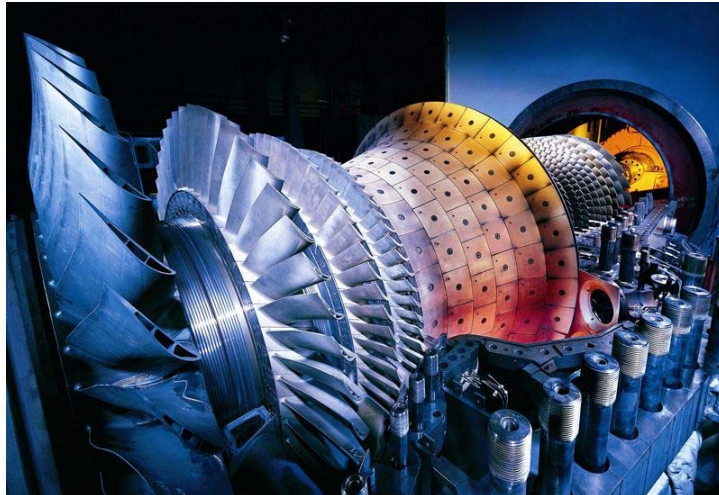# Computational and Experimental Development of Novel High Temperature Alloys

Matthew J. Kramer, Tyler R. Bell, Pratik K. Ray, Mufit Akinc
Prashant Singh, Linlin Wang and Duane D. Johnson

2015 Crosscutting Technology and Research Meeting
April 29, 2015

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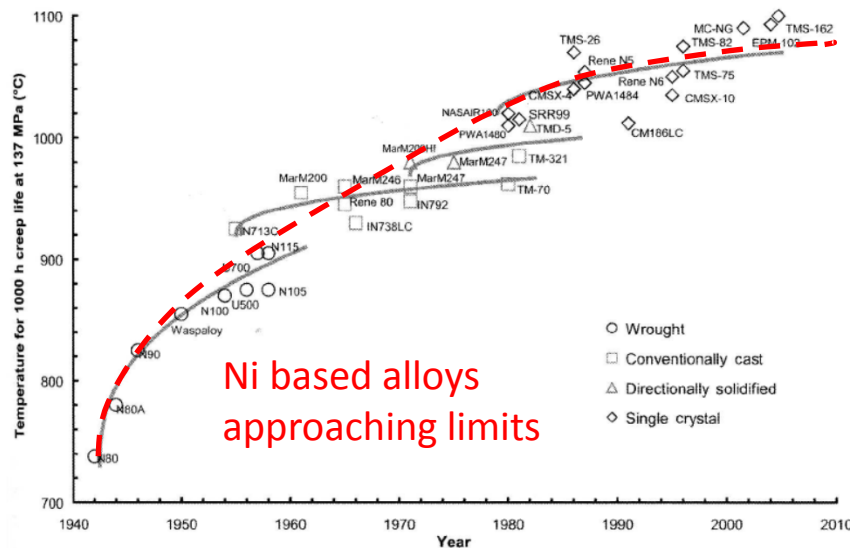U.S. DEPARTMENT OF ENERGY

IOWA STATE UNIVERSITY

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

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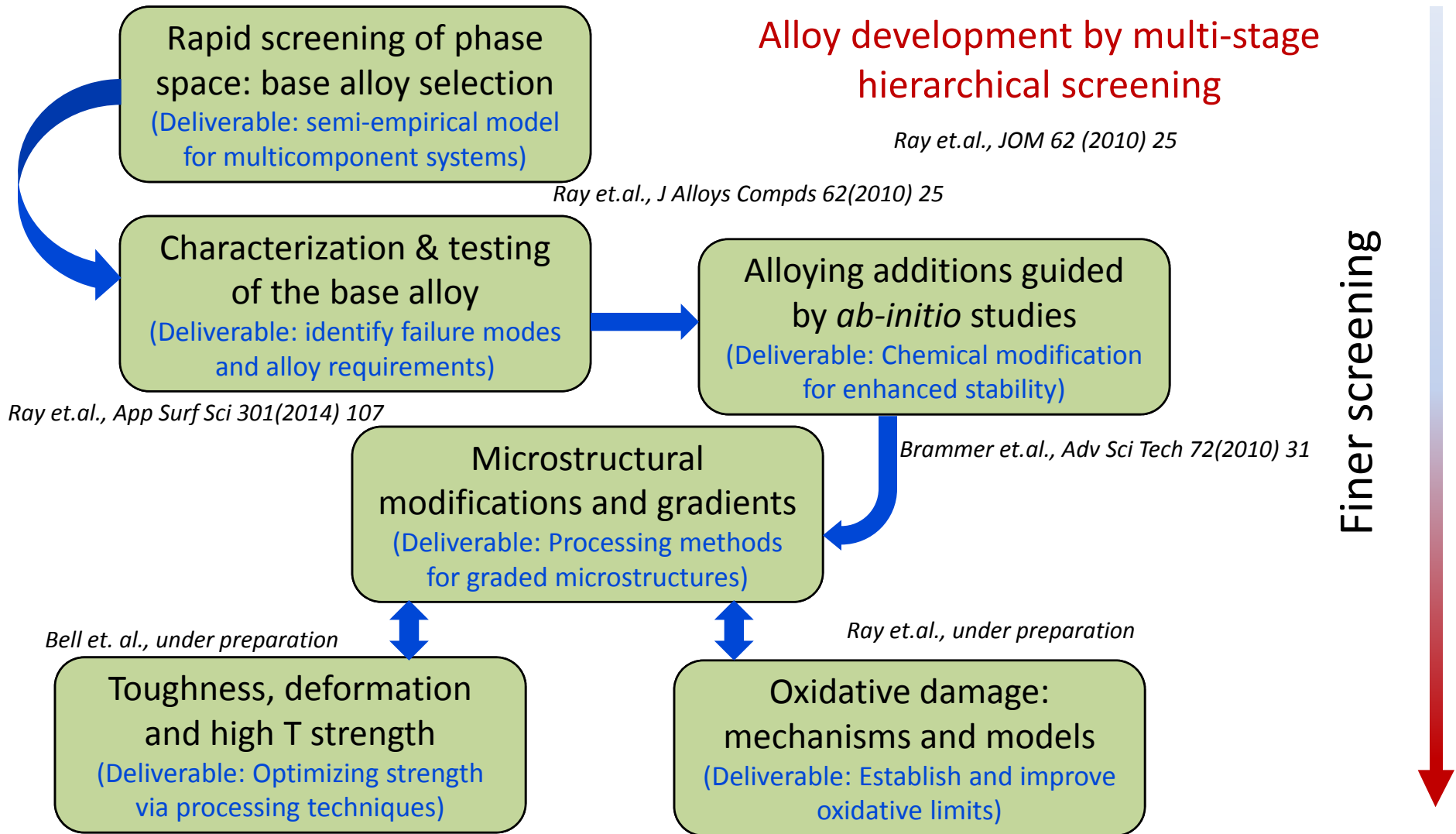- Can we develop a new alloy system?

Key metrics:
- High melting temperatures
- Microstructural stability
- Toughness $\geq$ 20 MPa•m$^{1/2}$
- Oxidative Stability

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

IOWA STATE UNIVERSITY

Conceptual approach

Alloy development by multi-stage hierarchical screening

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

Rapid screening of phase space: base alloy selection
(Deliverable: semi-empirical model for multicomponent systems)

Ray et.al., J Alloys Compds 62(2010) 25

Characterization & testing of the base alloy
(Deliverable: identify failure modes and alloy requirements)

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

Alloying additions guided by *ab-initio* studies
(Deliverable: Chemical modification for enhanced stability)

Brammer et.al., Adv Sci Tech 72(2010) 31

Microstructural modifications and gradients
(Deliverable: Processing methods for graded microstructures)

Bell et. al., under preparation

Ray et.al., under preparation

Toughness, deformation and high T strength
(Deliverable: Optimizing strength via processing techniques)

Oxidative damage: mechanisms and models
(Deliverable: Establish and improve oxidative limits)

Finer screening

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

IOWA STATE UNIVERSITY

Enthalpies of multicomponent alloys

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

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

Individual binaries calculated using Miedema's equation

$$\Delta H = c_A c_B \left(f_B^A \Delta H_{AB}^{i/c} + f_A^B \Delta H_{BA}^{i/c} \right)$$
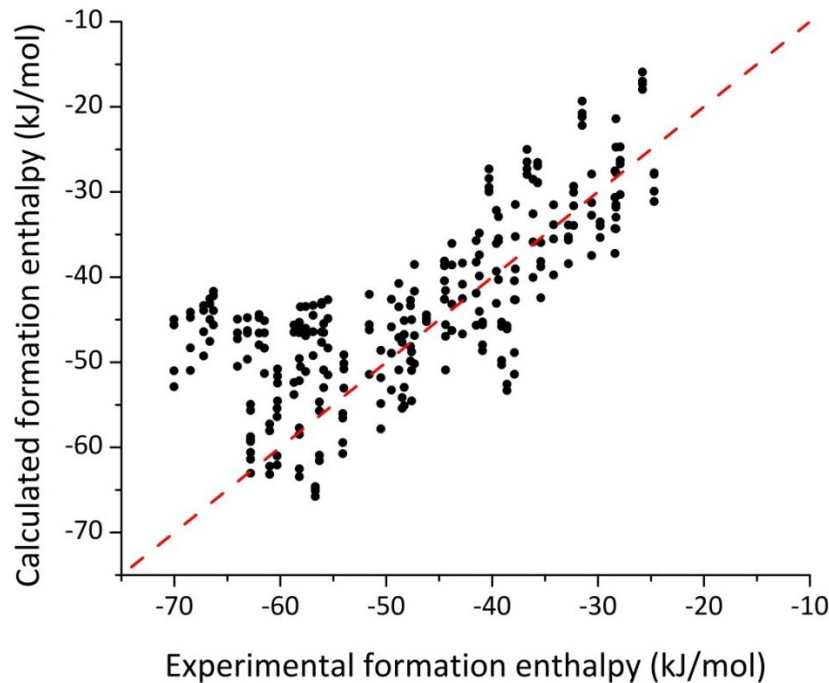
$$\sum_{i=1}^{3} \phi_i = 1$$

Mass balance constraints

$$\phi_1 \alpha + \phi_3 (1-\gamma) = x_A$$
$$\phi_2 \beta + \phi_1 (1-\alpha) = x_B$$
$$\phi_3 \gamma + \phi_2 (1-\beta) = x_C$$

Ray et.al., J. Alloys Compds. 62 (2010) 25

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

IOWA STATE UNIVERSITY

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

Passivating elements: Al, Si, Cr, Ga, Ge

Mo — Mo_3Al — Mo_7Ni_7 — $MoNi_{0.5}Al_{2.5}$ — Mo_5Al_{22} ht — Mo_4Al_{17} — $MoAl_{13}$ ht — Mo_3Al_8 — at.% Al — at.% Mo — L — Ni_2Al_3 — NiAl — at.% Ni — Ni_3Al — Al — Ni

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

IOWA STATE UNIVERSITY
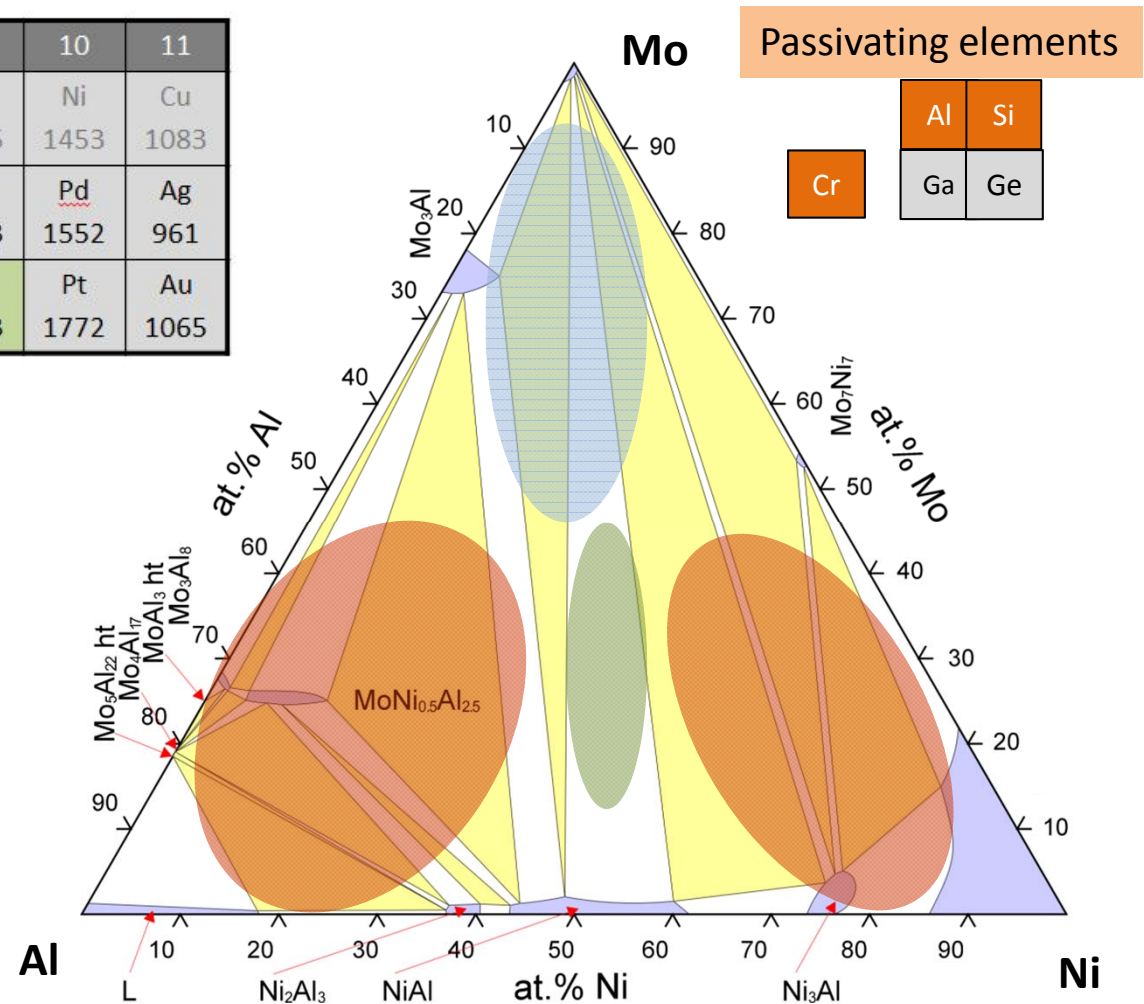
Processing and microstructures
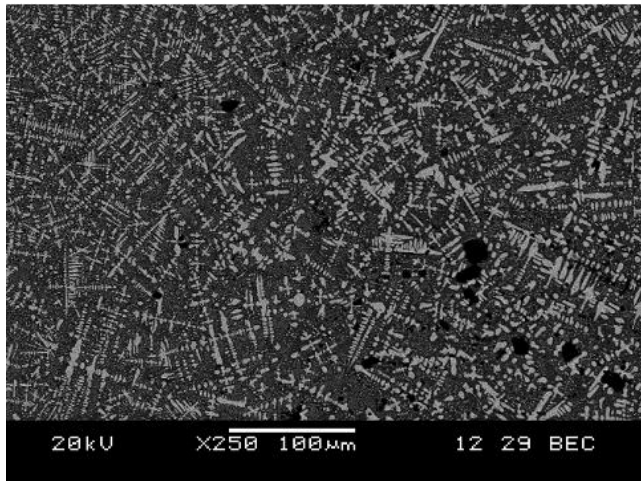
◀ Arc-melted

Directionally
solidified ▶
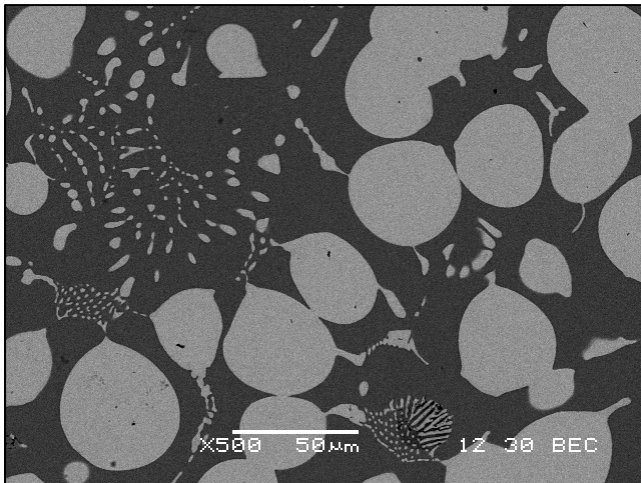
Liquid phase
sintered ◀
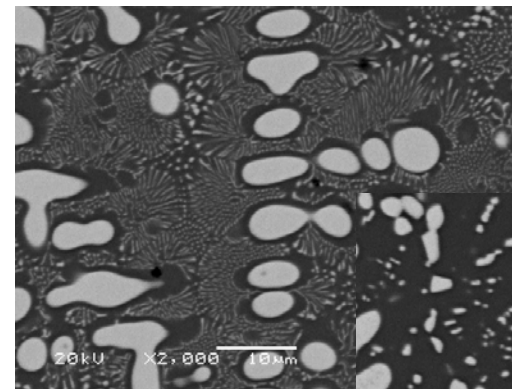
Stable microstructures
at 1500°C (12 hrs) ▶

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

IOWA STATE
UNIVERSITY
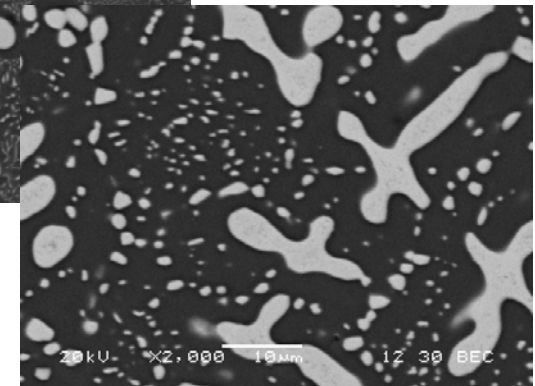
Fracture toughness of NiAl-Mo alloys

Mo forms the "backbone" for this alloy – creep and toughness

Toughness of NiAl ~ 5 MPa•m$^{1/2}$

Toughness of Mo-Si-B alloys ~ 12 MPa•m$^{1/2}$

Fracture toughness ascertained using four point bending method
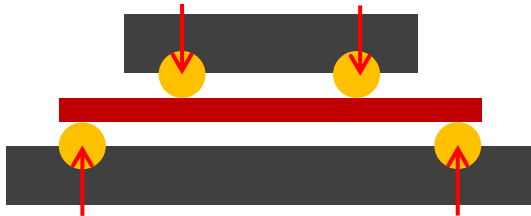
Force applied perpendicular to the growth direction [(0 0 1) direction]

Fracture toughness of NiAl-Mo alloys

Fracture toughness of NiAl-15%Mo [drop-cast] ~ 10 MPa•m$^{1/2}$

J. Kruzic, OSU

Fracture toughness of NiAl-15%Mo [DS] ~ 20 MPa•m$^{1/2}$

DS alloys shows a larger strain to failure
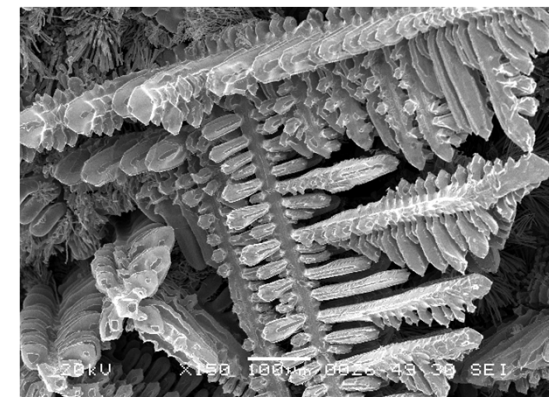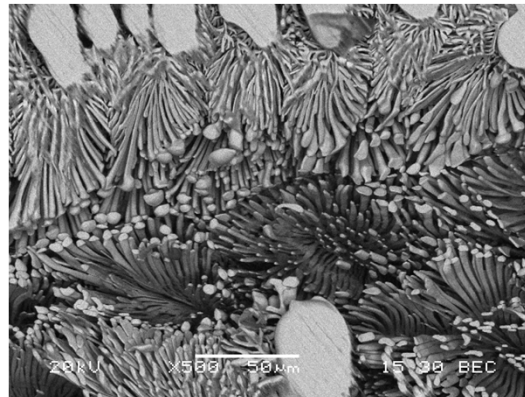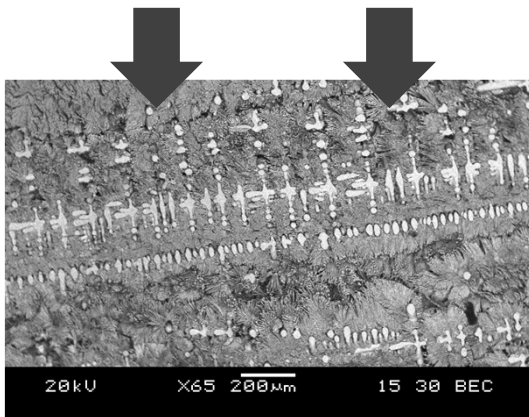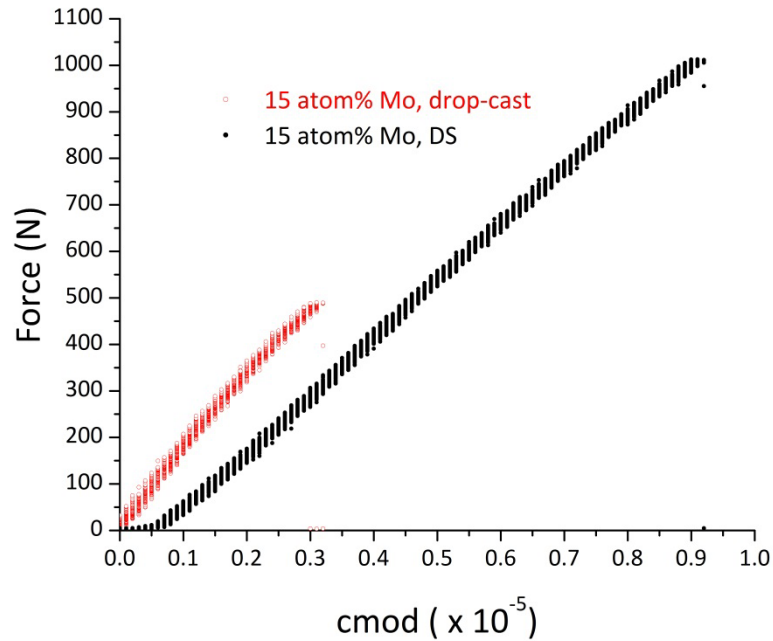
Flexural Strength
Drop-cast   ~ 400 MPa
DS alloys   ~ 850 MPa
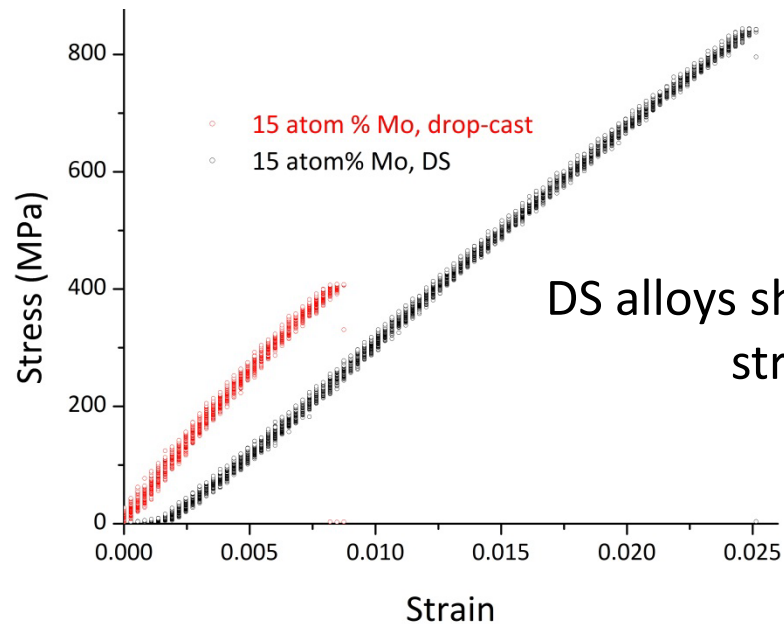
Fracture toughness of NiAl-Mo alloys
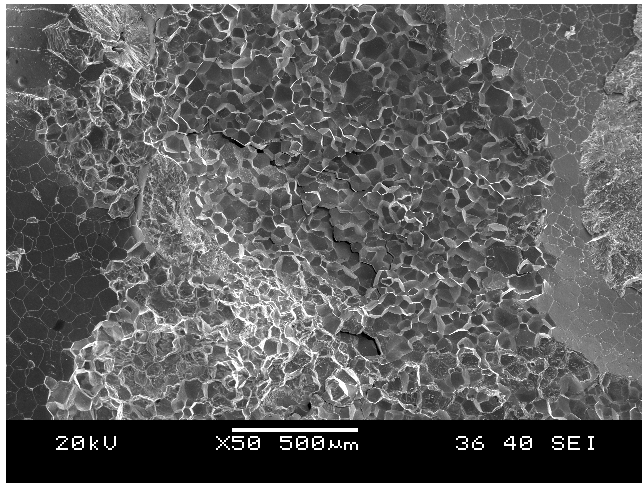
Fracture surface of drop-cast alloy ▲
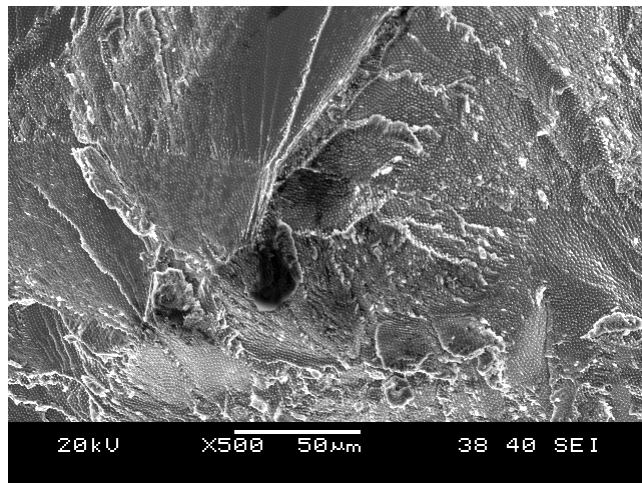
Fracture surface of DS alloy ▲

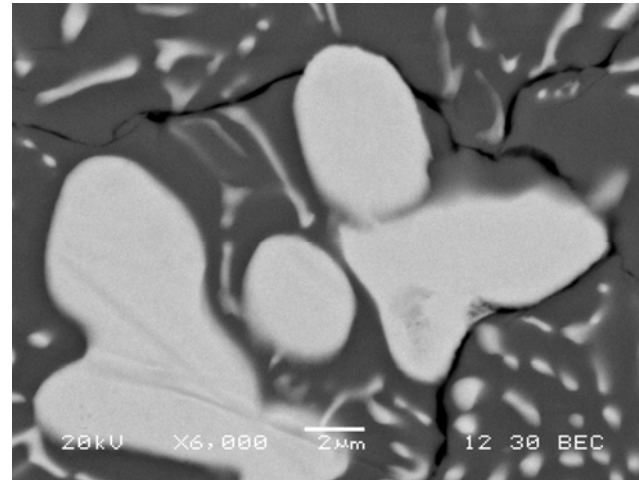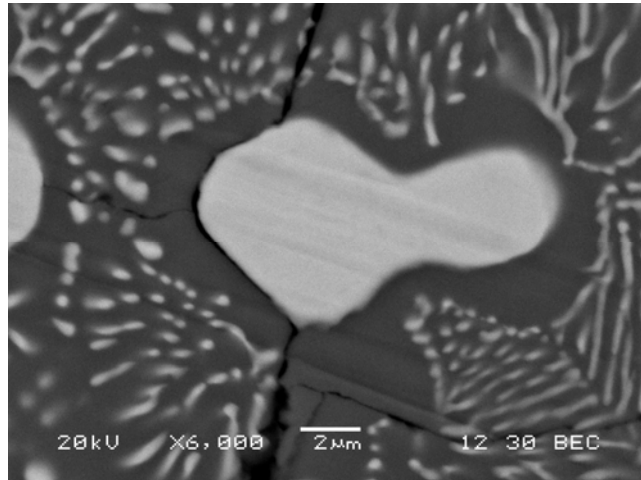Presence of Mo dendrite pull-outs ▶ indicate a contribution towards toughening
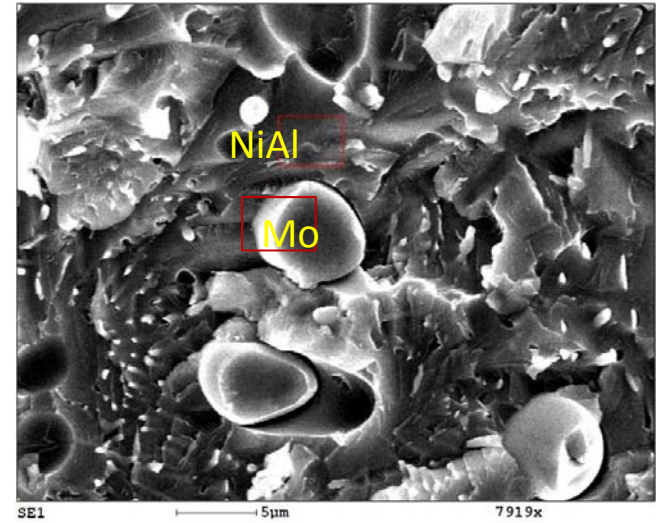
Some eutectic regions also showed the eutectic lamellae ▶ pull-outs
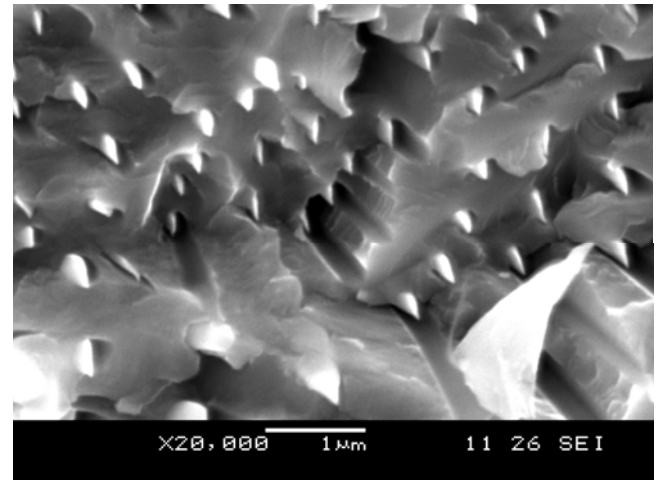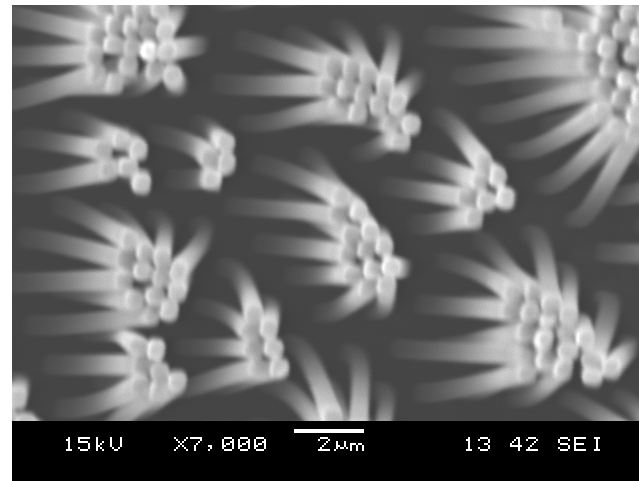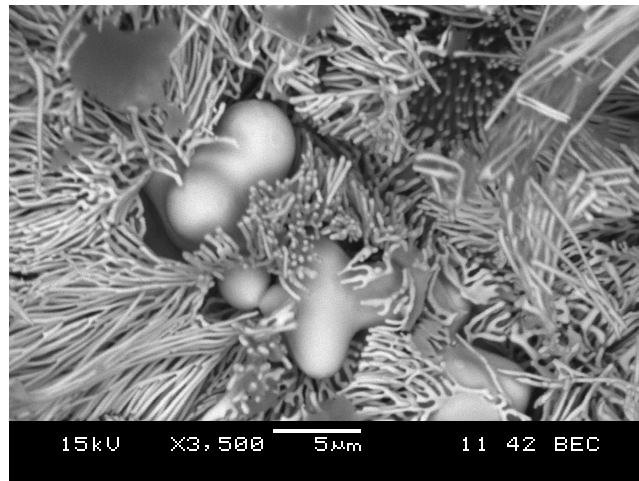

Bell et.al., article under preparation

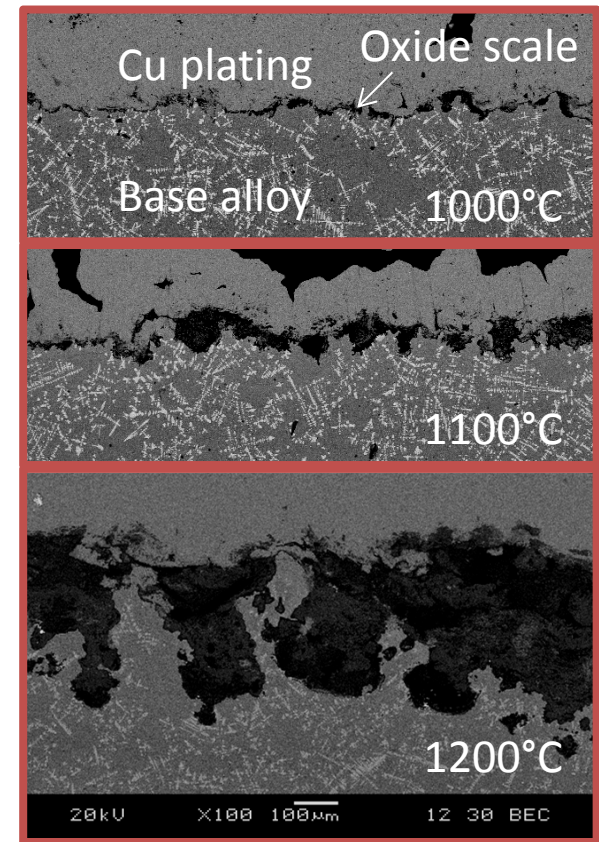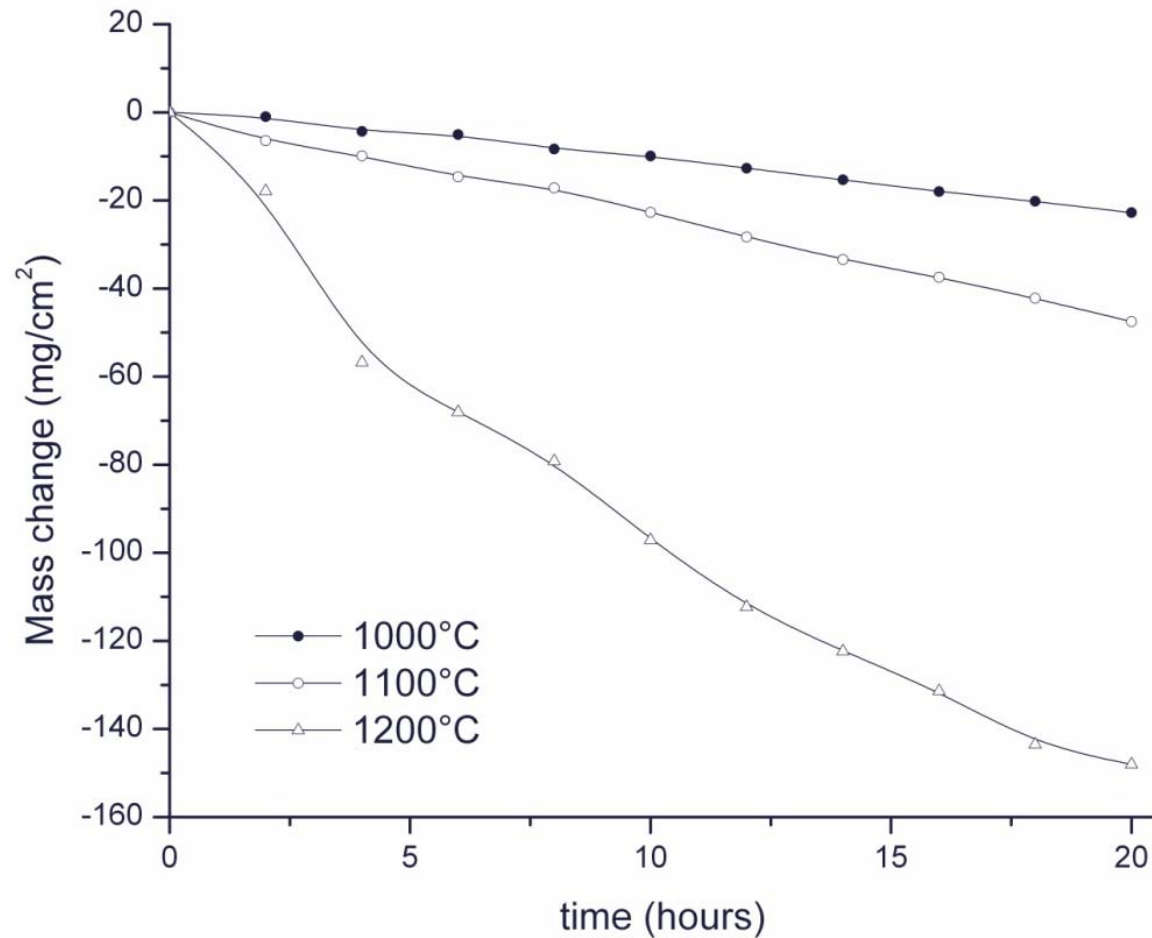# Fracture toughness of NiAl-Mo alloys

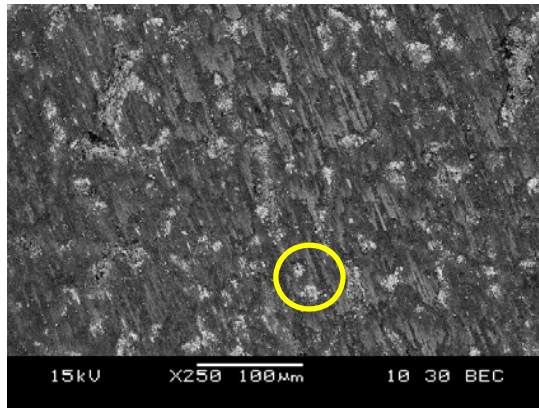◄ Mo serves to deflect crack path thereby imparting toughening

◄ Mo additions also appear to induce a small amount of plasticity
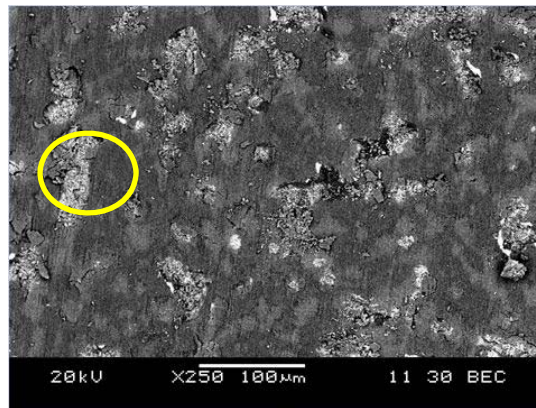
Effect of temperature on oxidation

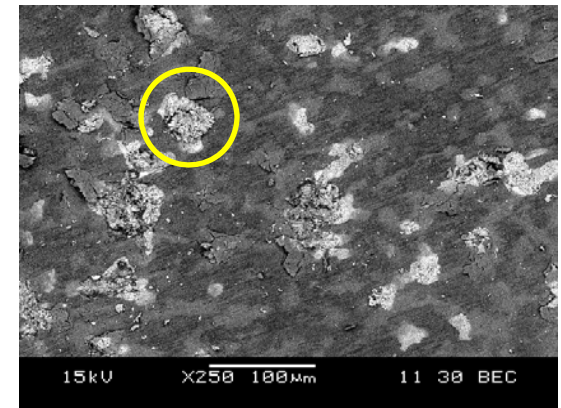Ray et.al., Appl. Surf. Sci. 301(2014) 107

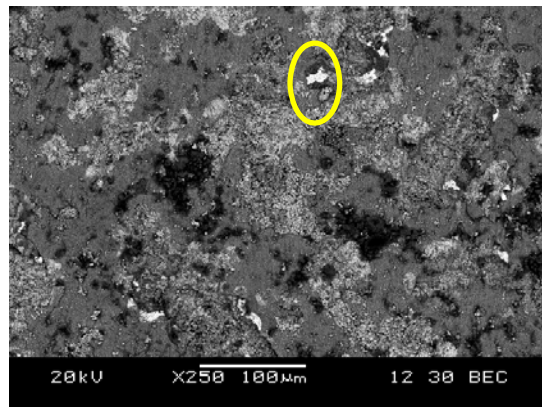# Evolution of the oxide scale with temperature

1000 °C

1075 °C
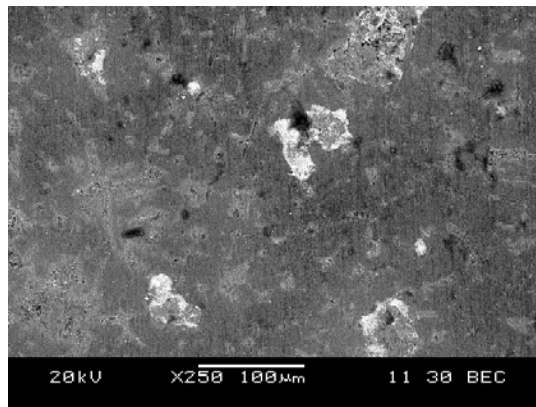

1100 °C

1125 °C

1200 °C

Oxidation time: 30 minutes

As temperature increases, $NiMoO_4$ regions grow larger, but they start disappearing above 1100 °C
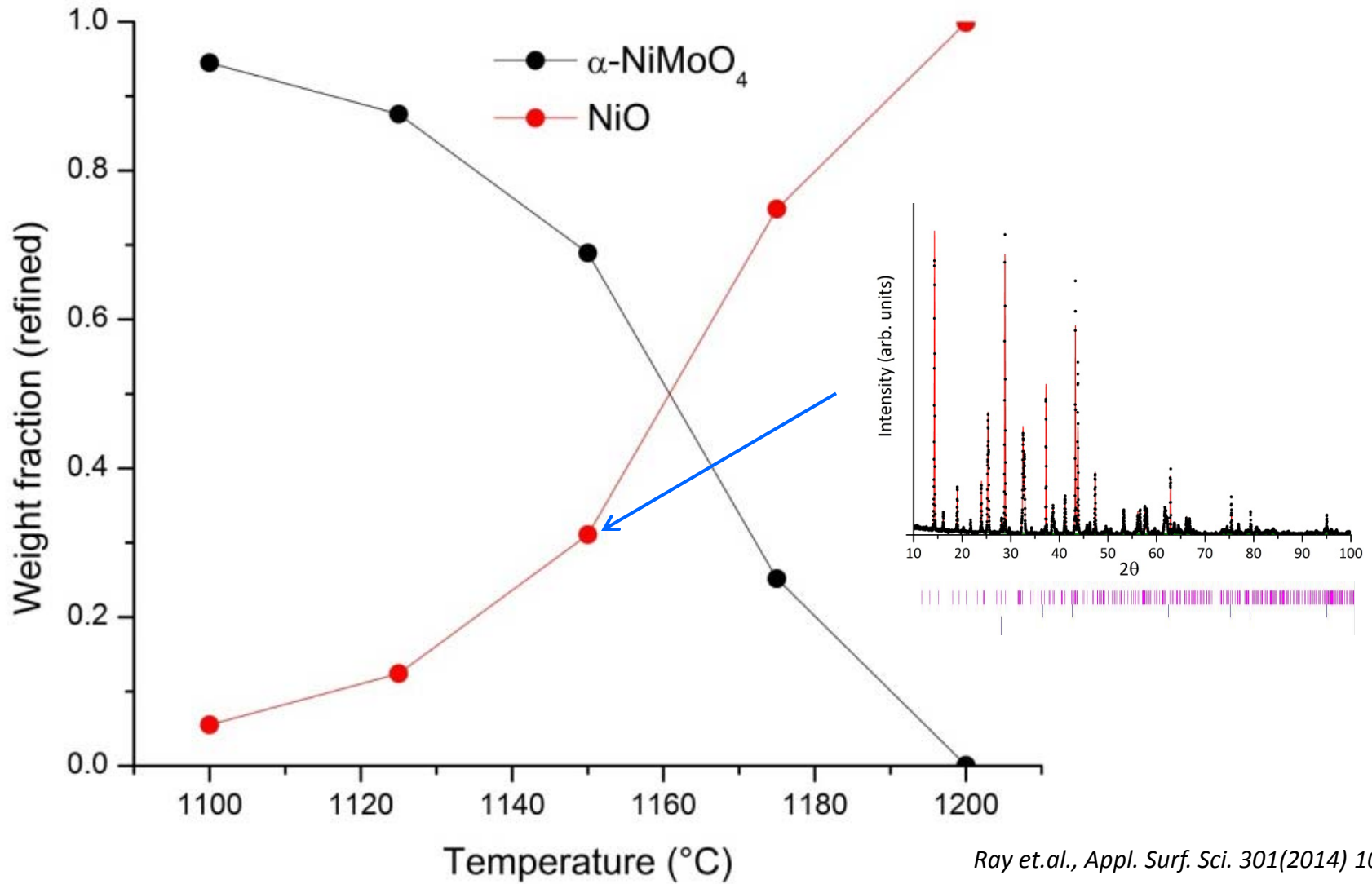
$NiAl_2O_4$ and NiO seem to predominate above 1125 °C

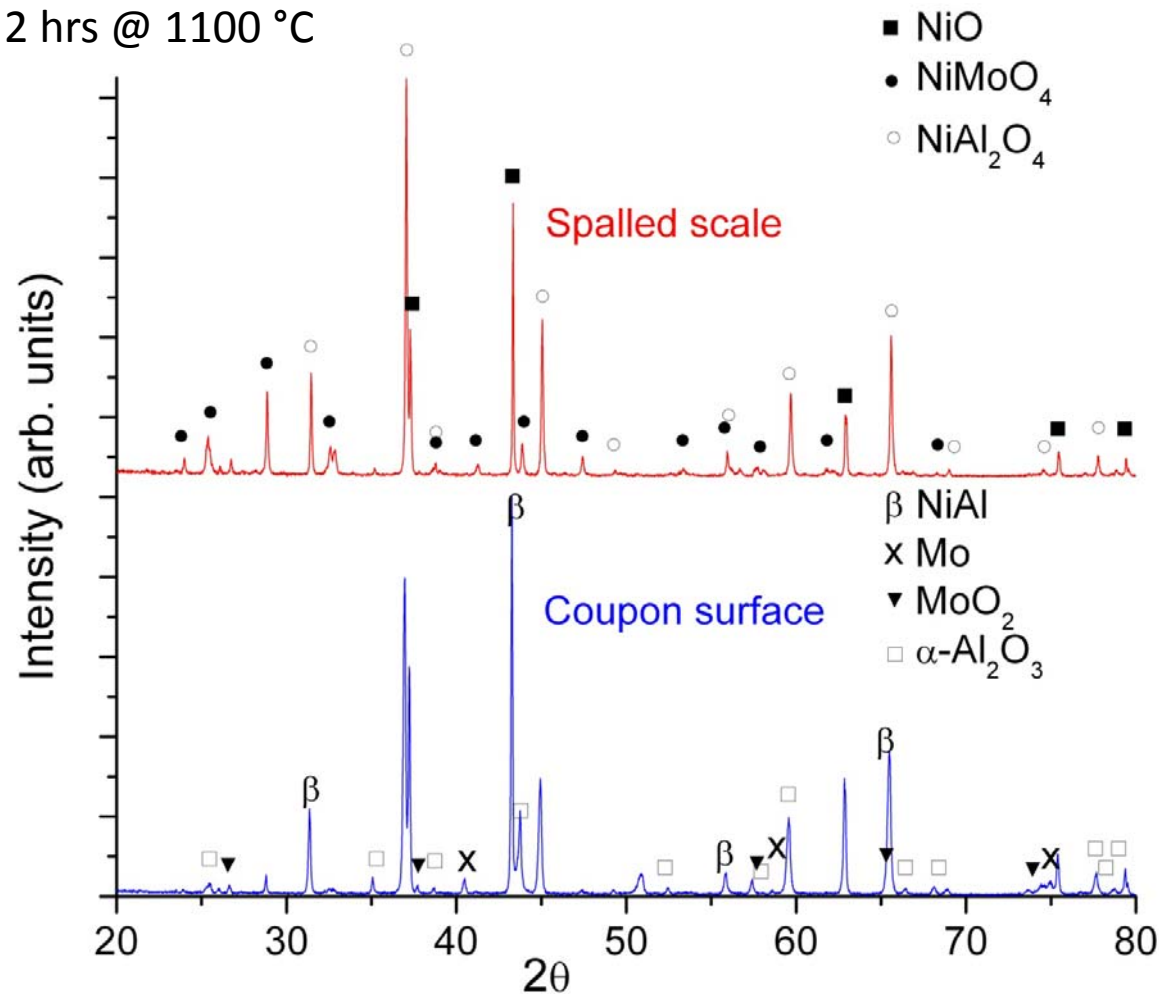# Stability of NiMoO$_4$

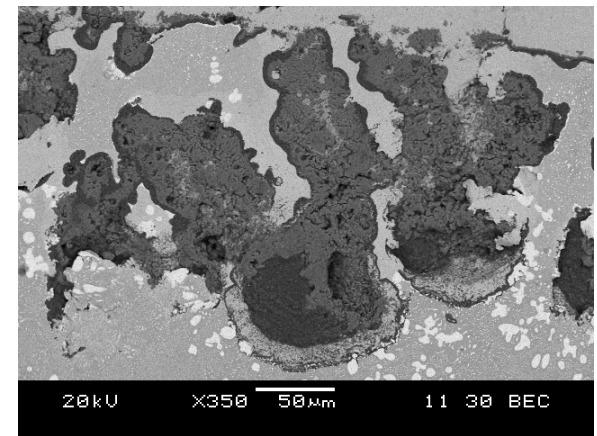Ray et.al., Appl. Surf. Sci. 301(2014) 107

Comparisons – spalled vs adherent scale

2 hrs @ 1100 °C

Legend:
- ■ NiO
- • $NiMoO_4$
- ○ $NiAl_2O_4$

Spalled scale

Coupon surface

- β NiAl
- x Mo
- ▼ MoO_2
- □ $\alpha\text{-}Al_2O_3$

Intensity (arb. units) vs 2θ

Major differences –
- o The amount of $NiMoO_4$ and NiO is drastically reduced in the coupon surface
- o The $\alpha\text{-}Al_2O_3$ and MoO_2 are virtually absent in the spalled scale.
- o $NiAl_2O_4$ shows up in both cases as a major phase.

20kU   X350   50μm   11 30 BEC

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

A physical model for oxidation

Al$_2$O$_3$

NiO

Al$_2$O$_3$

NiAl

NiAl$_2$O$_4$

NiMoO$_4$ dissociates progressively

NiMoO$_4$ → NiO + MoO$_3$

The NiO reacts with the underlying Al$_2$O$_3$ to form the spinel interphase

NiO + Al$_2$O$_3$ → NiAl$_2$O$_4$

NiMoO$_4$ dissociates: poor oxidation;
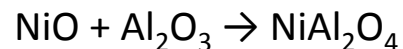NiMoO$_4$ doesn't dissociate: β→α transformation with 20% volume change

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$_2$ → MoO$_3$

NiMoO$_4$ forms at the interface along with alumina

2MoO$_3$ + 2NiAl + 3/2O$_2$ → 2NiMoO$_4$ + Al$_2$O$_3$
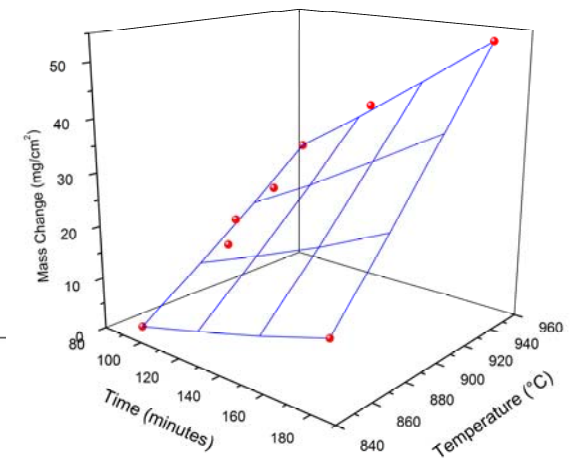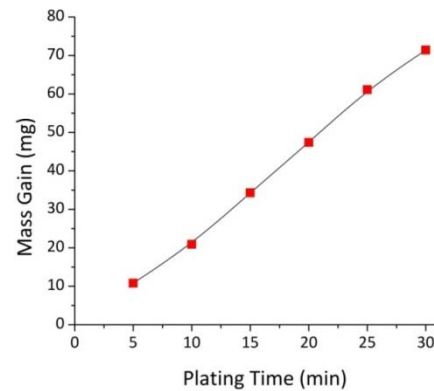
Ray et.al., article under preparation
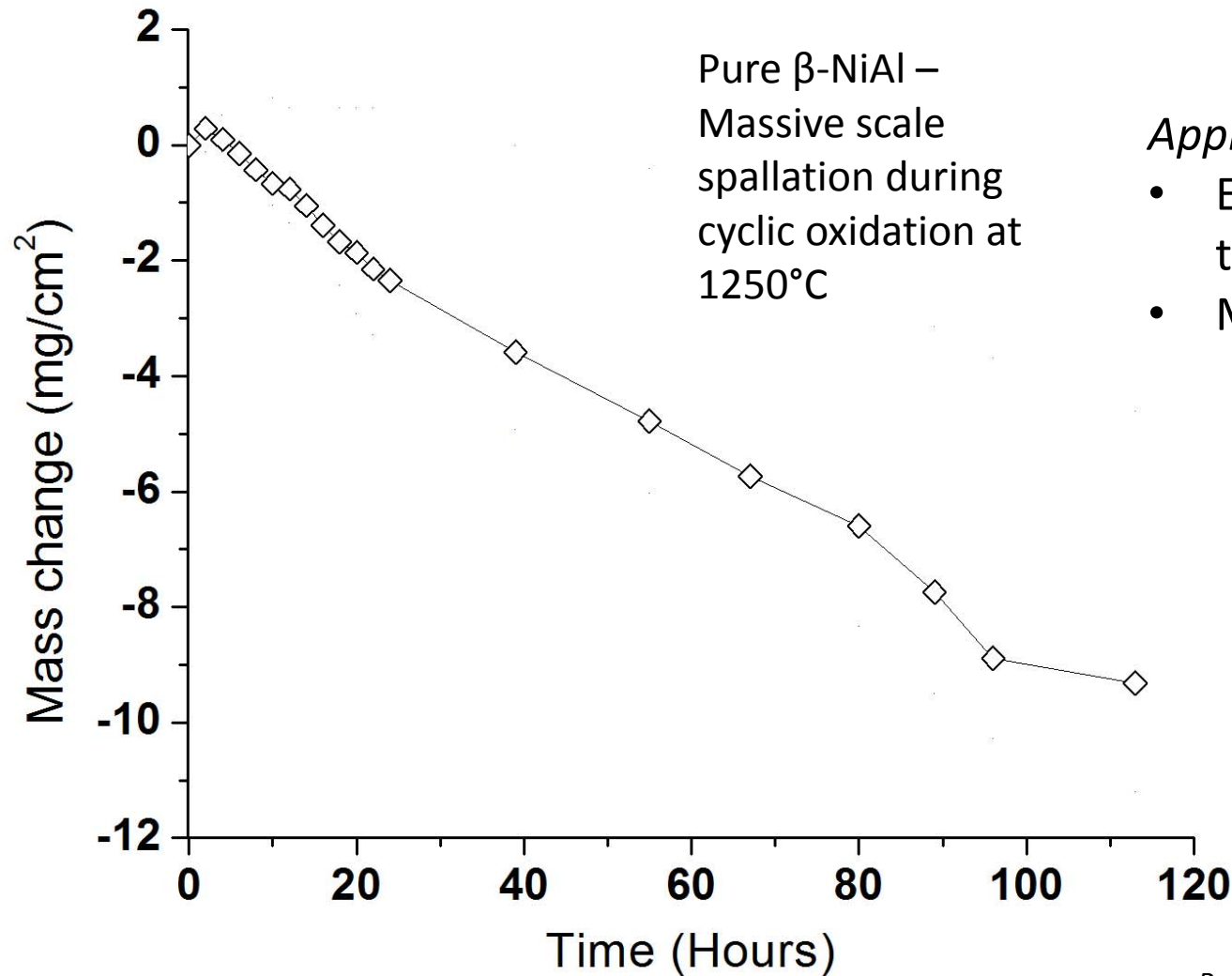
Coating methodologies
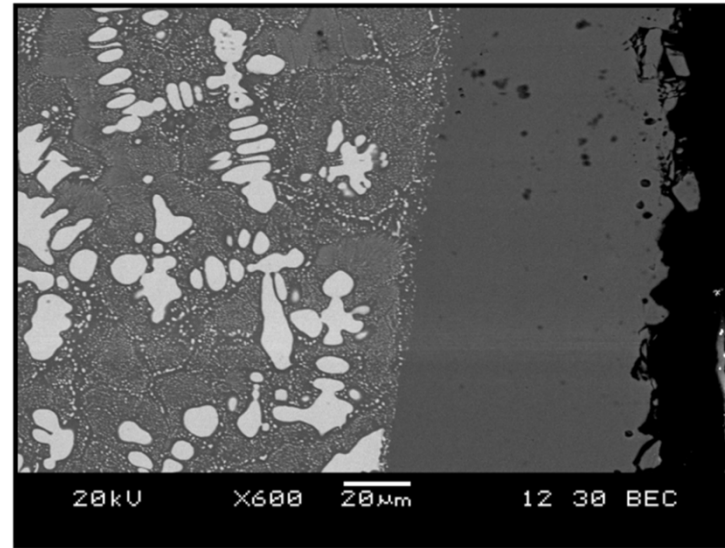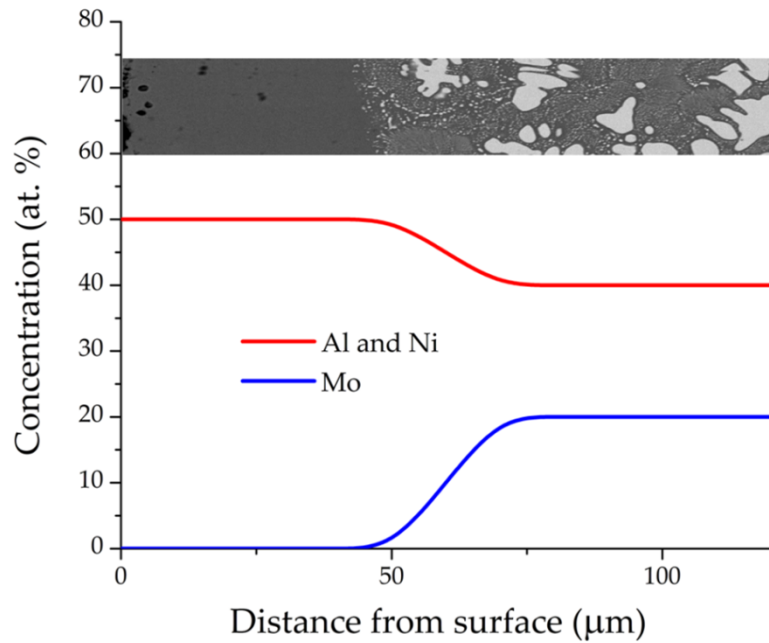
Coating process: Electrodeposition(Ni) and pack cementation (Al); anneal at 1350°C for 2 hours

Accurate statistical models of electroplating and pack cementation for controlling thickness

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

IOWA STATE UNIVERSITY

Oxidation of NiAl

Pure β-NiAl –
Massive scale
spallation during
cyclic oxidation at
1250°C

Approaches –
- Enhanced melting temperature
- Microstructure

Ray et.al., JOM 62 (2010) 65

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

IOWA STATE UNIVERSITY

Alloying additions: computational screening

Brammer et.al., Adv. Sci. Tech. 72 (2010) 31
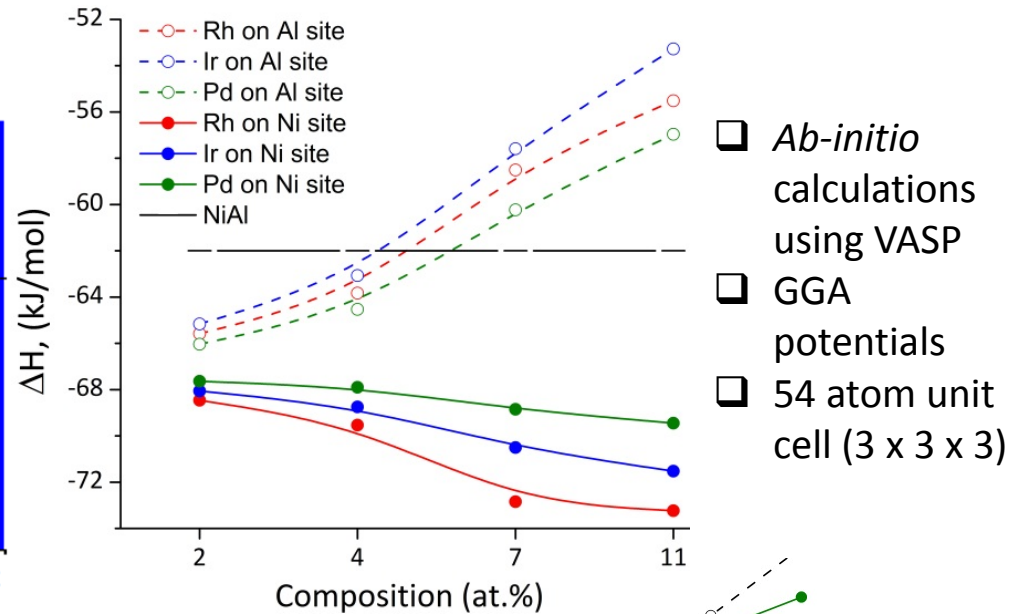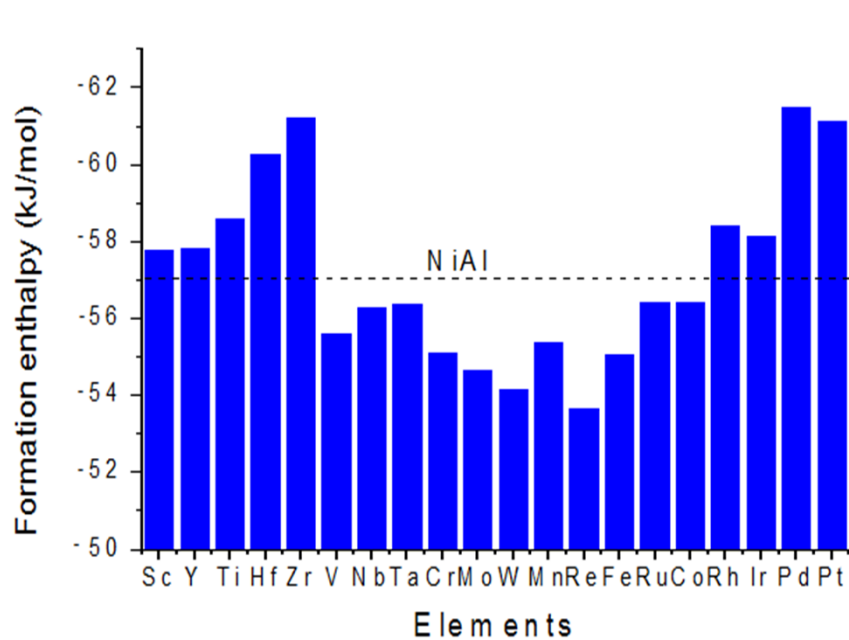
❑ *Ab-initio* calculations using VASP
❑ GGA potentials
❑ 54 atom unit cell (3 x 3 x 3)

$$T_m = 0.032 \frac{E^c}{k_B}$$

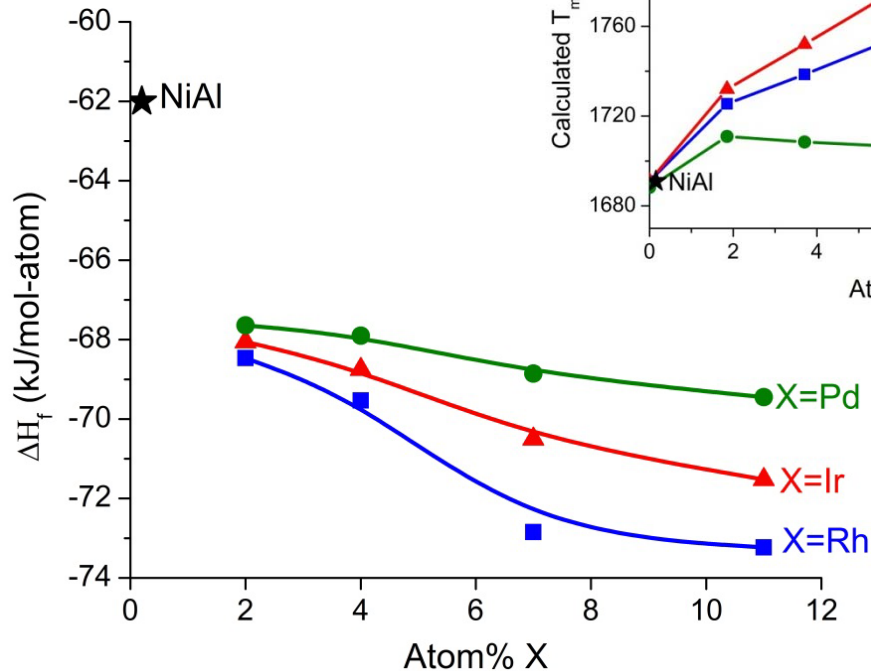Rose-Ferrante theory of Universal Binding Curve
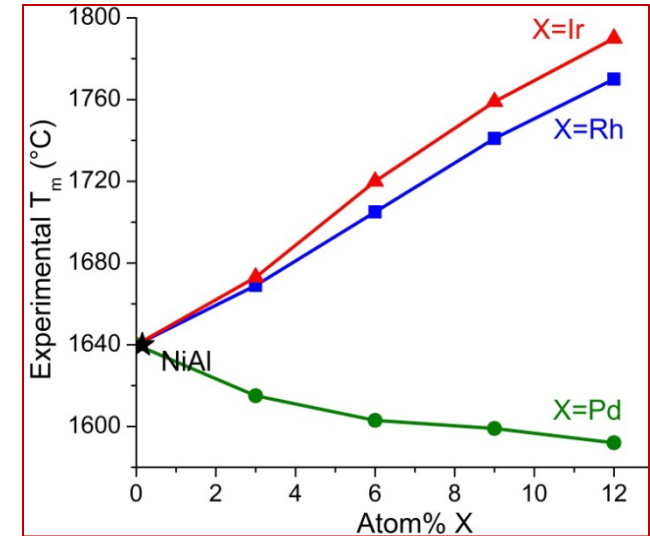
$$E^c = x_1 E_1^c + x_2 E_2^c + x_3 E_3^c - \Delta H_f$$
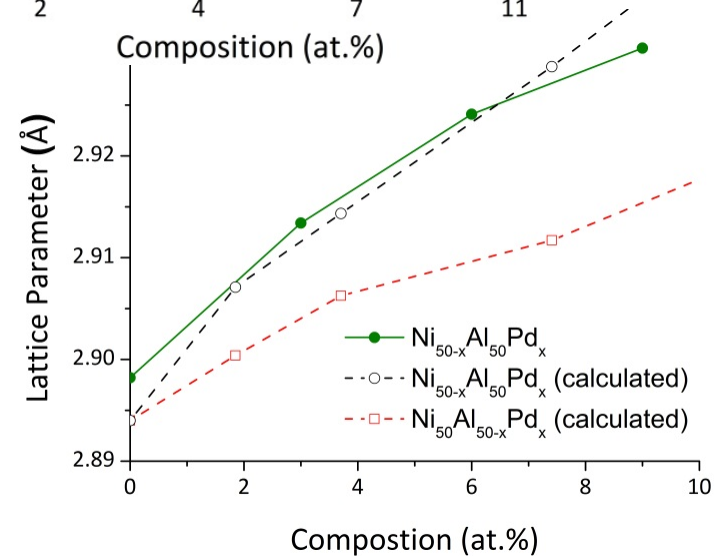
Ab-initio studies on the role of PGM additions

$$T_m = 0.032 \frac{E^c}{k_B}$$

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

Formation enthalpies estimated using the VASP code with GGA potentials
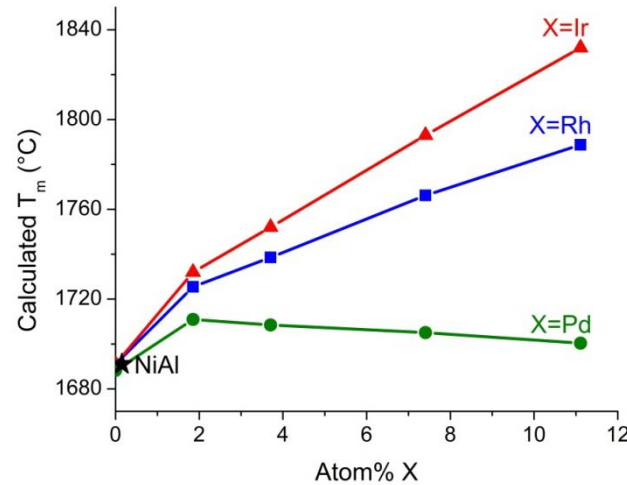
Metal	Cohesive E (kJ/mol)	Metal	Cohesive E (kJ/mol)
Al	327	Ir	670
Ni	428	Pd	376
Rh	554		

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

IOWA STATE UNIVERSITY

Effect of PGM additions on oxidation
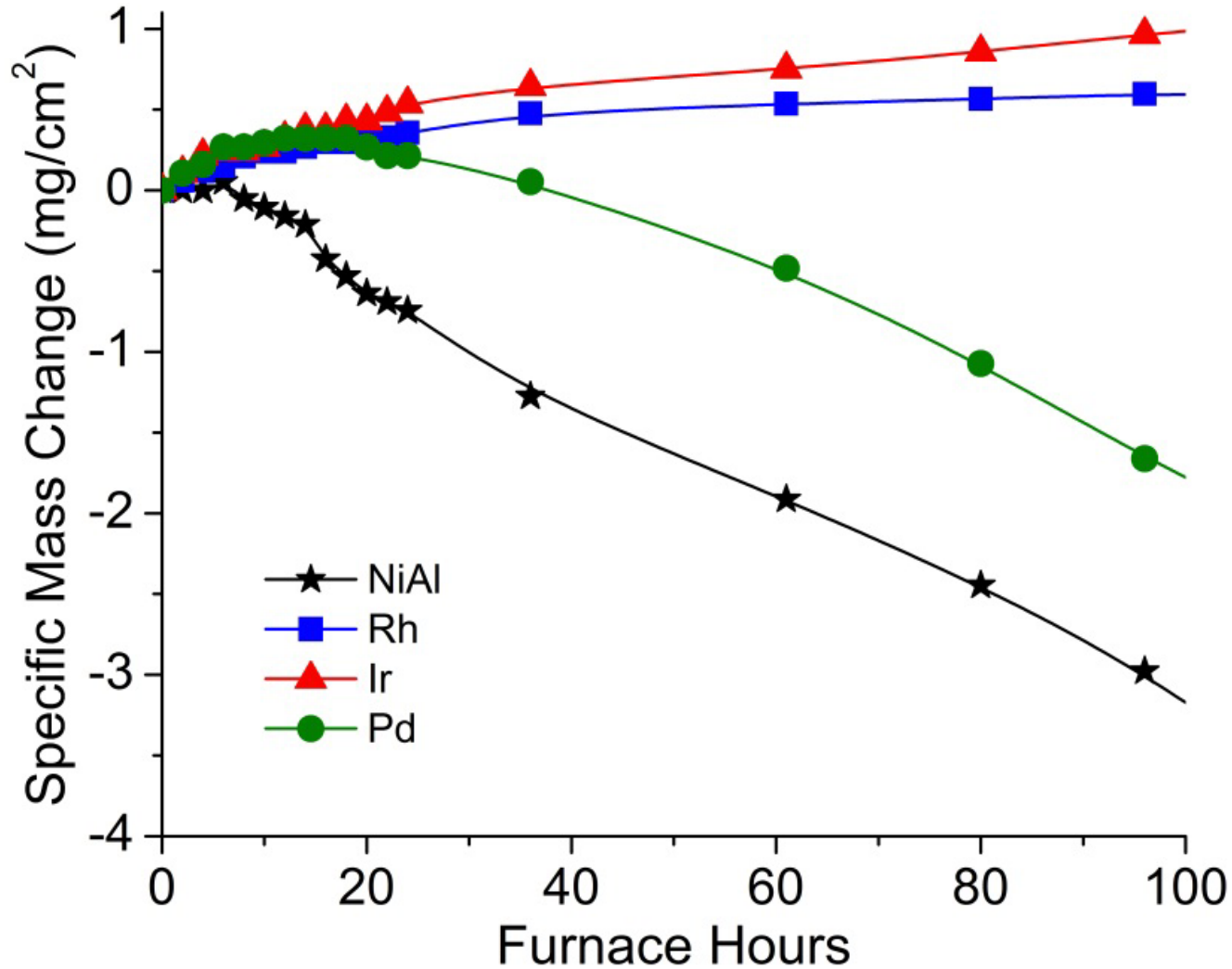
Pure β-NiAl –
Massive scale
spallation during
cyclic oxidation at
1250°C

Addition of 6 atom%
of PGM results in a
significant increase
in the oxidation
resistance

Ray et.al., JOM 62 (2010) 65

The role of grain size

β-NiAl

β-NiAl + 9% Ir

β-NiAl + 9% Ir + 0.05% Hf
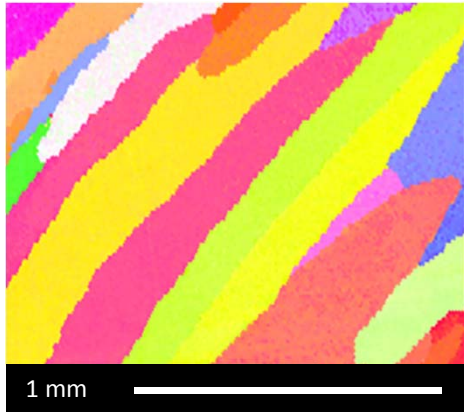

β-NiAl + 9% Ir after 100 hours at 1300°C

β-NiAl + 9% Ir + 0.05% Hf after 100 hours at 1300°C

1150°C   1200°C

y-axis: $mg^2 \cdot cm^{-4} \cdot s^{-1}$

■ As-cast (635 μm)

■ Melt-spun (126 μm)*

After annealing for 6 hours at 1350°C
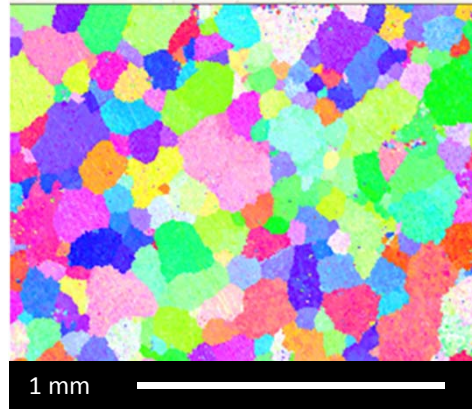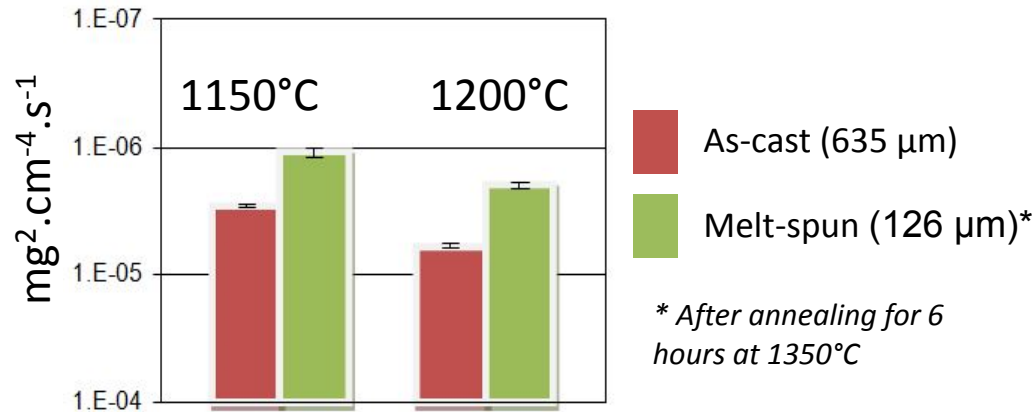
Brammer et.al., article under preparation

Failure mechanisms for the coatings
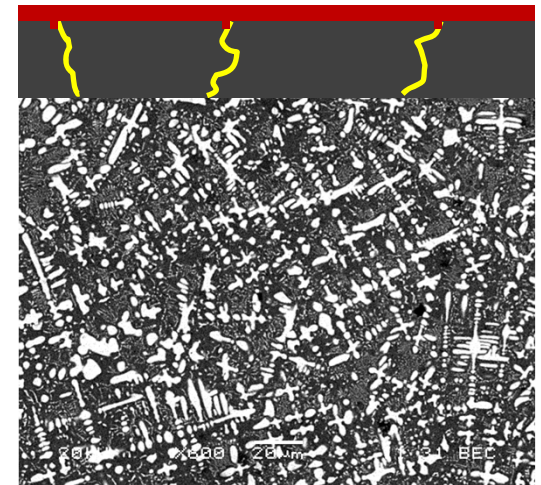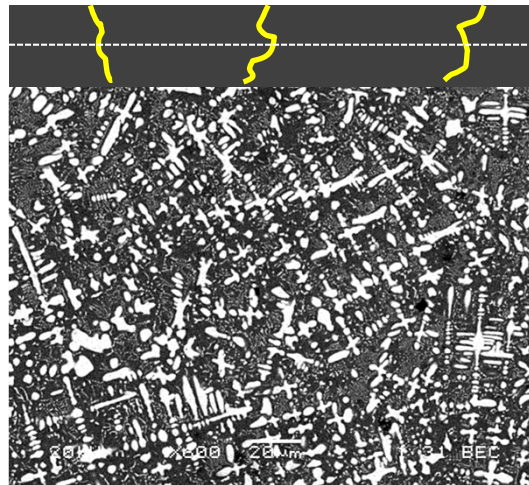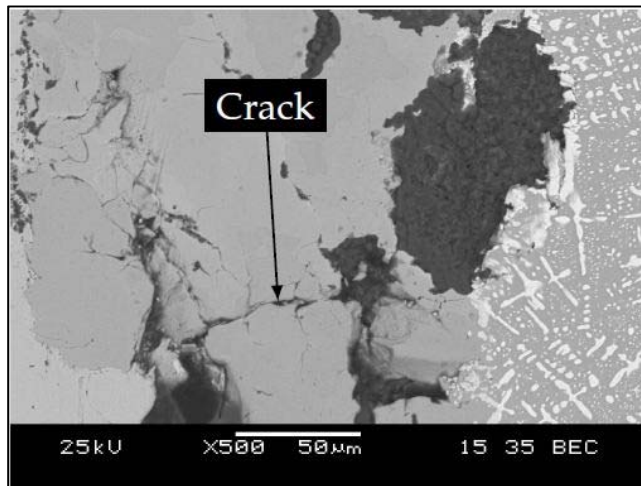
- Pre-existing cracks provide oxidation pathways.
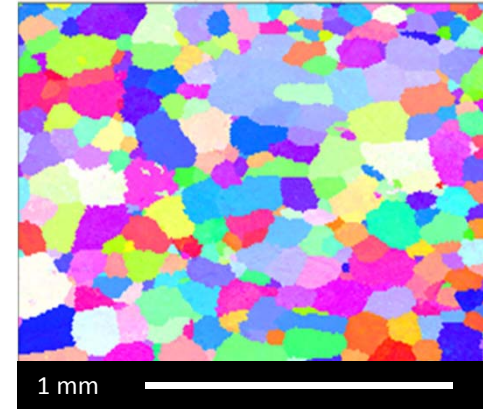- Integrity is a function of NiMoO$_4$ formation vs Al$_2$O$_3$ coverage.

- T dependence is function of Al$_2$O$_3$ growth rate and MoO$_3$ vapor pressure

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

IOWA STATE UNIVERSITY
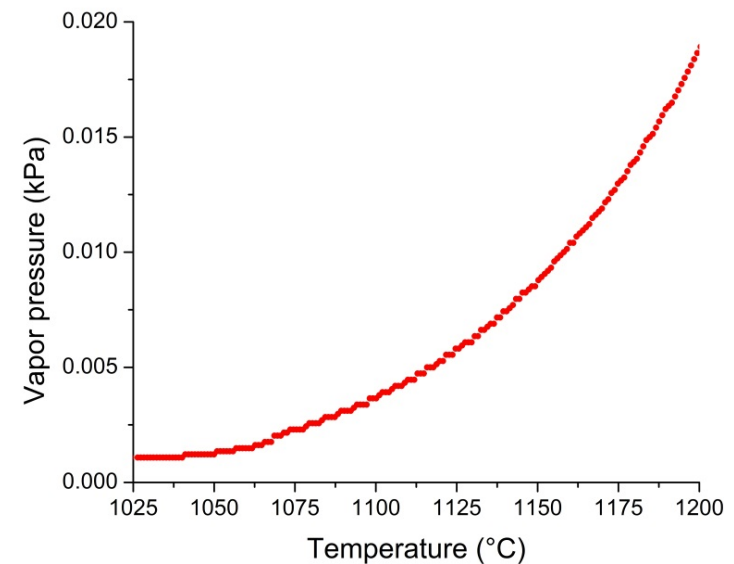
Oxidation behavior of coated alloys 1150°C
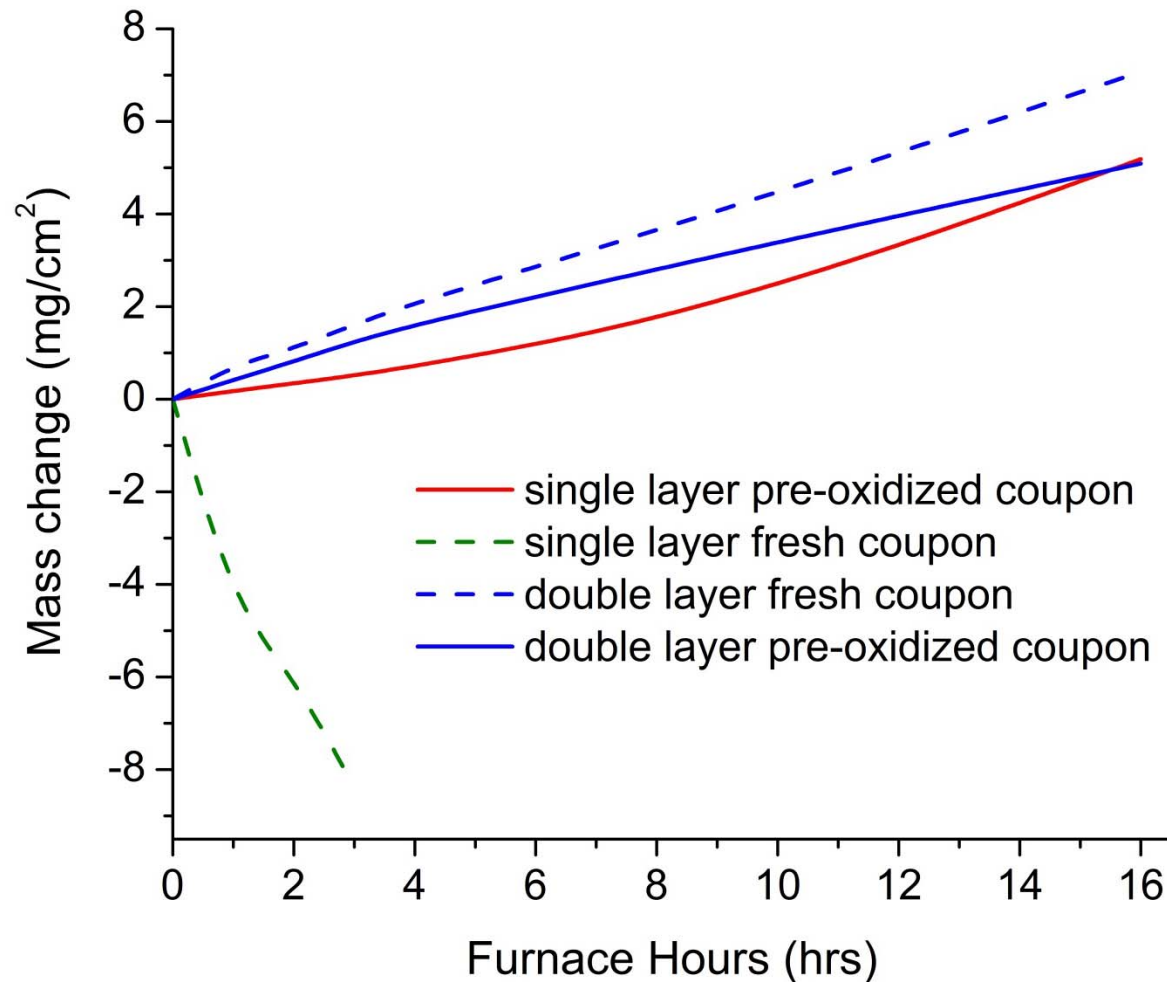
Optimal coating approach:

Double layered coatings

Pre-oxidized at 1100°C for 5 hours

Bell et.al., article under preparation

Perspectives

- Semi-empirical techniques assisted in initial selection; further work resulted in an alloy with high melting temperature and adequate toughness, with oxidatively stable coatings.

- Computational methods were not used for down-selecting materials on the basis of oxidation resistance, due to a relatively small playground once criteria for high melting temperature and tough "backbone" phase were fulfilled

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

IOWA STATE UNIVERSITY

Expanding the toolbox

- Need for more accurate models for materials genomics, especially with multiple principal components which presents a greater complexity of challenges

- Standard DFT based approaches are more suited to ordered materials rather than disordered solid solutions like HEAs

- Looking ahead – use computational tools for oxidation resistance, while selecting alloy systems that retain structural stability with temperature (Entropically Stabilized Alloys – studied using KKR-CPA) when oxidized (system selection using new computational tools – GSSNEB)

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

IOWA STATE UNIVERSITY

Short Range Ordering in N-component Alloy

- Atomic SRO can be calculated using *all-electron, first-principles KKR-CPA-based linear-response code* addressing inhomogeneous chemical fluctuations.

- We can uniquely identify atomic SRO in alloy using Concentration Wave analysis using an analytic N-dimensional transform for Gibbs' (chemical) space.

- Approach was tested and verified on

  - Ternary A2 (bcc) $Nb_{25}Al_{25}Ti_{50}$
  - Quinary A1 (fcc) $Ni_{20}Cu_{20}Al_{20}Ti_{20}Zr_{20}$

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

IOWA STATE UNIVERSITY

Ti$_{50}$Nb$_{25}$Al$_{25}$: SRO unstable eigenmodes

SRO indicate the unstable chemical modes
All mode determined simultaneously,
just like for (second-order) phonon modes.

Lowers energy

Costs energy

Alloy-specific partially-ordered B2 phase

Nb/Al   <111>

A2 phase   H → Ti   B2
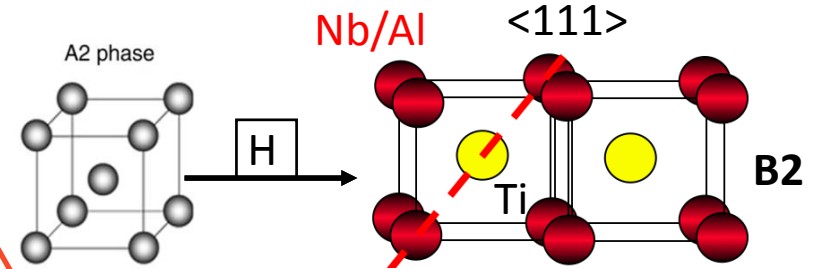
Strong partially-ordered B2 (H-pt) ordering

First unstable mode (H-point)
k$_0$ → <100> = <111>

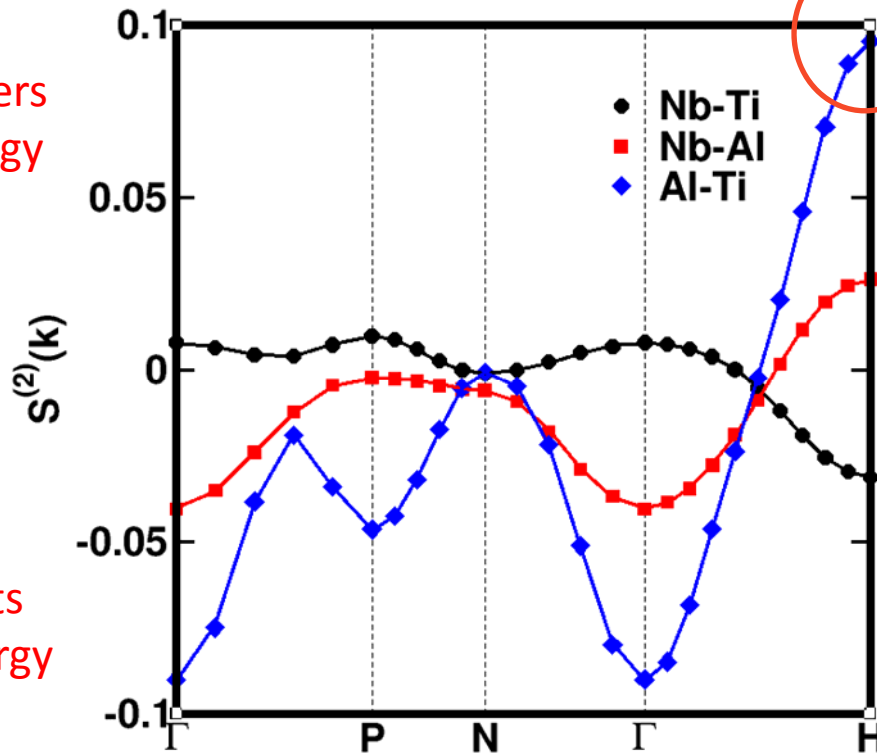**Temperature Scale**
Theory spinodal   T$_{sp}$ = **1750 K**
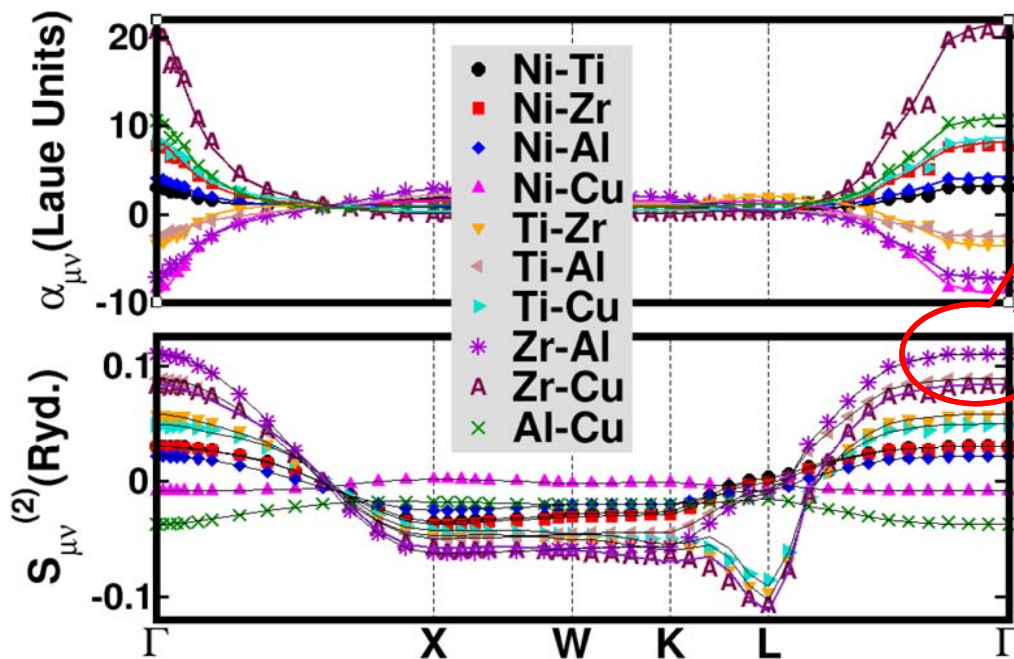Experimental B2 order: **1713 K**

D.D. Johnson et al., Phil Mag. Lett 79, 551 (1999)

SRO in Quinary NiTiZrAlCu

Direct Calculation KKR-CPA
Formation Energy = +16.4 mRyd
T_c = 1610 K

Experimental findings – HEA by MA, multiphase intermetallics by casting

SRO: k_0 = [000] Clustering
SRO: Unstable Modes (Zr-Cu)
$S^{(2)}$: competing Zr-Al, Zr-Cu, Ti-Al
T_{sp} = 1510 K (estimated)

Real Space decomposition of $S^{(2)}$ upto 5-shells.

Shell$_{RS}$/Modes	Zr-Al	Zr-Cu	Ti-Al
$S_0^{(2)}$	+10.4	+9.39	+8.55
$S_1^{(2)}$	-0.07	+2.37	-0.55
$S_2^{(2)}$	-0.01	-1.92	-0.05
$S_3^{(2)}$	-0.10	-4.27	+0.12
$S_4^{(2)}$	-0.01	+0.50	-0.01

Kinetic Barriers for MnBi: HTP to LTP

Nudged elastic band (NEB)
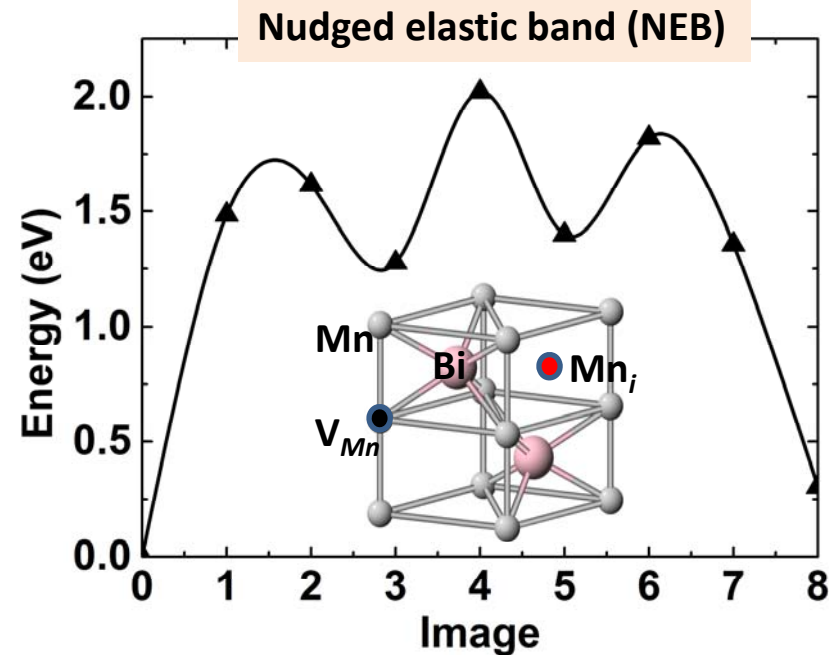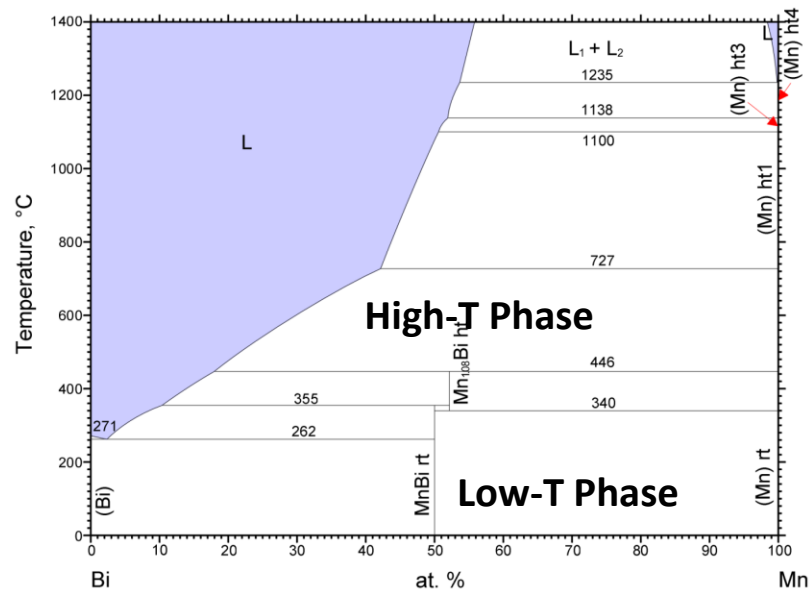
- In HTP, interstitial Mn couples anti-ferromagnetic and reduces magnetization
- Interstitial-vacancy pair (Mn_i-V_{Mn}) only costs 0.3 eV when separated by 1 atom.
- Barrier in between is as high as 1.7-2 eV, which limits kinetic for HTP → LTP
- Kinetically stable HEA desirable for mechanical properties.

Summary

"*Explore the development of graded oxidation resistant microstructures with high-entropy precursors*"

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

IOWA STATE UNIVERSITY