Computational and Experimental Development of Novel High Temperature Alloys

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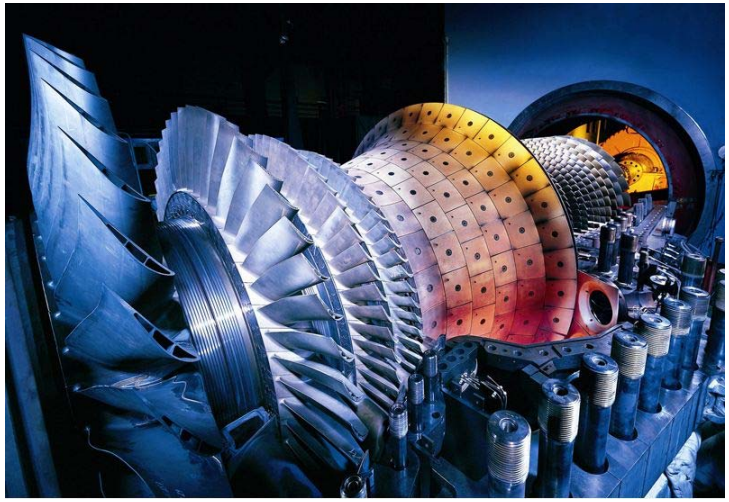
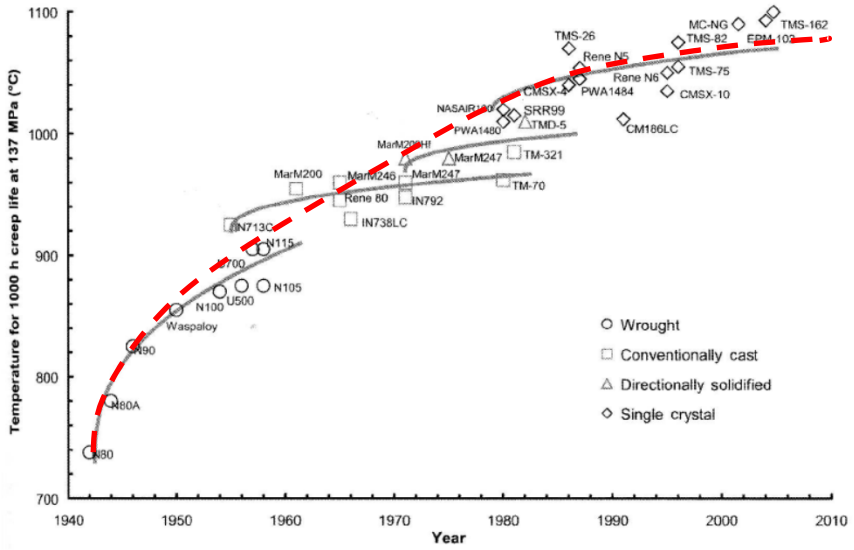
The High Temperature challenge



Higher temperatures → Higher energy efficiencies

Challenges –

- High T oxidation
- Moisture
- Creep and high T deformation
- Toughness & manufacturability
- Highly variable coal combustion environments

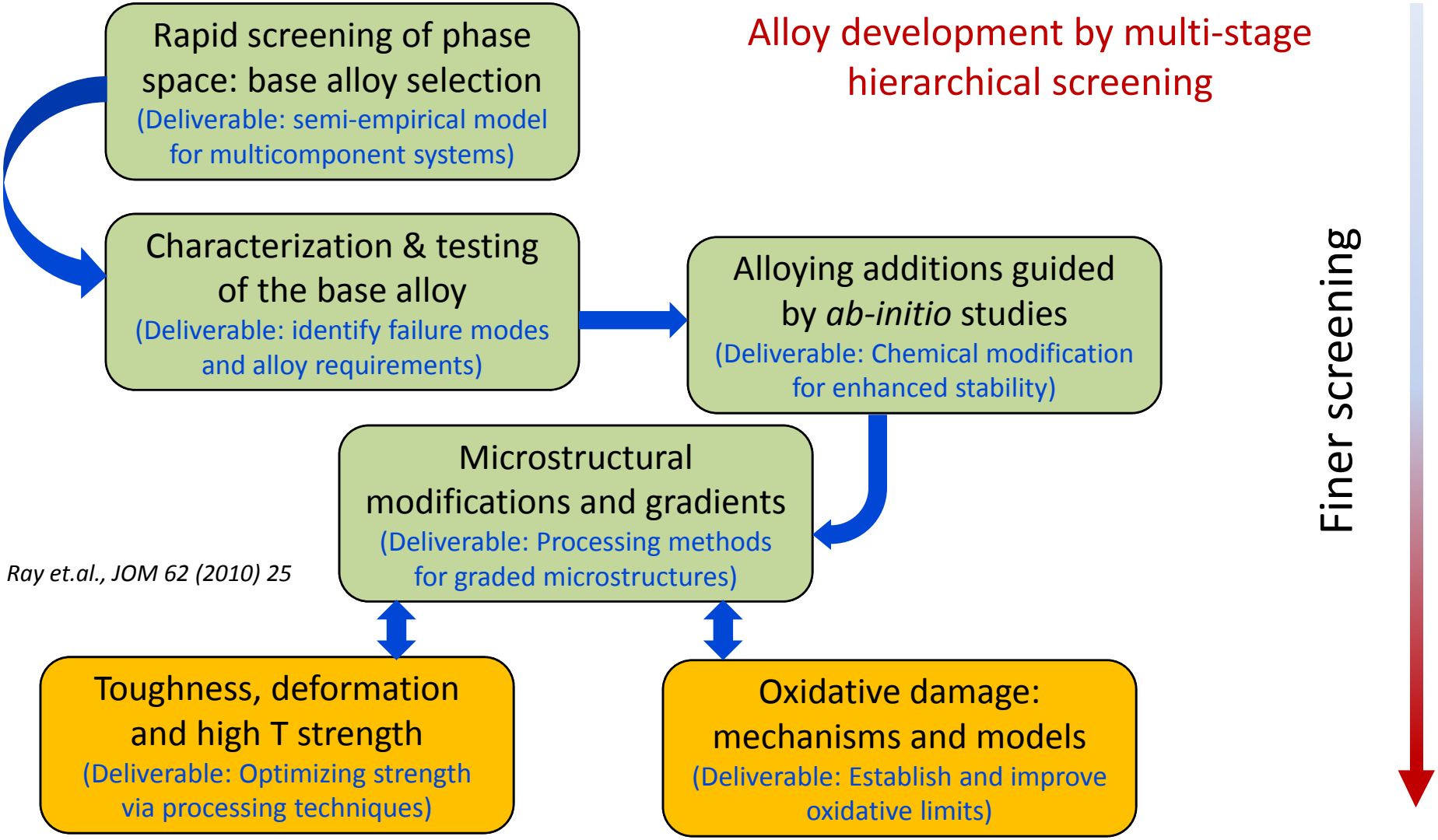


- Ni based alloys approaching limits
- Silicides form a borosilicate scale susceptible to moisture

The problem:

- Are there effective ways of tweaking existing systems?
- Can we develop a new alloy system?

Conceptual approach

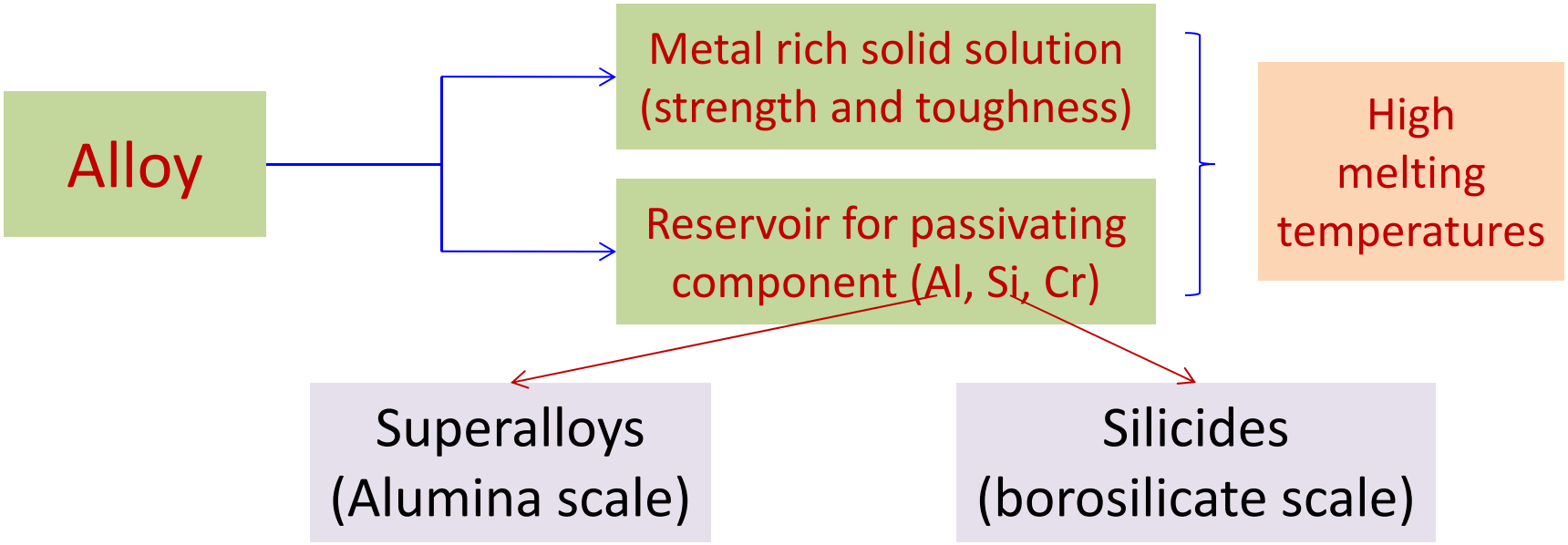


Alloy architecture

Key requirements

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

How do we develop stronger, oxidation resistant alloys that operate at very high temperatures?



Alloy selection: a coarse-grained approach

Estimation of formation enthalpies (ternary alloys)

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

Boundary conditions for energy minimization

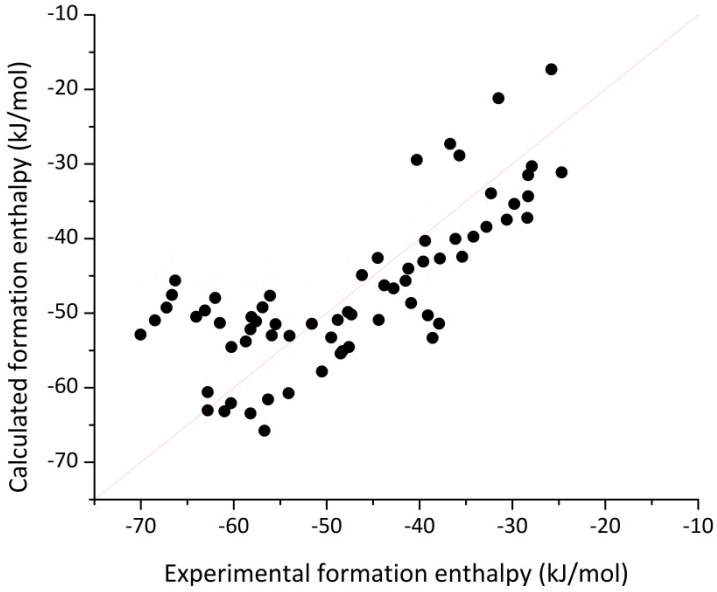
$$\sum_{i=1}^{3} \phi_i = 1$$

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

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

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

# of elements	Combinations
3	3160
4	82160
5	1.58 x 10^6
6	2.40 x 10^7



Semi-empirical thermodynamics: the initial screen

Ray et.al., J. Alloys Comp 489 (2010) 357

Alloy selection: the NiAl-Mo system

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

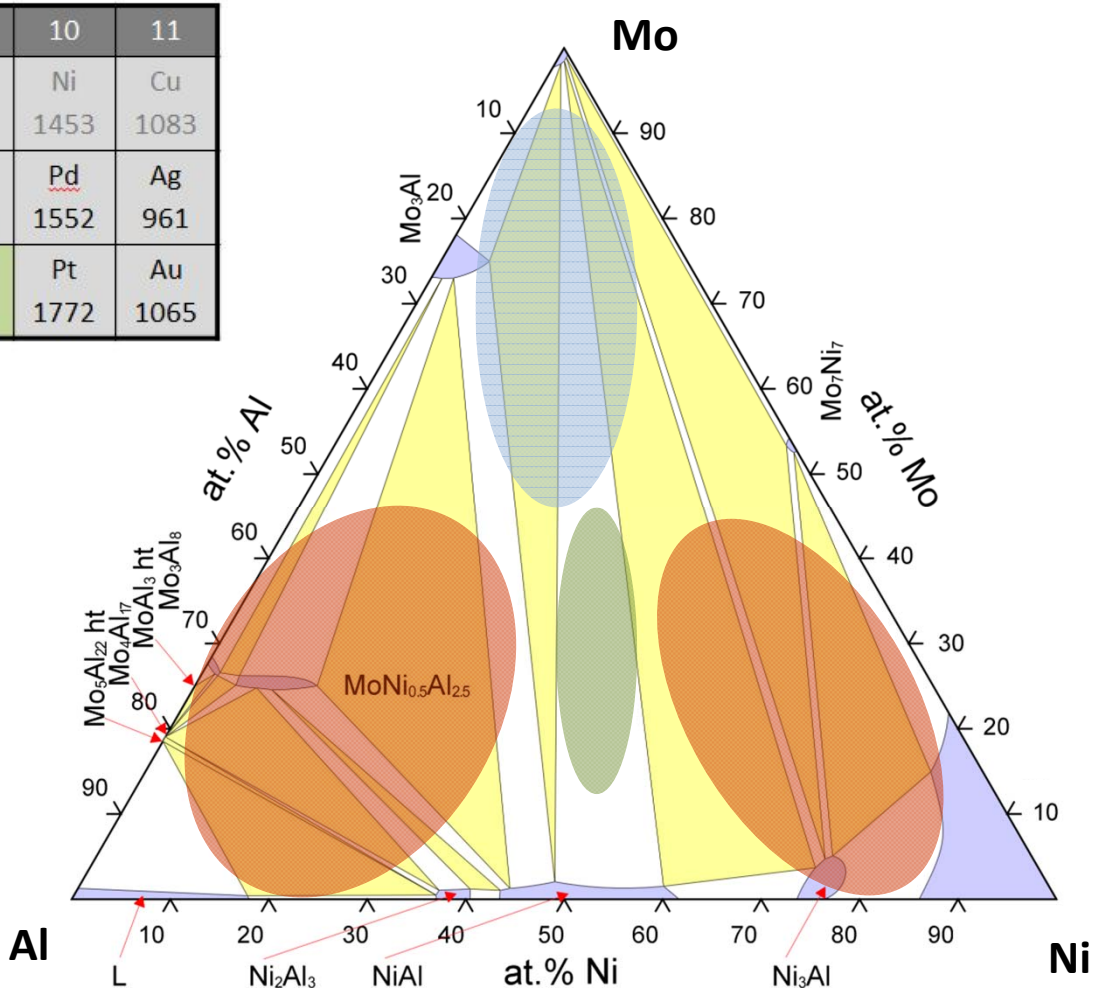
Requisites

- High temperature oxidation resistance
- High thermal stability

High melting + poor oxidation

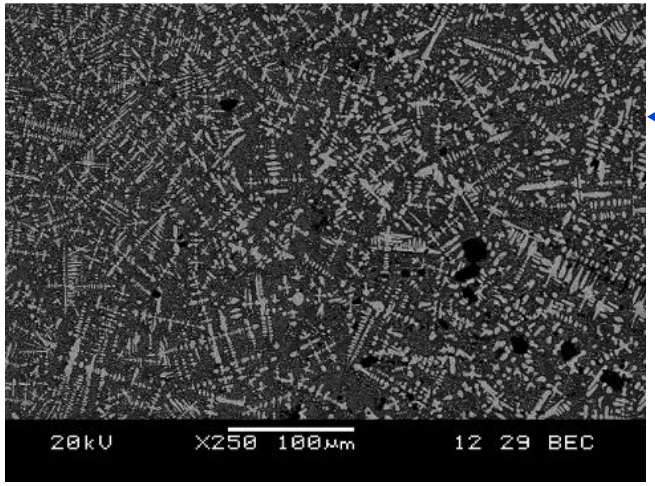
Low melting + good oxidation

Mix of oxidation and melting & possibly creep strength



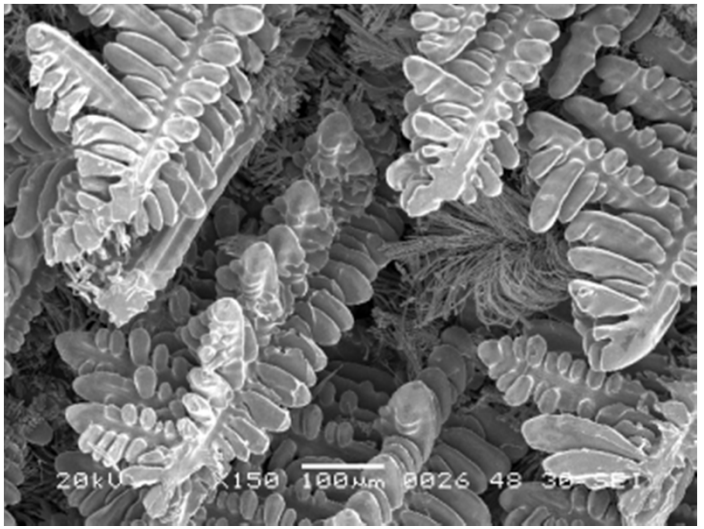
Haenschke et.al., J. Phys. 240(2010) 012063
Bei & George, Acta Mater 53(2005) 69

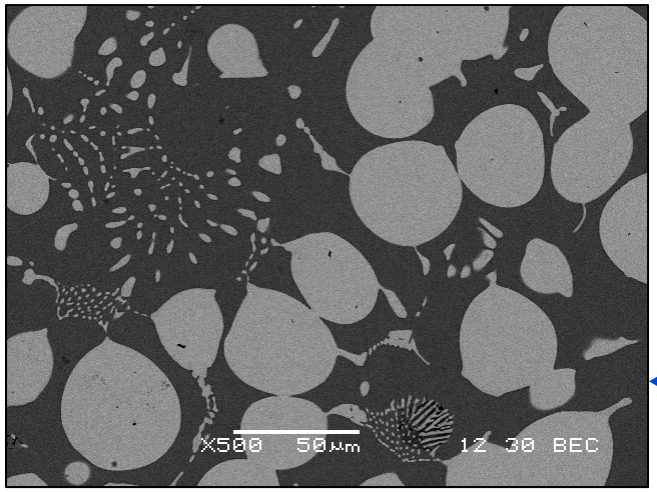
Processing and microstructures



Arc-melted

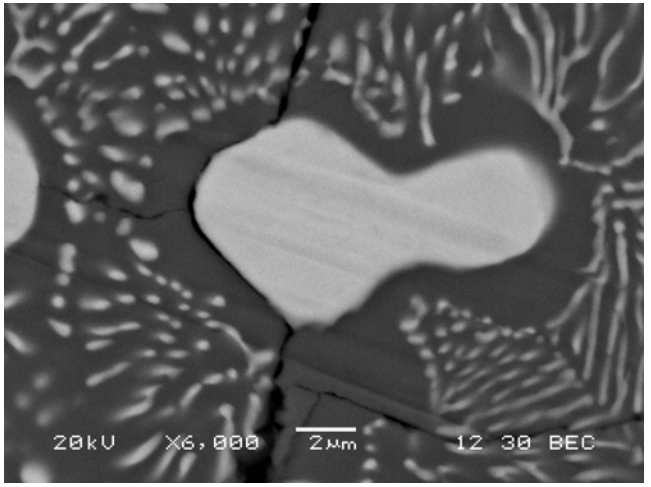
Directionally solidified



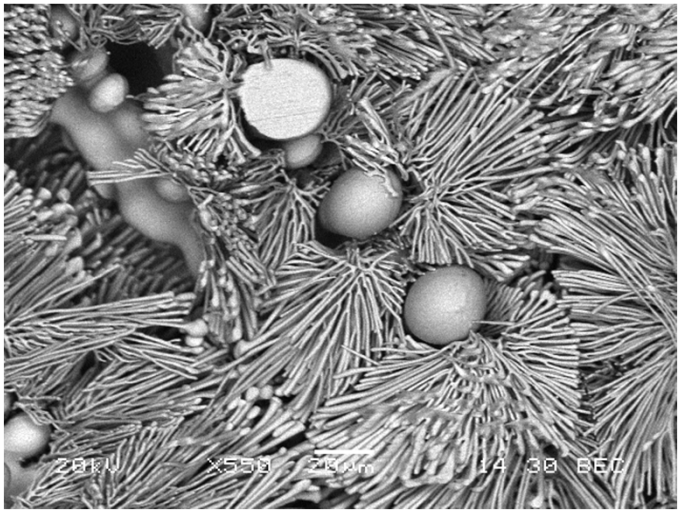


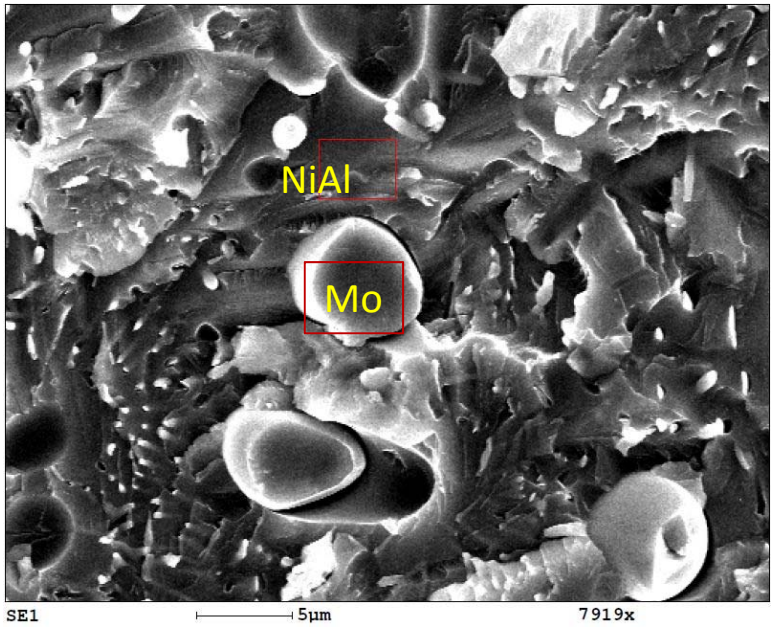
Liquid phase sintered

Significance of Mo distribution – Mo helps in crack deflection



Fracture Toughness





- Drop-cast and DS 15 atom% Mo alloy
- Fracture toughness ~ 9.4 MPa.m$^{1/2}$
  - Jamie Kruzic, OSU
- 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

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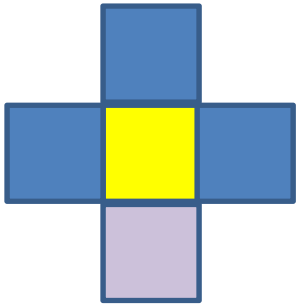
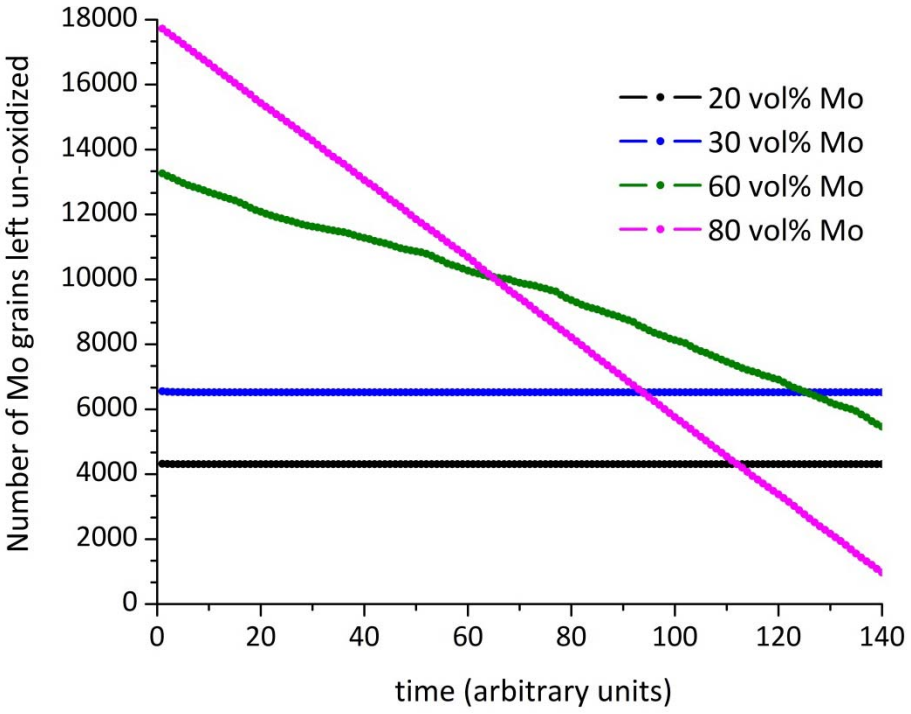
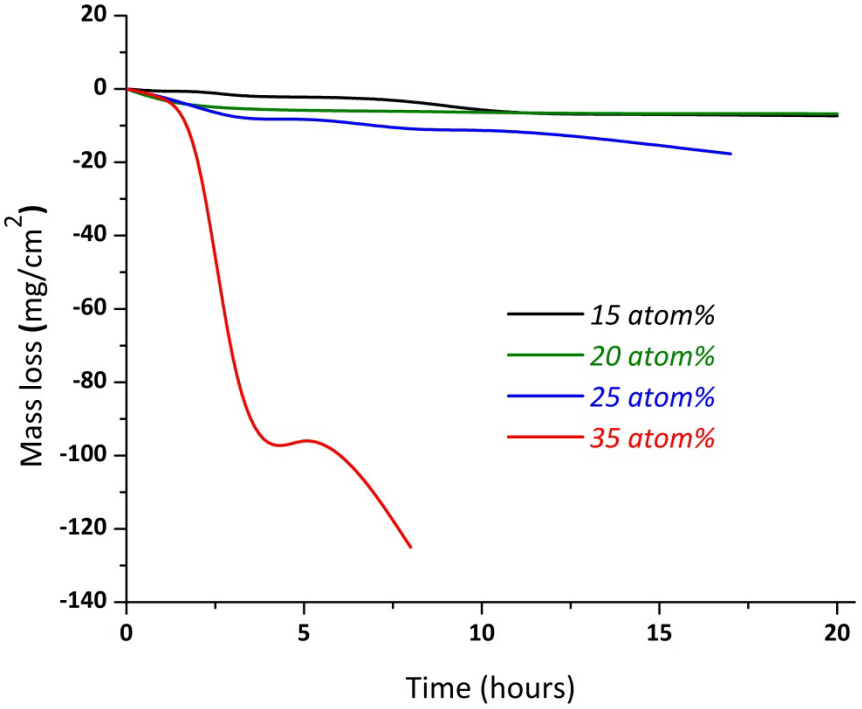
Composition optimization – Oxidation mitigation



CA model assuming Von-Neumann environment

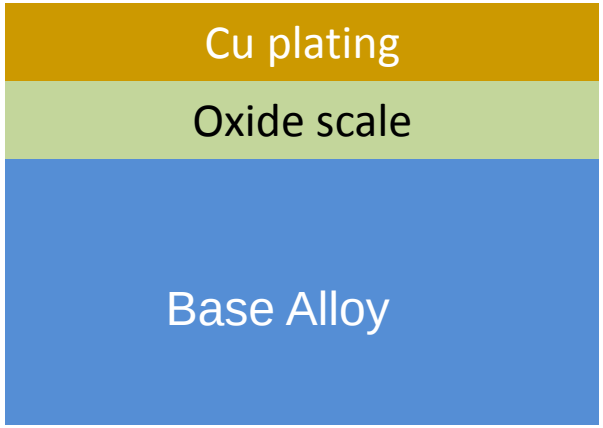




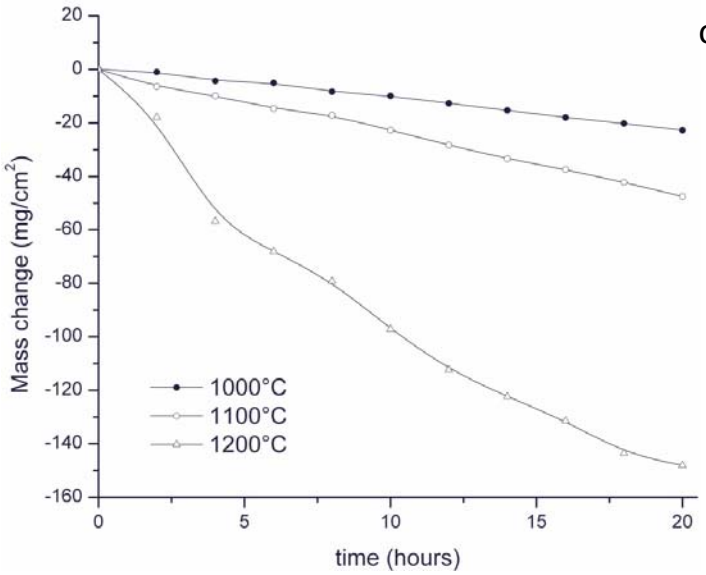
Isothermal oxidation at 1200°C

Composition used for rest of the presentation: $Mo_{20}Ni_{40}Al_{40}$

The effect of temperature

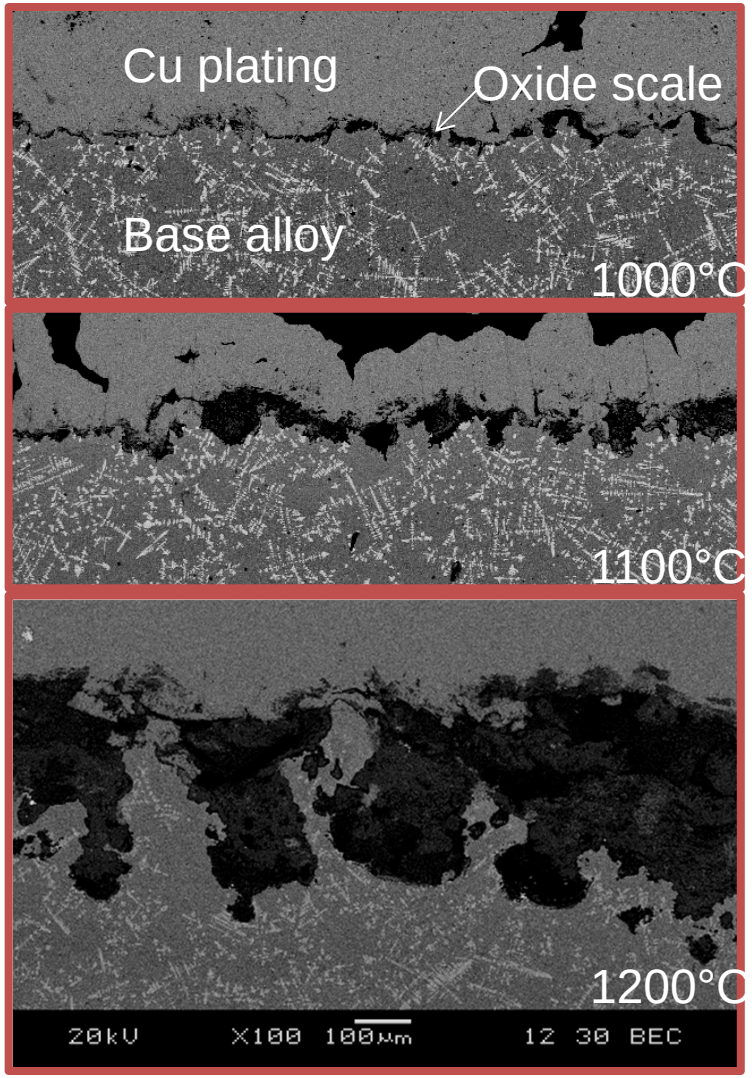


Sample prep schematic



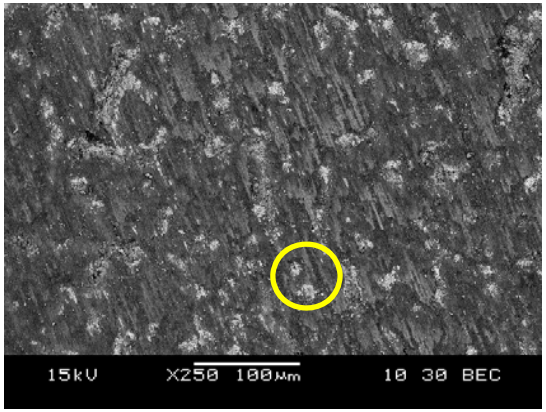
Mass change during oxidation at different temperatures

Cross-section micrographs after 10 hours of oxidation

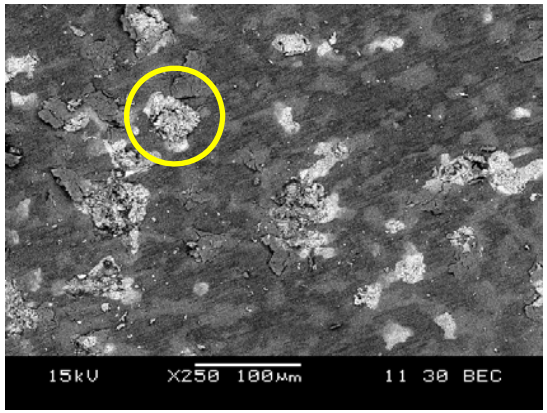


Ray et.al., Appl. Surf. Sci. 301(2014) 107

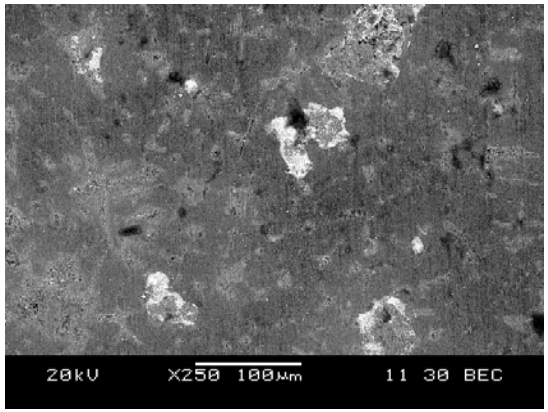
Oxidized surfaces



1000 °C



1100 °C



1200 °C

Ray et.al., manuscript under prep

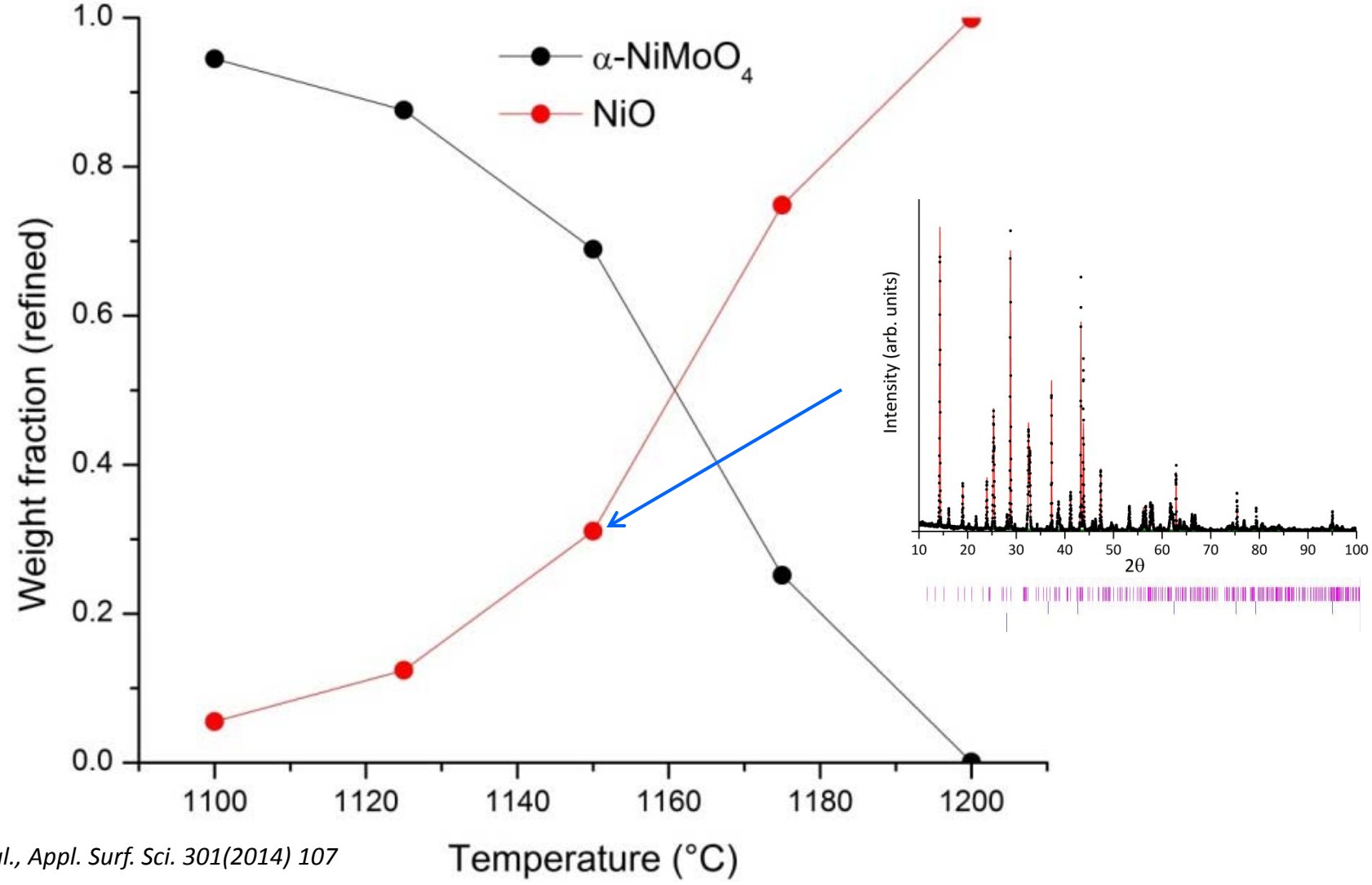
Oxidation time: 30 minutes

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

$NiAl_2O_4$ and NiO seem to predominate above 1100 °C

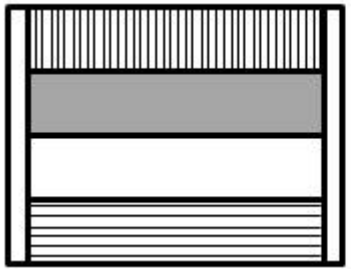
Oxidation possibly results in a multi-layered scale

Stability of $NiMoO_4$



Ray et.al., Appl. Surf. Sci. 301(2014) 107

Oxidation mechanism



$NiO + NiMoO_4$

$NiAl_2O_4$ + traces of NiO and $NiMoO_4$

α-Al_2O_3

$MoO_2 + \alpha$-Al_2O_3

Phase transformation in $NiMoO_4$

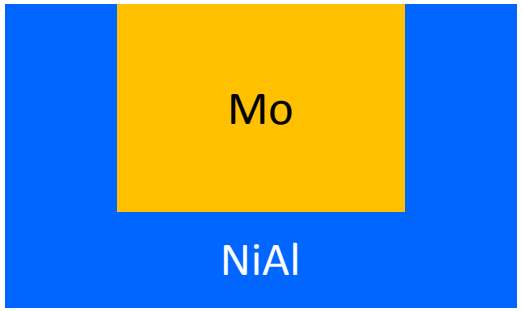
Heating $\alpha \longrightarrow \beta$ @ 602 °C

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

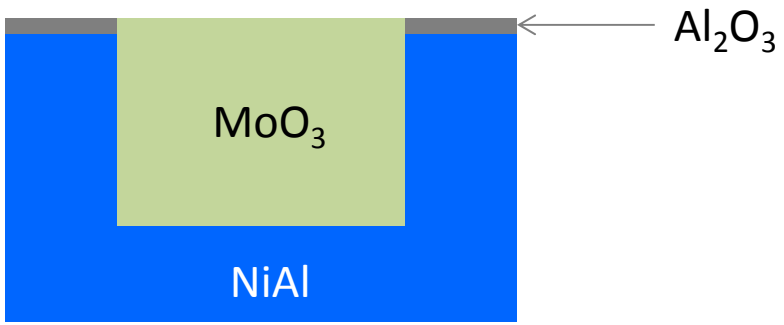
Oxidation mechanism



Consider the oxidation of a Mo rich region of the surface.

Ray et.al., article under preparation

Oxidation mechanism



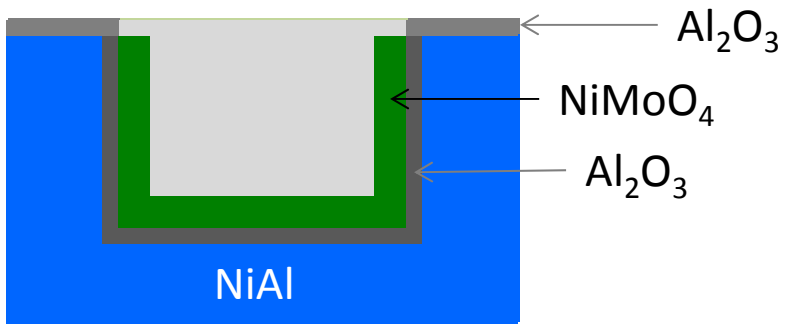
Consider the oxidation of a Mo rich region of the surface.

Initial oxidation of Mo results in the formation of MoO_3 which later volatilizes.

$Mo + 3/2\ O_2 \rightarrow MoO_3$

Ray et.al., article under preparation

Oxidation mechanism



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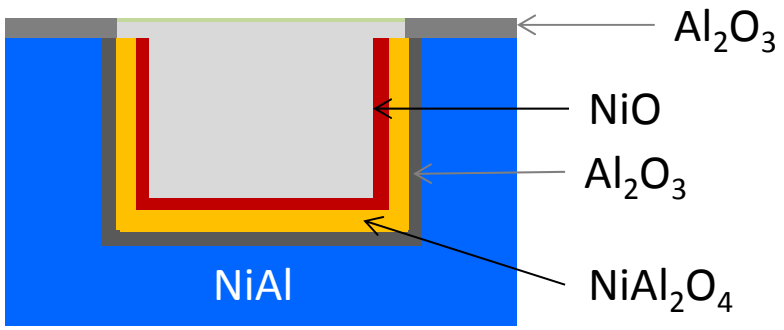
$Mo + 3/2\ O_2 \rightarrow MoO_3$

$NiMoO_4$ forms at the interface along with alumina

$2MoO_3 + 2NiAl + 3/2O_2 \rightarrow 2NiMoO_4 + Al_2O_3$

Ray et.al., article under preparation

Oxidation mechanism



$NiMoO_4$ dissociates progressively

$NiMoO_4 \rightarrow NiO + MoO_3$

The NiO reacts with the underlying Al_2O_3 to form the spinel interphase

$NiO + Al_2O_3 \rightarrow NiAl_2O_4$

Ray et.al., article under preparation

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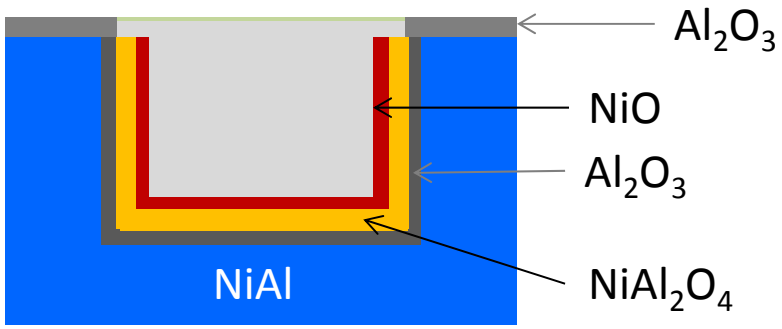
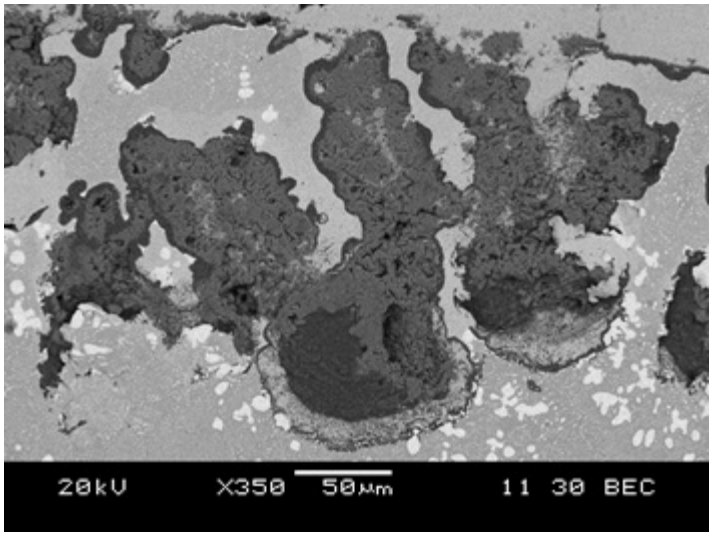
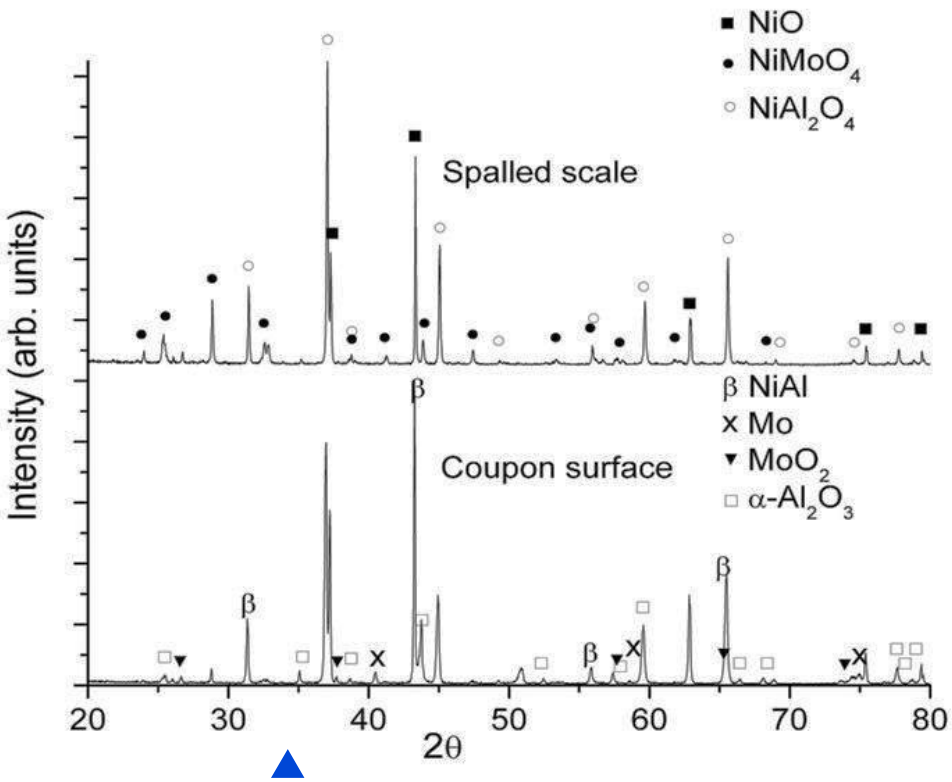




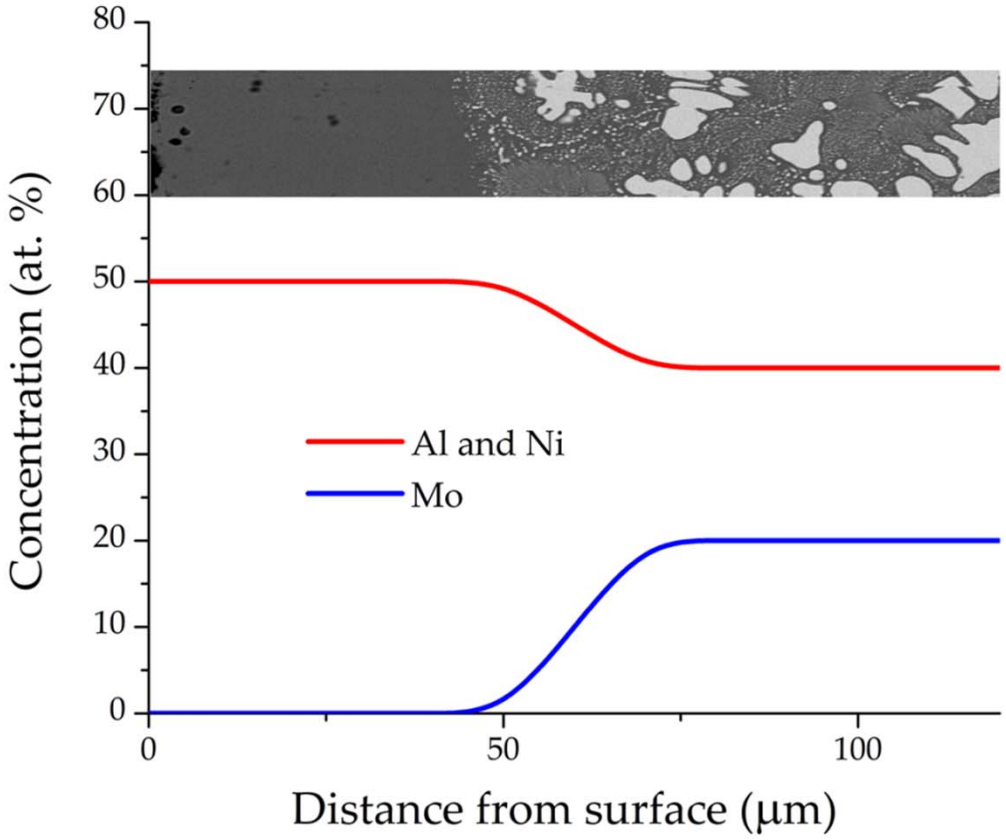
Oxidized micrograph (1200°C, 10 hours)



X-rays of the spalled and the surface scale

Ray et.al., article under preparation

Designing microstructural gradients



The coating should be:
-Oxidation Resistant
-Compatible with the base alloy

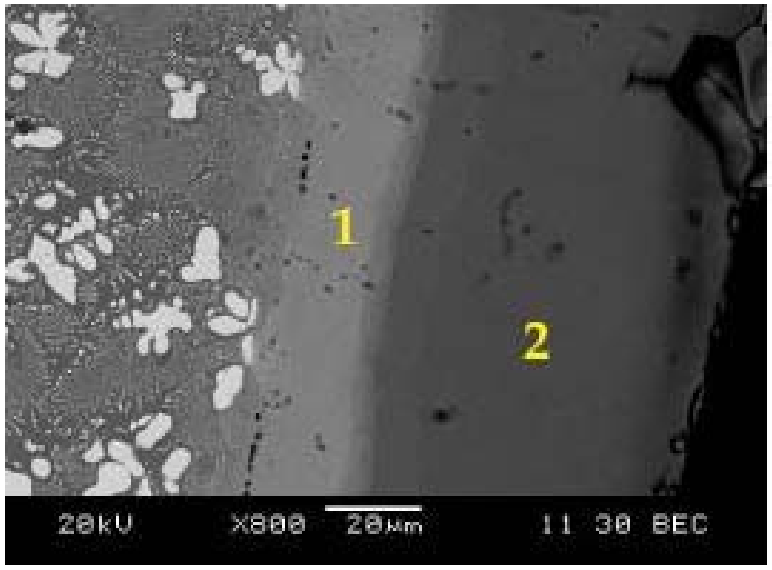
By using β-NiAl as a coating, on top of the MoNiAl alloy, chemical gradients are decreased, which can prolong the life of the coating

Designing microstructural gradients

The two phase (Mo)+NiAl microstructure of the cast alloy necessitates a two step coating method.

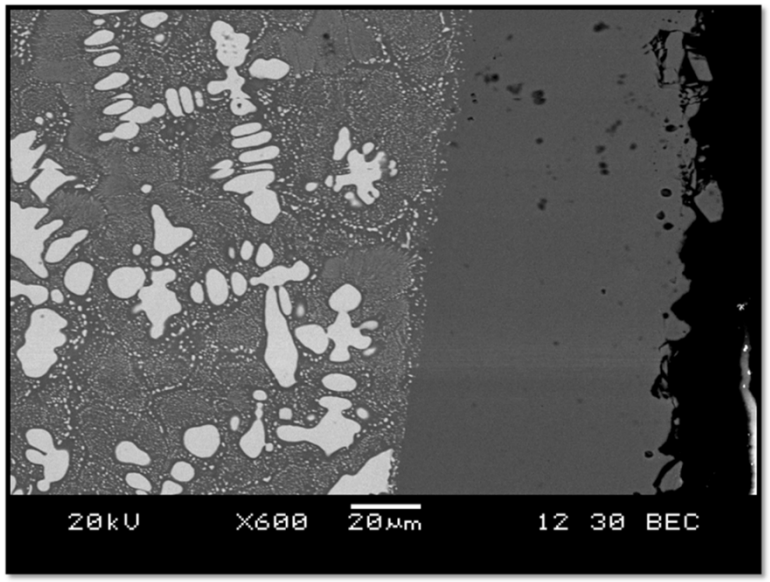
Ni / Al coating

In order to form the β-NiAl coating, Ni has to be deposited on the surface to avoid formation of Al-Mo intermetallics.

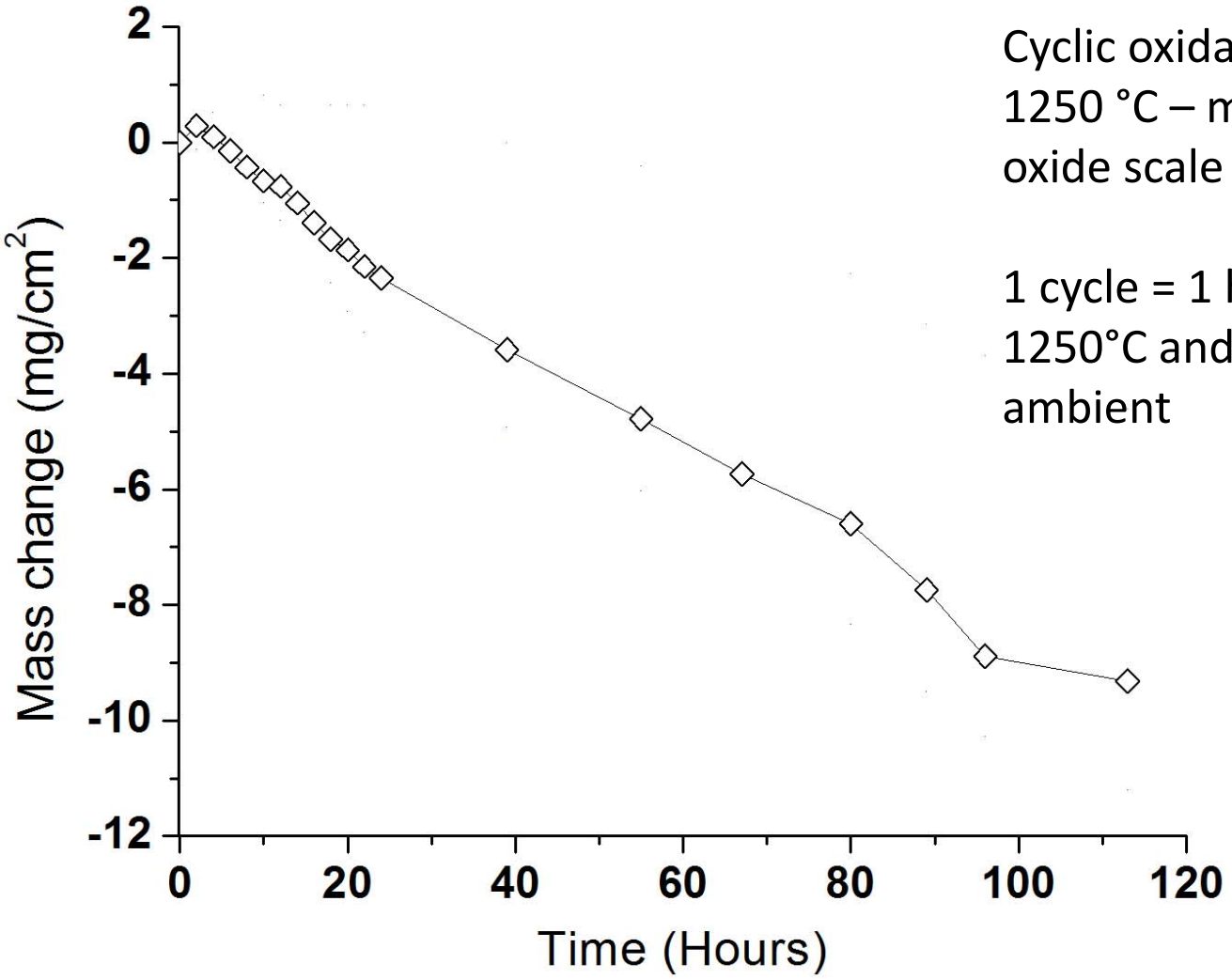


Annealed coating

Easily controllable process to adjust amount of Al deposited to form the β-NiAl



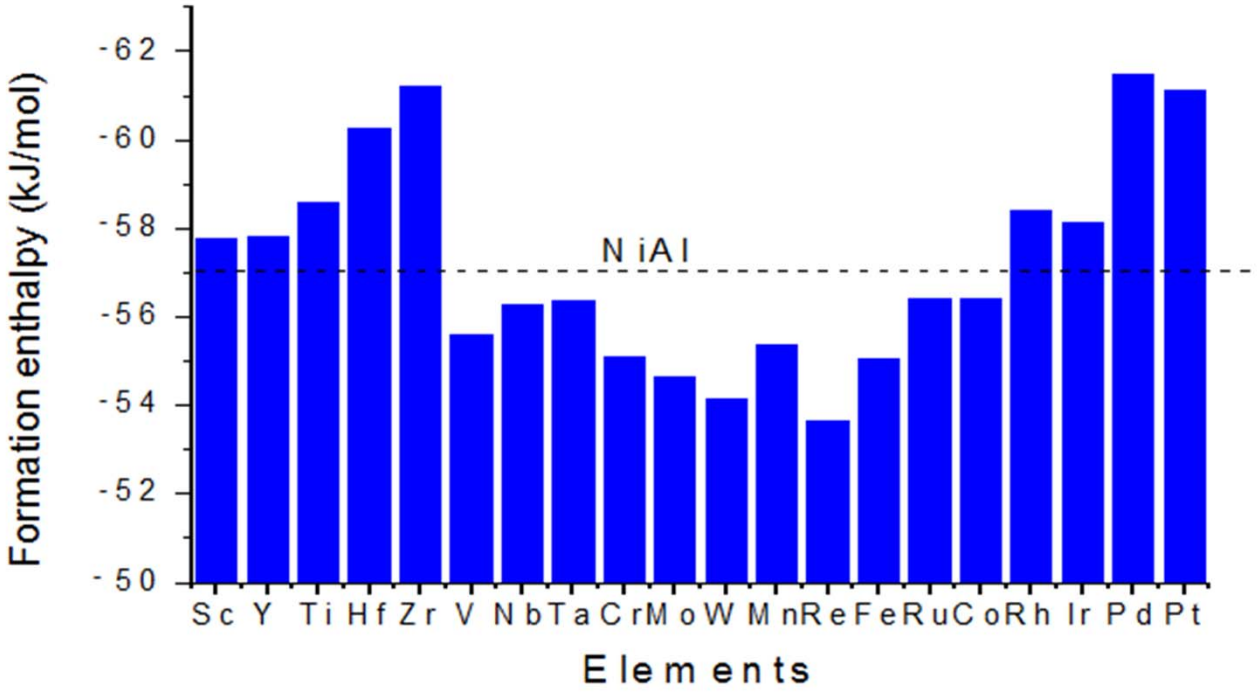
Improve the NiAl coating



Cyclic oxidation at 1250 °C – massive oxide scale spallation

1 cycle = 1 hour at 1250°C and 30 min at ambient

Alloying additions: computational guide



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

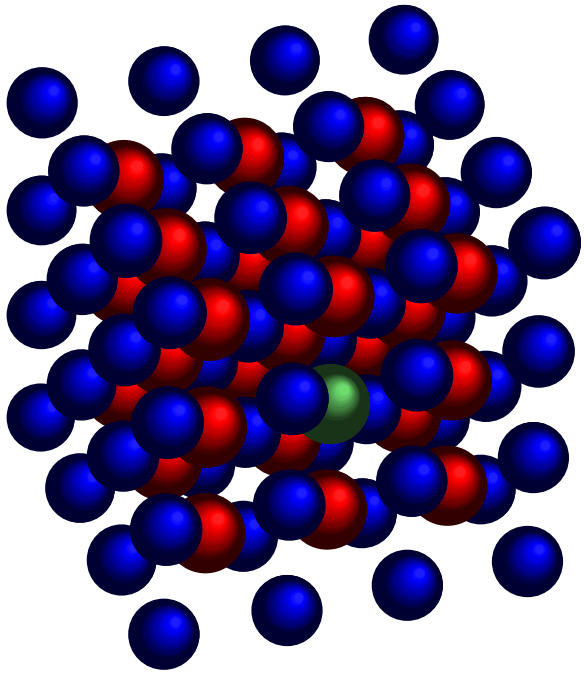
From Debye's theory of solids, derived by Smith, Rose and Ferrante, *Appl. Phys. Lett (1984)*

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

Brammer et.al., Adv. Sci. Tech. 72(2011) 31

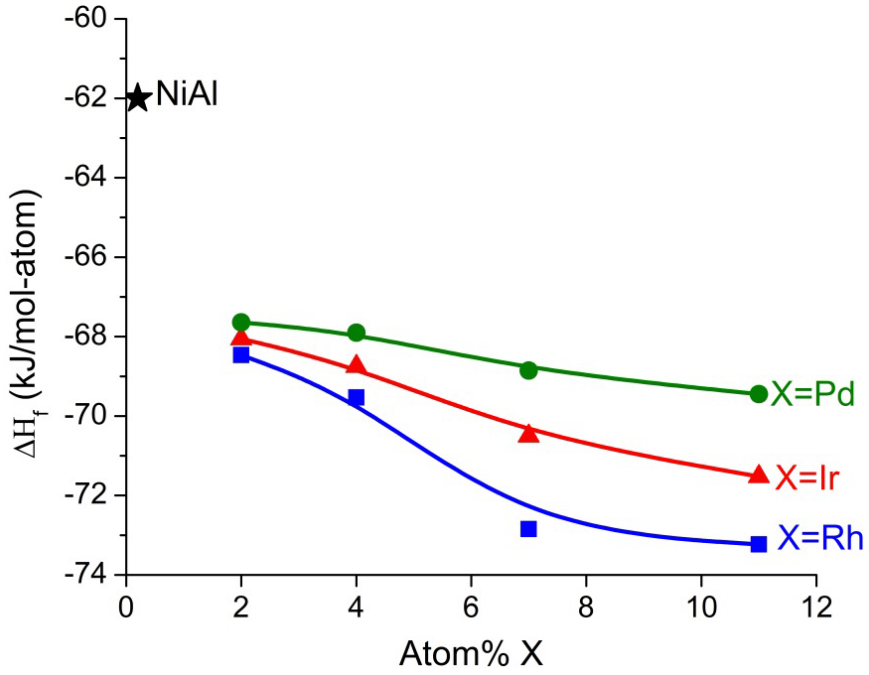
Alloying additions: computational guide

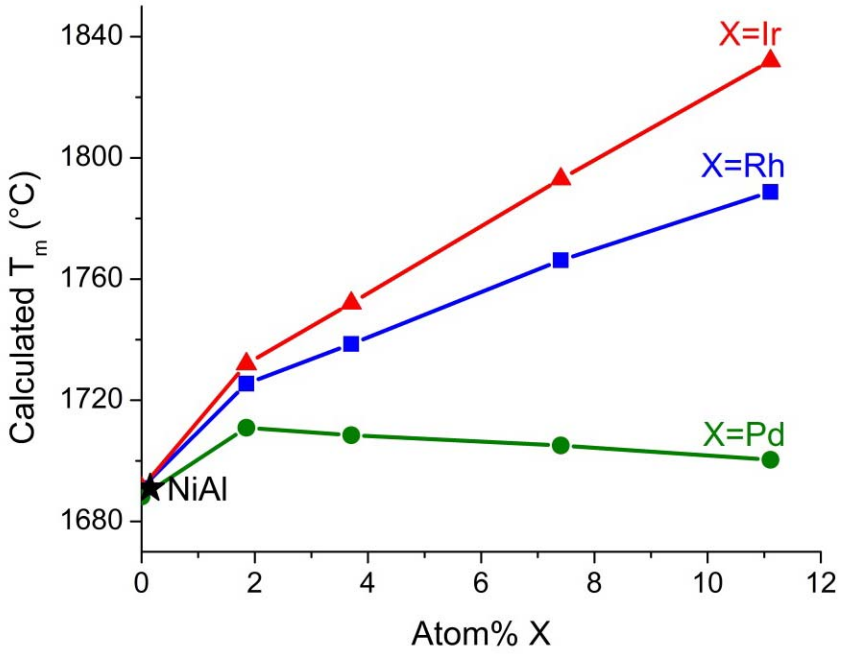
Objective: electronic stability (DOS)
Site preference



- Ab-initio studies on alloying additions down-selected by Miedema
- VASP, GGA potentials
- 54 atom unit cell [3 × 3 × 3]
- Site preference tested (both Ni and Al) sites

Alloying additions: computational sieve





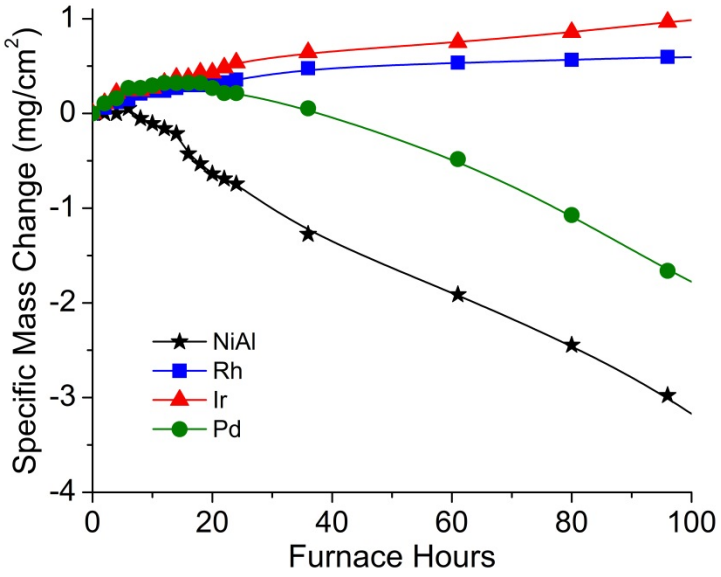
$$T_m = 0.032\, E^c / k_B$$

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

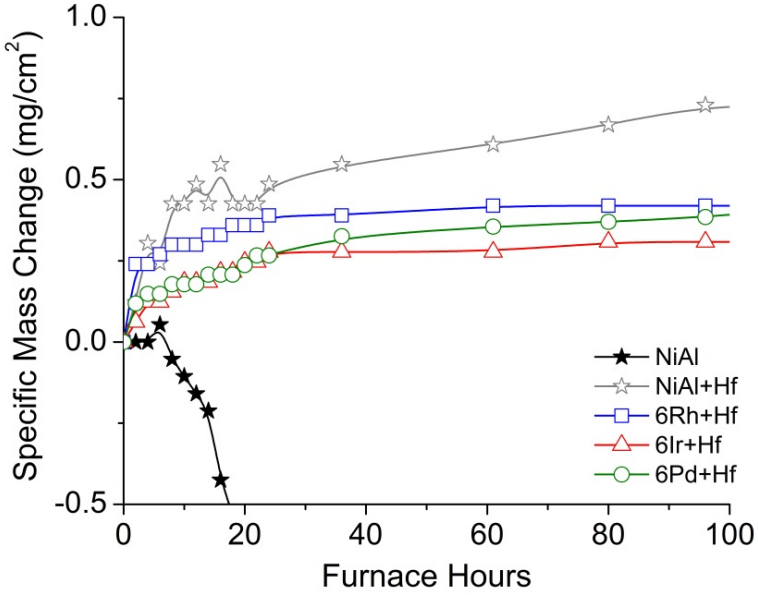
Brammer et.al., Adv. Sci. Tech. 72(2011) 31

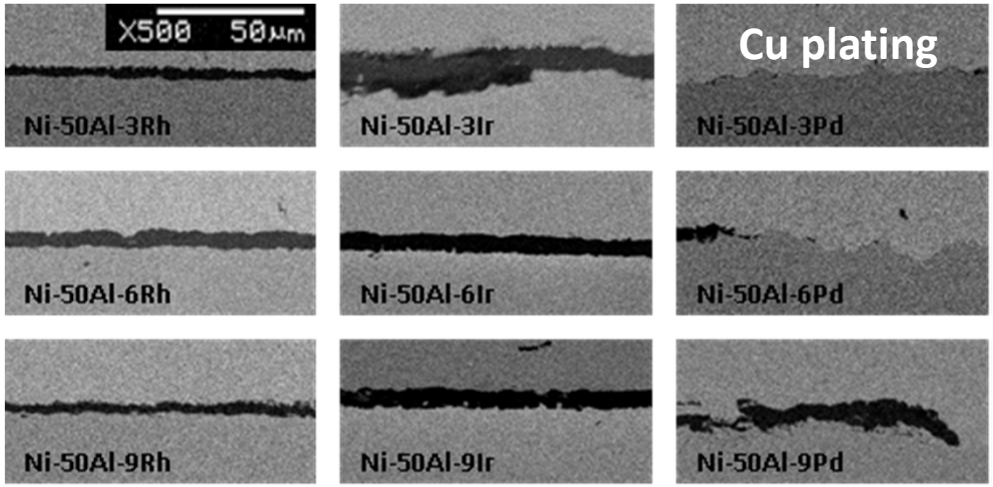
Metal	Cohesive E (kJ/mol)	Metal	Cohesive E (kJ/mol)
Al	327	Ir	670
Ni	428	Pd	376
Rh	554		

Alloying additions: experimental sieve



1250 °C
6% PGM



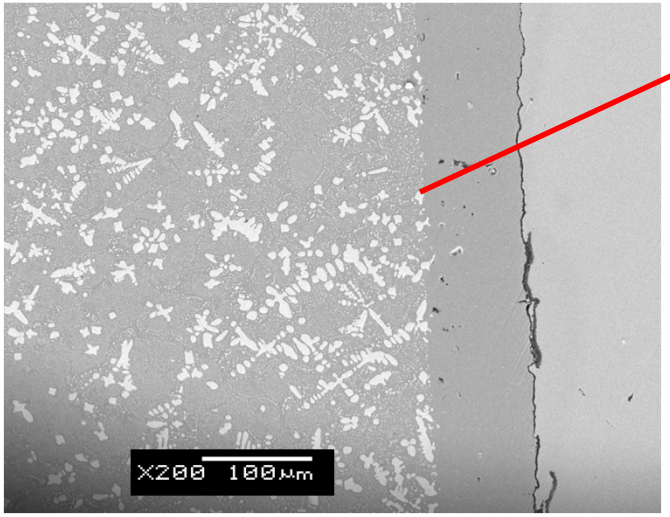


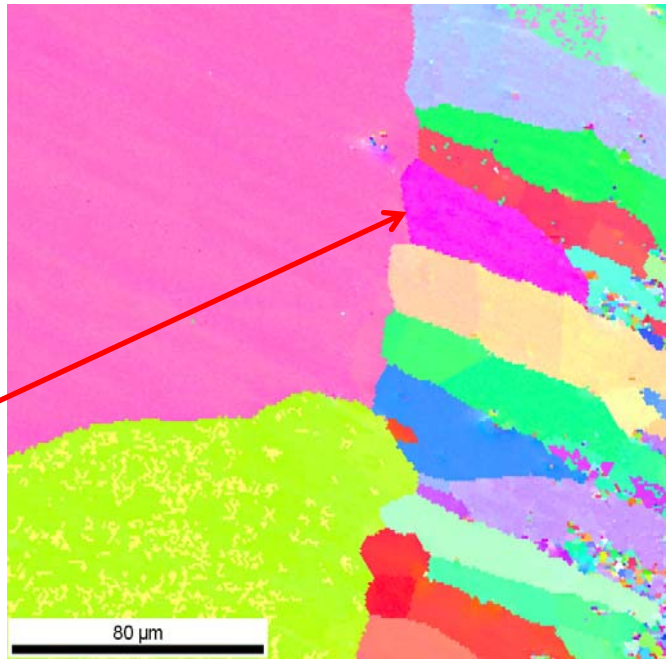
- Addition of PGM elements helps in avoiding spallation.
- Hf addition further reduces the growth rate of the oxide scale.

Ray et. al., JOM 62(2010) 25

Putting it all together

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



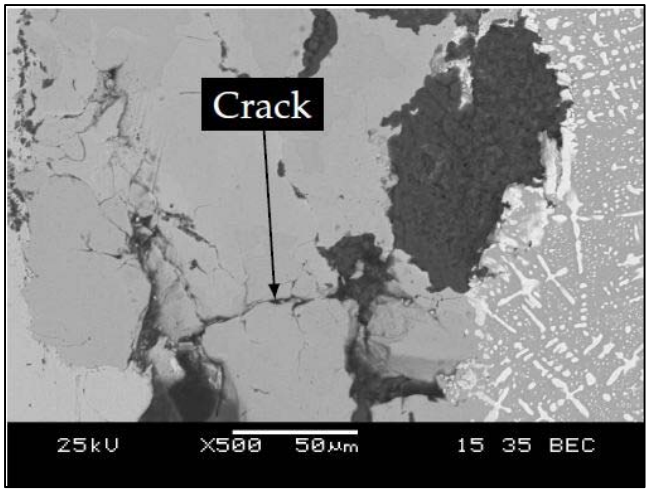


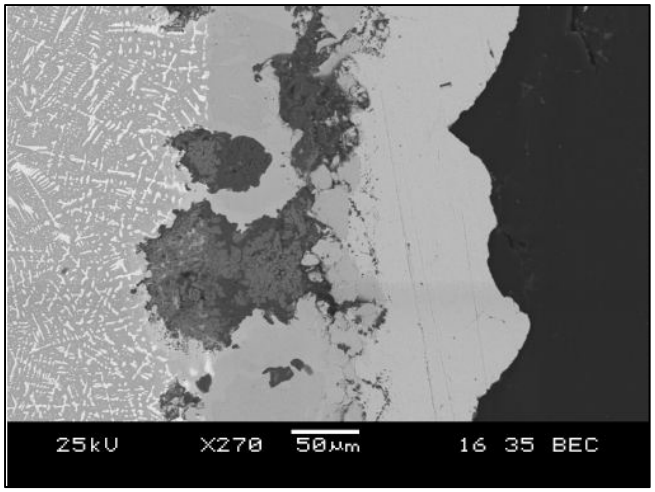
OIM of NiAl coating

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

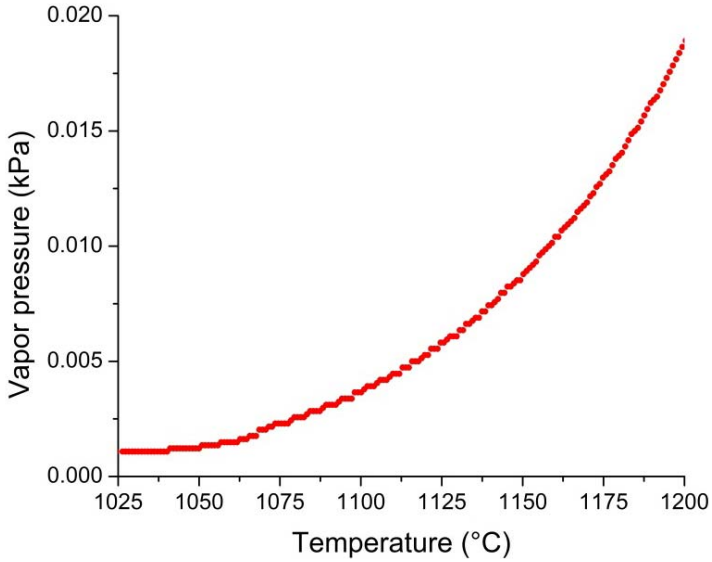
Severs et.al., article under perparation

Failure mechanisms

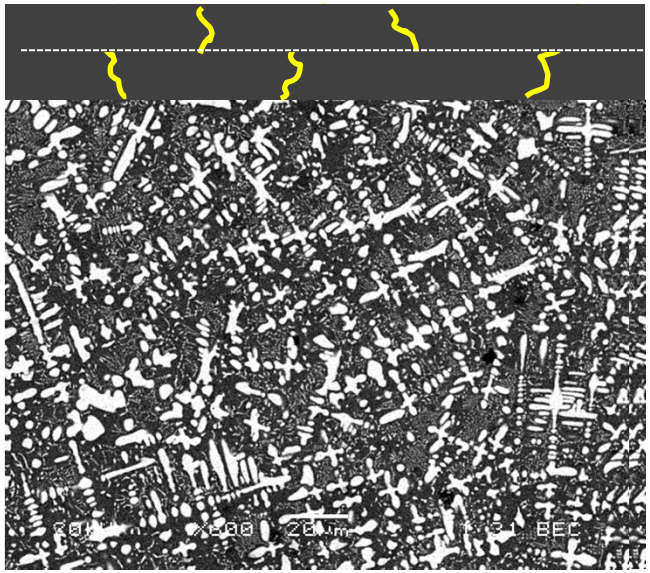




- Pre-existing cracks provide oxidation pathways.
- Integrity is a function of $NiMoO_4$ formation vs Al_2O_3 coverage.
- T dependence is function of Al_2O_3 growth rate and MoO_3 vapor pressure

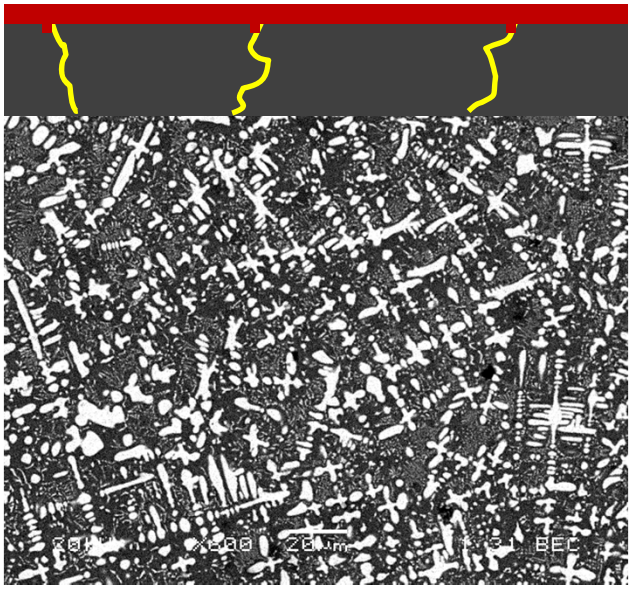


Approach



Cracks in a layer of NiAl appears during the coating process

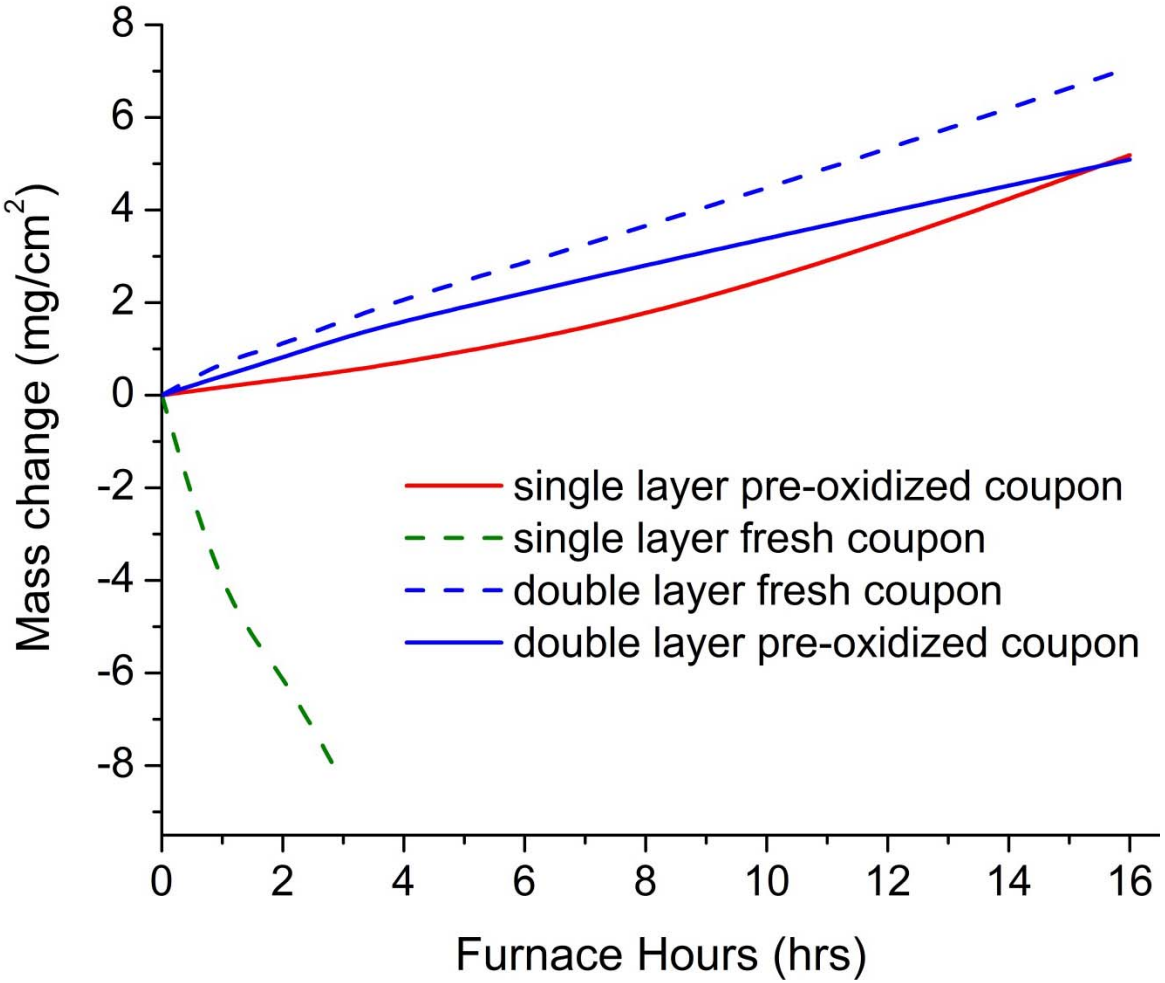
Probability of aligned cracks is very low in a double layered coating



Additionally, pre-oxidation at lower temperatures can help cover cracks

Time and temp = balance of Al_2O_3 growth rate vs $NiMoO_4$ growth rate

Cyclic oxidation @ 1150°C

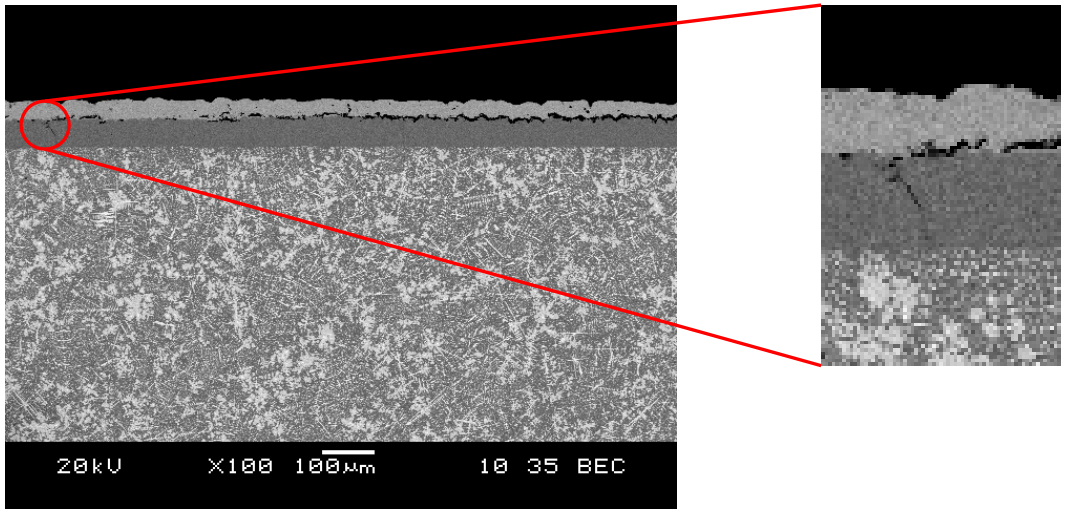


Optimal coating approach:

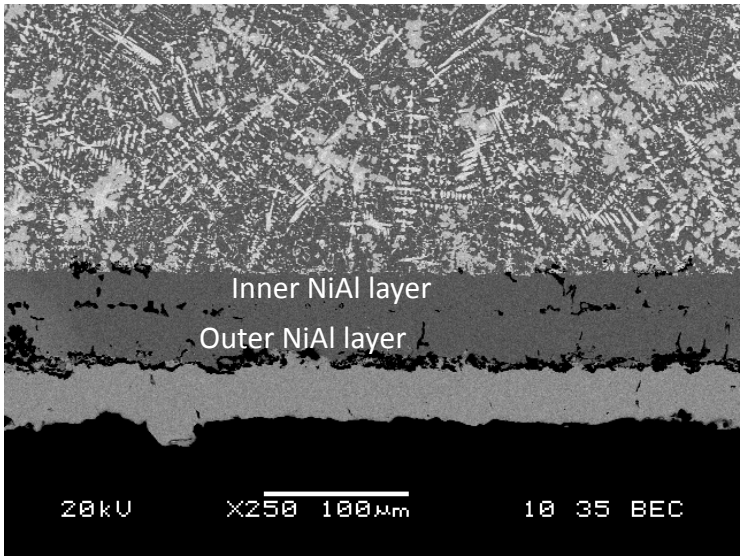
Double layered coatings

Pre-oxidized at 1100°C for 5 hours

Oxidized microstructures



Double layered coating, pre-oxidized at 1100°C for 5 hours, followed by 20 hours of cyclic oxidation at 1150°C



Cracks in the two layers of NiAl don't coincide – results in a barrier for the oxygen pathway into the alloy

Formation of significant quantities of $NiMoO_4$ could be mitigated.

Al_2O_3 scale could be observed instead

Summary

- Double layer coatings, pre-oxidized at lower temperatures result in improved oxidation resistance – alloy oxidation is now governed by the coating integrity
- Using Hf + PGM (Ir or Rh), the NiAl can perform adequately at 1200°C. Packaging the NiAl-Ir+Hf layers on NiAl-Mo alloy could result in a significantly improved alloy at 1200°C
- A multi-scale hierarchical approach to alloy design can provide a viable alternative to Edisonian methods of alloy design

<u>On-going/future work</u>

- Modeling and optimization of the pre-oxidation process
- Mechanical testing