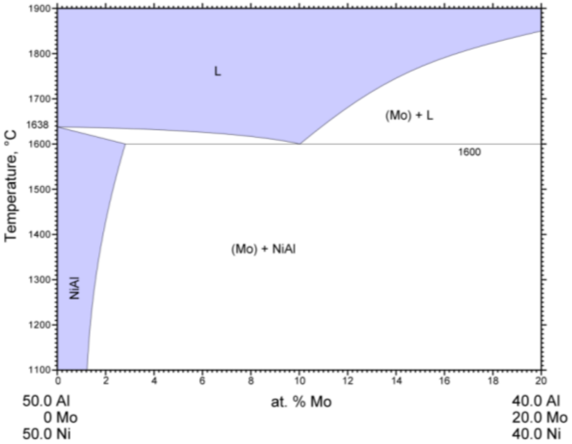
The “dendrite” on left is actually a top section of the longer primary dendrite (growing out of plane).

Microstructural control









Directional solidification is a promising technique for orienting the microstructures For optimal mechanical properties. The major issue is the processing temperature.