Improving Aluminide Bond Coat Performance: Optimizing Composition and Understanding Co-Doping Effects

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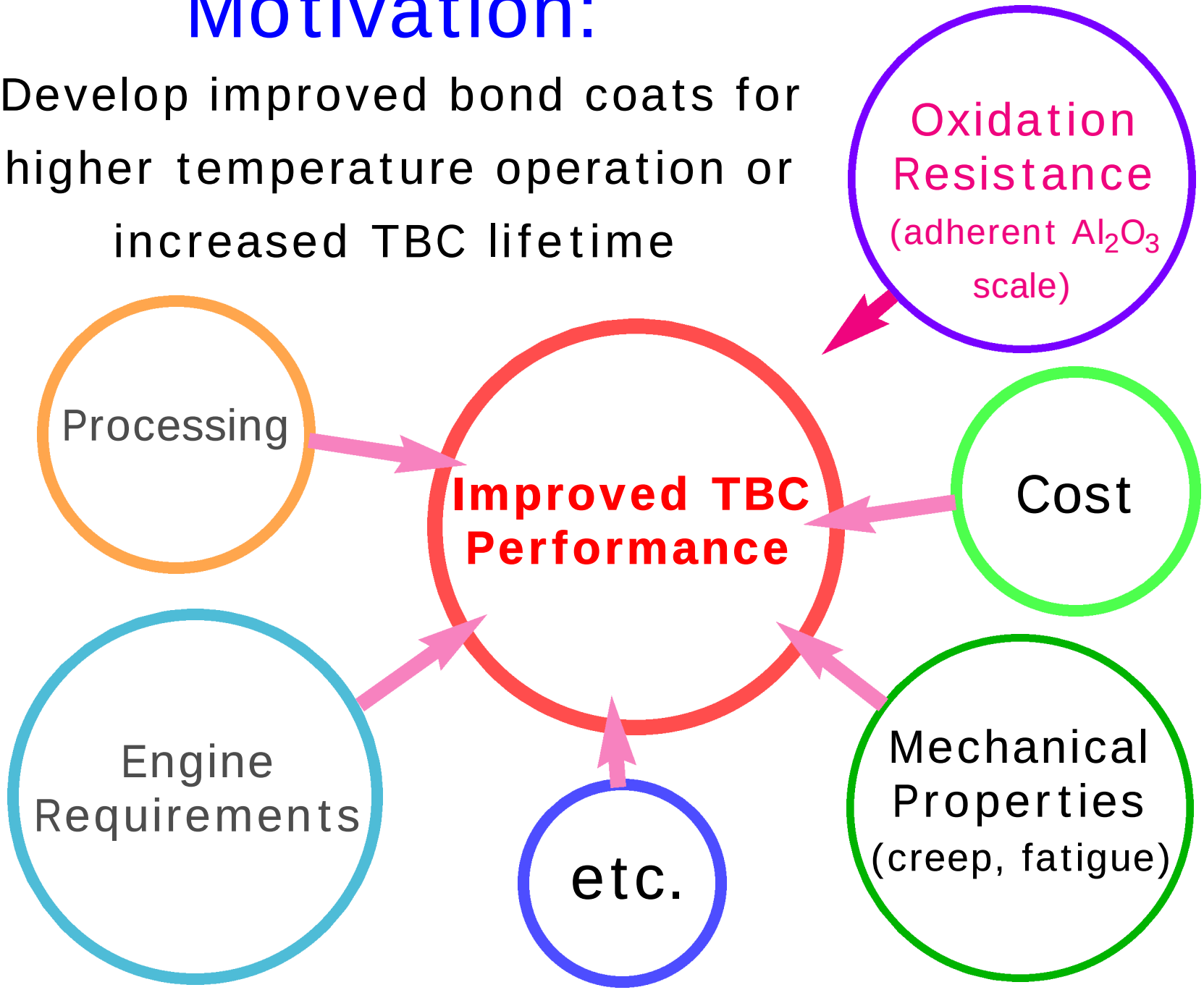
  Joe Doychak "take a look at Hf, it worked really well" 1994
  Jim Smialek "you are going to have to optimize each addition in order to compare them" 1993

- Thomas Edison (for setting example of common sense research)

Motivation:

Develop improved bond coats for higher temperature operation or increased TBC lifetime



Experimental Strategy/Procedure

Make castings to study composition effects

- feed information into coating research (Haynes/Zhang)

Castings:

≈400g water-chilled copper molds, ≈15mm diameter

ICP & Combustion analysis

anneal 1300°C 4h

Oxidation tests:

specimens polished to 0.3µm

contained :alumina crucibles, box furnace, air-> total mass

uncontained : hanging by wire in tube furnace -> specimen mass

automated thermal cycling rig based on NASAdesign

Characterization including:

Cu-plate prior to metallographic sectioning

Field-emission gun SEM

TEM sample preparation by Focused Ion Beam (FIB)

High-Temperature XRD - alloy phase composition

How to improve aluminide bond coat performance:

- starting from Pt-modified low activity (one phase) by CVD

1. Add a reactive element (RE) -> Hafnium is best!

   (Adding Hf: Howmet, W. Lee at Stevens Institute)

2. Keep the Pt

   Hf improves scale adhesion

   but Pt improves selective oxidation

Interdiffusion with substrate: (diffusion barrier?)

3. Increase Al in coating (or reduce loss to substrate)

   Hf can't help problems of Ni_3Al

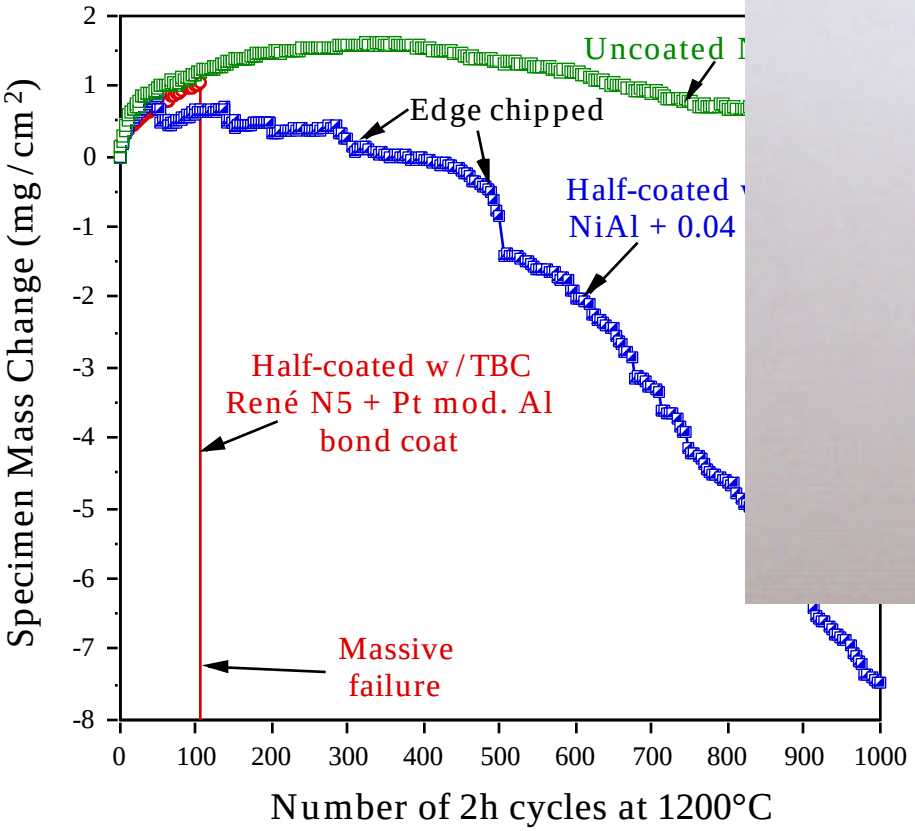
4. Decrease elements from the substrate

   Other elements diffusing into coating diminish

   the Hf benefit

RE + high Al :1 fe!

EB-PVD TBC, furnace C



edge

EB-PVD, 125 μm (5mil)

β-NiAl+0.04at%Zr

Using NiAl+Zr as the substrate - an adherent alumina former

Commercial Pt-modified aluminide coating on René N5 life = **106** cycles

On NiAl+Zr, 20% of face has not spalled after **1000** 2h cycles

- mass loss from edge spallation
- test began in 1995 (coating from Nagaraj, GEAE), ended in 2000

Hf-modified Aluminide Bond Coat

Material selection:

why aluminides?

why Hafnium?

does it need Pt?

Base casting: NiAl+0.05at%Hf

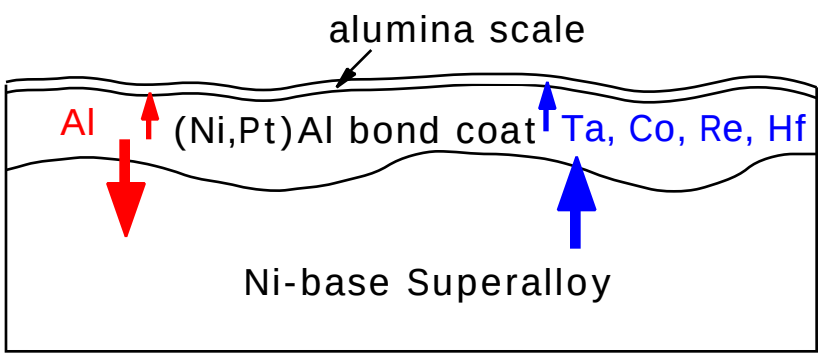
Practical problems:

substrate elements

hot corrosion

Al content + depletion

diffusion barrier

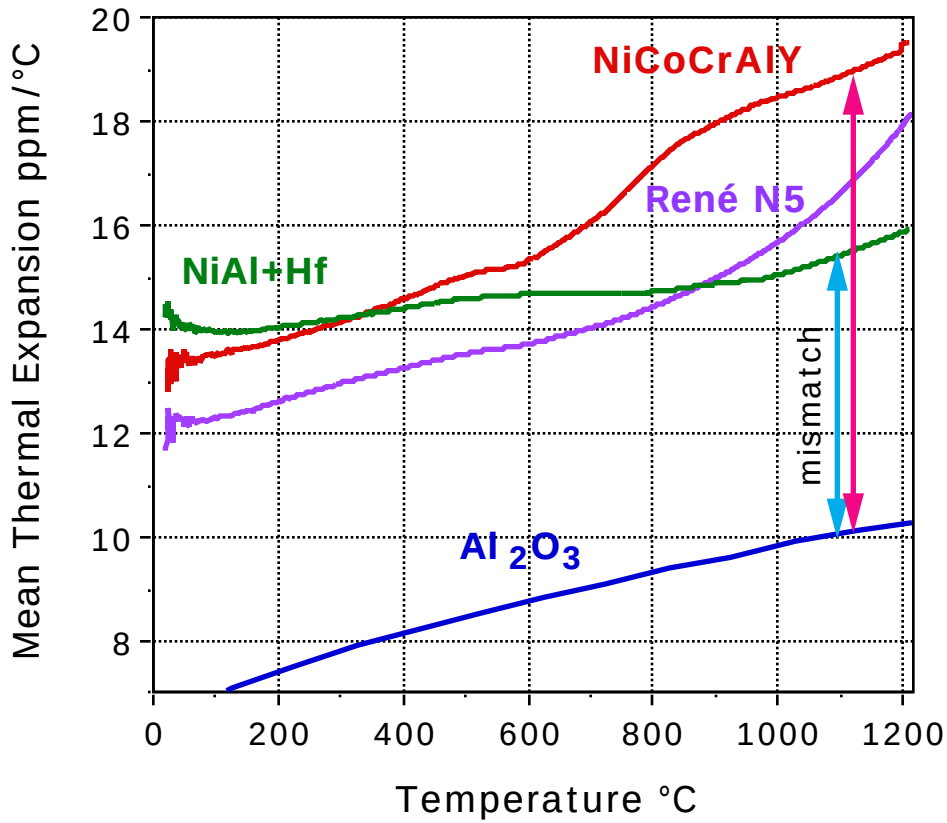


Processing issues

How to make it (?)

β-NiAl has lower CTE than MCrAlY

Mean thermal expansion not constant with temperature



Oxidation view:
Aluminides more promising at higher temps. for TBCs

Measurements at ORNL on cast, annealed alloys using dual push rod dilatometer

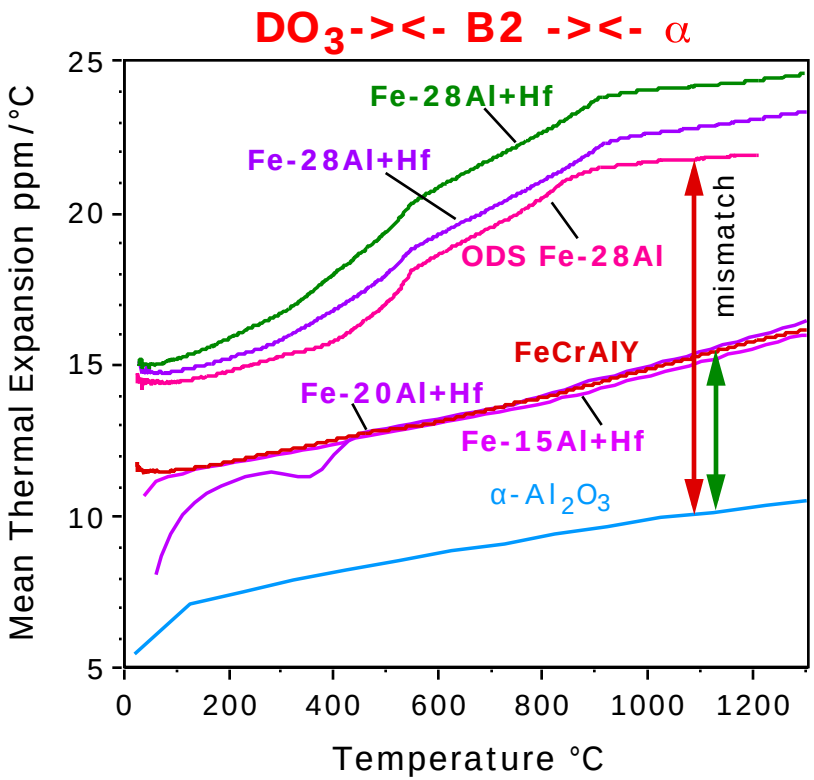
Average for Al_2O_3 at 1100°C is ≈10

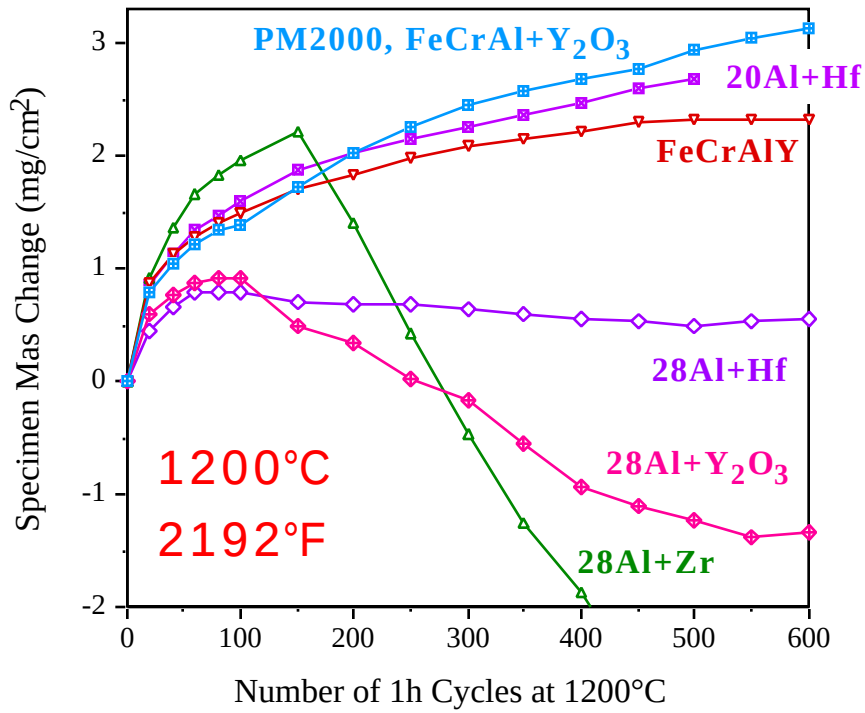
Larger difference between metal and oxide represents more strain

Thus, thermal expansion mismatch is a first order spallation mechanism

Lesson learned with Fe_3Al

High CTE alloys spall despite reactive elements!





Additions of Zr, Hf and Y_2O_3 to Fe-28Al alloy don't prevent spallation

- De-sulfurizing ODS Fe_3Al showed no improvement

Lowering the Al content in Fe-Al alloys:

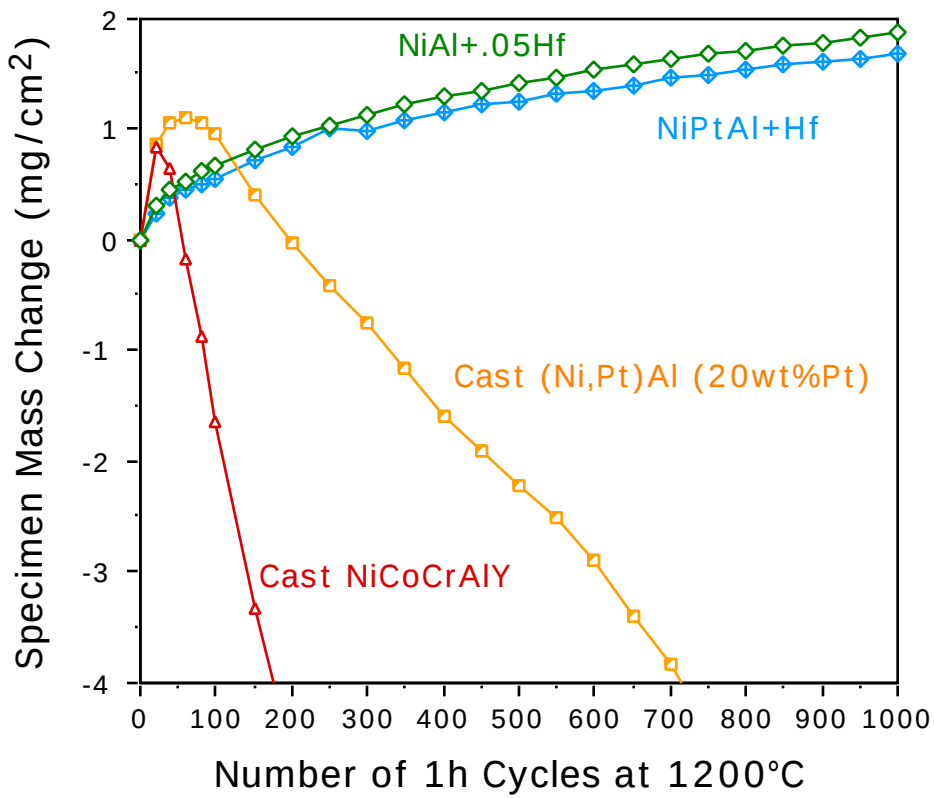
- Avoids the DO_3 phase and related transformations to B2 and α
- Improves scale adhesion similar to FeCrAl alloys

Smialek and Doychak first suggested CTE problem for Fe-40Al in 1990

Improved scale adhesion of Hf-doped NiAl

performance comparison in 1h cycles at 1200°C

1200°C, 2192°F

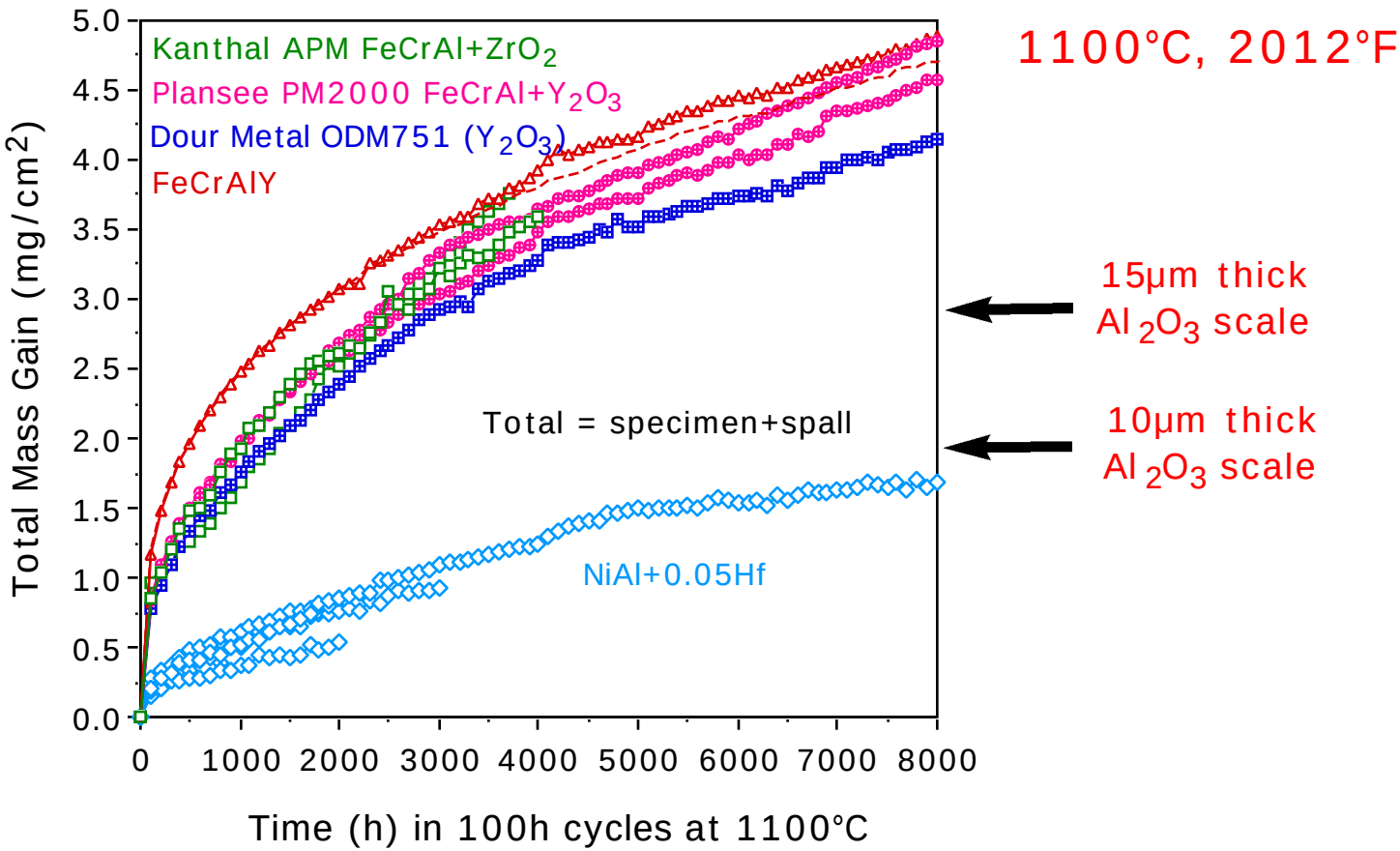


In cyclic testing, castings of both MCrAlY and Pt-modified aluminides show more spallation than NiAl with a reactive element like Hf.

Reactive element can't correct CTE problem of NiCoCrAl

Hf addition: Slows alumina growth rate

comparison in 100h cycles at 1100°C



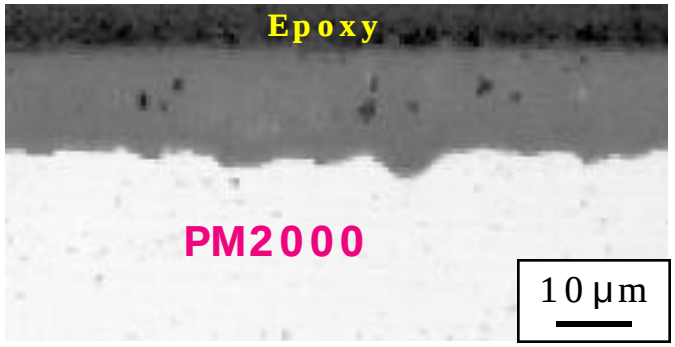
Many alloys form adherent alumina scales

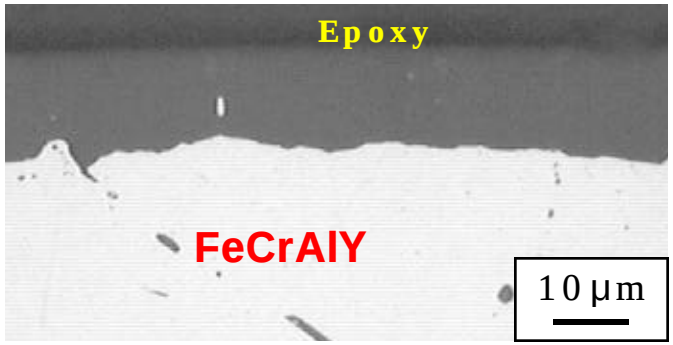
Growing slowly is the key factor

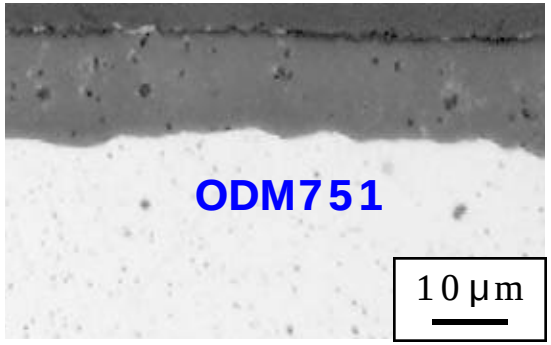
For operation at 1100°C, much longer time to critical scale thickness of 10-15µm where spallation occurs in many applications

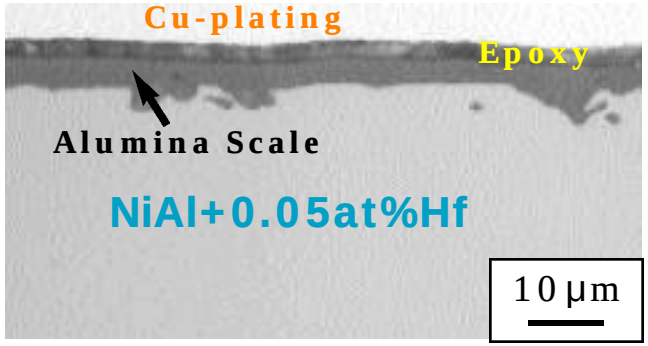
Metallographic sections of alumina scales

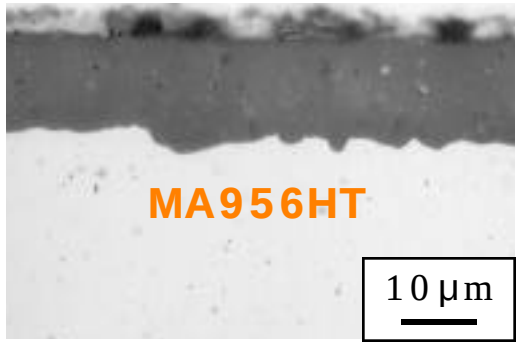
all after 2000h (20x100h) at 1100°C in air

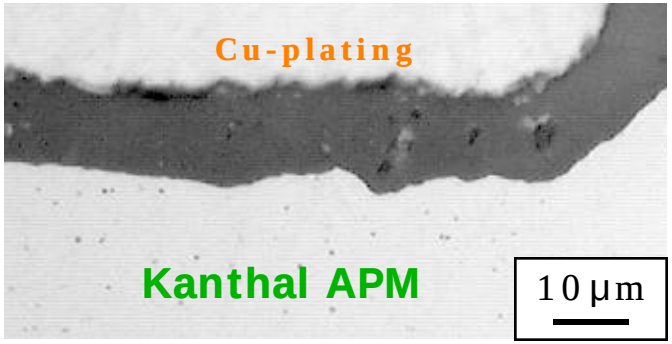


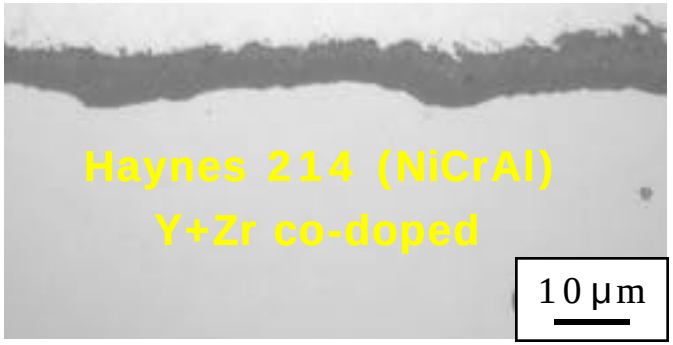












thinner scale with Hf-doped NiAl

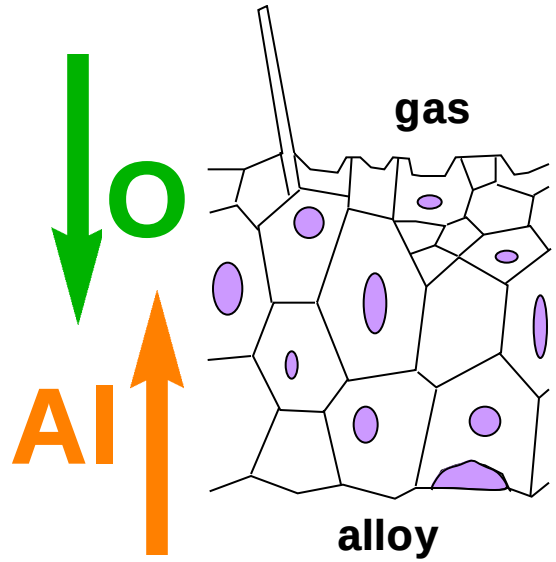
#1: Why does Hf work?

#1a: How do Reactive Elements work?

#1b: What is the growth mechanism of undoped alumina?

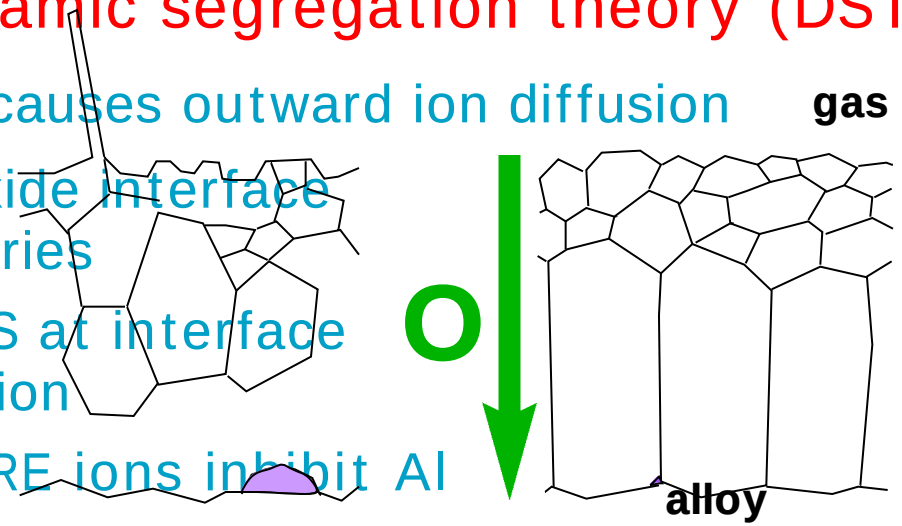
#1b: It depends on the phase:

- θ-Al_2O_3 grows by Al diffusion outward (blades!)
- α-Al_2O_3 grows by grain boundary diffusion of Al and O



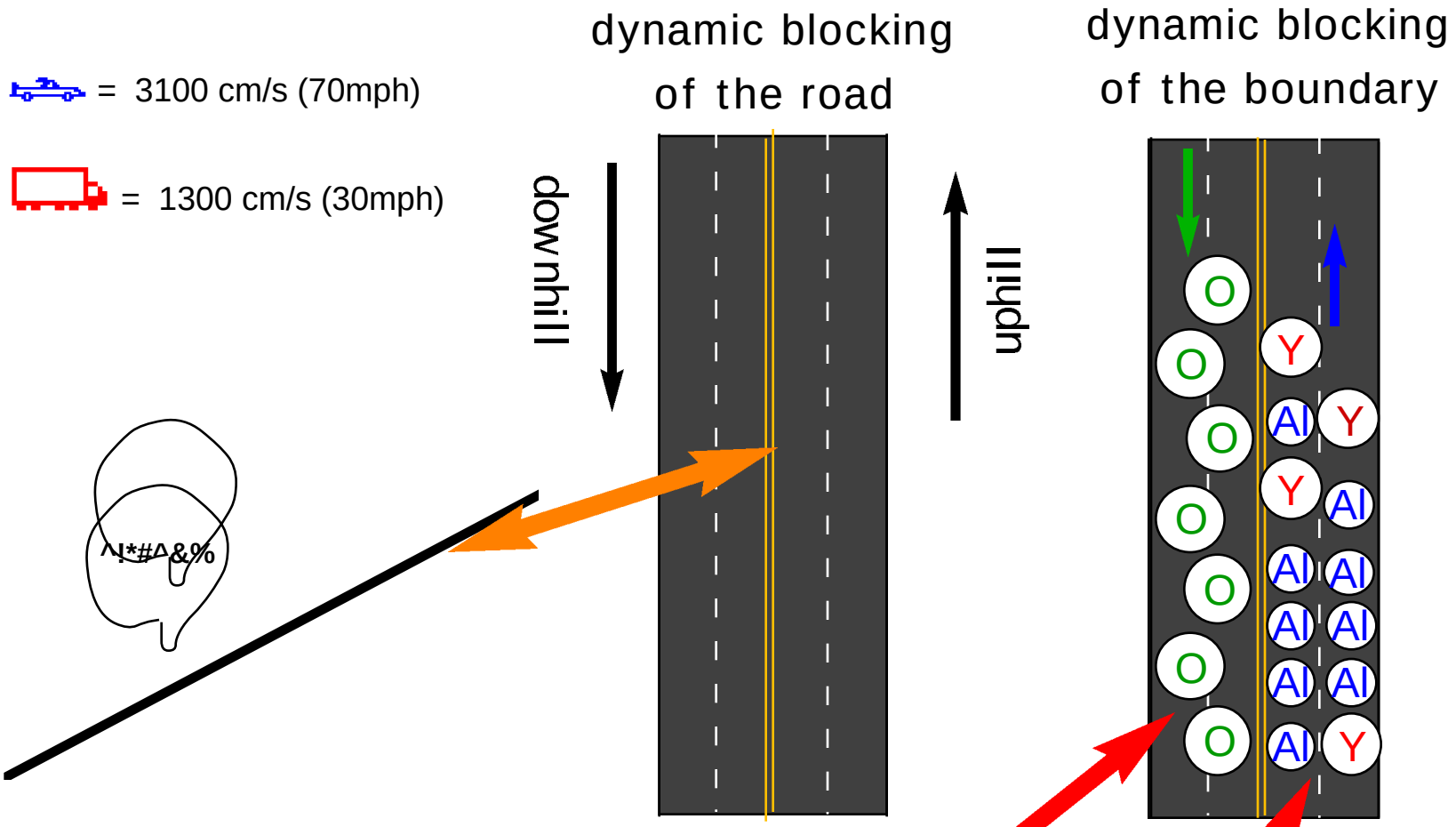
#1a: Explained by the dynamic segregation theory (DST)

- oxygen potential gradient causes outward ion diffusion
- ions segregate to metal-oxide interface and scale grain boundaries
- inhibit the segregation of S at interface and reduce void formation
- diffusing slowly outward RE ions inhibit Al



Jellico Mountain Example

I-75 north of Knoxville, on my way home from Mom's



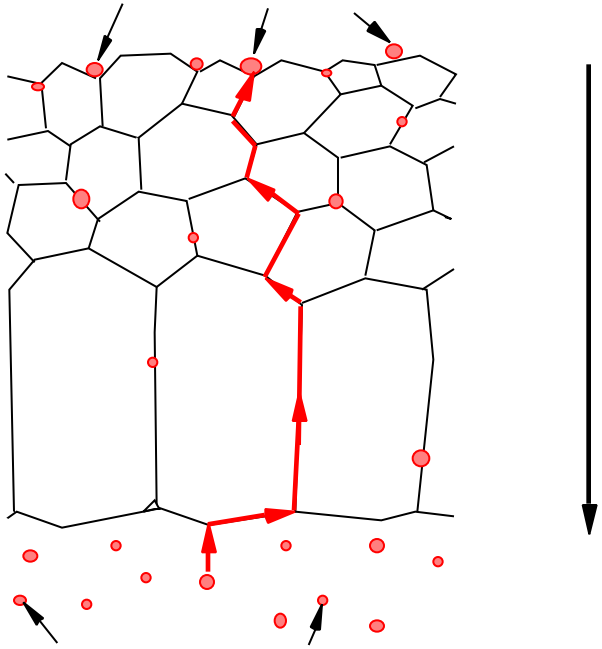
downhill - anion sublattice, no effect of trucks or Y

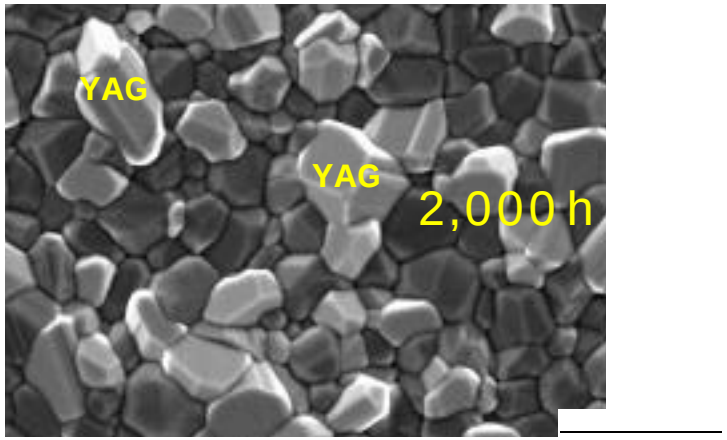
uphill - slow moving trucks and Yions block faster moving travellers

no hill - like an undoped boundary - both Al and O move at similar rate

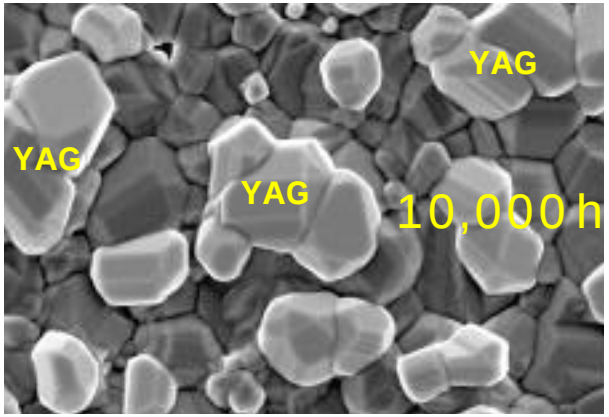
What about gettering S?

ODS alloys suggest Sgettering is not important for scale adhesion





PM2000: FeCrAl+Y_2O_3

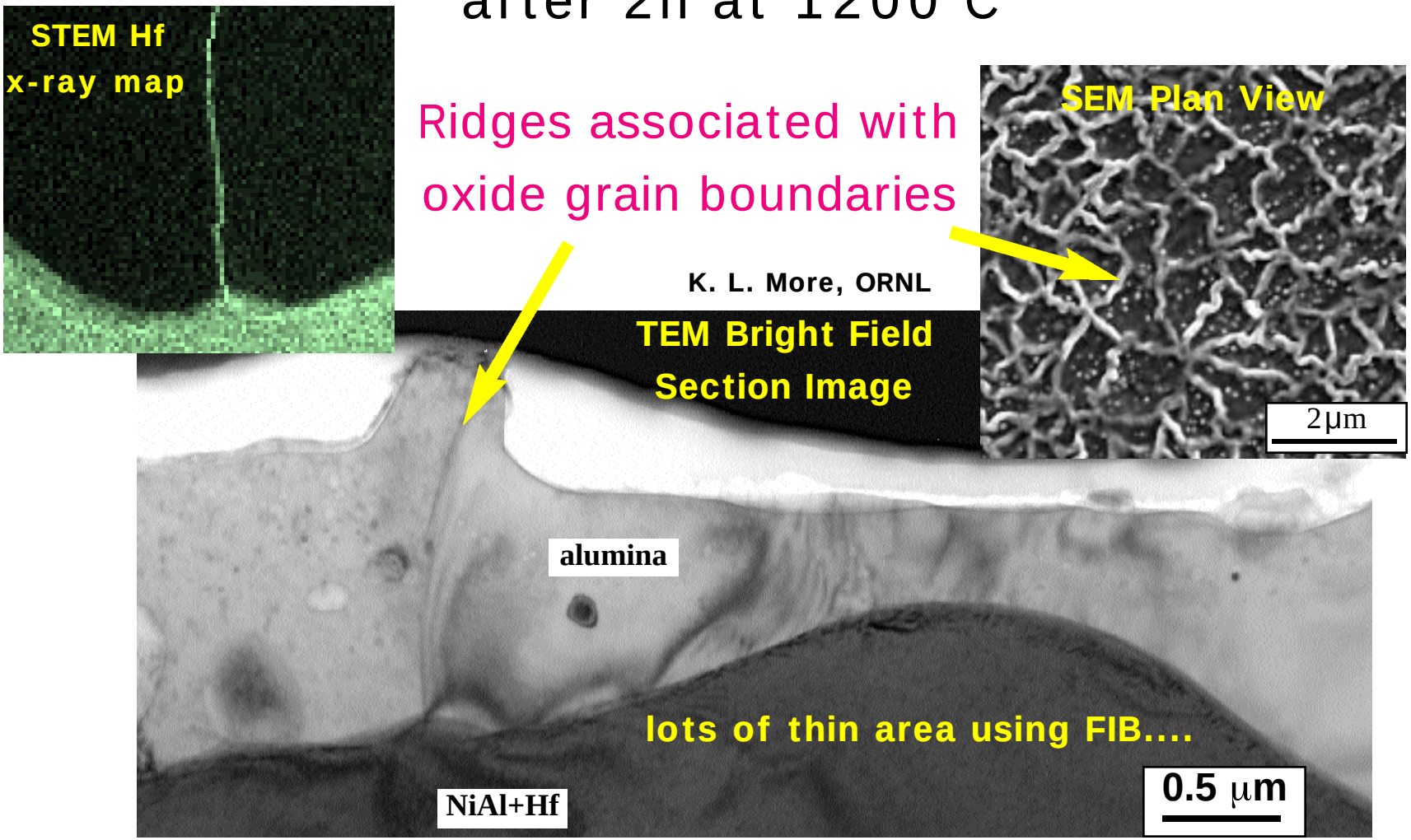


ODS alloys contain Y_2O_3, high (30-100ppm) Slevels but great behavior

- no observations of sulfides or S at dispersoid-metal interface
- Y ends up at gas interface - Y-rich particles grow with time
- Y as oxide or oxy-sulfide would dissolve to enter scale

Scale on Hf-doped NiAl

after 2h at 1200°C



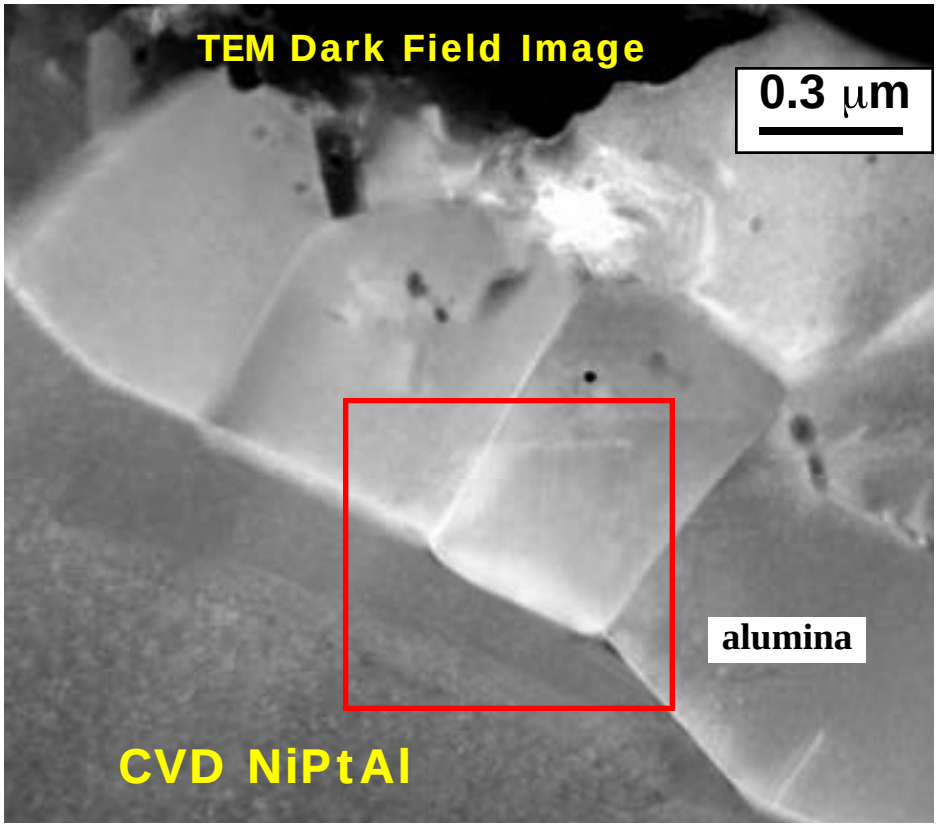
Overall scale is thinner with Hf doping but...

away from grain boundary the scale is even thinner

Scale grows by boundary diffusion where Hf ions segregate

CVD Pt-modified Aluminide Coating

Low-S René N5 substrate, after 100h at 1150°C



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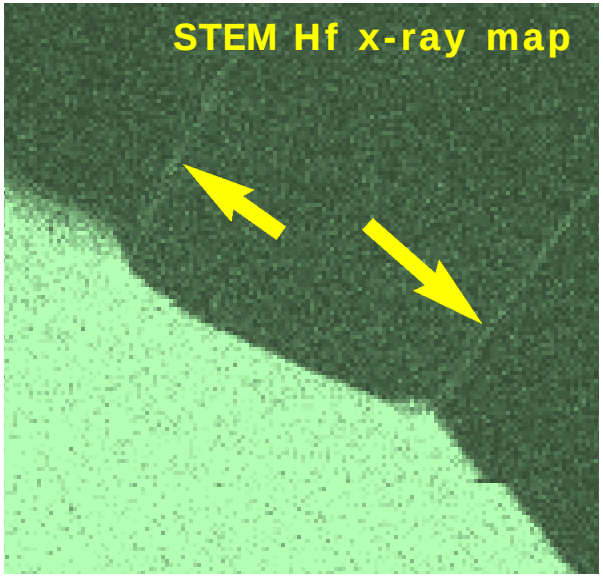
Hf ionic segregation at Al_2O_3 grain boundaries



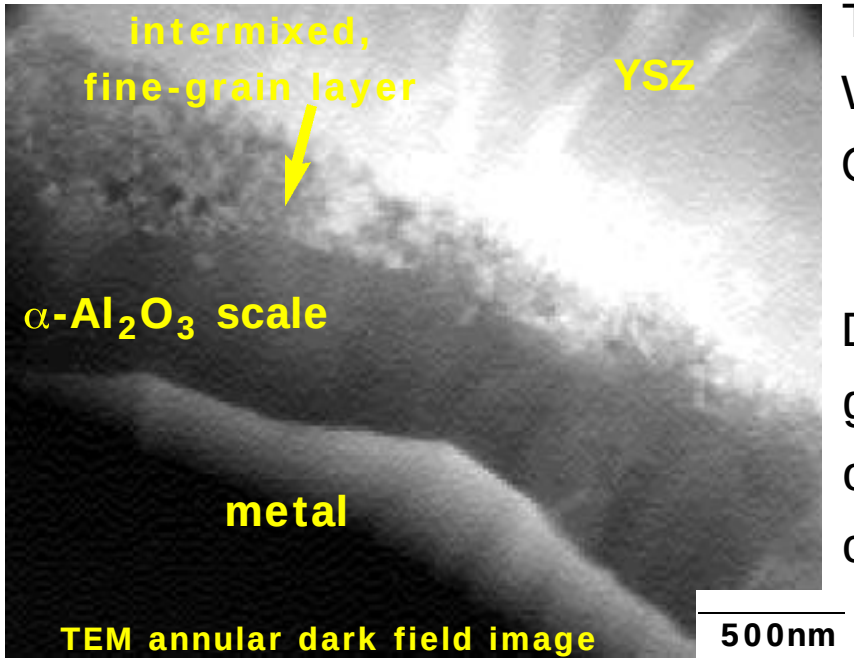
When Hf is present in the substrate (500ppma) in N5

Hf is in the coating and the Al_2O_3 scale

May be less than optimum dopant level (?)

What about dopants in TBC?

Lots of Y, Zr, Hf around why doesn't it help?



K. B. Alexander, ORNL

TBC specimen is covered with RE

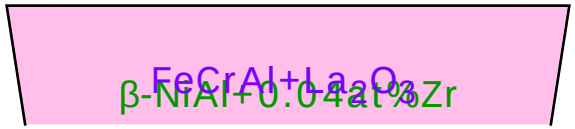
Why add more?

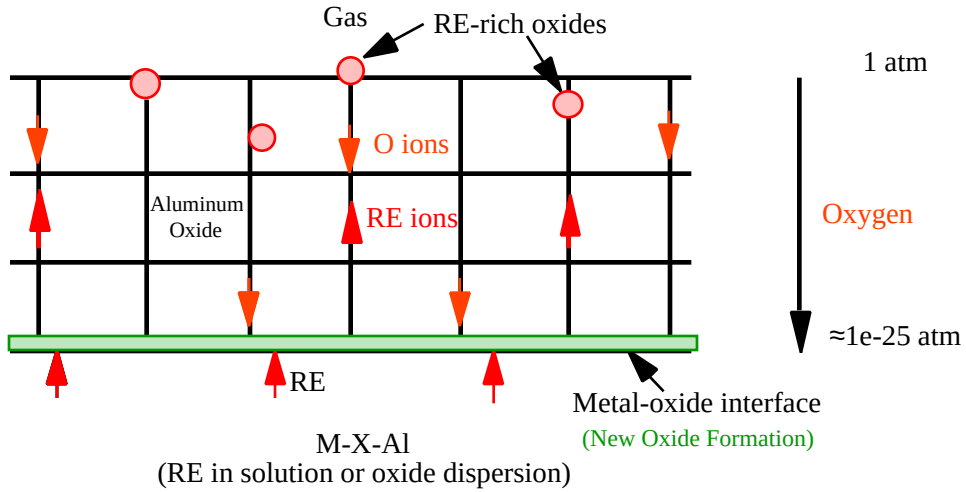
Observations are that Y in TBC doesn't improve scale adhesion

DST explanation: chemical potential gradient prevents back diffusion of oxygen active elements from top coat into scale

Test the model:

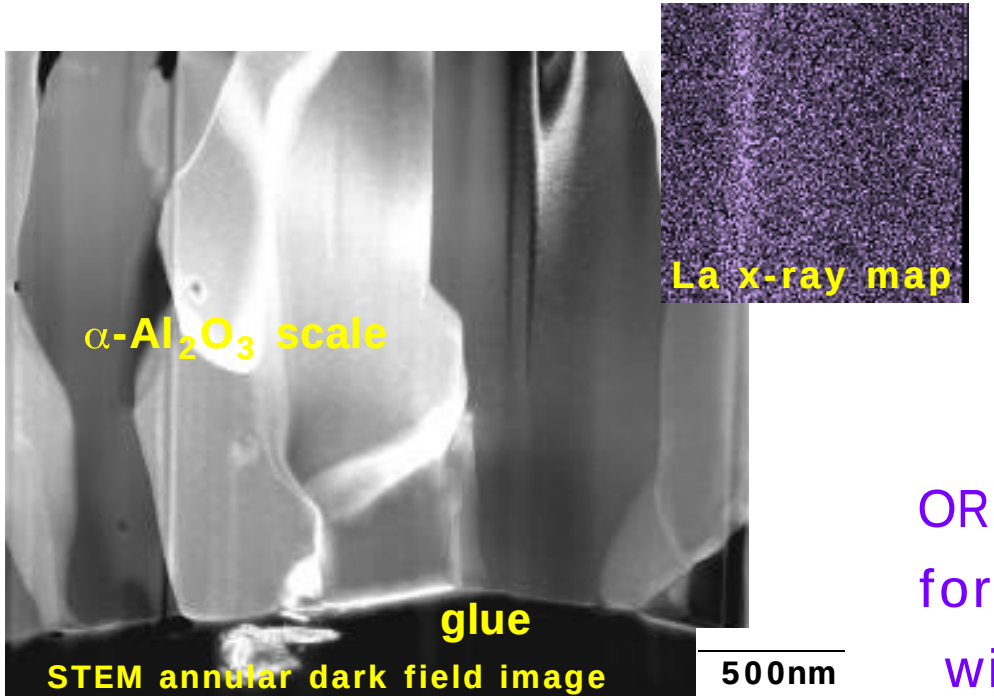
EB-PVD, 125 µm (5 mil) from DLR (C. Leyens)





Only La ions on grain boundaries!

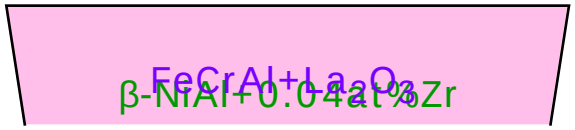
EB-PVD on FeCrAl+La_2O_3 oxidized 200h at 1200°C



K. L. More, ORNL

Test System:

EB-PVD, 125 µm (5mil)
from DLR (C. Leyens)



ORNL-made La-doped FeCrAl:
forms adherent alumina scale
without Y, Zr or Hf in alloy

Lower, columnar alumina grains:

- Zr, Y or Hf from YSZ top coat were not detected
- Only La ions were detected on the alumina g.b.'s

Equiaxed alumina grains near Al_2O_3-ZrO_2 region:

- Zr and La ions were detected on grain boundaries

#1 Why does Hf work so well?

DST says two factors are important for dopants:

(1) Oxygen affinity (correlates with S affinity)

(2) Ion size

No thermodynamic data supports that Hf has higher oxygen affinity than other elements like Y, Sc, Er

Ionic radius: handbook says Hf = 0.83Å CN=8

Y, Nd, La all have larger ion sizes

Most info comes from calculations of hard sphere model

Possible that Hf has a higher "effective" radius than other dopants when present on an α-Al_2O_3 grain boundary

Needs to be investigated experimentally/theoretically

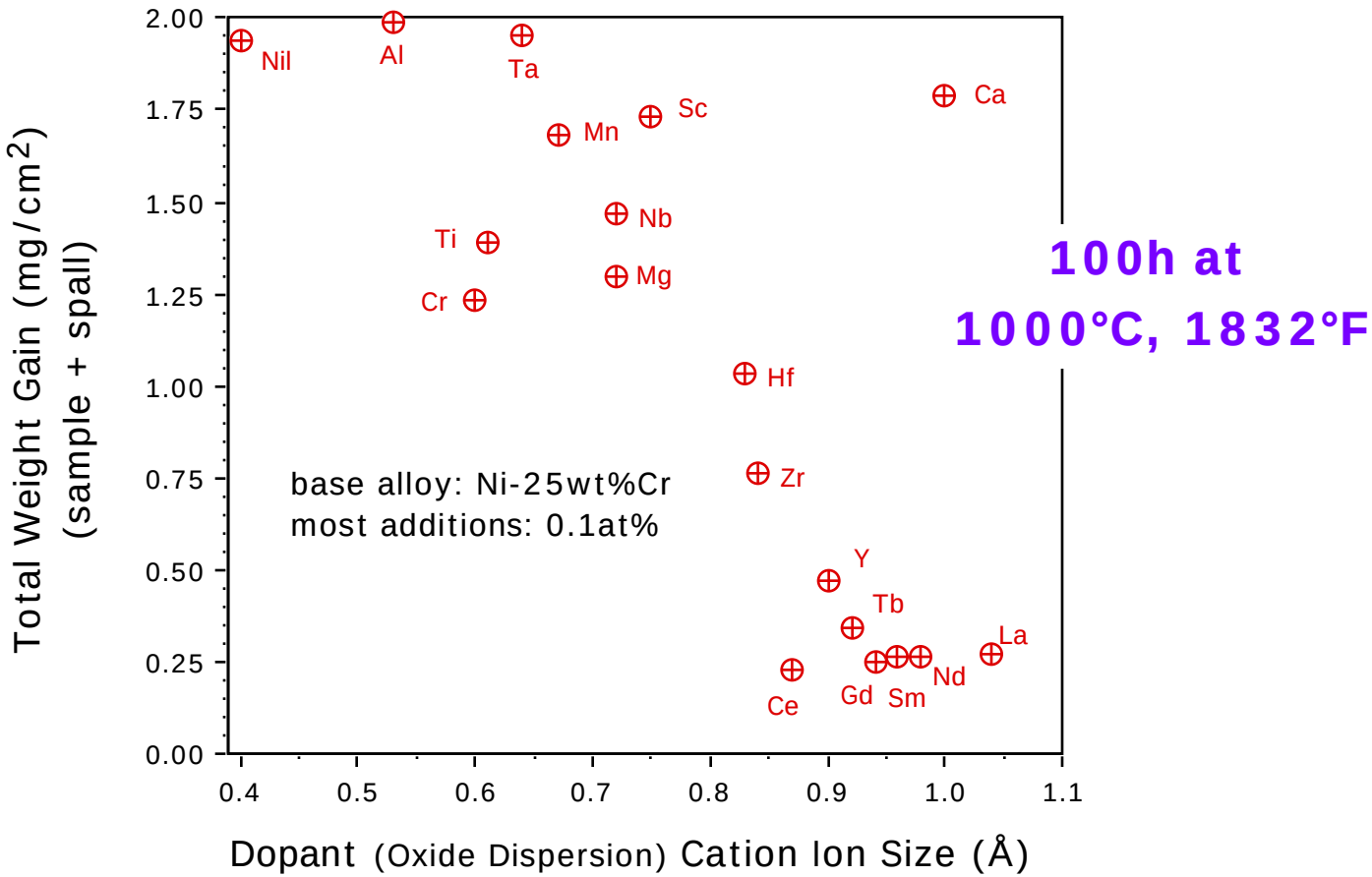
Alternatively, Hf doping results in a larger alumina grain size

If Hf slows θ->α phase transformation, i.e. fewer nuclei

Slower scale growth because fewer O transport paths

Ion size correlates well with dopant effects

Example: dopant oxide dispersions in Ni-25wt%Cr



Larger ion size decreases Cr_2O_3 growth rate

Up to an order of magnitude reduction in this case

Smaller ions (e.g. Sc, Hf!) are less effective

Practical issues for improving coatings

Translate idealized lab work into real coating...

#1 Hard to get 0.05at%Hf in coating - processing issue
already being addressed by others

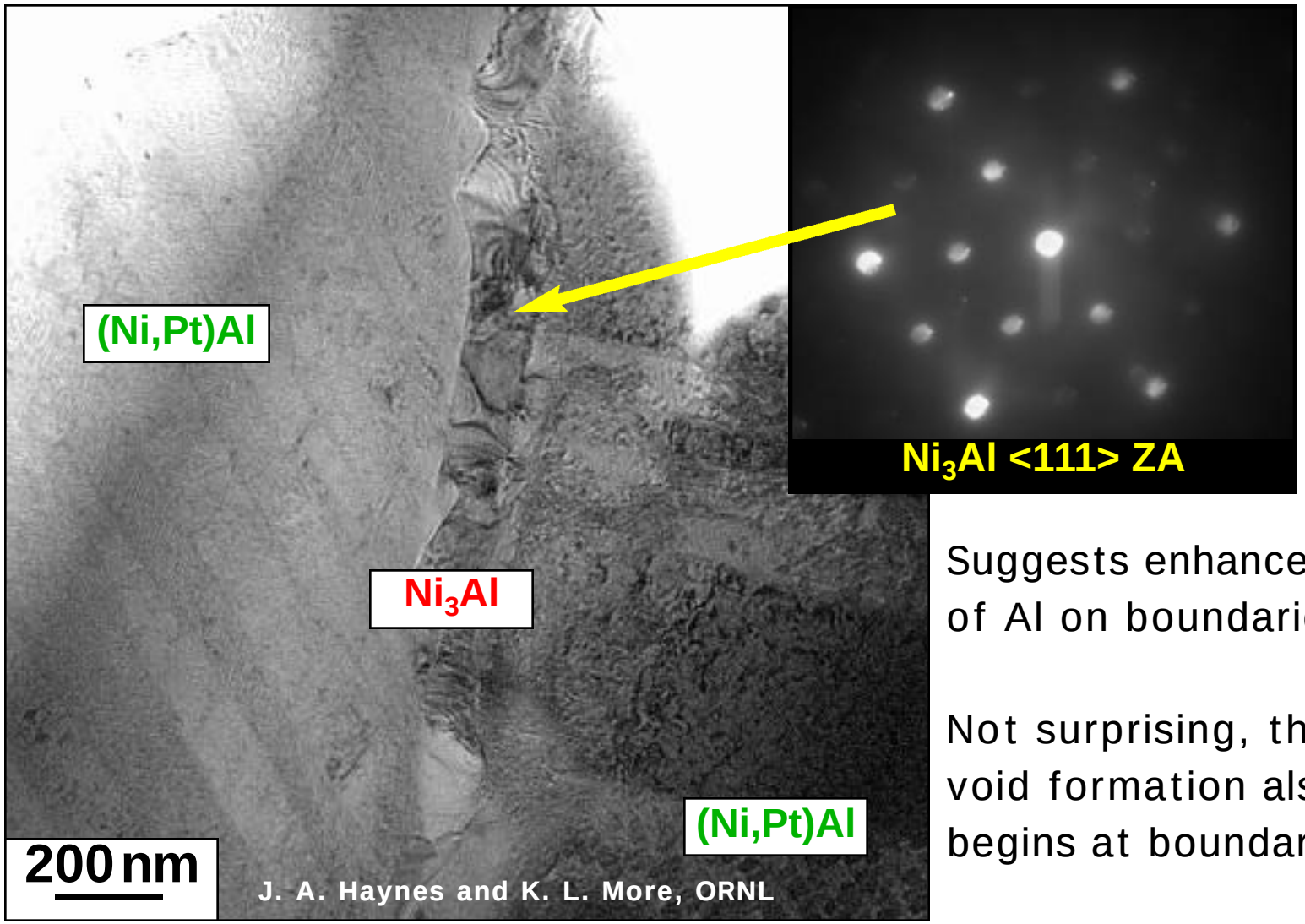
#2 Coatings almost never contain 50at% Al
most contain <40at%Al and end up having some Ni_3Al

#3 Additional elements entering the coating from
the substrate

TEM of CVD(Ni,Pt)Al coating on René N5

Grain Boundary Transformation to Ni_3Al

after 100h at 1150°C



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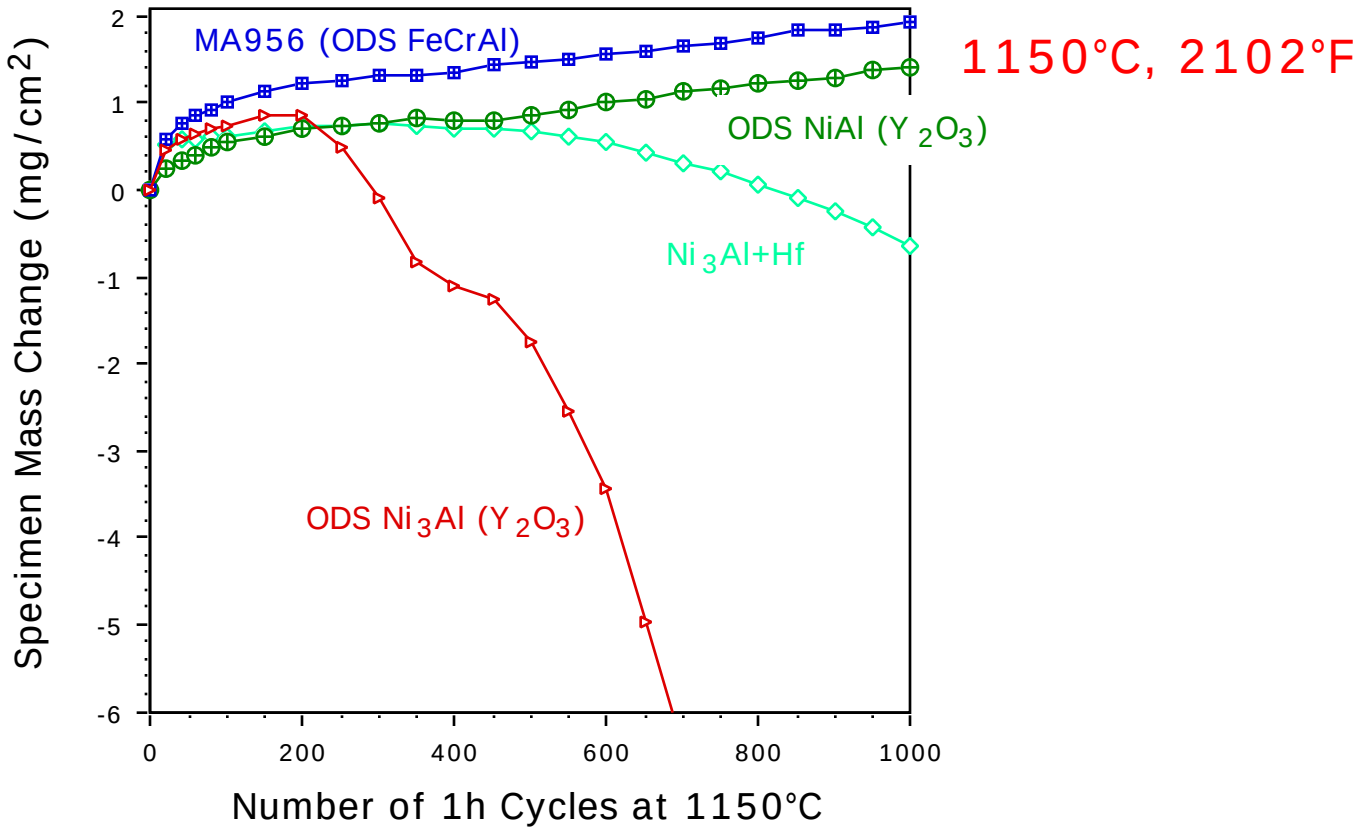
Suggests enhanced loss of Al on boundaries

Not surprising, that void formation also begins at boundaries.

Problems with scale adhesion on Ni_3Al

comparison of ODS (all Y_2O_3) alloys in 1h cycles at 1150°C



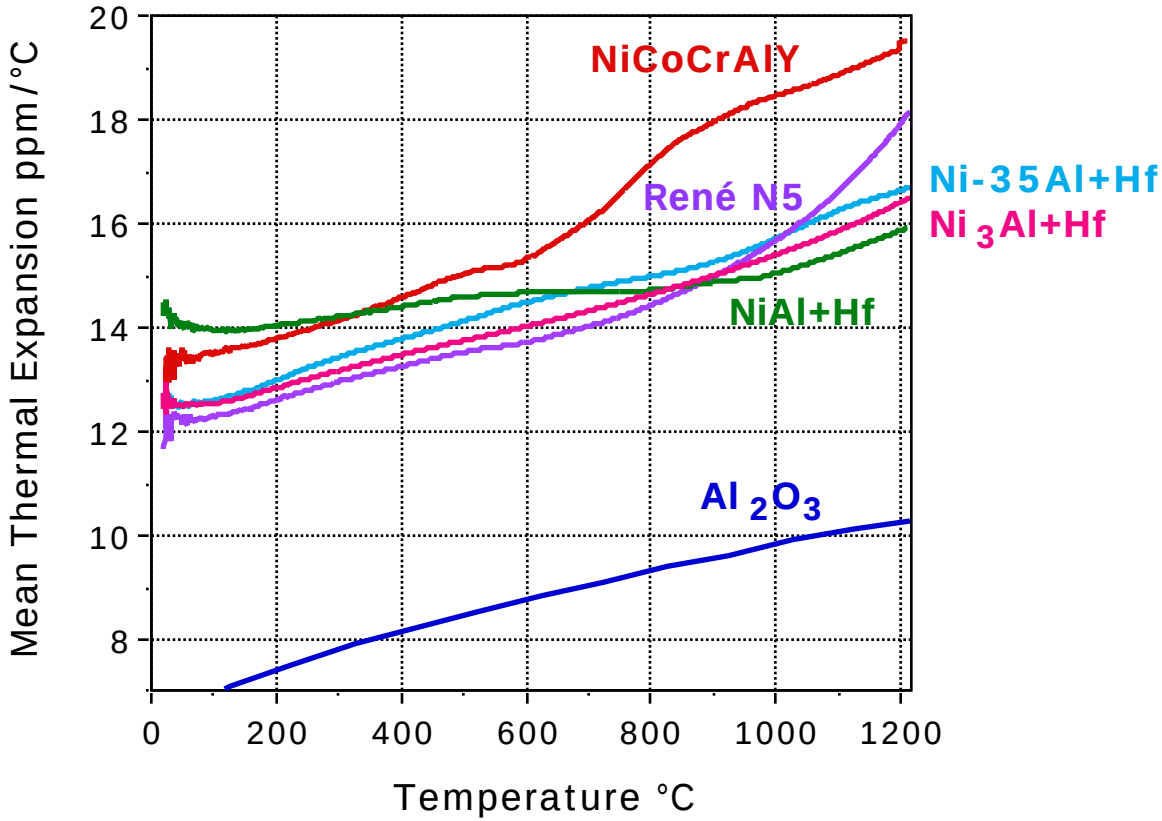
Problems with scale adhesion on Ni_3Al - also 1000°, 1100° &1200°C

Not even Hf prevents the onset of spallation after 500h

Subject of a recent paper in Oxidation of Metals

Thermal Expansion of Ni-Al+Hf

mean thermal expansion similar from 25-50at%Al

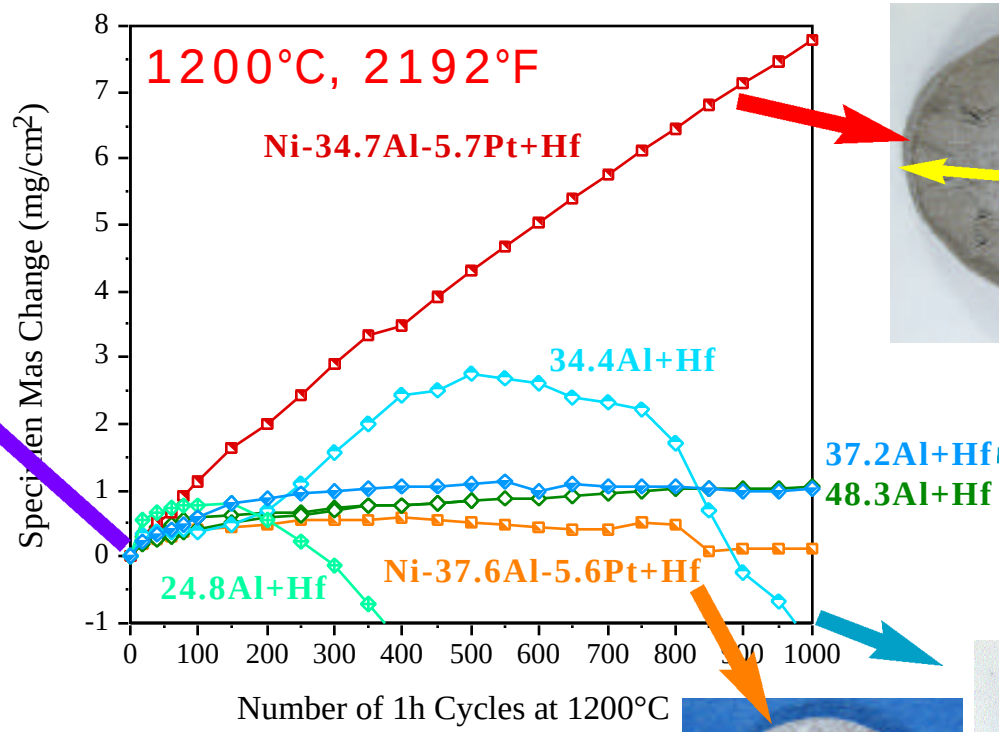


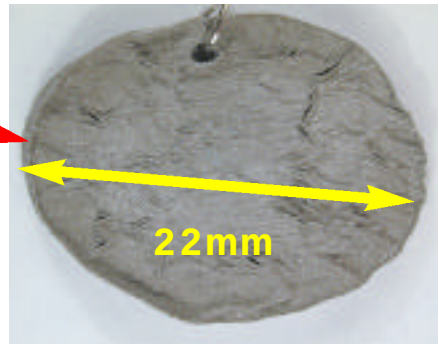
No strong indication from thermal expansion that Ni-35Al or Ni_3Al should have a scale adhesion problem

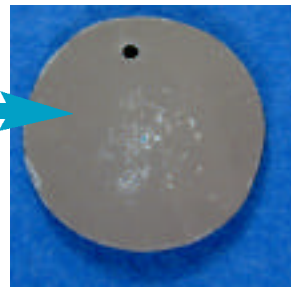
Ni_3Al problem may be one of scale cracking and rehealing?

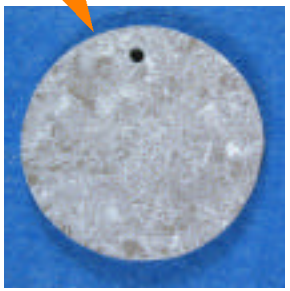
Ni-Al+Hf: Critical Effect of Al content

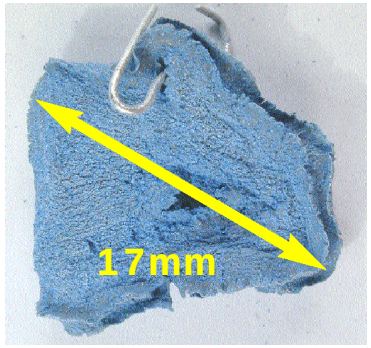
cast alloys, oxidized 1000x1h cycles at 1200°C in O_2











Critical range: 35-37.5%

two phase vs. one phase?

Al contents below 37.5at% have significant oxidation problems

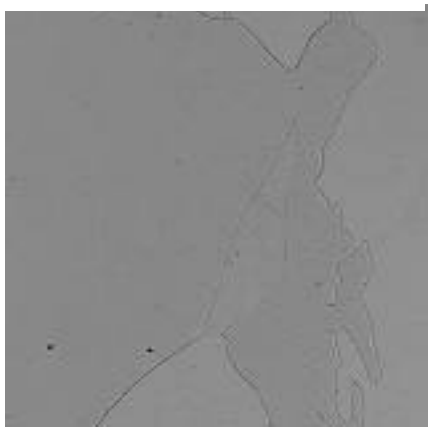
Macroscopic deformation occurs for low-Al two phase alloys

Addition of Pt does not stop deformation or spallation but no blue oxide!

Ni-Al+Hf - Effect of Al Content

annealed microstructure (4h 1300°C)

Ni-24.8Al+Hf

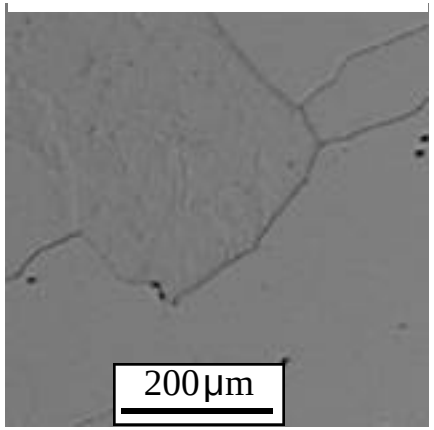


Nice one phase alloys

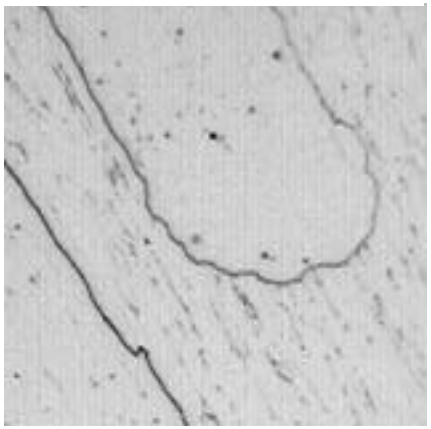
<- γ'

β ->

Ni-37.2Al+Hf



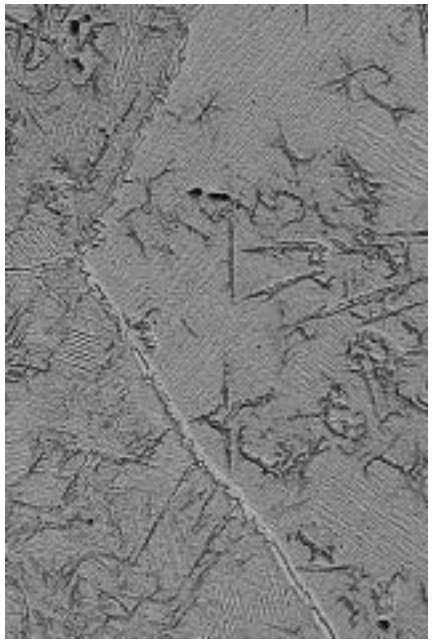
Ni-50.1Al+Hf



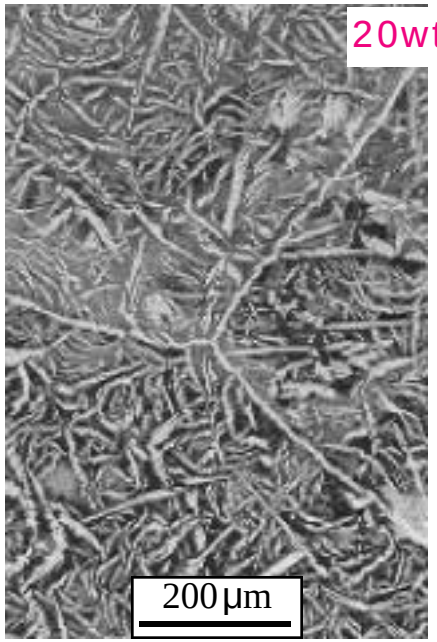
Two phase alloys

By XRD:
Room T:
γ' + β

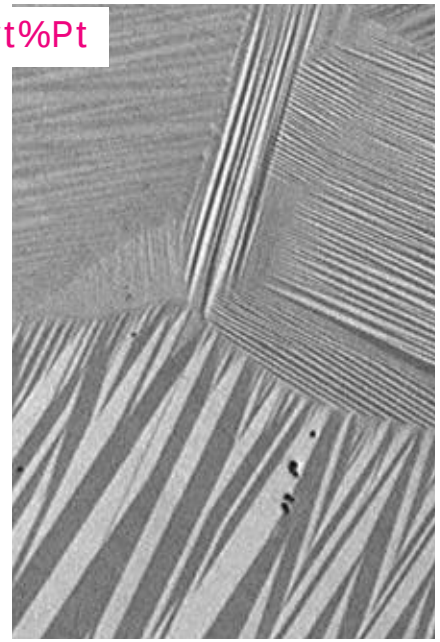
At 1100°C one phase β?



Ni-34.4Al+Hf

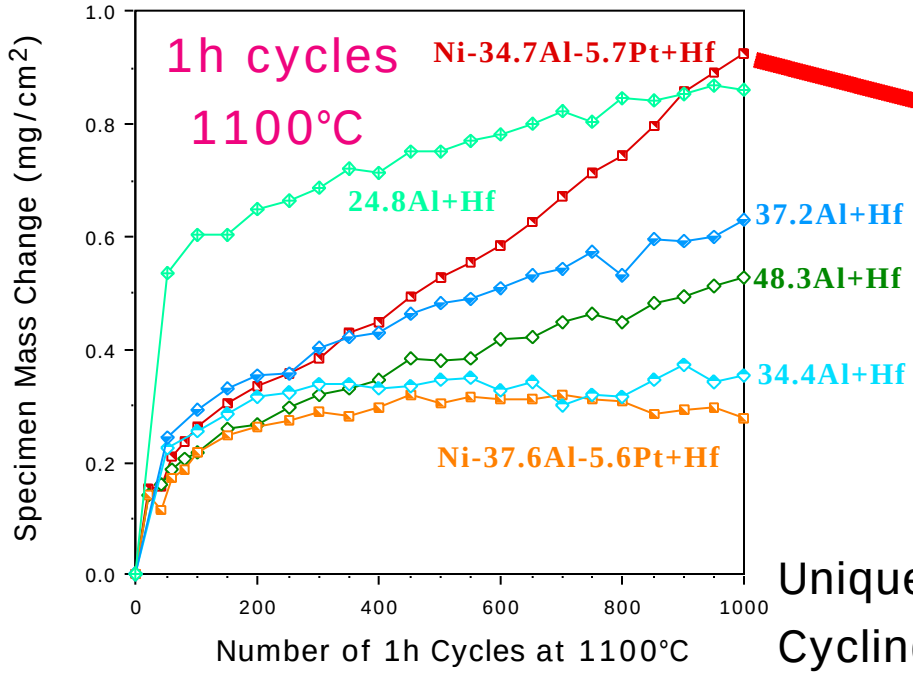


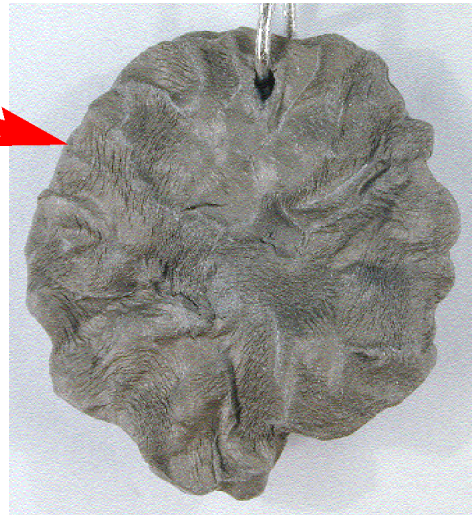
Ni-34.7Al-6Pt+Hf



Ni-37.6Al-6Pt+Hf

Deformation depends on T & cycle frequency

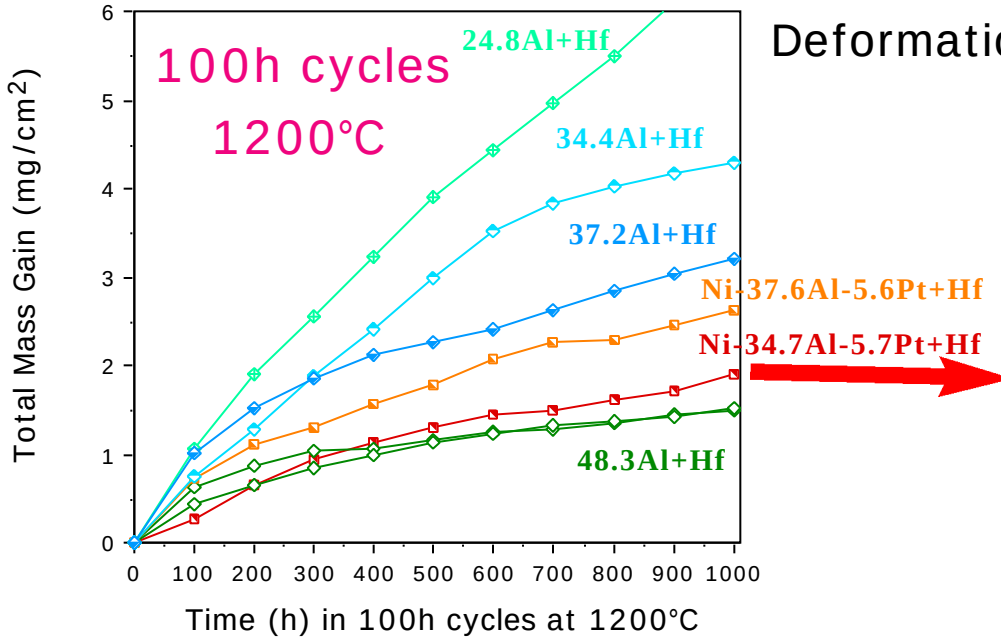


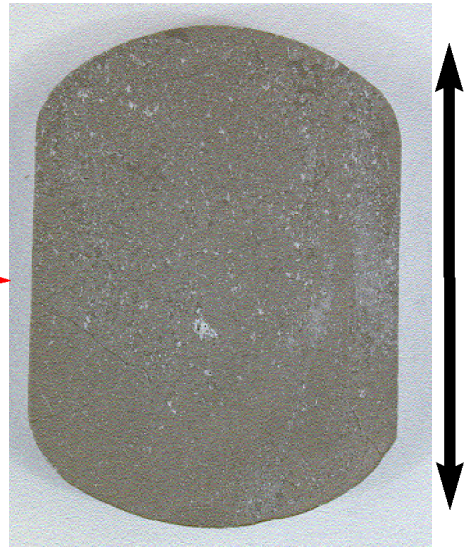


Unique behavior of Ni-34.7Al-5.7Pt+Hf

Cycling causes repeated phase change

Deformation similar to aluminide coatings!





sides ground to fit in crucible

What does Pt do?

(Based on observations from cast alloys)

Pt does:

- improve scale adhesion
- reduce the number of interfacial voids (compared to NiAl)
- increase the number of oxide intrusions (don't ignore keying effect)
- reduce the coefficient of thermal expansion
- improve the selective oxidation of Al
- increase the amount of Hf internal oxidation (compared to NiAl+Hf)

Pt does not:

- change scale growth rate or microstructure
- act like a reactive element
- prevent macroscopic deformation of Ni-Al

Observations from CVD coating work (Allen Haynes)

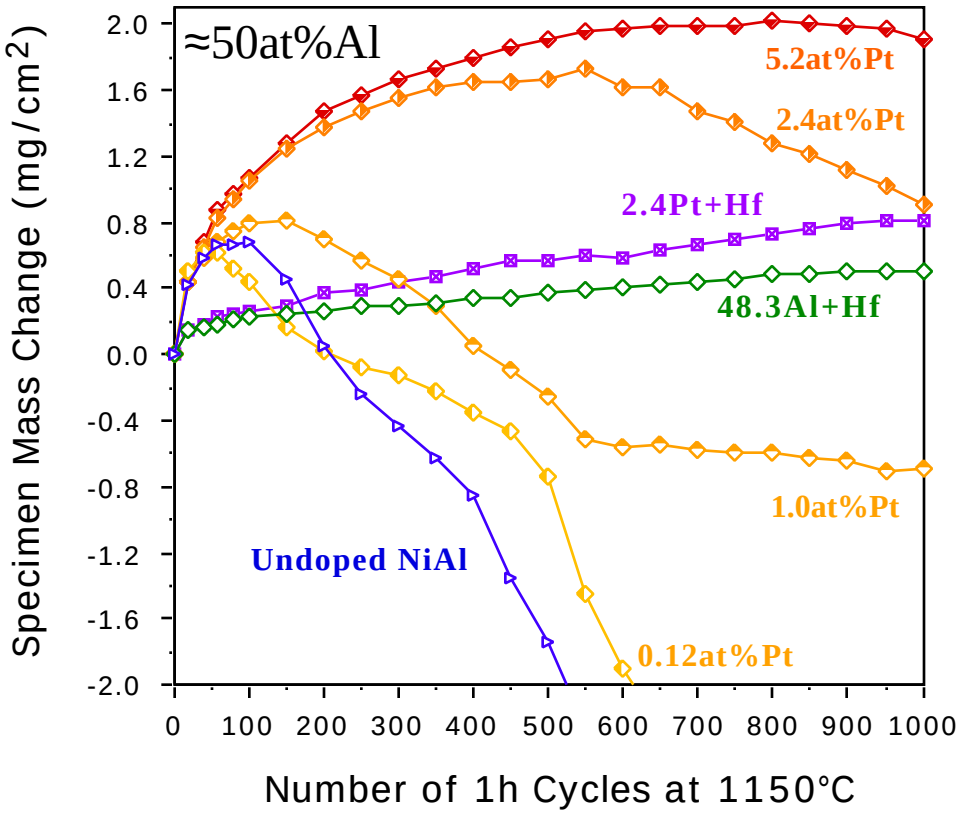
Pt does not:

- significantly change the coating Al content
- significantly change the coating refractory content

Pt-modified coating can tolerate more S than simple aluminide

More Pt is beneficial to scale adhesion

cast ≈ 50at%Al alloys, oxidized 1000x1h cycles at 1150°C in O_2



1150°C, 2102°F

With 50at%Al, increasing Pt contents show improved scale adhesion

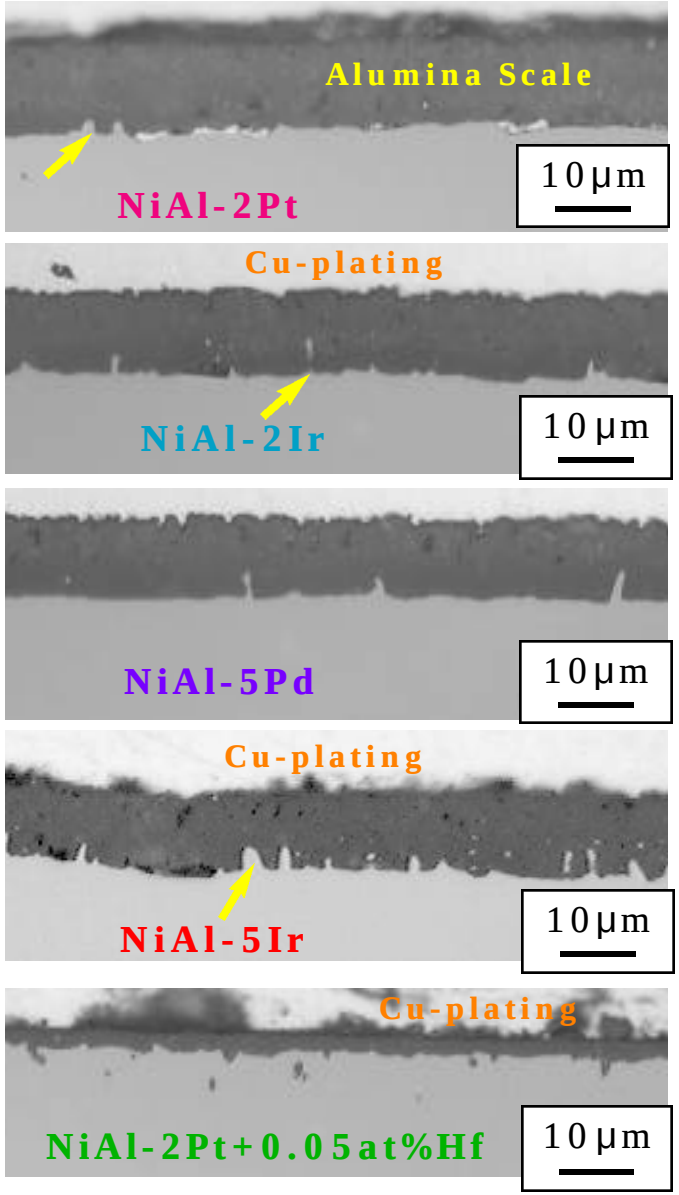
Lower mass gain for Hf-doped alloys due to slower alumina growth

not scale spallation

No additional benefit of combining Pt and Hf

Precious metal effect on alumina scales

cast ≈50at%Al alloys after 100h at 1200°C in O_2



Alloy protrusions are the major feature observed for NiPtAl

2at%=10wt%Pt; 5at%= 20wt%Pt

Similar microstructure for 2at%Pt 2at%Ir and 5at%Pd

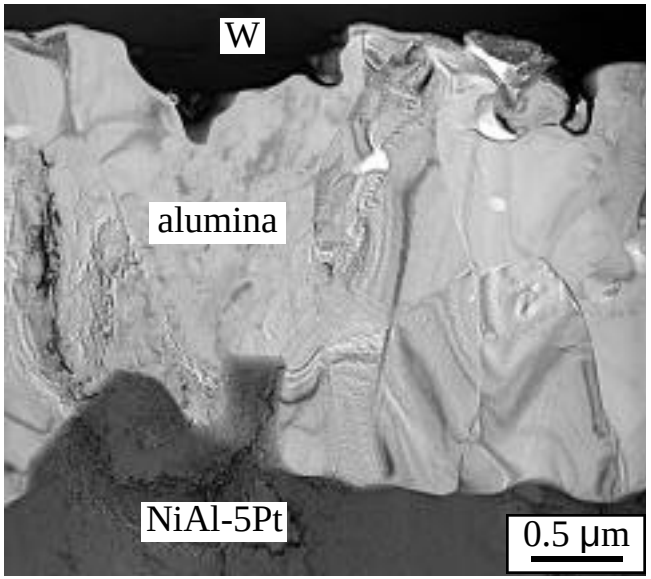
More protrusions may explain superior performance of 5at%Ir

Same magnification:

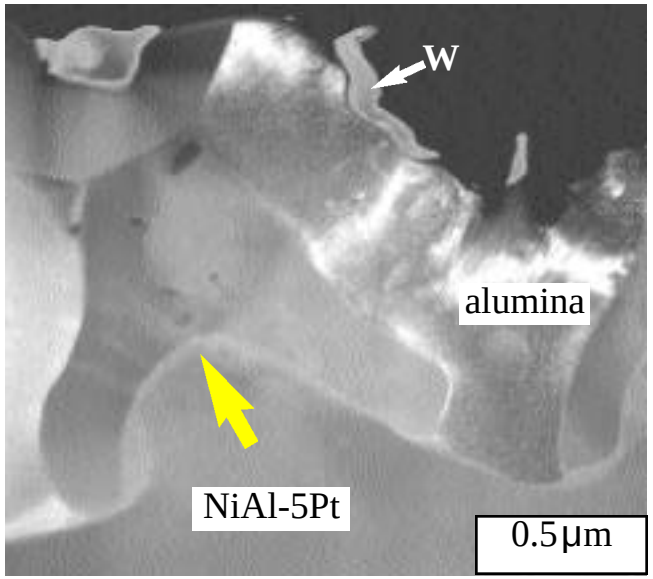
Hf effect on NiPtAl is evident

Effect of Pt on scale on cast NiPtAl

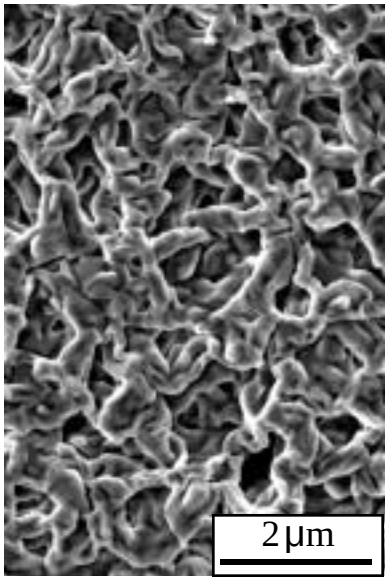
TEM/STEM of scale after 2h at 1200°C



TEM bright field image



STEM annular dark field image



SEM plan view

Scale is 2 grains thick, no interfacial voids

Neither gas or metal interface is smooth

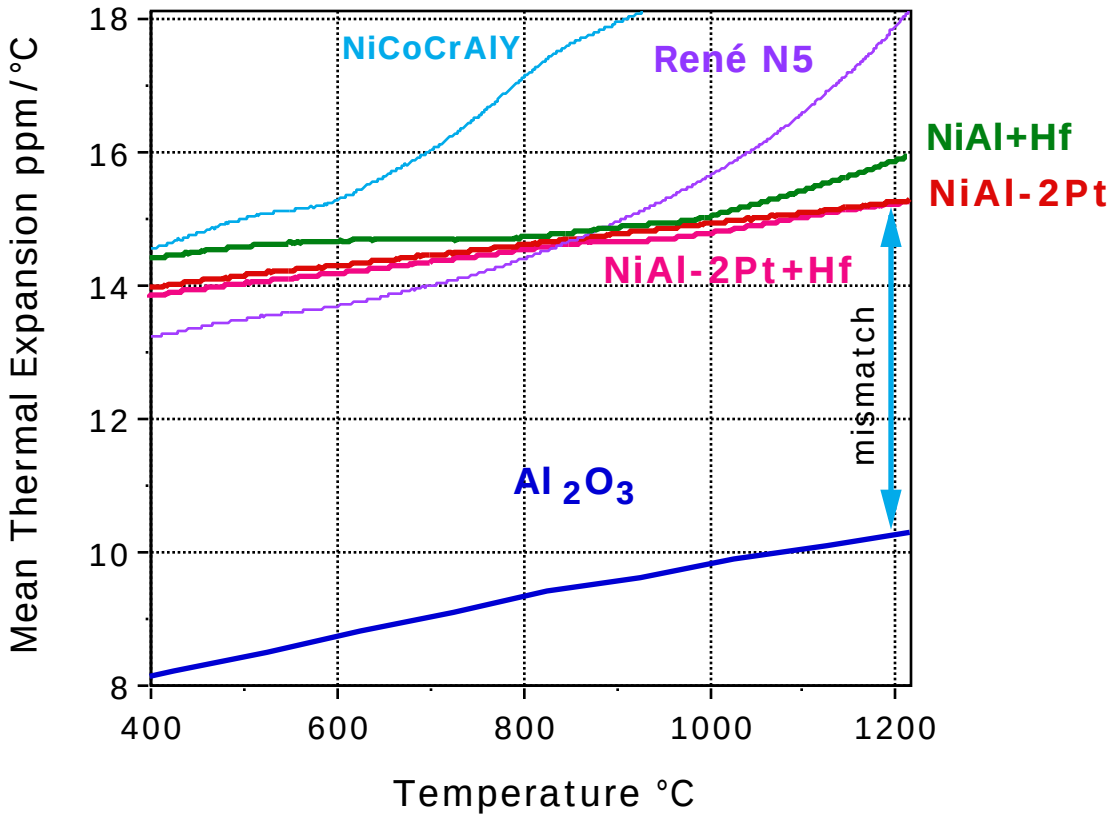
(intrinsic oxide ridges similar to undoped NiAl)

Metal protrusions are associated with a single alumina grain and are actually oxide protrusions

On undoped NiAl, this type of oxide growth would likely cause a void

Effect of Pt on thermal expansion

mean thermal expansion with and without 10wt%Pt



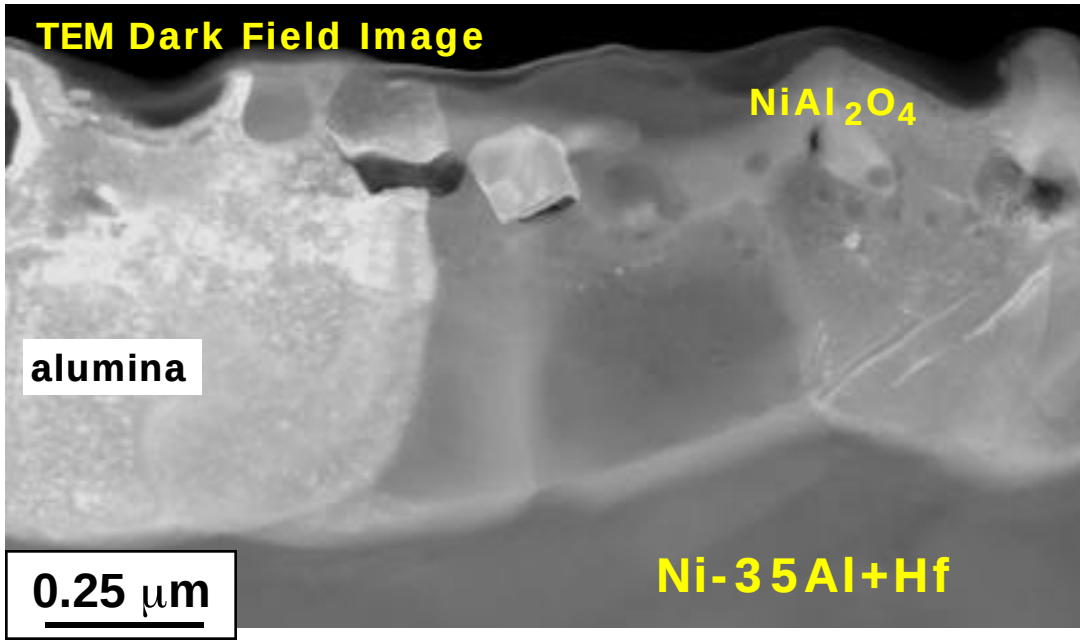
with J. A. Haynes & W. D. Porter, ORNL

Lower CTE with same crystal structure (β) suggests lower equilibrium vacancy concentration

Lower [V] may inhibit interfacial void formation on NiPtAl

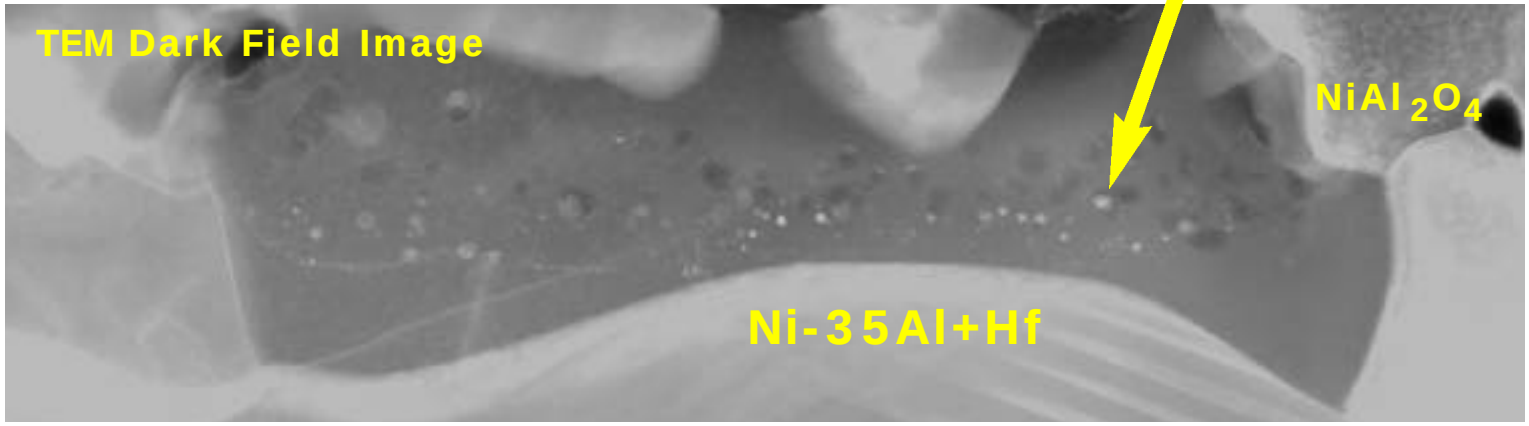
TEM of scale on Ni-35Al+Hf

cast alloy after 2h at 1200°C



Ni-rich oxide forms on top (result of low Al)

More voids in α-Al_2O_3 scale

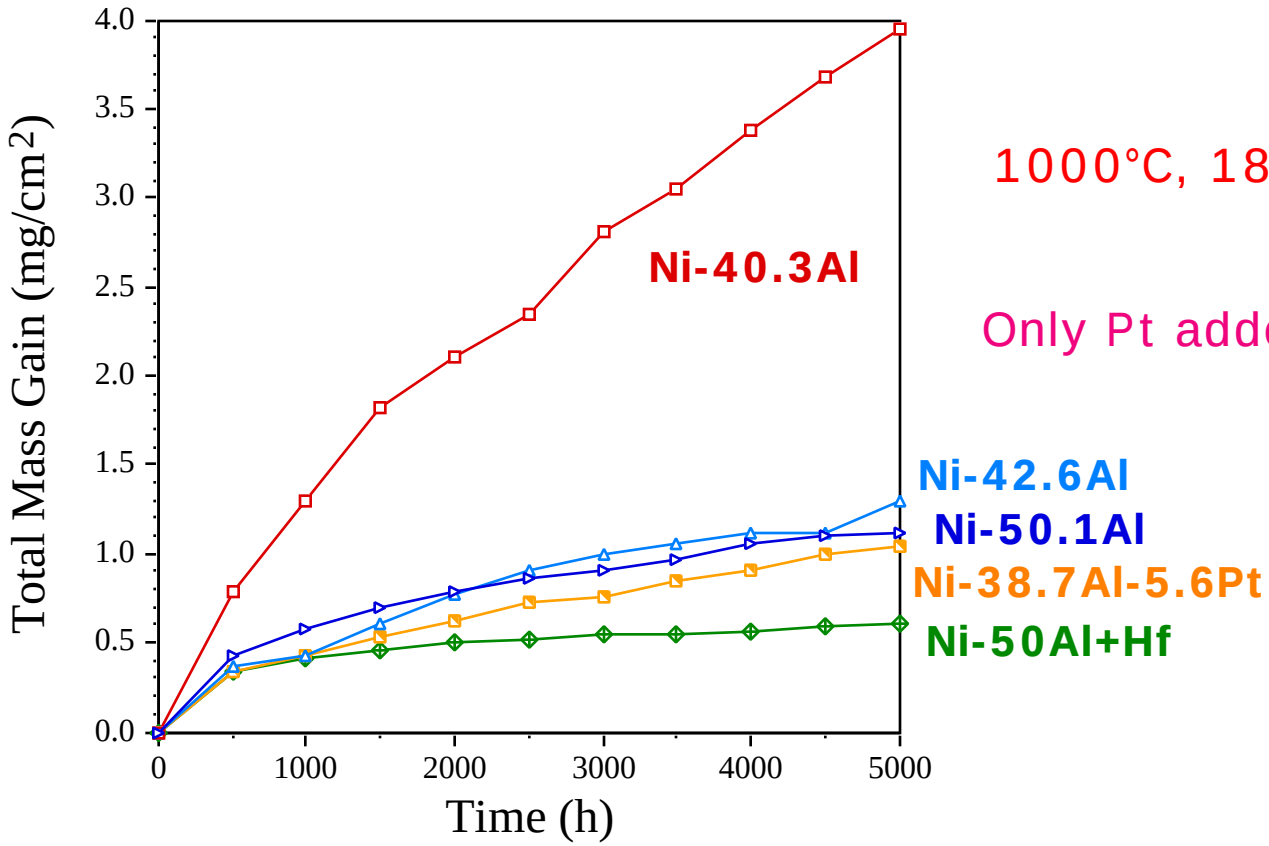


$NiAl_2O_4$-Al_2O_3 interface contains voids and is know to be weak

Need diffusion barrier to prevent Al depletion in the coating...

Improved Selective Oxidation with Pt

Total Mass Gain during 500h cycles at 1000°C



1000°C, 1832°F

Only Pt added, no Hf

NiAl+Hf - lower because of better adhesion and slower growth rate

Ni-42.6Al & Ni-50.1Al - undoped alumina growth +some spallation

Ni-40.3Al - spinel formation increased total mass + some spallation

Ni-38.7Al-5.6Pt(20wt%) - better selective oxidation, i.e. no spallation

What is “co-doping”?

Recently: adding 2 reactive elements to improve oxidation behavior

Examples:

- Y-Hf: René N5 10-100ppma Y, 500ppma Hf
- Y-Zr: Haynes 214 10-50ppma Y, 100-150ppma Zr
- Y-Hf: ORNL lab experiments on FeCrAl and NiCrAl
- similar to Y-Ti: commercial ODS FeCrAl (Quadakkers, et al.)

Formerly: adding a quaternary non-reactive element addition to NiAl

Why co-dope?

It works! Especially in NiCrAl-type alloys

Lower Y alloy addition avoids NiY_x internal oxidation problem

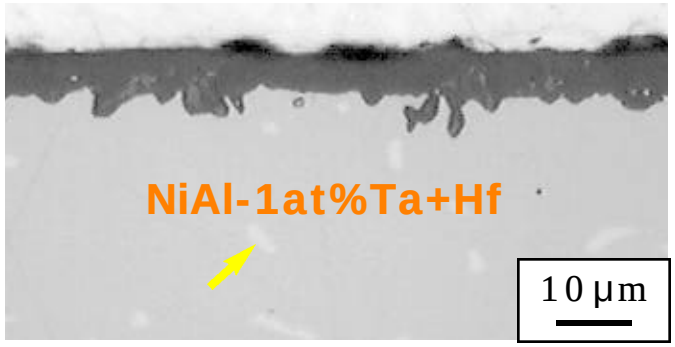
How do I co-dope an alloy?

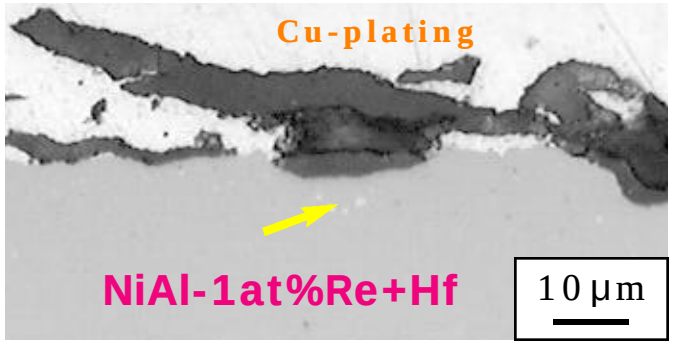
Empirically: Add Y until [Y]/[S] > 1

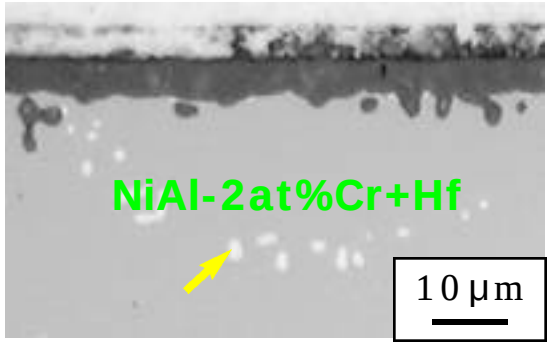
- add larger quantities of a more-soluble dopant like Zr or Hf
- Zr or Hf additions alone are not nearly as effective

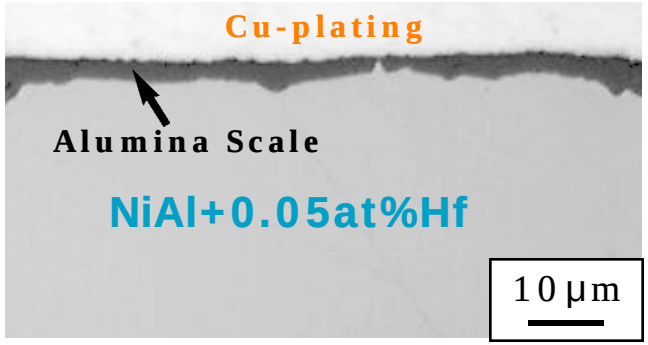
Quaternary additions are detrimental to NiAl+Hf

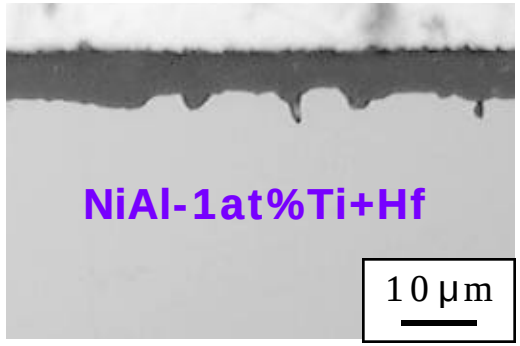
metallography after 1000x1h at 1150°C in O_2

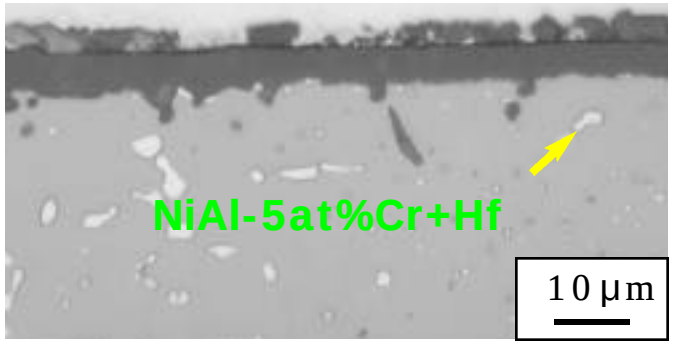


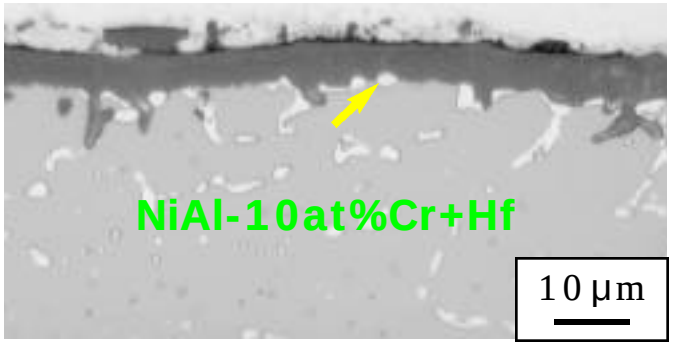










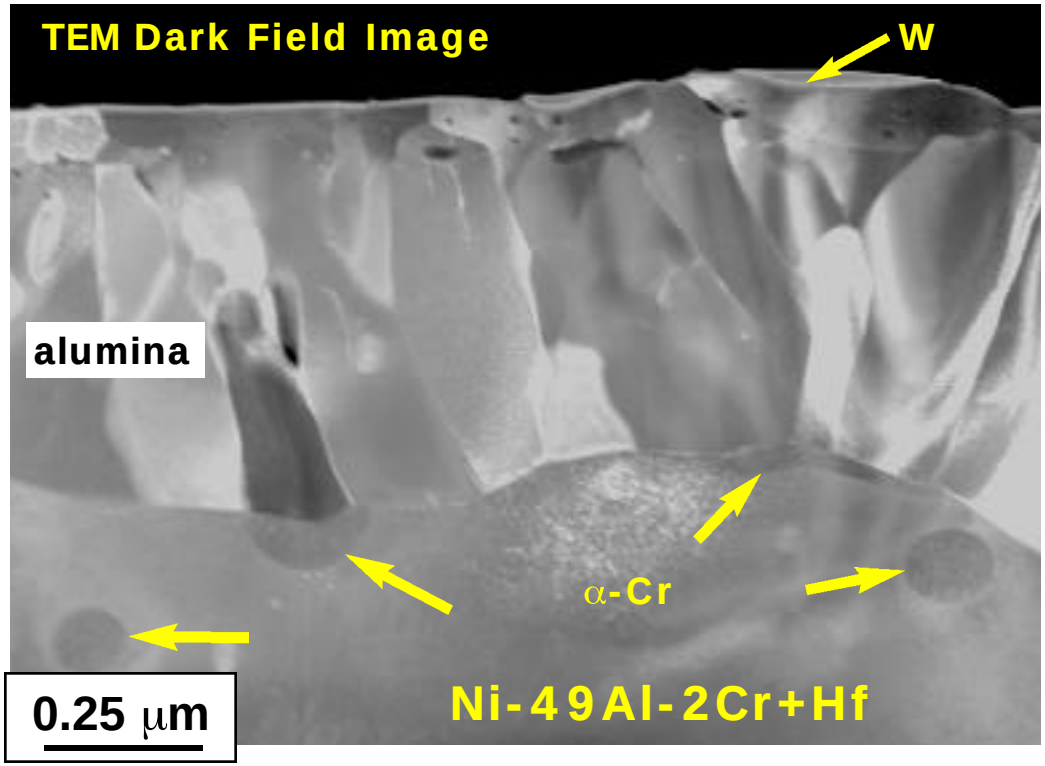


All additions accelerate scale growth rate compared to NiAl+Hf

Problems with scale adhesion with Cr and Re -> precipitates

Cr effect on Hf-doped scale

scale on Ni-49Al-2Cr+Hf after 500x1h at 1100°C



NiAl+Hf:

With Cr:

fine columnar grains

α-Cr at interface

Without Cr:

larger grains

Thicker scale forms than on NiAl+Hf (<0.01Cr)

With Cr, finer columnar grains ->more diffusion paths

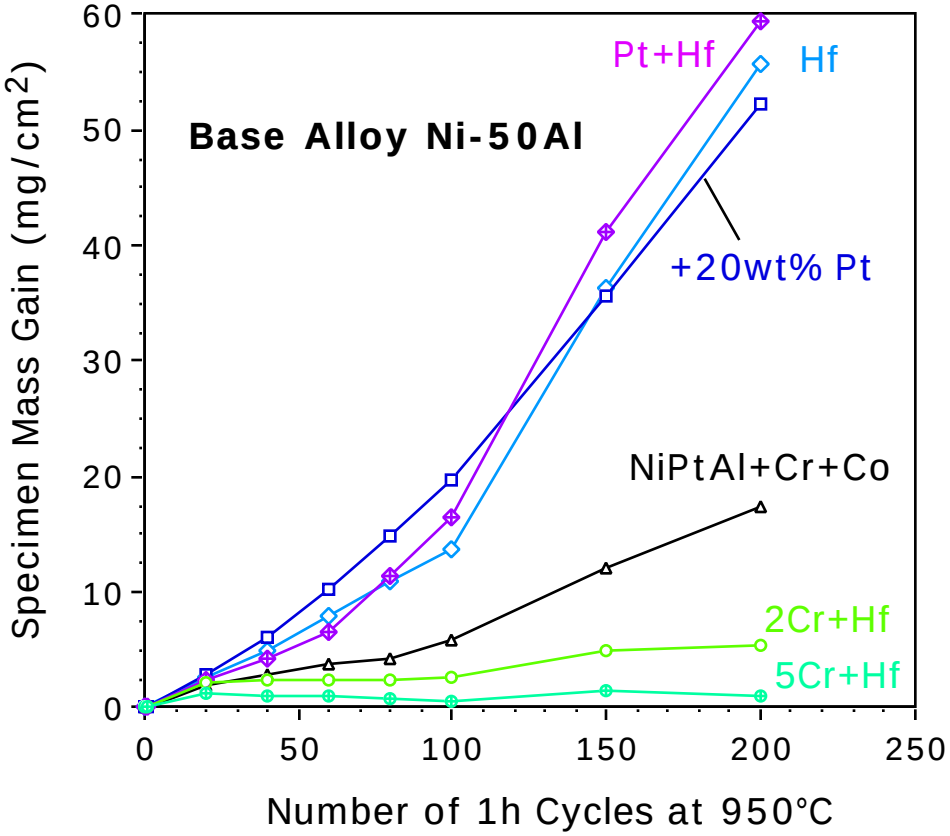
Might be effect of Cr on Al_2O_3 phase transformation

Brumm/Grabke suggested faster α nucleation with Cr

But Cr may be defeating the slow (large grain) nucleation with Hf

Hot Corrosion at 950°C

1h cycles with surface coat of Na_2SO_4



C. Leyens while at ORNL

Na_2SO_4 strongly attacks alumina scales

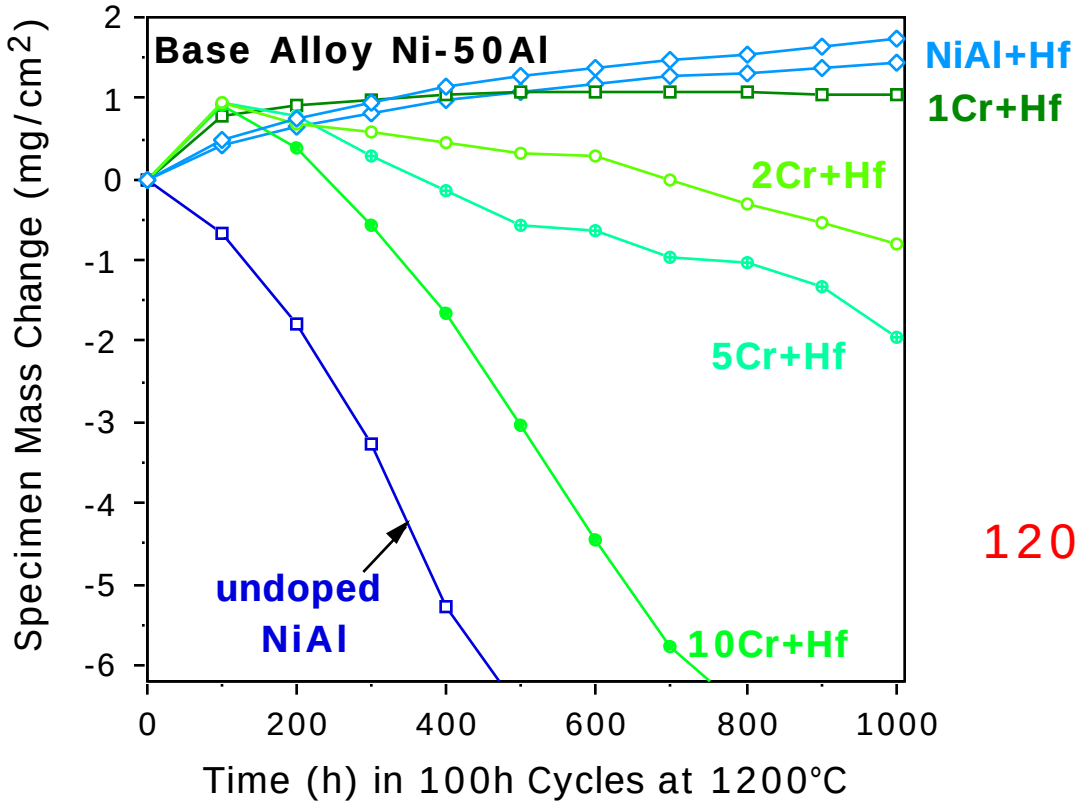
Hf and Pt additions have little effect on β-NiAl

Significant improvement with the addition of Cr

(confirms role of Cr proposed by R. Rapp)

Increased Scale Spallation with Cr Additions

Cast alloys in 100h cycles at 1200°C



1200°C, 2192°F

Hf-doped NiAl shows virtually no spallation

With Cr additions, significant spallation occurs

(commercial coatings contain approx. 5at%Cr)

α-Cr particles at metal-oxide interface may cause spallation(?)

Chromium

Without Cr, no hot corrosion resistance for NiAl
(Commercial Pt-modified coatings contain≈5at% Cr)

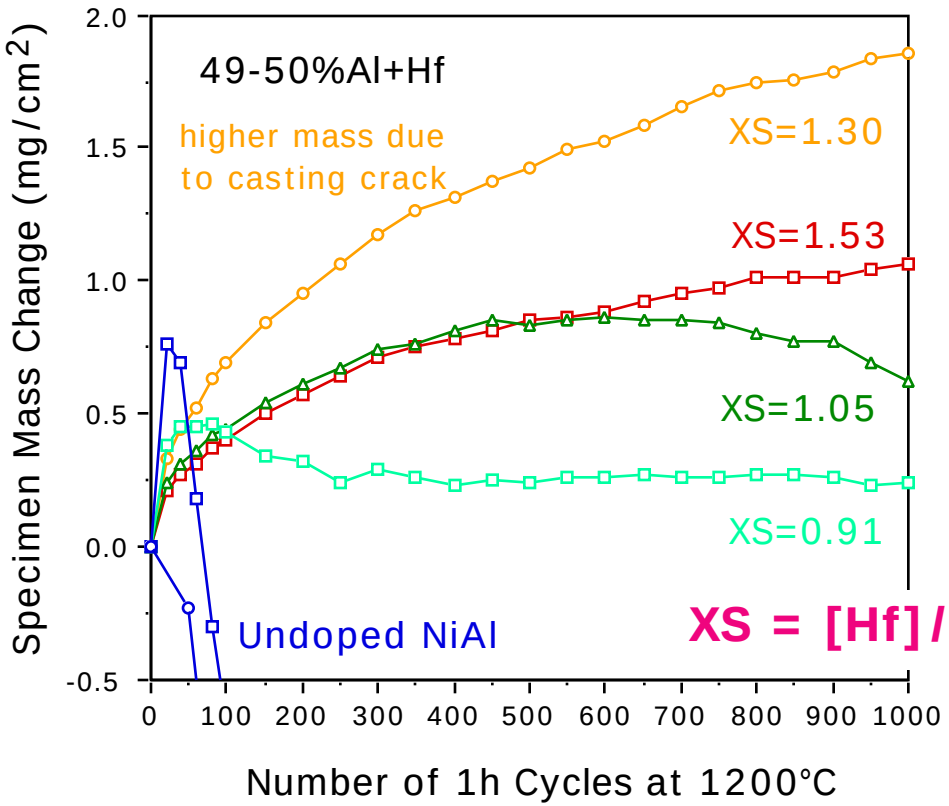
With Cr, the scale on NiAl+Hf grows at a faster rate
and is more prone to spallation
(likely due to α-Cr formation at metal-oxide interface)

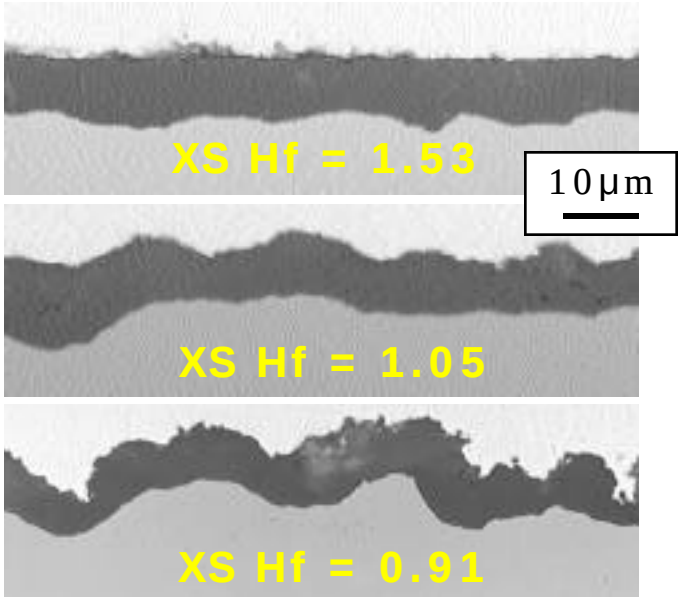
Resistance to hot corrosion and exceptional oxidation resistance appear to be mutually exclusive goals

Application will determine which compositions should be pursued.

Effect of C-doping on NiAl+Hf

testing in 1h cycles at 1200°C





XS = [Hf]/([C]+0.5[O]+[N])

after 100h at 1200°C

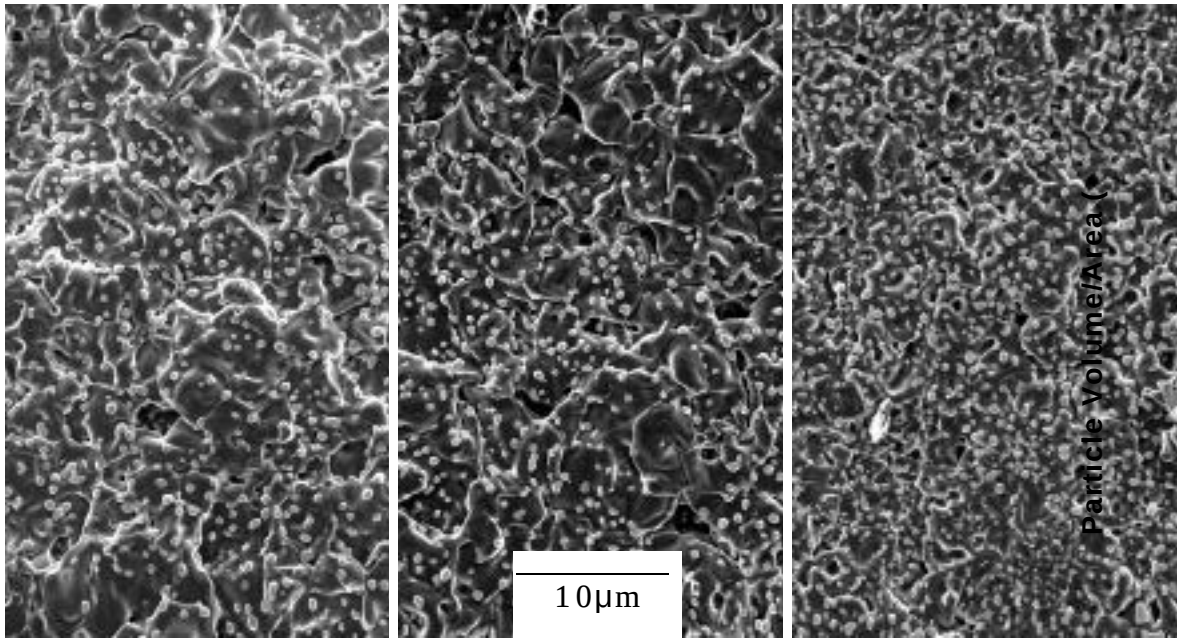
Typically, [Hf] = 450-550ppma (plasma analysis)
[N] = <4ppma (LECO) [S] = <2ppma (by GDMS)
[0] = 20-30ppma (LECO)

XS varied by changing [C] -> making graphite additions to the casting

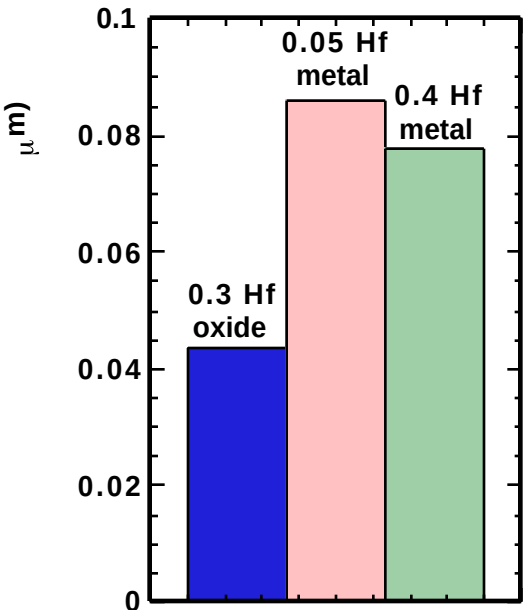
Is XS > 1 a critical parameter?

HfO_2 Formation at 1500°C

Comparison on NiAl after 4h at 1500°C



0.30at%Hf as HfO_2 | 0.05at%Hf | 0.40at%Hf



Particle size/volume were quantified using SEM BSE image analysis

With HfO_2 in the alloy, smaller particles and lower volume fraction due to a lower Hf activity? (idea proposed by Univ. of Pitt. team)

For NiAl+Hf, higher Hf meant more smaller particles but no increase in the volume fraction (same observation with NiAl+Zr)

Does something similar occur for HfC formation?

Improve aluminide bond coat performance by:

1. Adding best reactive element ->Hafnium

   slows the alumina growth rate and improves adhesion

2. Maintain ≈10-20wt%Pt in coating

   not for scale adhesion or deformation problem
   but Pt improves selective oxidation (less $NiAl_2O_4$)

3. Critical performance break between 35 & 37.5%Al

   Hf can't help problems of Ni_3Al, two phase alloys

4. Decrease elements from the substrate

   Other elements diffusing into coating diminish
   the Hf benefit

5. Control carbon content to maximize Hf benefit

   Hf/C ratio appears critical for getting the best behavior

General note: thermal expansion is a first order adhesion parameter