Computational and Experimental Development of Novel High Temperature Alloys

Pratik K. Ray, Kevin R. Severs, Karen A. DeRocher, Mufit Akinc, Matthew J. Kramer

*This work was supported by the **DOE-FE (AMR program)** through Ames Laboratory contract no. DE-AC02-07CH11358*

THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

IOWA STATE UNIVERSITY

The Problem

- Increasing efficiency require higher operating temperatures, goal ~1300°C is very aggressive
  - Loss in creep strength
  - Dramatic Increase in oxidation rates
- Fossil fuel 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 ?

Conceptual Approach

- Rapid Screening of potential systems
  - Edisonian approach is not an option
  - Computational Thermodynamics
  - *Ab initio*
  - Approximate methods
    - Extend and use the Miedema approach for downselecting the base alloy

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}

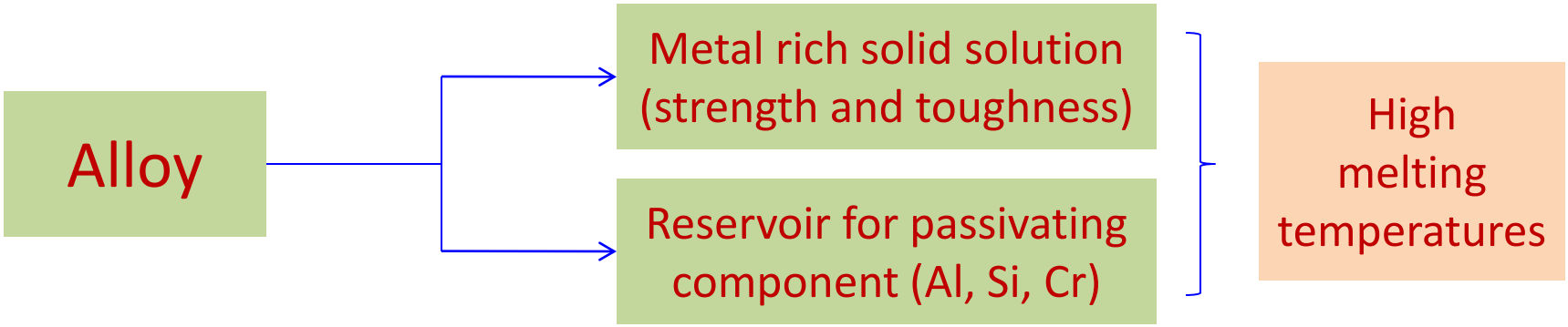
The need for rapid and effective hierarchical screening!!

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

Architectural framework

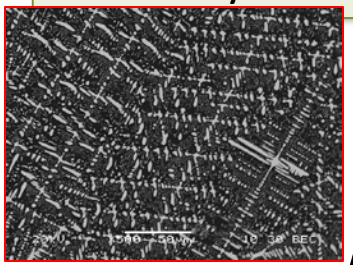
<u>Key requirements</u>

A. High melting temperatures
B. Adequate strength and toughness
C. Good oxidation resistance



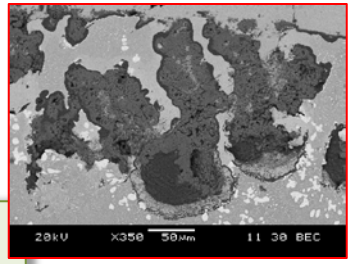
Overview

Base alloy selection

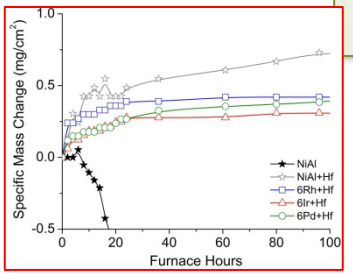


Selection via Semi-empirical thermodynamics

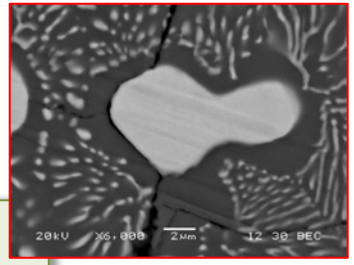
Oxidation mechanisms in the base alloy



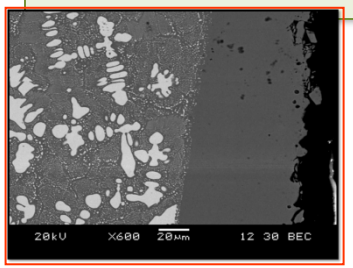
Development of coating materials



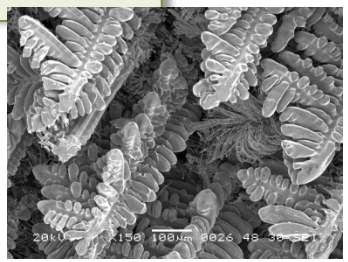
Preliminary mechanical testing



Development of coating methods & characterization



Microstructure optimization



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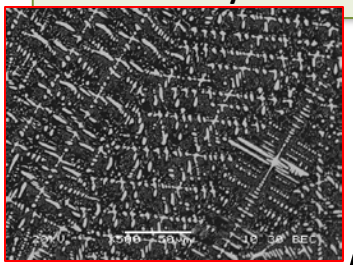

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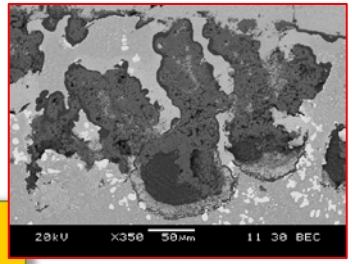

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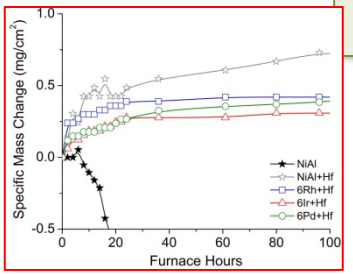

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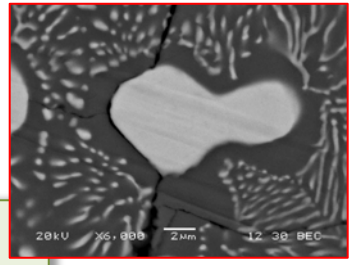

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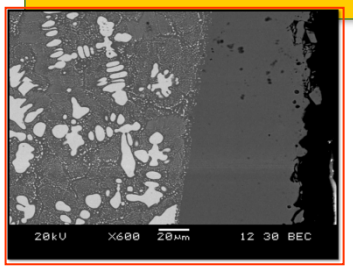

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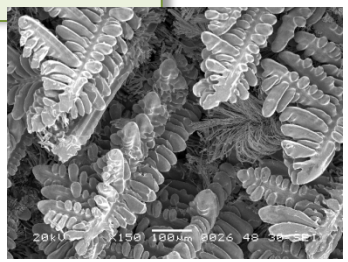
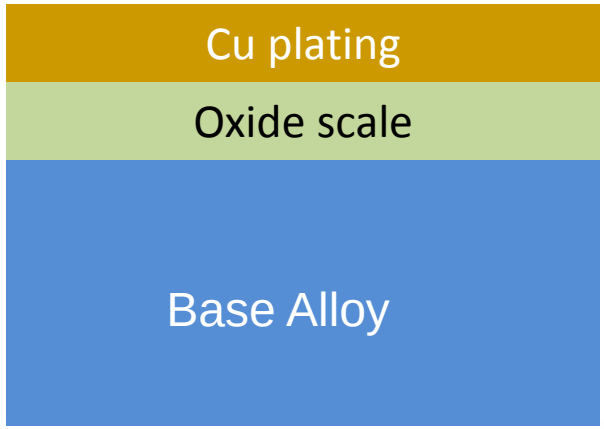
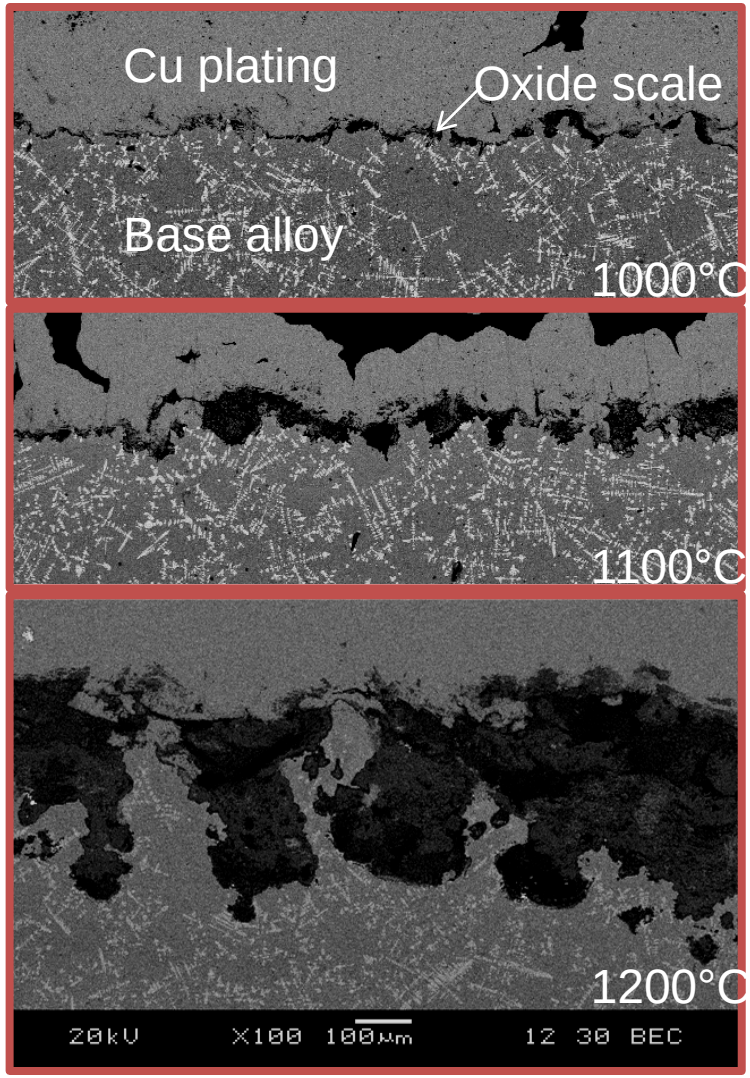


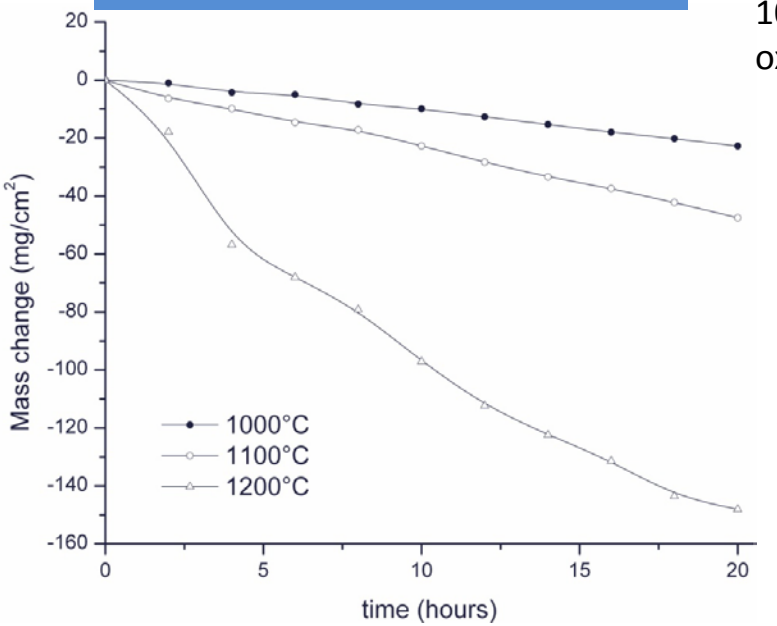
The effect of temperature



Sample prep schematic

Cross-section micrographs after 10 hours of oxidation

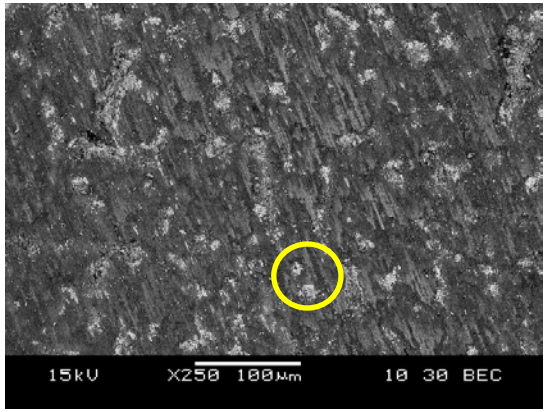




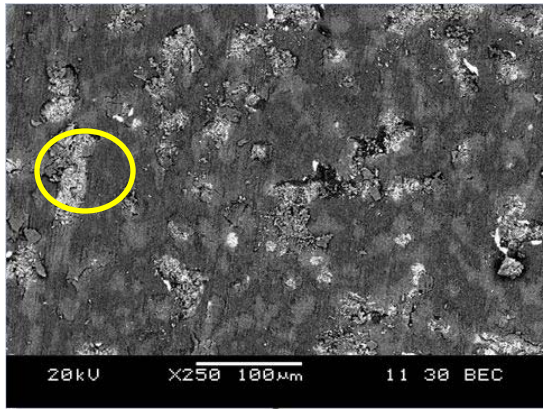
Mass change during oxidation at different temperatures

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

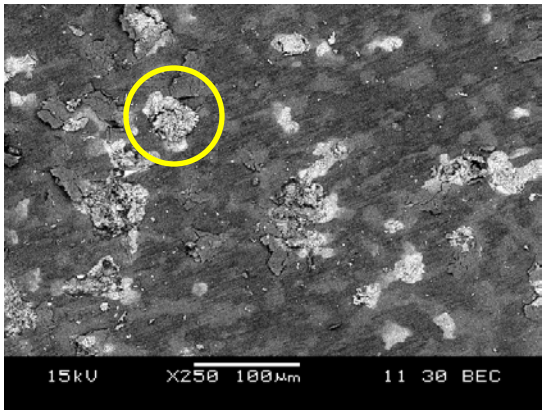
The effect of temperature: surface



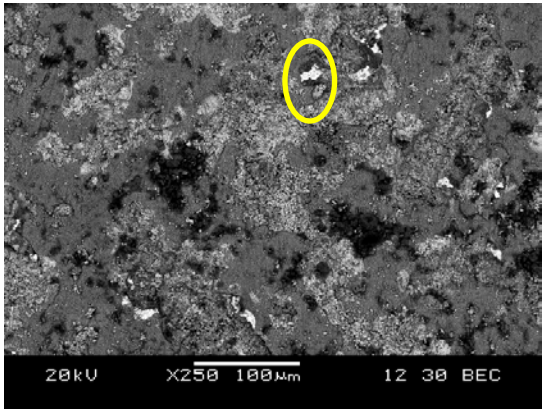
1000 °C



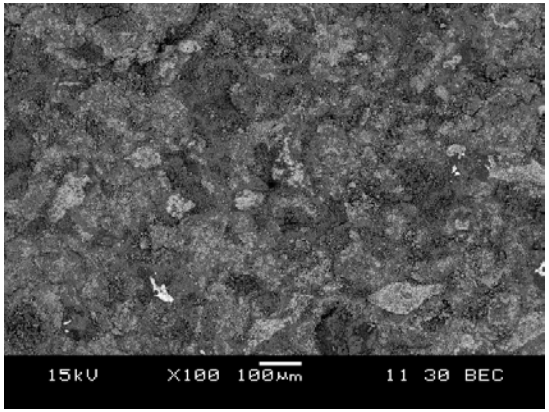
1075 °C



1100 °C



1125 °C



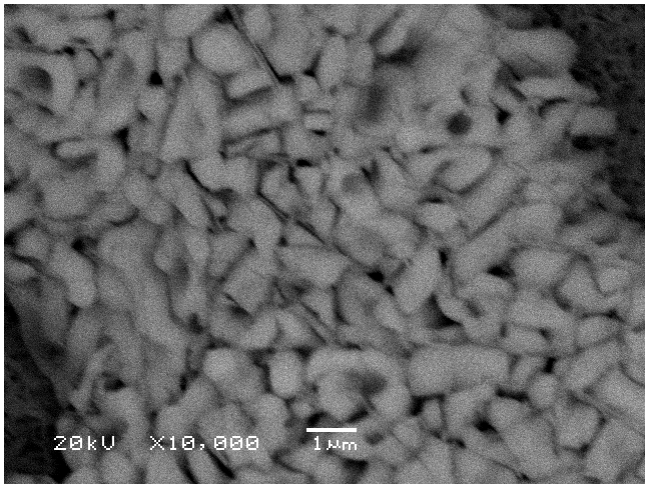
1200 °C

Oxidation time: 30 minutes

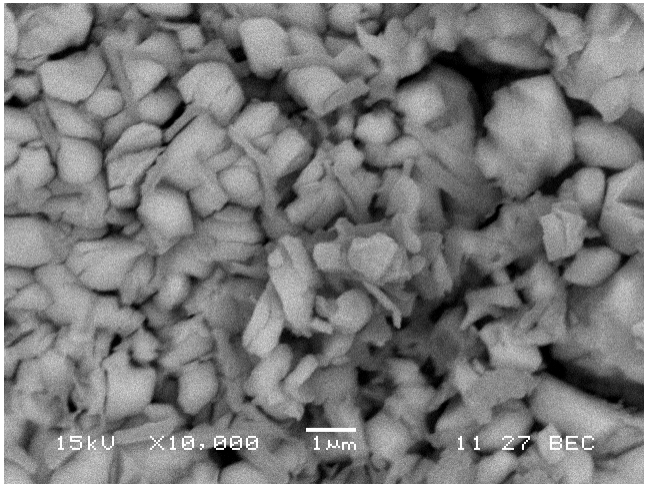
As temperature increases, $NiMoO_4$ regions grow larger, but they start disappearing above 1100 °C

$NiAl_2O_4$ and NiO seem to predominate above 1125 °C

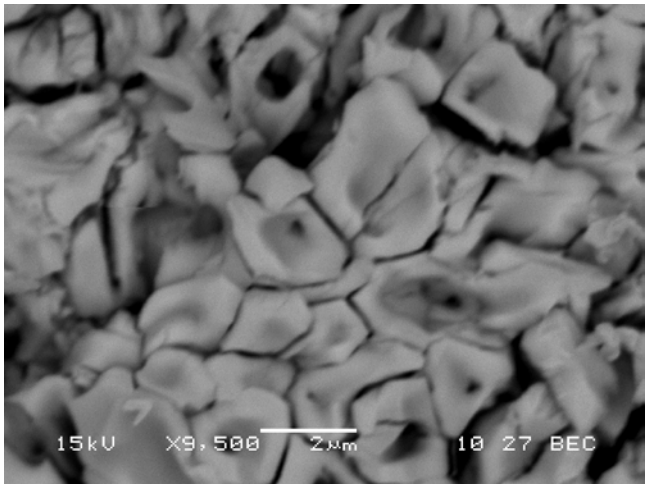
Formation of $NiMoO_4$



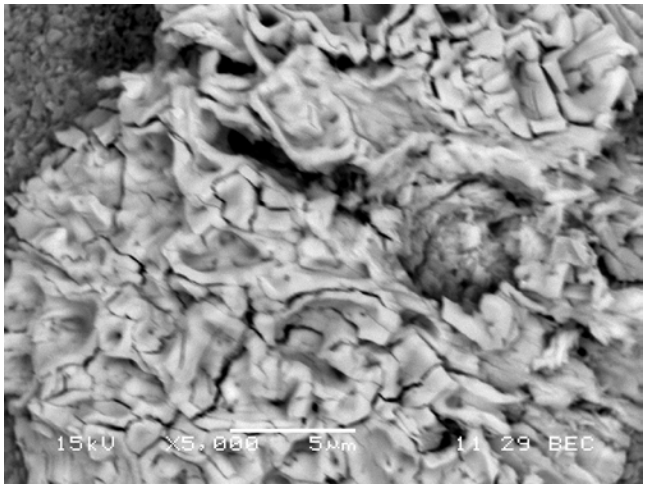
1000 °C



1075 °C



1100 °C



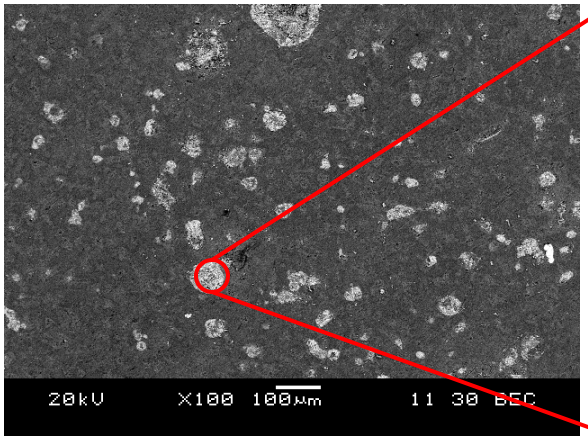
1125 °C

Oxidation time – 30 minutes

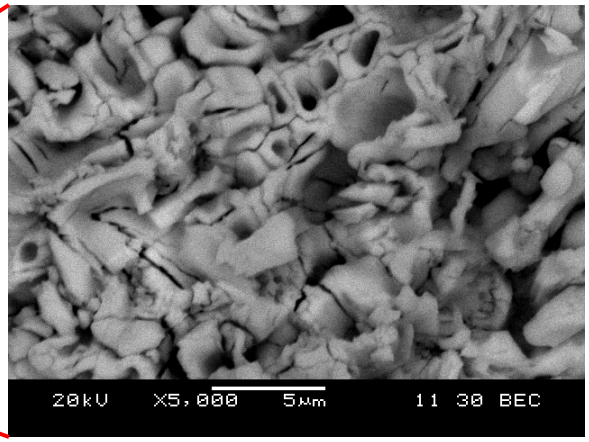
Growth of $NiMoO_4$ grains as a function of temperature.

Change in morphology – crystals increasingly seem “concave”

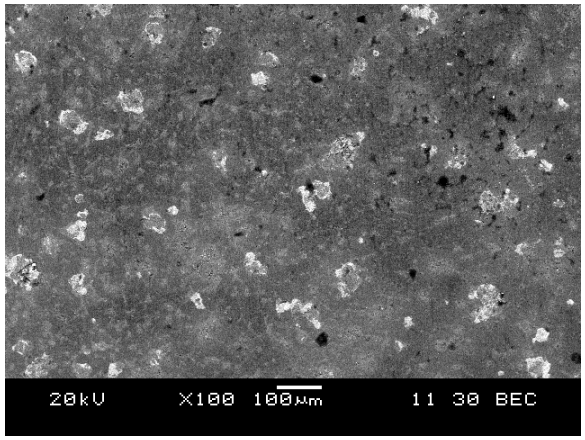
Observing $NiMoO_4$ at 1200 °C



5 minutes

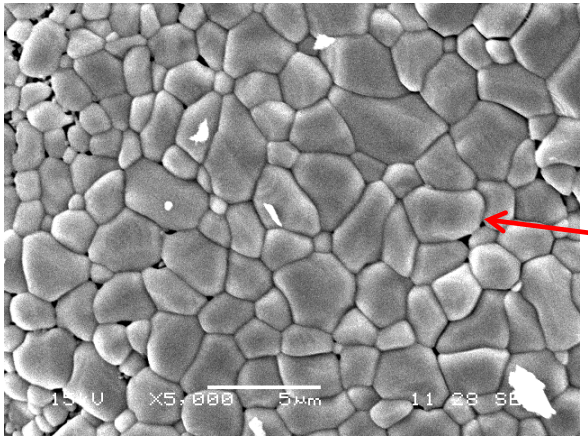


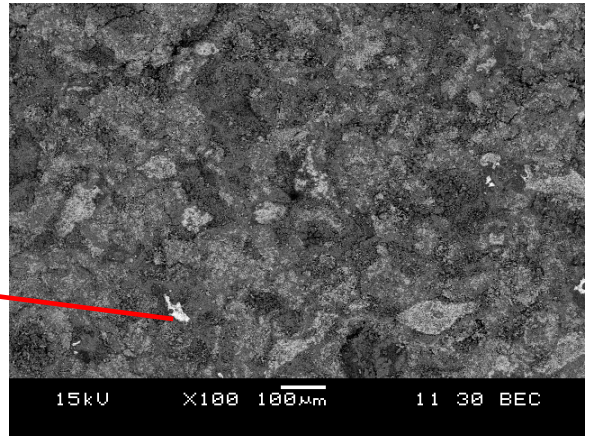
5 minutes



15 minutes

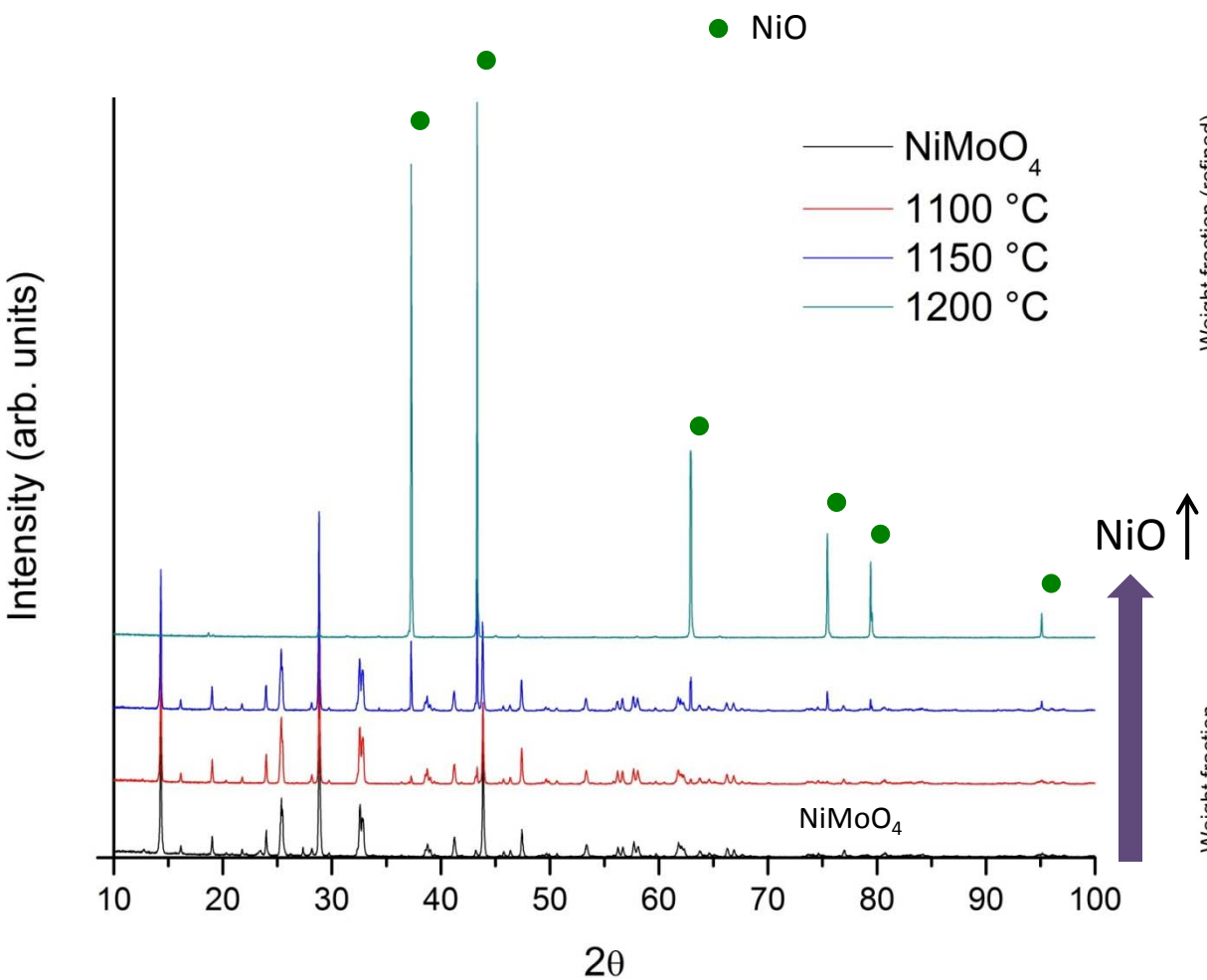
$NiMoO_4$ can be observed on the surface only at very short oxidation times. The morphology is comparable to long term oxidation at 1000 °C

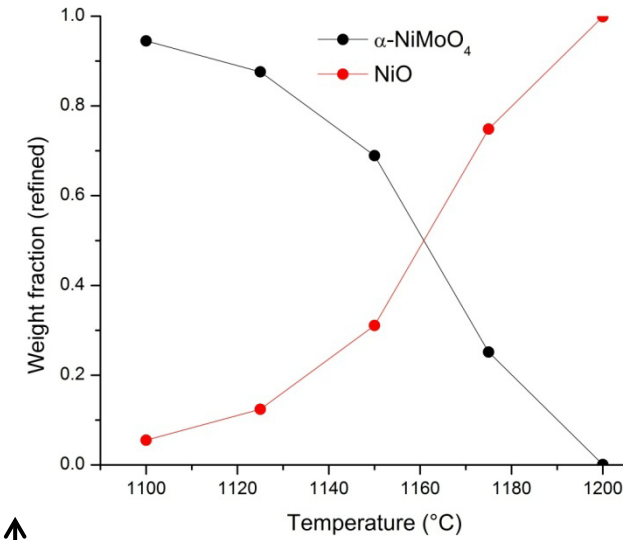




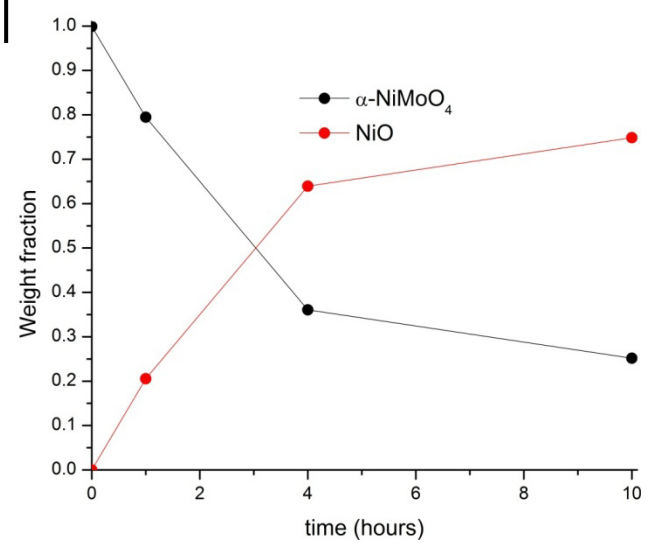
10 hours

Thermal stability of $NiMoO_4$



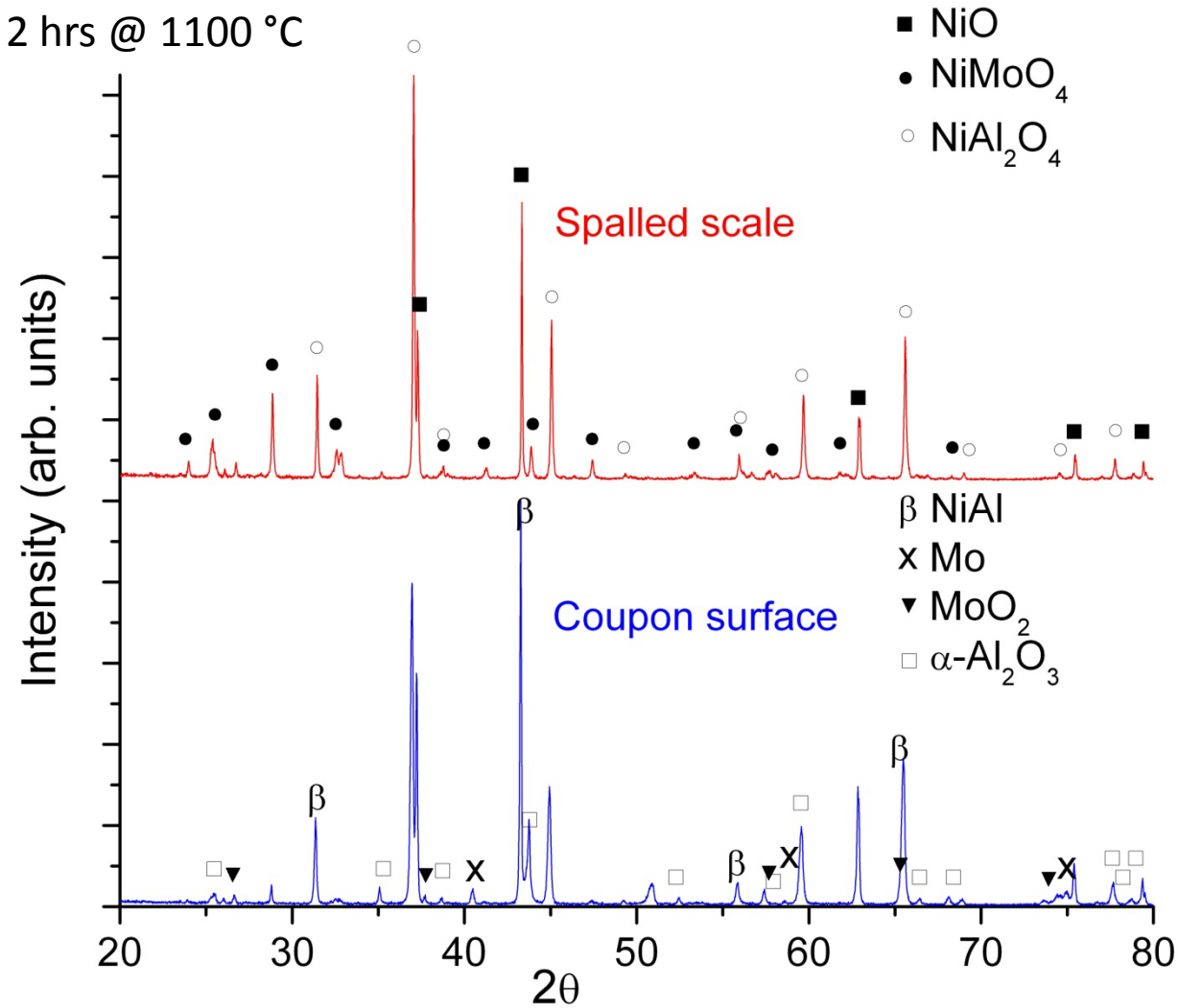


NiO ↑



Heat treatment time = 10 hrs

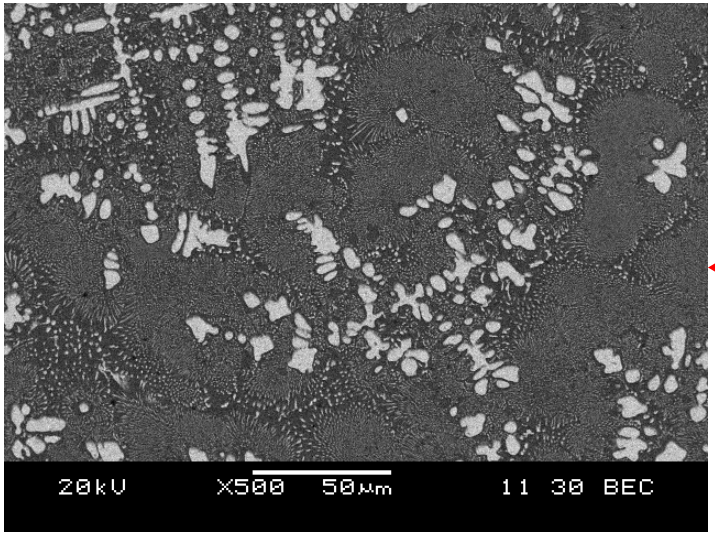
Comparisons – spalled vs adherent scale



Major differences –

- The amount of $NiMoO_4$ and NiO is drastically reduced in the coupon surface
- The α-Al_2O_3 and MoO_2 are virtually absent in the spalled scale.
- $NiAl_2O_4$ shows up in both cases as a major phase.

Low magnification micrographs

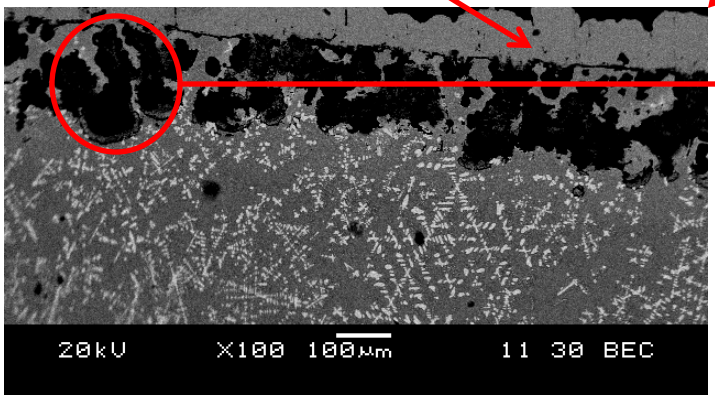


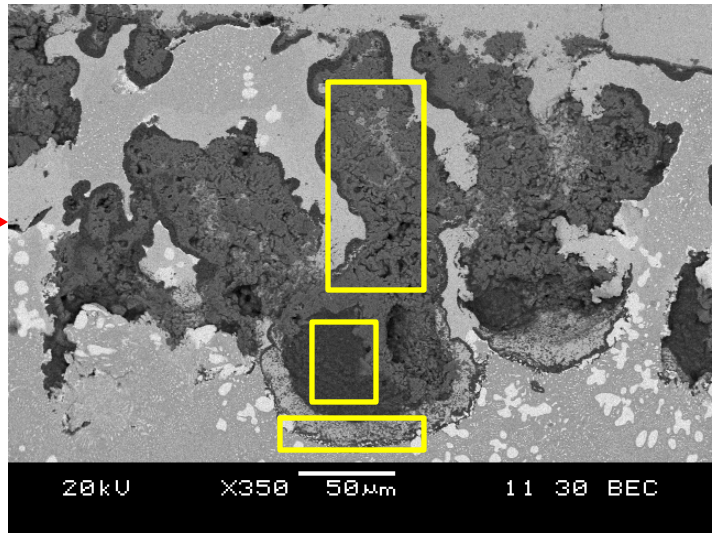
<u>Oxidation conditions</u>
Isothermal, 1200 °C, 2 hrs

Alloy interior post-oxidation

Oxide scale (BEC image – dark contrast)

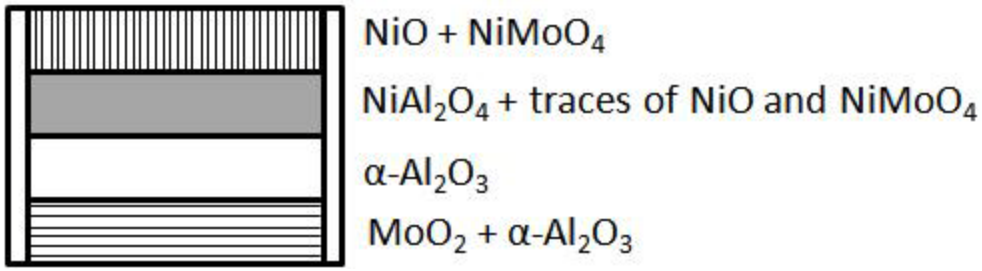
Cu plating





Multilayered scale formation: Schematic 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



<u>Phase transformation in $NiMoO_4$</u>

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

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

Volume change associated with transformation on cooling ~ 20%

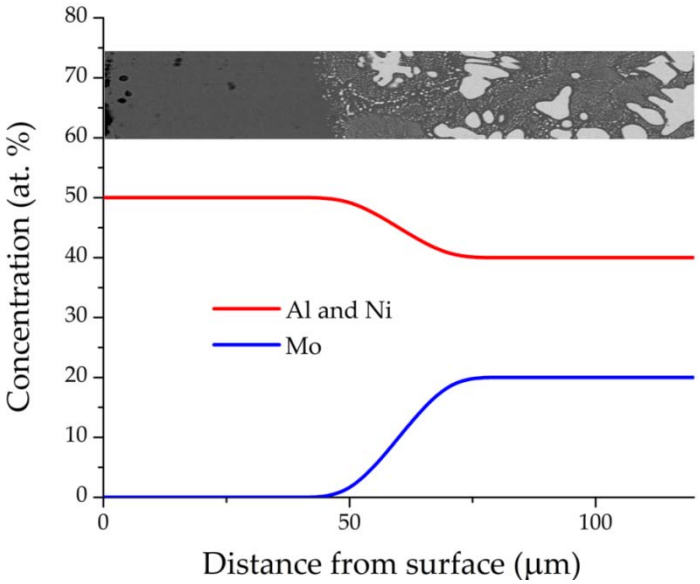
Massive volume change is responsible for spallation – hence its only the layers containing $NiMoO_4$ that will spall off

Addressing spallation

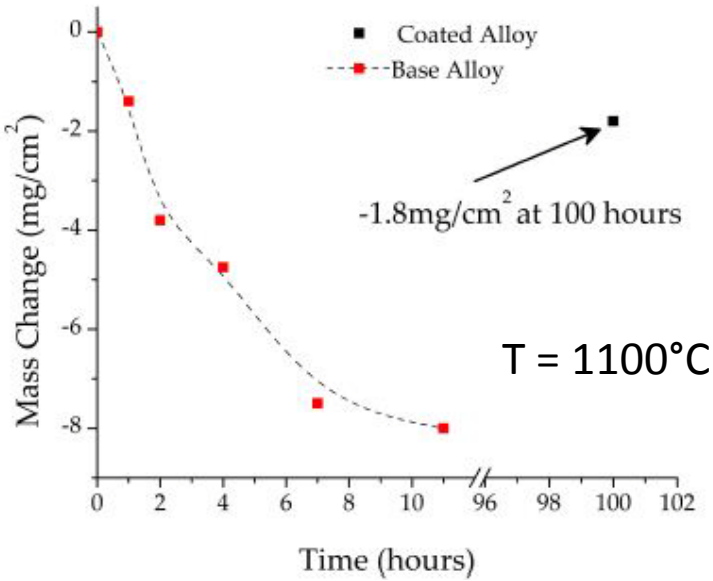
Primary failure mechanism – phase transformation in $NiMoO_4$ resulting in a significant volume change, which results in spallation of the oxide scale

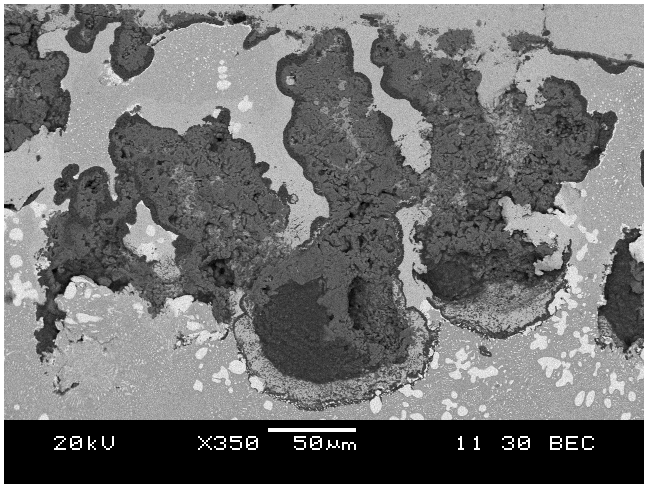
- Prevent its formation (shielding, i.e. coatings)
  - Control the Mo content in the base alloy
  - NiAl coatings – excellent compatibility with the base alloy
  - Chemical modifications to improve performance
- Stabilize the $NiMoO_4$ (control over chemistry)
  - Stability of off-stochiometric compositions
  - Substitutions (W)

Coatings



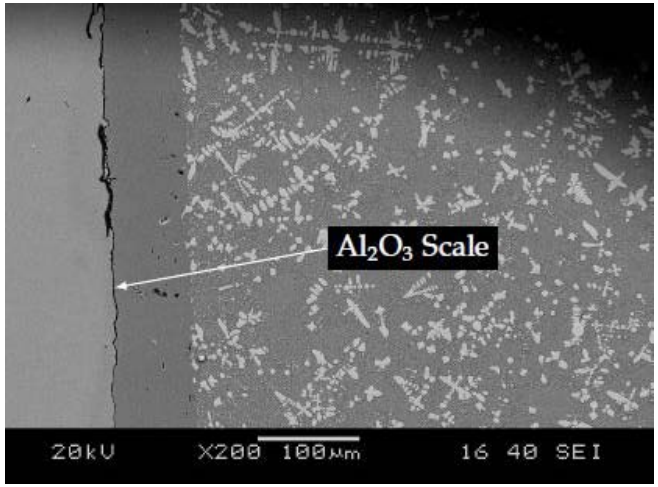
Coatings result in a significant improvement in oxidation resistance



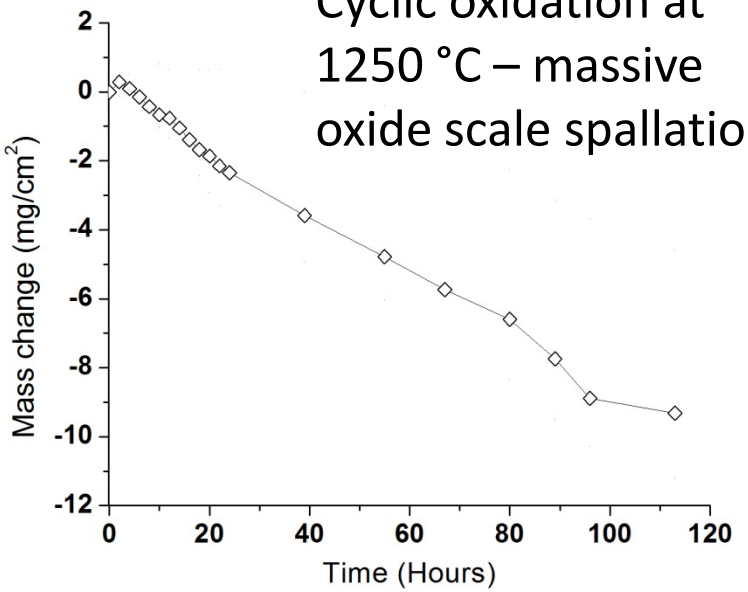


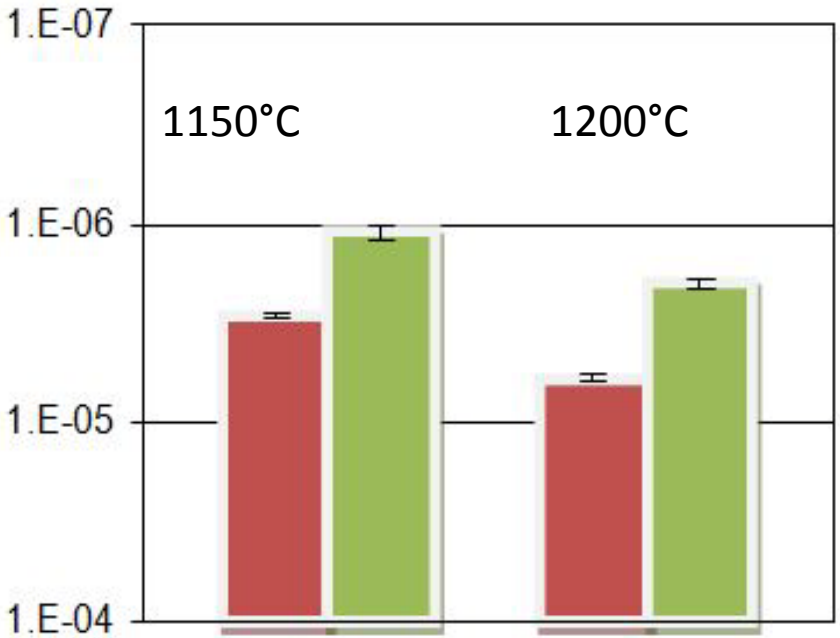
◀ Uncoated alloy

Coated alloy ▶



Can we enhance high T oxidation resistance?





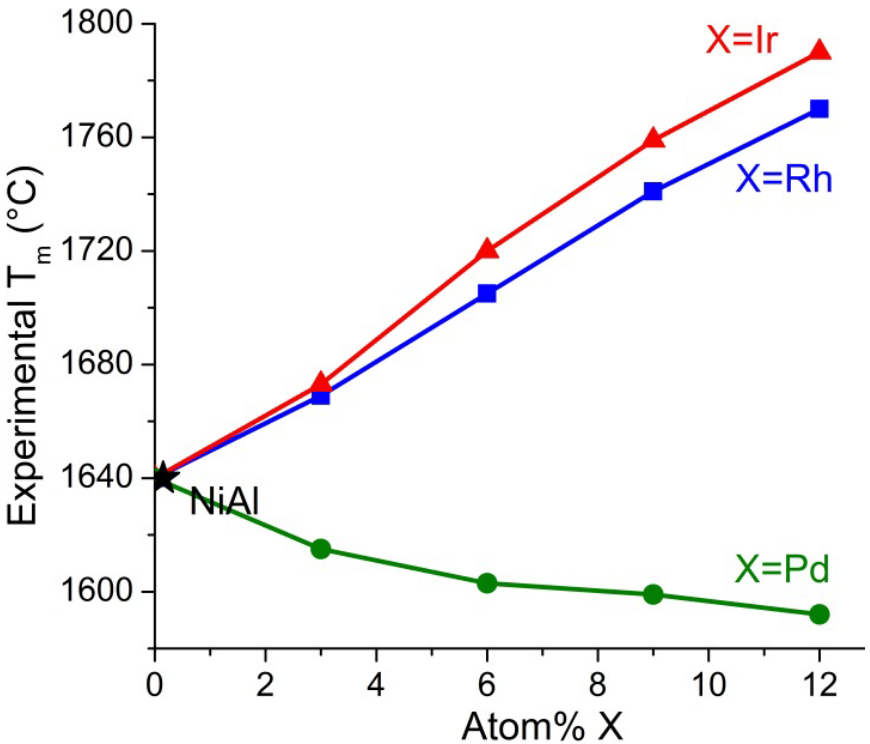
Modifications → Microstructural ↔ Chemical

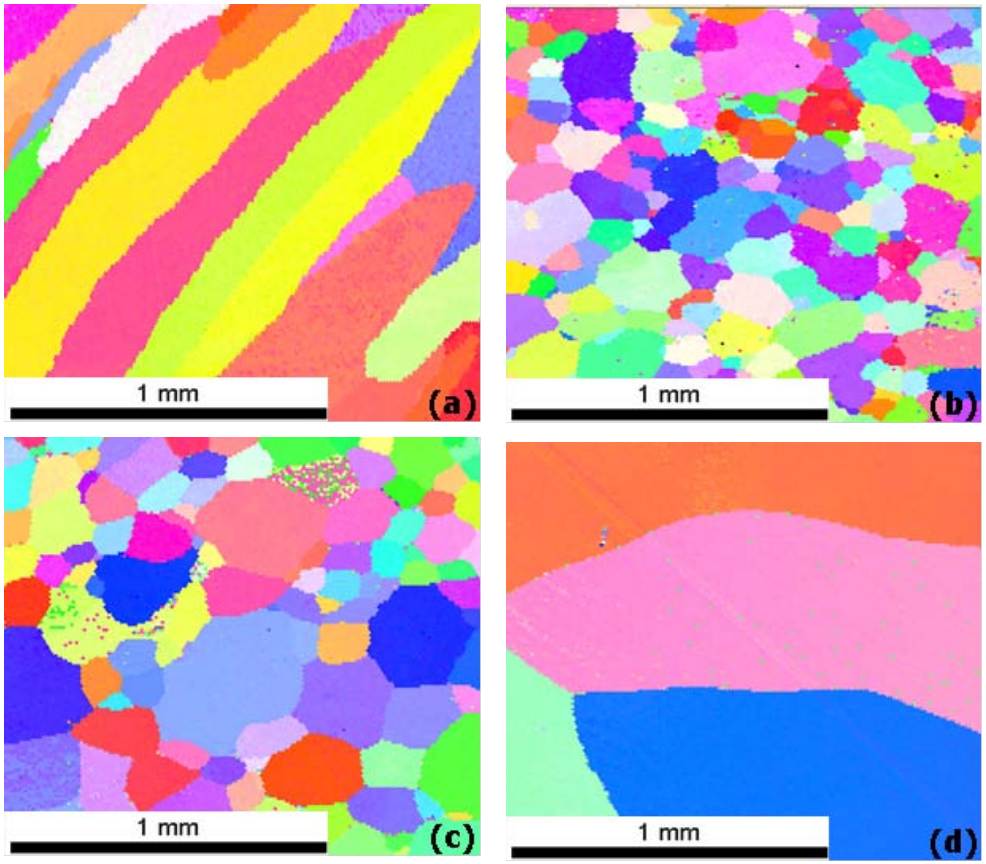
As-cast (~ 635 µm)

Melt-spun (~ 125 µm)*

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

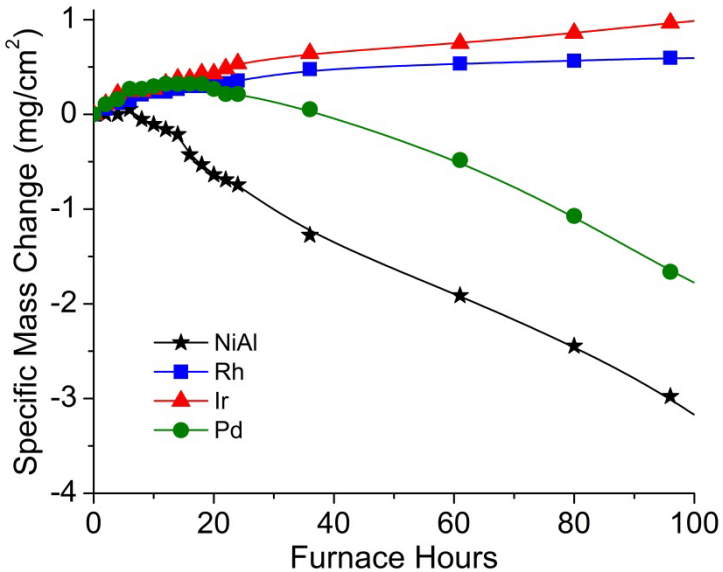
Selecting alloying additions



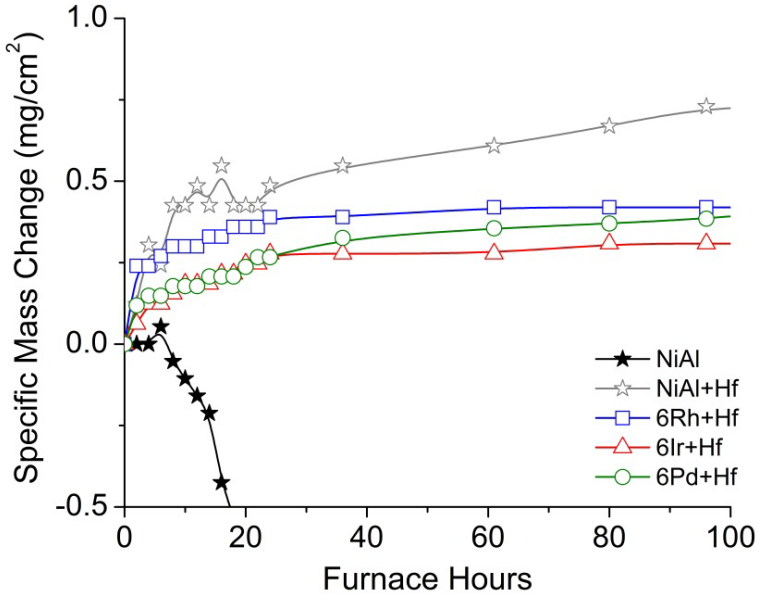


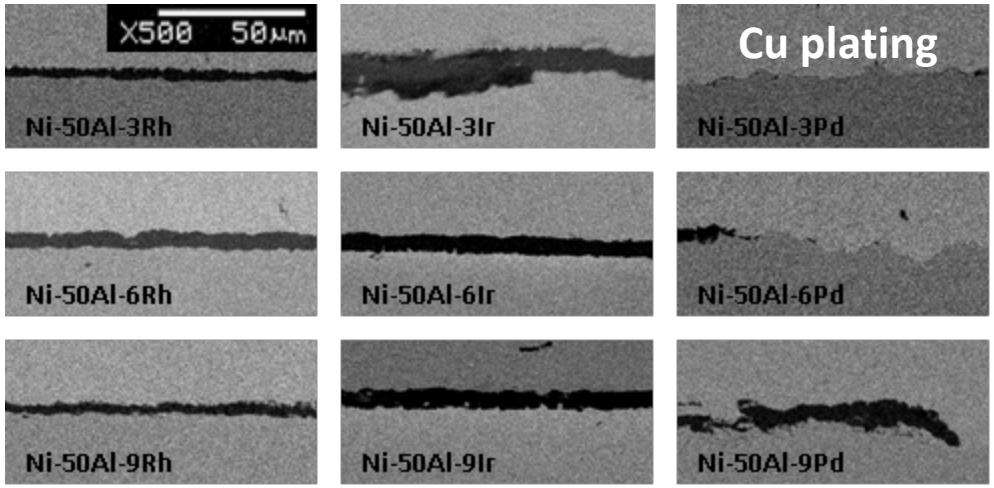
Grain size of (a) NiAl, (b) 3% Ir, (c) 3% Rh and (d) 3% Pd in as-cast conditions.

Effect of PGM and Hf



1250 °C
6% PGM

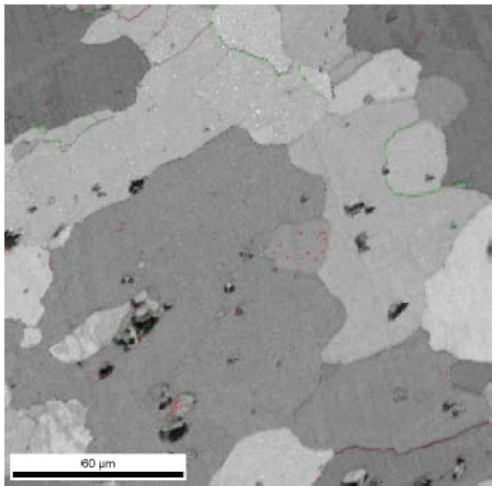


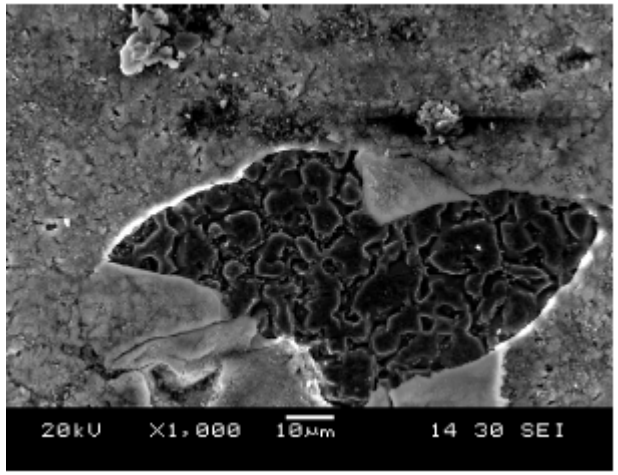


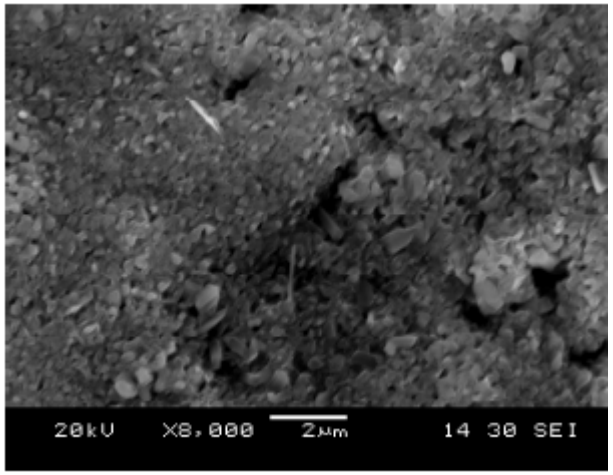
- Addition of PGM elements helps in avoiding spallation.
- Hf addition further reduces the growth rate of the oxide scale.

P.K. Ray et. al., "A multi-stage hierarchical approach to alloy design", JOM 62(2010) 25

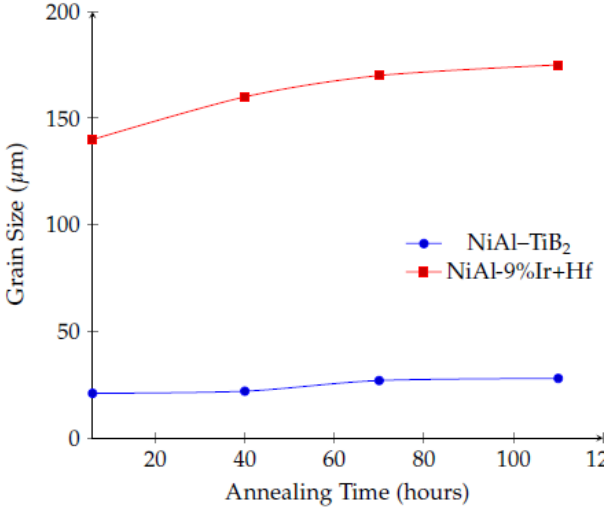
NiAl-TiB_2 composite coatings

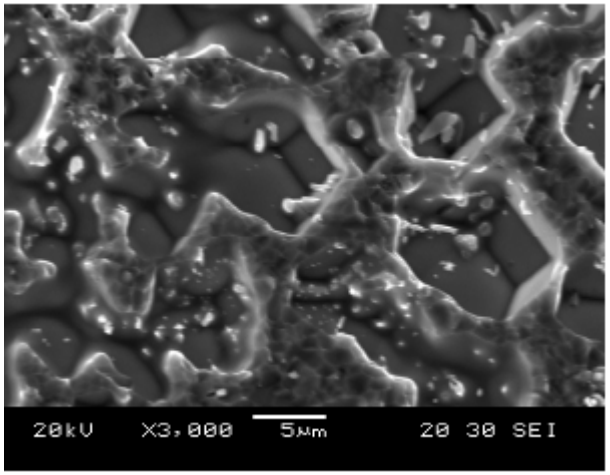


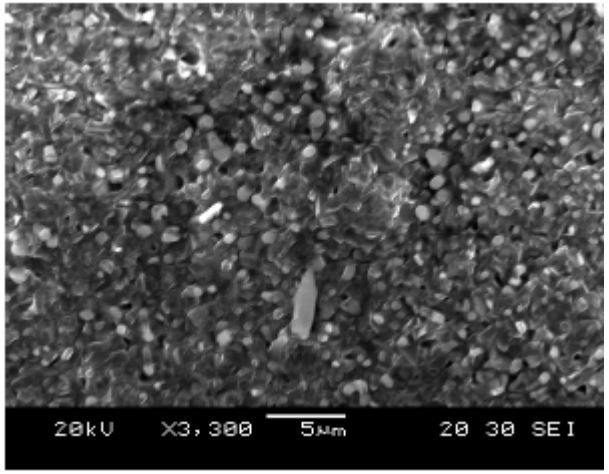




1100°C



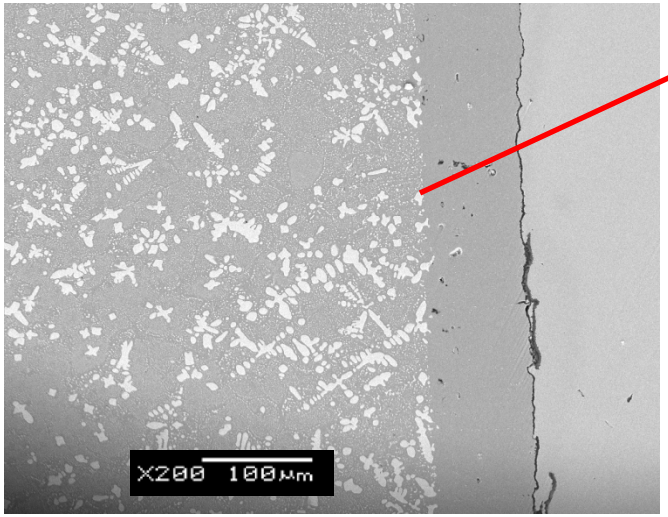


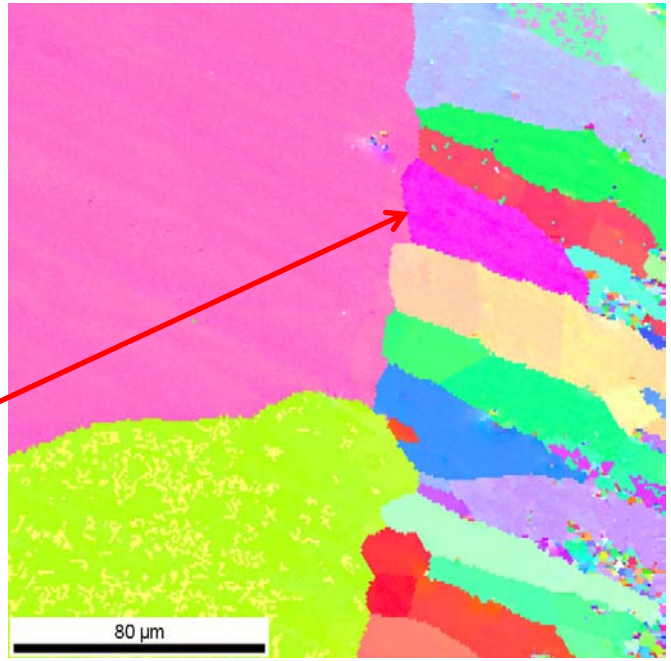


1200°C

Putting it all together

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

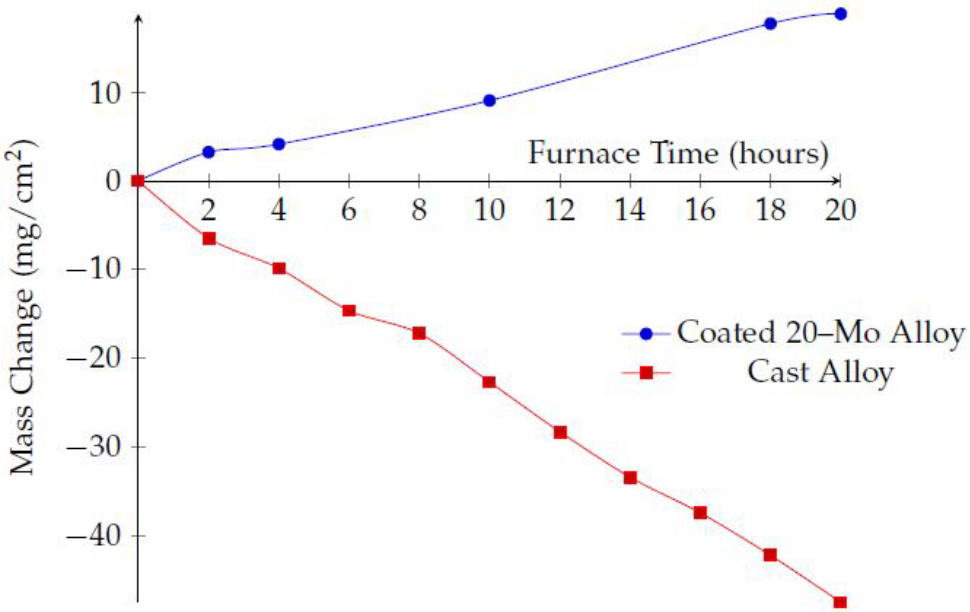


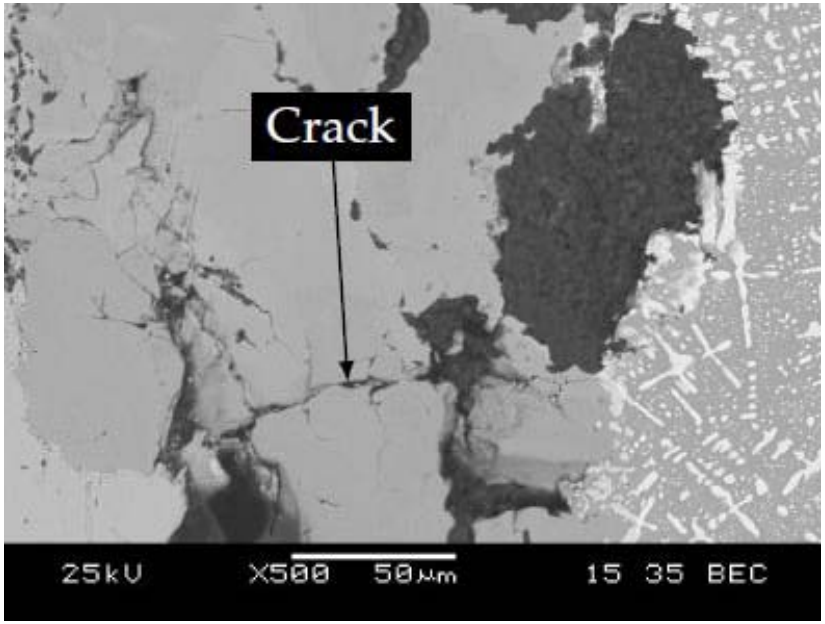


OIM of NiAl coating

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

Future Work: Coating process optimization

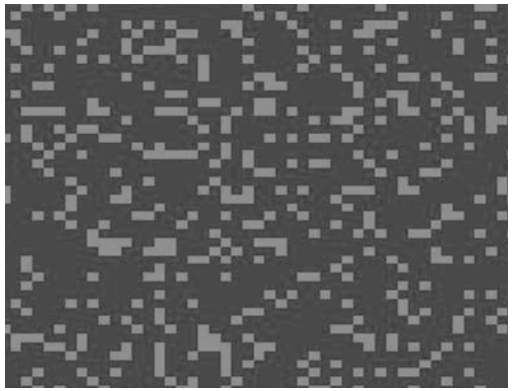




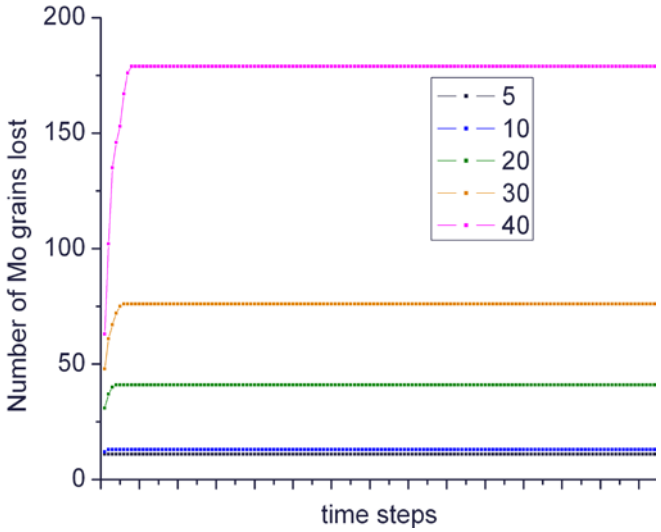
Coating cracks affect the performance

Critical Mo content – a percolation approach

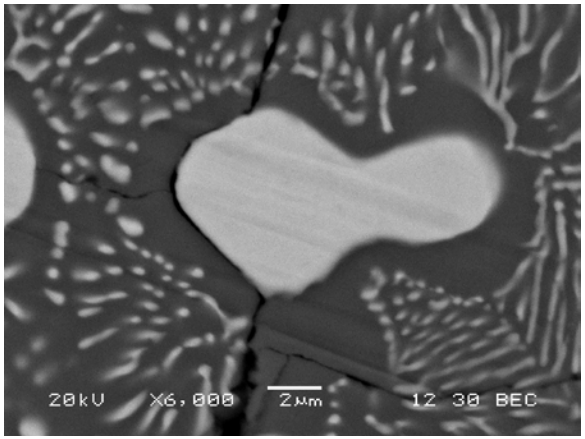
- Mo reacts with oxygen to form MoO_3 which volatilizes or reacts with Ni to form $NiMoO_4$ which later spalls off . That cell is then taken up by fresh oxygen.
- If NiAl gets exposed, it forms Al_2O_3 and seals the surface and does not spall.
- A 2D section accurately represents the alloy.
- A grain is represented by a single cell.
- Periodic boundary conditions are assumed at the vertical edges. Hence, the simulation cell "wraps around" in a cylindrical manner.

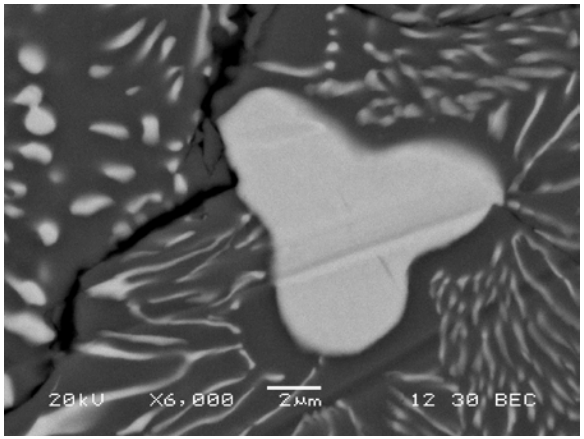


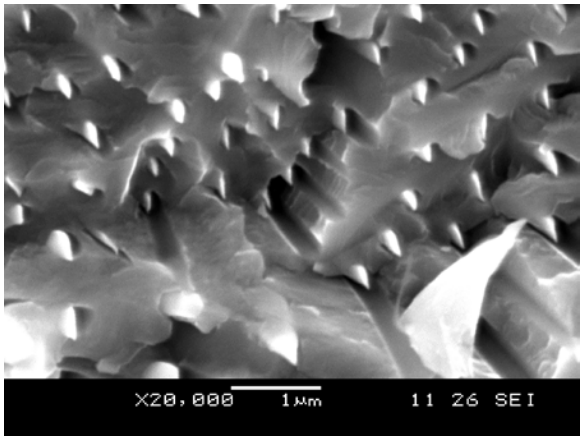
A typical grid, with about 20 atom% Mo

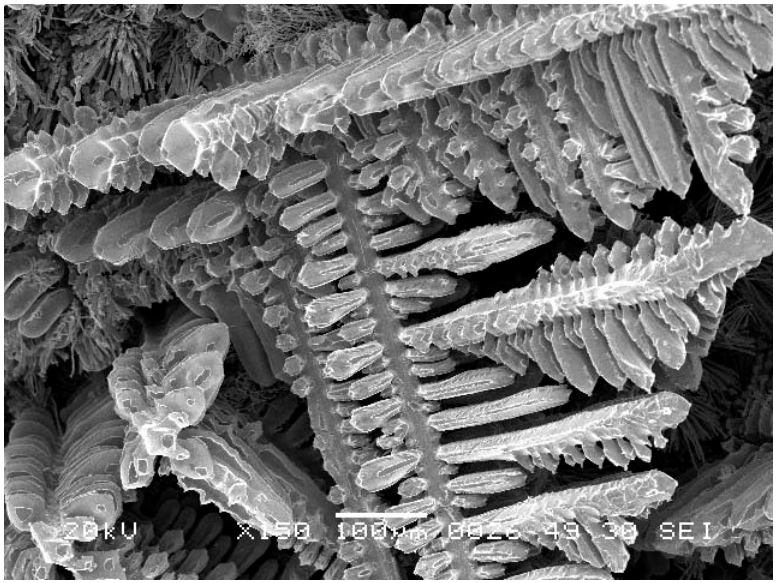


Fracture surface







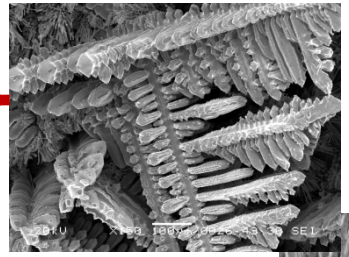


Improved mechanical properties with DS alloys?

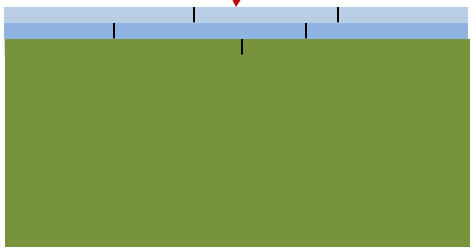
Mo dendrites help with crack deflection during the fracture process.

In the eutectic regions, fracture occurs with cleavage of NiAl and pull out of Mo lamellae.

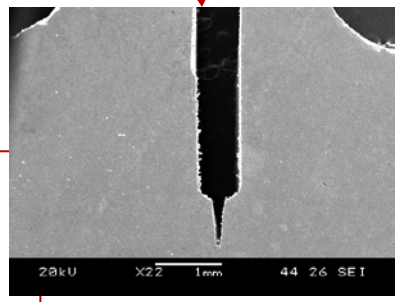
Proposed work



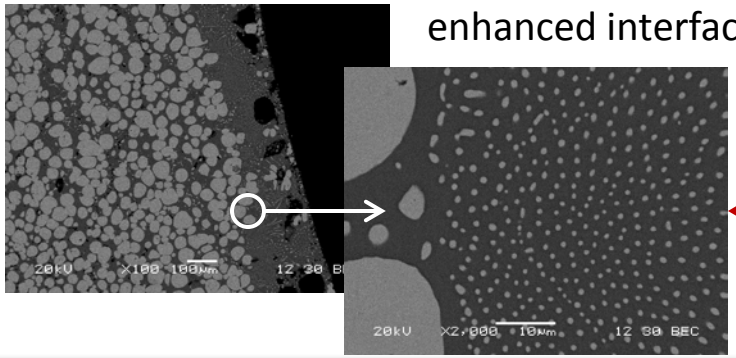
Microstructure control in the base alloy

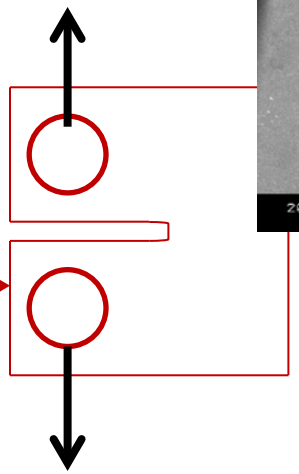


Multilayered coatings – prevent aligned cracks / improve oxidation resistance



Graded microstructures with enhanced interfacial compatibility

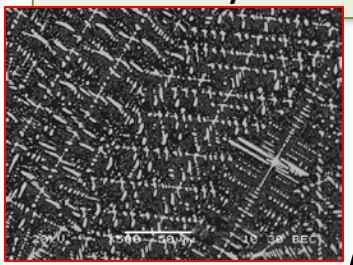




Fracture toughness & deformation

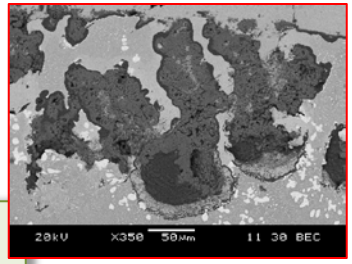
Summary

Base alloy selection

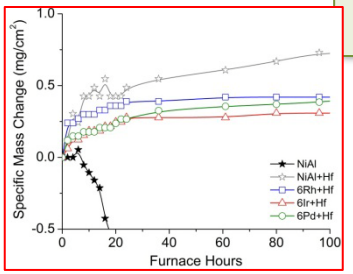


Selection via Semi-empirical thermodynamics

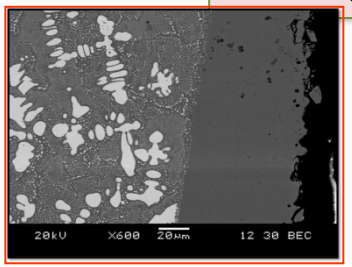
Oxidation mechanisms in the base alloy



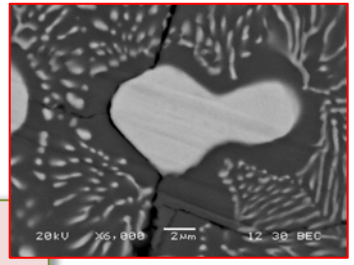
Development of coating materials



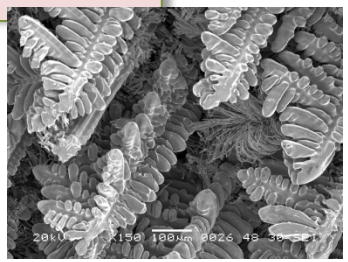
Development of coating methods



Preliminary mechanical testing



Microstructure optimization



Acknowledgements

- This work was supported by the **DOE-FE (AMR program)** through Ames Laboratory contract no. DE-AC02-07CH11358

- Program Manager: Vito Cedro

- OIM studies: Fraan Laabs