Extended Alloy Lifetimes Through Improved Coating Performance and Composition Optimization

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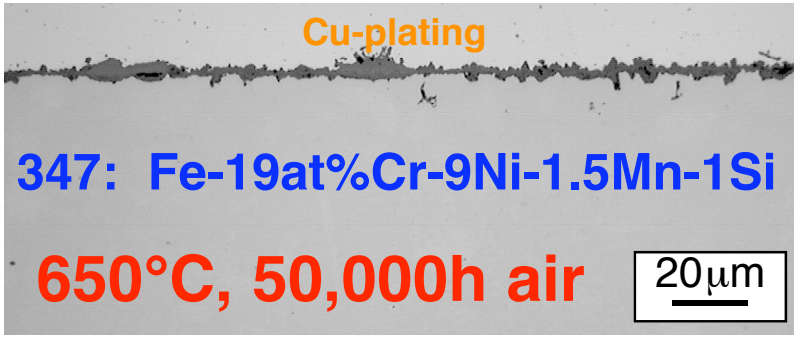
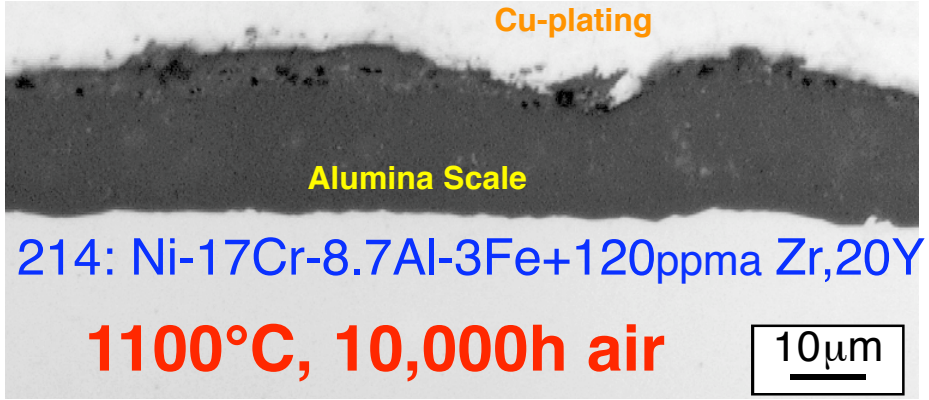
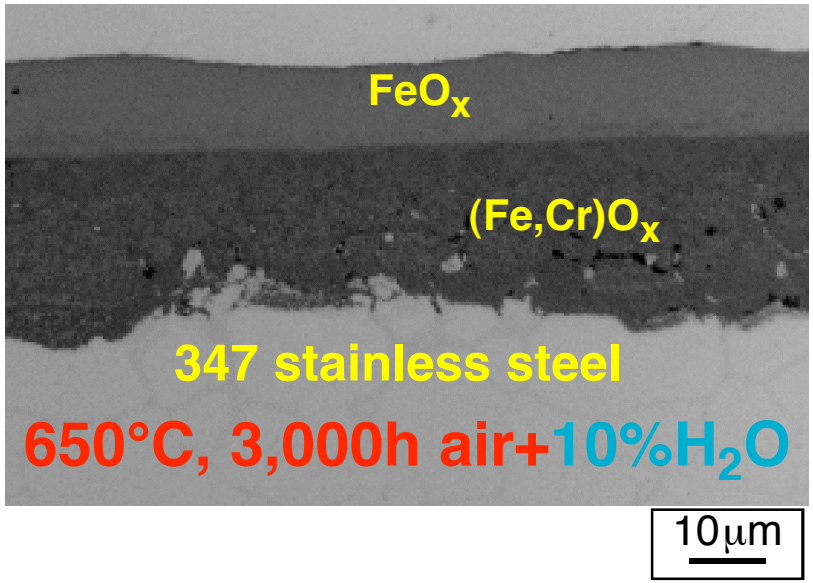
High Temperature Oxidation

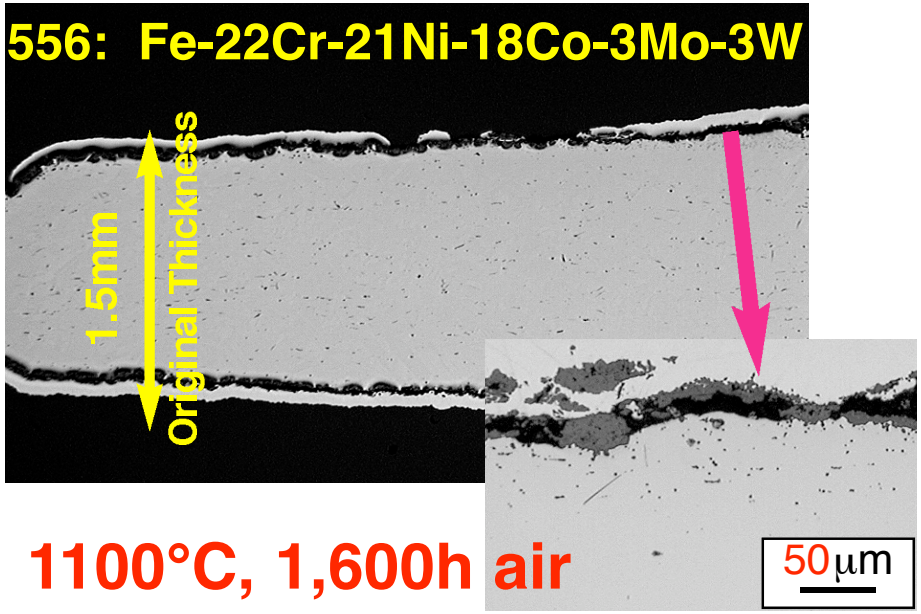
What we like:





Sometimes, what we get:





One solution: Coatings

Applications: Next generation power plants

Ultra-supercritical steam - up to 760°C from ~575°C

higher efficiency, lower emissions

Coal gasification - low P_{O_2}, high P_{S_2}

high natural gas prices driving interest

Benefits of Fe-Al coating:

- resist sulfidation/carburization (well-studied)
- Al_2O_3 surface oxide resistant to water vapor

  (important in combustor, heat exchanger/recuperator, steam)

Extensive work by Rapp et al. on Fe-Al coatings

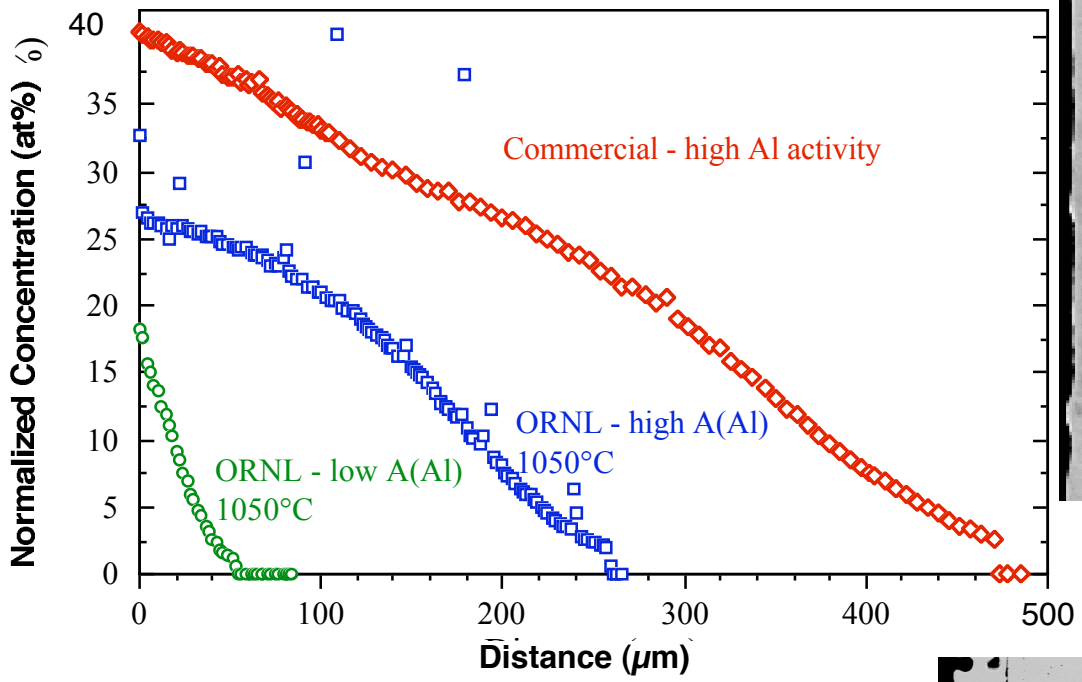
Before coatings are widely employed, critical questions need to be answered about benefits:

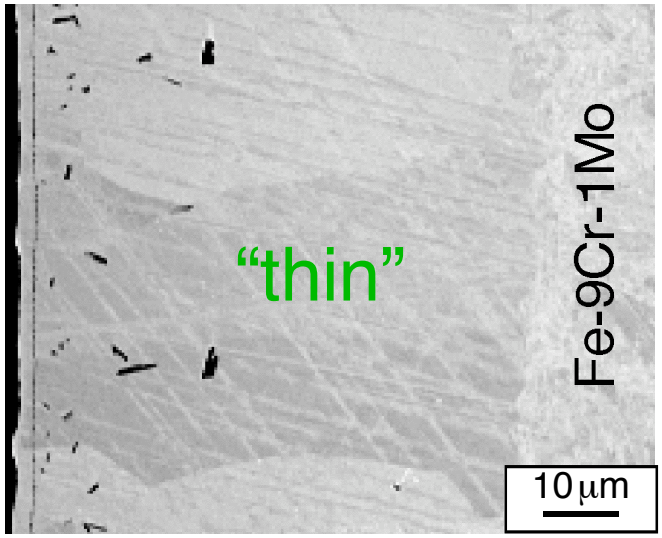
- maximum temperature for oxidation resistance
- need sufficient Al -> diffusion into substrate
- thermal expansion mismatch with oxide & substrate
- coating effect on substrate mechanical properties

As-deposited coating on Fe-9Cr

1050°C chemical vapor deposition at ORNL

EPMA composition profile

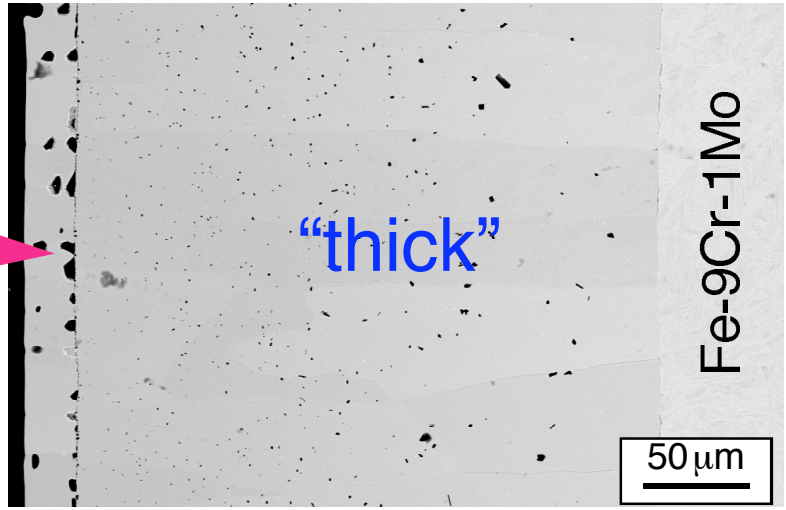




*Model process where Al reservoir can be varied (surface Al & depth)

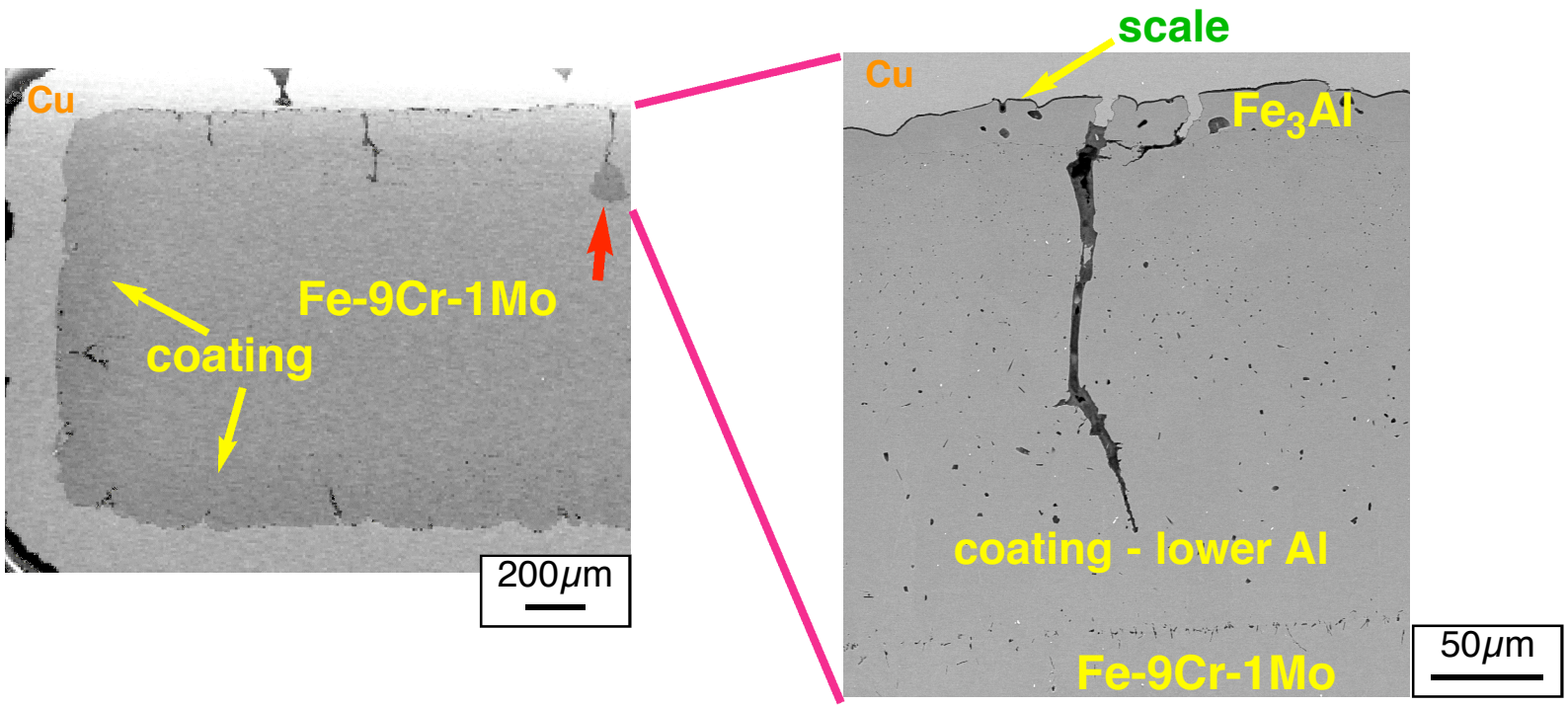
*Thin, outer Al-rich layer and inner ferritic Fe(Al) layer

*Also coatings on P92 (Fe-9Cr-2W) and austenitic 304L (Fe-18Cr-8Ni)



Aluminized Fe-9Cr-1Mo

Characterized after 2000 x 1h at 700°C in humid air



Thin, protective scale formed, BUT
Deep cracks observed through coating
Coating breached in one location (red arrow)

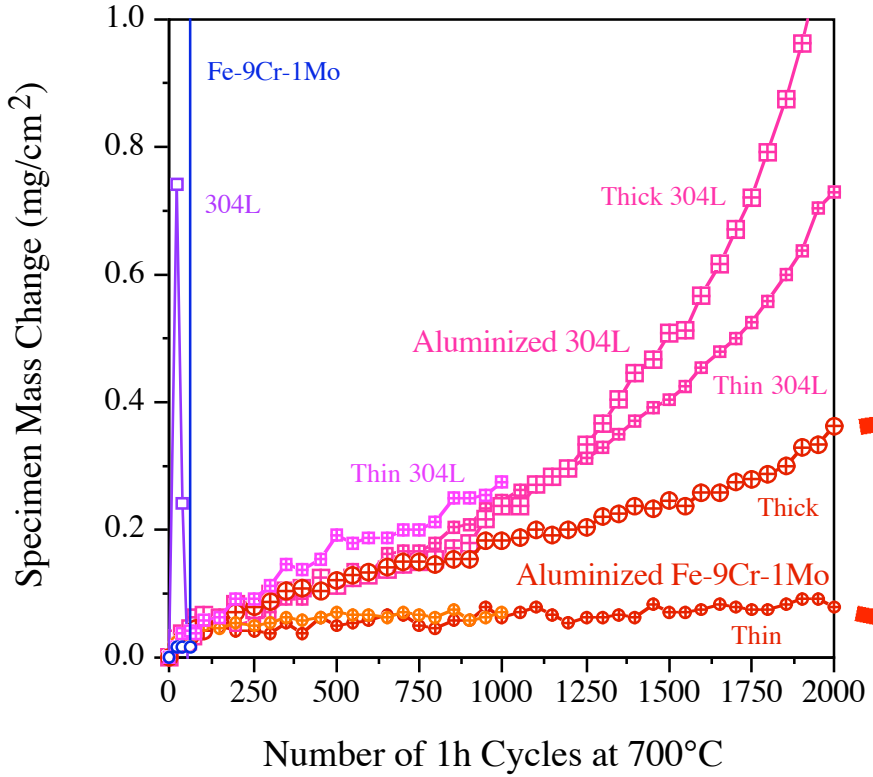
Problem source:

Thermal expansion mismatch between Fe_3Al and Fe-9Cr-1Mo

(Zhang et al., Surf. Coat. Tech. 188-189 (2004) 35)

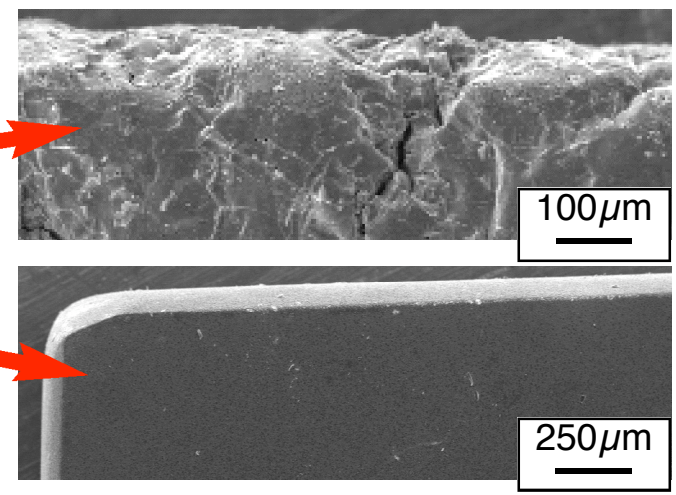
If CTE mismatch is problem, does coating thickness affect performance?

Thin & thick CVD coatings, 1h cycles, 700°C, humid air



$$\sigma_{coating} = f(\Delta\alpha_{coat\text{-}sub})$$

$$\varepsilon_{coating} = f(\delta_{coating})$$



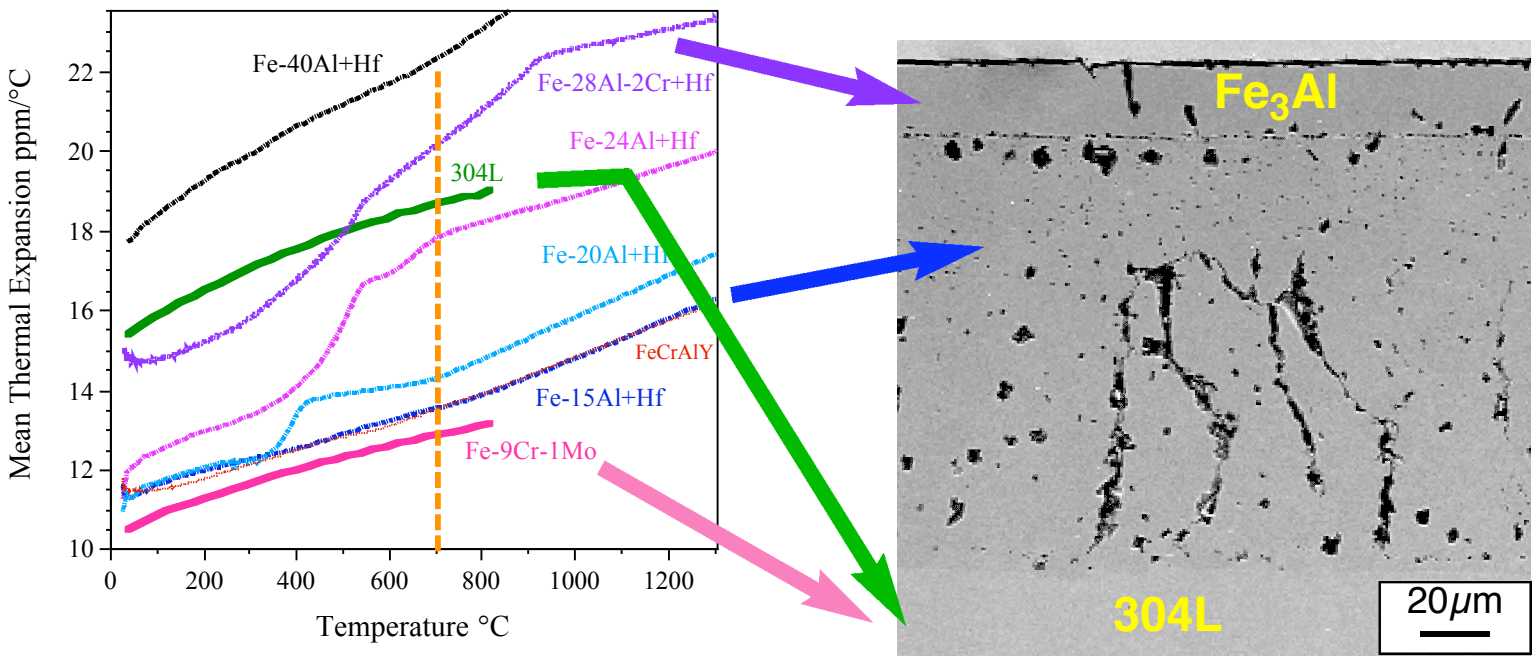
For Fe-9Cr-1Mo, thinner coating not showing signs of degradation after 2000 cycles at 700°C, similar to 2001 result (stop at 1000h)

For 304L, thin and thick coatings showing similar performance

why the difference between ferritic and austenitic?

Additional problem for austenitics

Likely explanation is the thermal expansion mismatch



For coated Fe-9Cr-1Mo:

Outer Fe_3Al layer different, inner coating & substrate are ferritic

For coated 304L,

Al addition likely created a ferritic inner layer

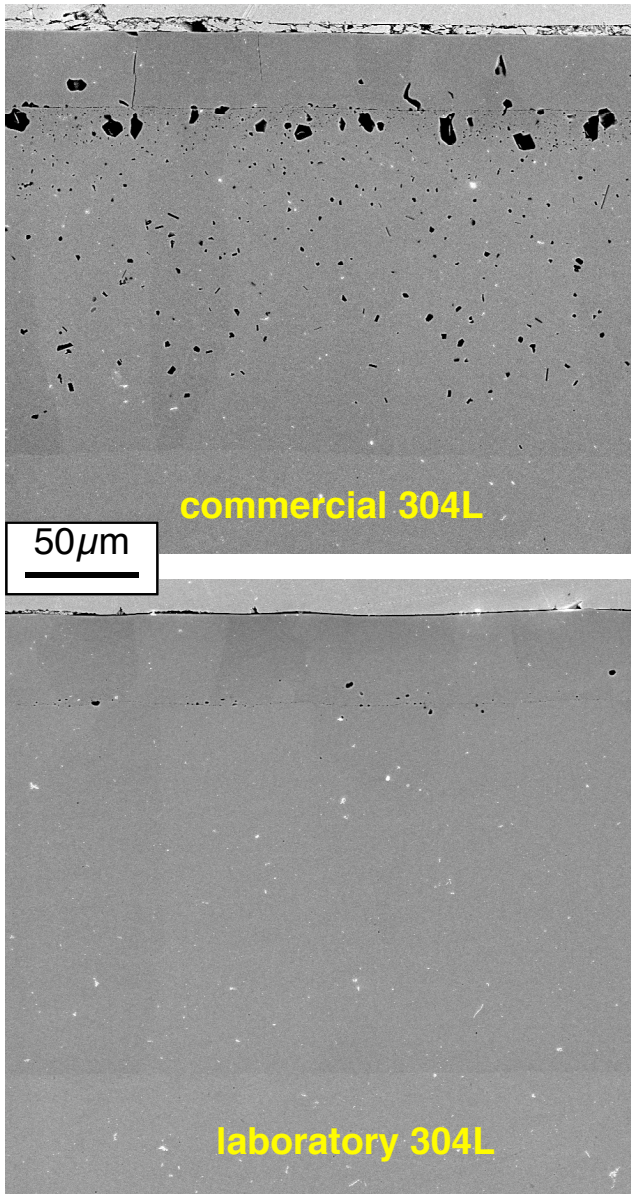
Three layers have distinct thermal expansion behavior (hi/low/hi)

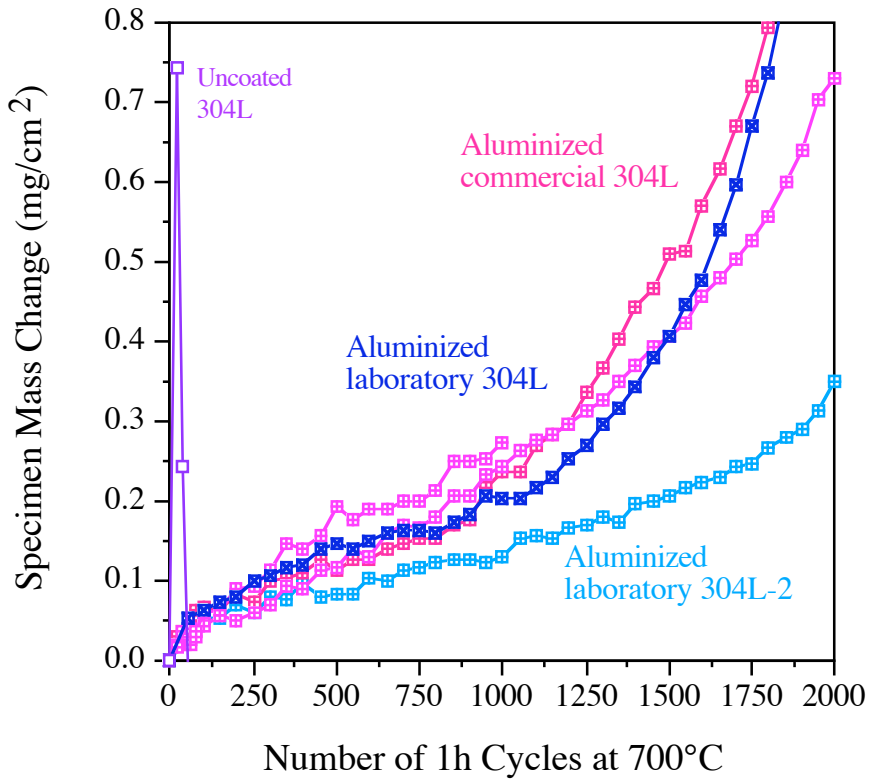
Mismatch may have resulted in stress sufficient to crack coating

What about defects in the coatings?

Substrate chemistry control - low N

Less cracking, fewer defects in coatings





Testing at 700°C, 1h & 100h cycles and 800°C 100h cycles

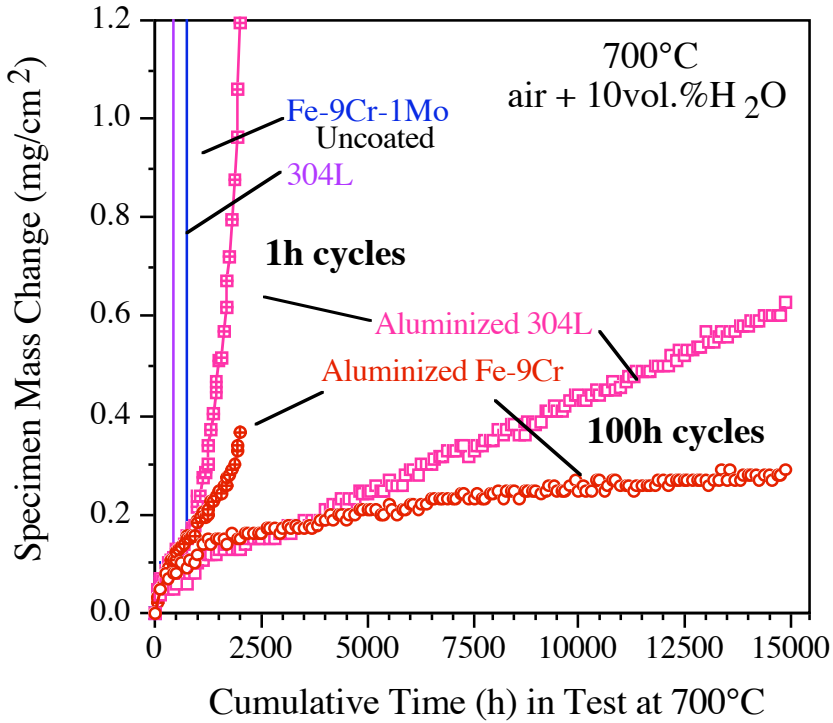
No clear benefit, some times better

But N needed for alloy strength

Zhang et al., Surf. Coat. Tech. (2005)

Effect of cycle frequency at 700°C

In 100h cycles, coatings have reached ~15,000h



700°C, 1292°F

100h cycle before cooling to room temperature

Higher mass gain for austenitic 304L substrate

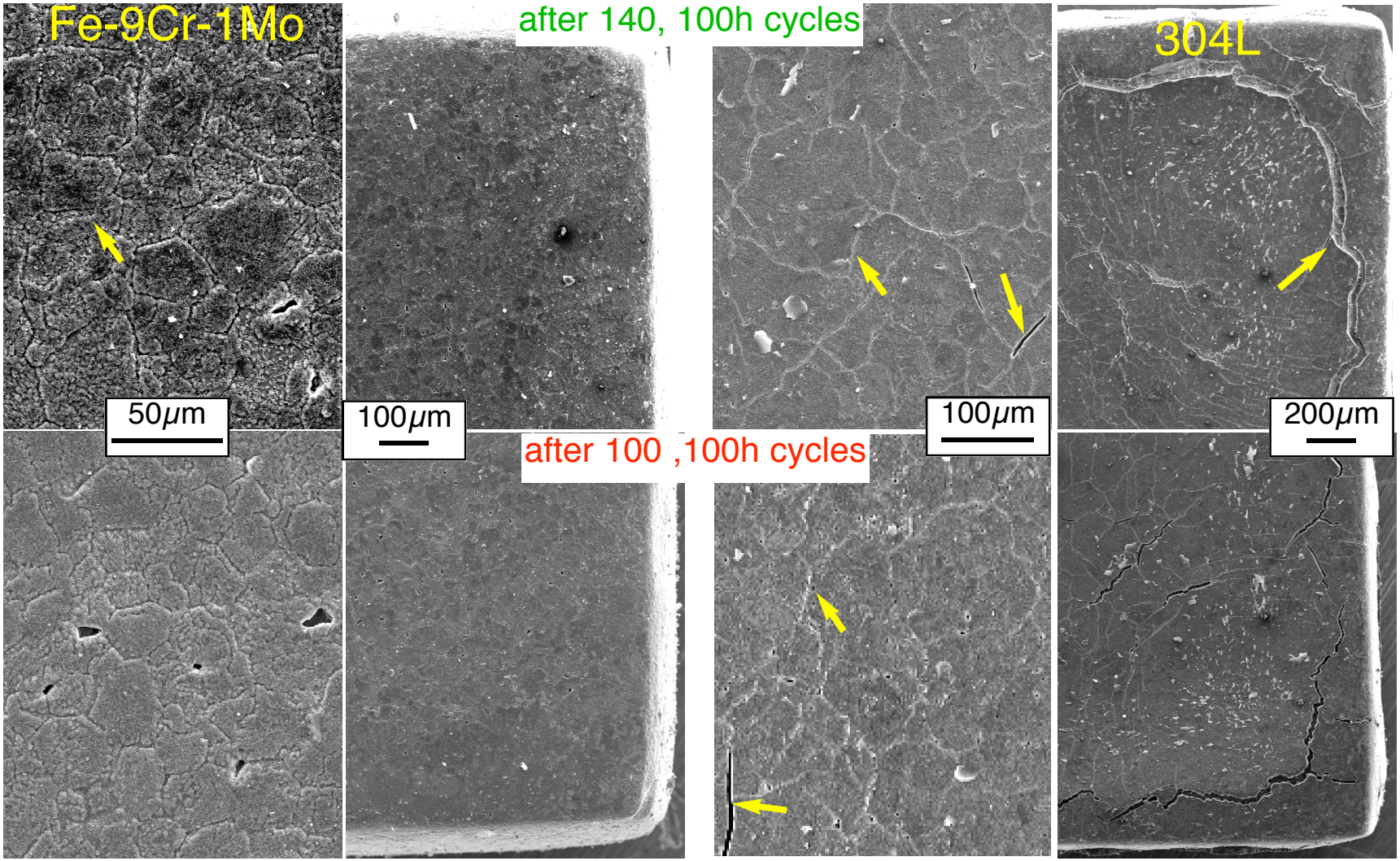
No signs of accelerated attack due to H_2O

Lower mass gain than observed for 1h cycles

(Details in Zhang et al., Surf. Coat. Tech. 188-189 (2004) 35)

Surface plan view after cycling

increase in surface damage after 140, 100h cycles

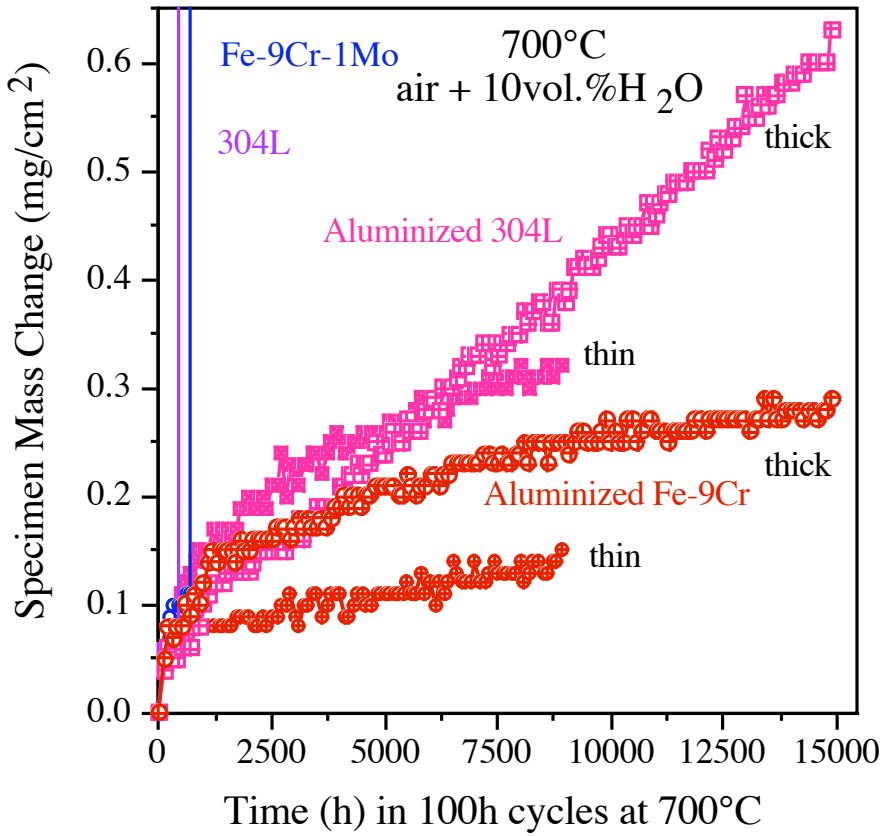


Fe-9Cr-1Mo: cracks in specimen face but no edge cracking

304L: scale spallation and macro-cracking on face and at coating edge

Effect of coating thickness

In 100h cycles at 700°C



700°C, 1292°F

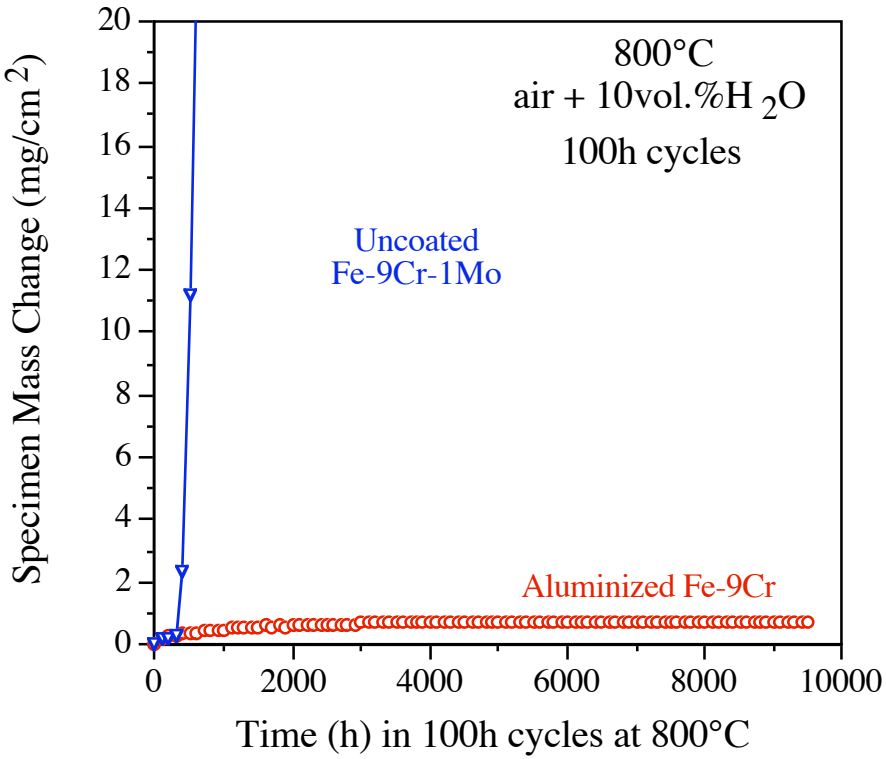
Lower mass gain, less cracking for thin coatings

As with 1h cycles, 304L coatings (thin and thick) show higher mass gain and more cracking

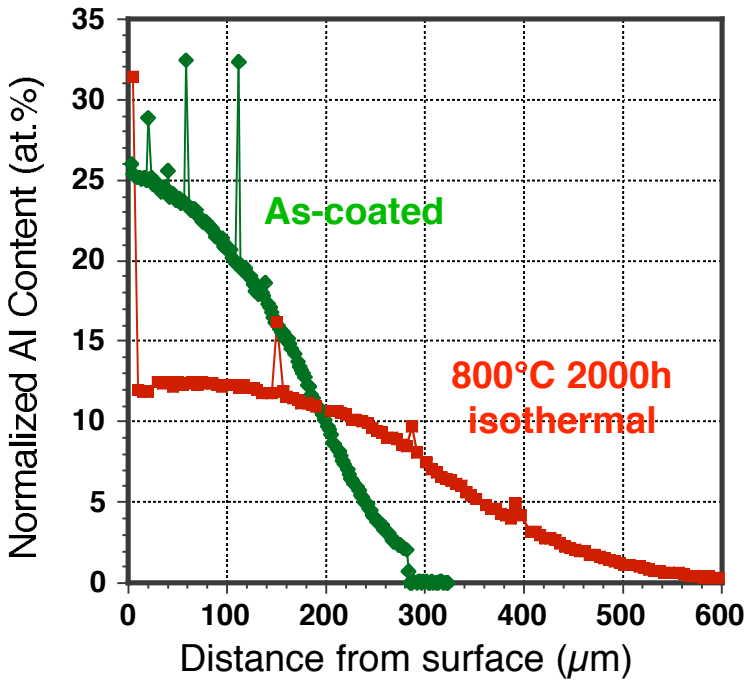
Thick 304L coating appears to be near end of life

Accelerated testing: 800°C

100h cycles, air+10%H_2O



800°C, 1472°F



Aluminized Fe-9Cr-1Mo specimen recently reached 9,500h

Diffusion test (isothermal, air) showed coating had dropped to 12 at.%Al at surface after 2,000h at 800°C

Calculation show Al down to <8at.%Al and Al tail to specimen center!

Coating Program Update

Model developed based on diffusion-oxidation data

Missing is critical Al content C_b at coating failure

Based on cast Fe-Al alloys: ≈10at.%

≥9%Cr in coating lowers C_b below Fe-Al value

Finer grain size in coating should lower C_b

Determining C_b:

At 700°C, coating at 14,700h and counting

- duplicate coating to be stopped at 10,000h
- testing "thin" coating, lower Al reservoir

At 800°C, (accelerated test) coating at 9,500h

- diffusion model suggests Al diffused to center
- duplicate coating stopped recently at 5,000h
- make thin coating on thicker (3mm) substrate?

Lower as-coated defects by reducing alloy N content

Currently showing mixed results in testing

Modeling Oxidation-Limited Alloy Life

Lifetime model developed by Quadakkers, Bennett, et al. for ODS FeCrAl tubes with 1-3 mm cross-sections

Premise: Calculate time to breakaway (FeO_x formation) by knowing total Al reservoir available and rate of Al consumption

Model inputs:

- initial Al content (**C_o**)
- the critical Al content where Al_2O_3 will no longer form: (**C_b**)
- the thickness of the specimen (**d**) and density (ρ)
- Al consumption rate (e.g. **kt^n**), **t** is time (**n**=0.5 for parabolic)
  consumption rate is higher when scales spall, **n** -> **1!**

$$(C_o - C_b)/100 \cdot d/2 \cdot \rho = k \cdot t^n \cdot \frac{\text{(mole Al)}}{\text{mole O in } Al_2O_3}$$

Assuming: (1) Al concentration profile is flat in alloy
(2) oxidation can be described by constants **k** and **n**

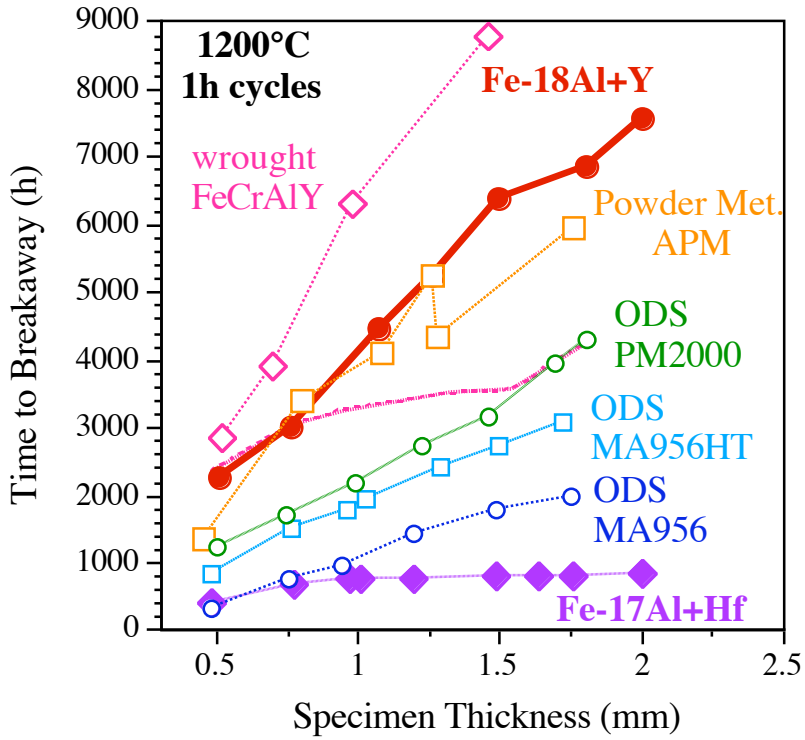
How extend life? Reduce consumption or increase reservoir

Affect **k** and **n**(?) by slowing scale growth & reducing spallation

Thicker components or new alloys with higher C_o-C_b value

Alloy Development Program

Goals: better alumina-forming alloys & feedback for coatings



Y

Hf

Real life:

n≈1 for FeCrAl

Fe-17Al+Hf

Al gradients

lower life

(Mater. Sci. Forum 2004)

Looking for Fe-base alloys with longer life than FeCrAlY

Y/Hf co-doped increase 37% (J. Am. Ceram. Soc. 2003)

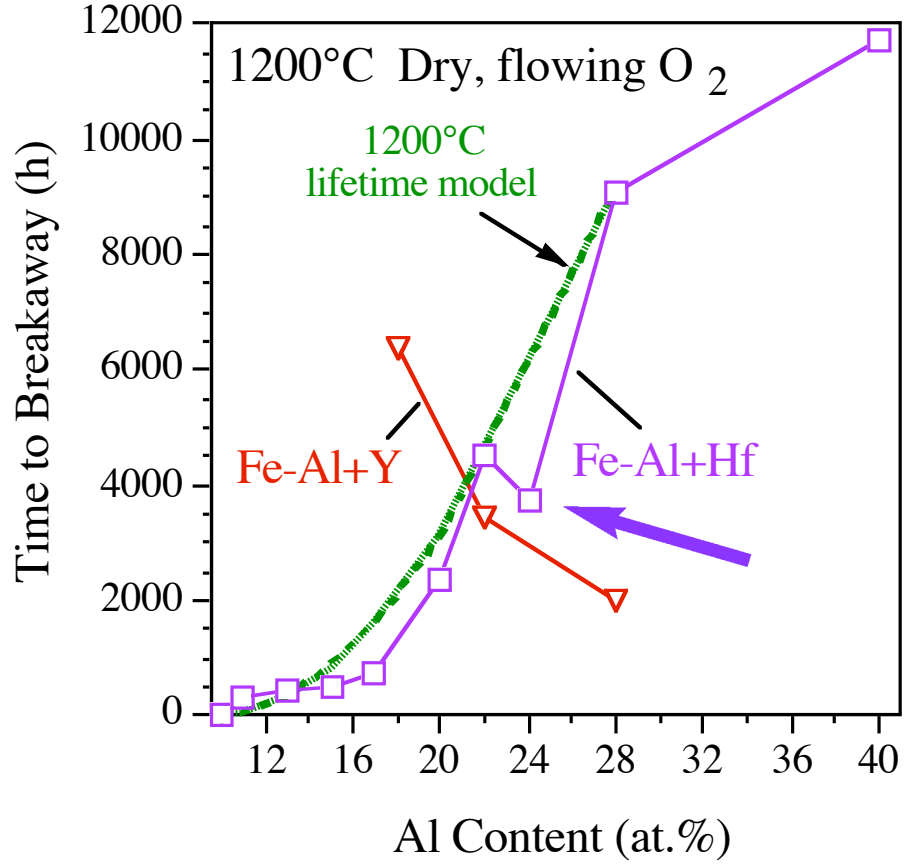
Fe-Al alloys with higher Al contents (C_o) than FeCrAl

Intermetallic Fe-Al spalls too much

Ferritic Fe-Al have more potential - optimized with Y

Problems with Y-doped Fe-Al

Increasing Al >18% did not increase 1200°C lifetime!



1200°C, 2192°F

Quadakkers' model explained results for Fe-Al+Hf (w/ I. Wright)

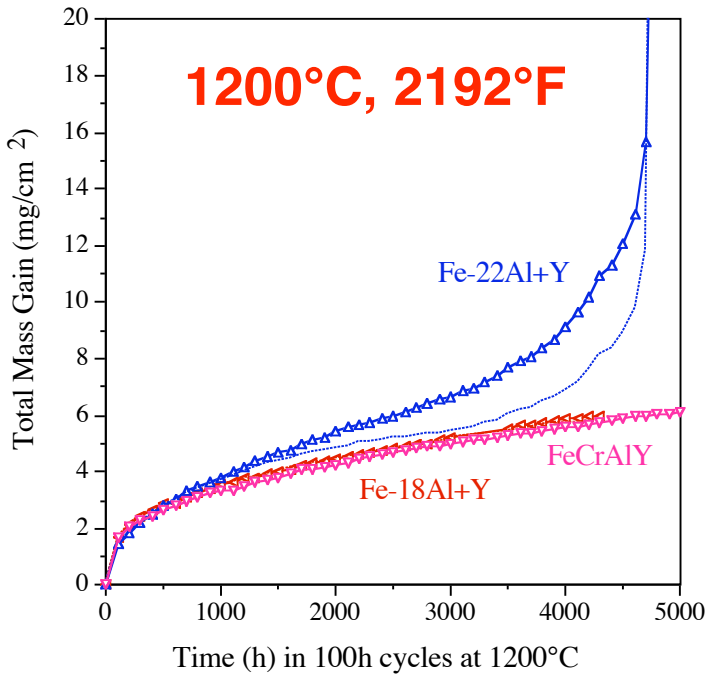
Premature failures for Fe-22Al+Y and Fe-28Al+Y

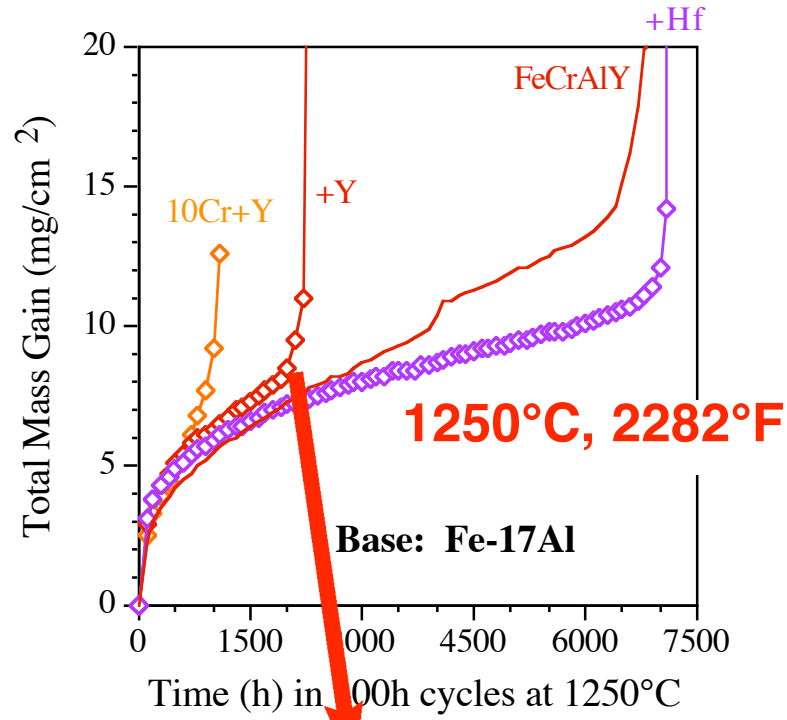
at 1200°C, 1h cycles (similar to lower life for Fe-22Al+Hf)

What is the problem?

“Broccoli” attack of Fe-Al+Y

Long-term at 1200°C & 1250°C showed accelerated attack





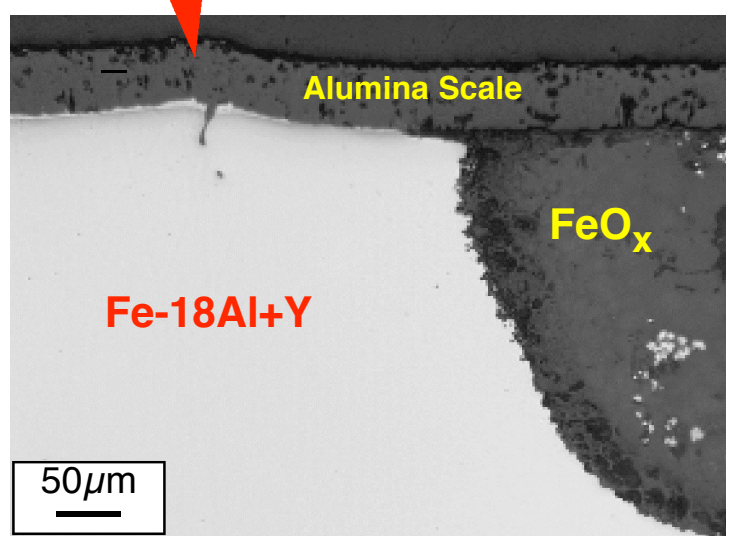
Accelerated attack at alloy grain boundaries: Quadakkers’ “broccoli”

Internal attack of gb carbides?

No strong carbide-formers with Y

Worse with addition of Cr

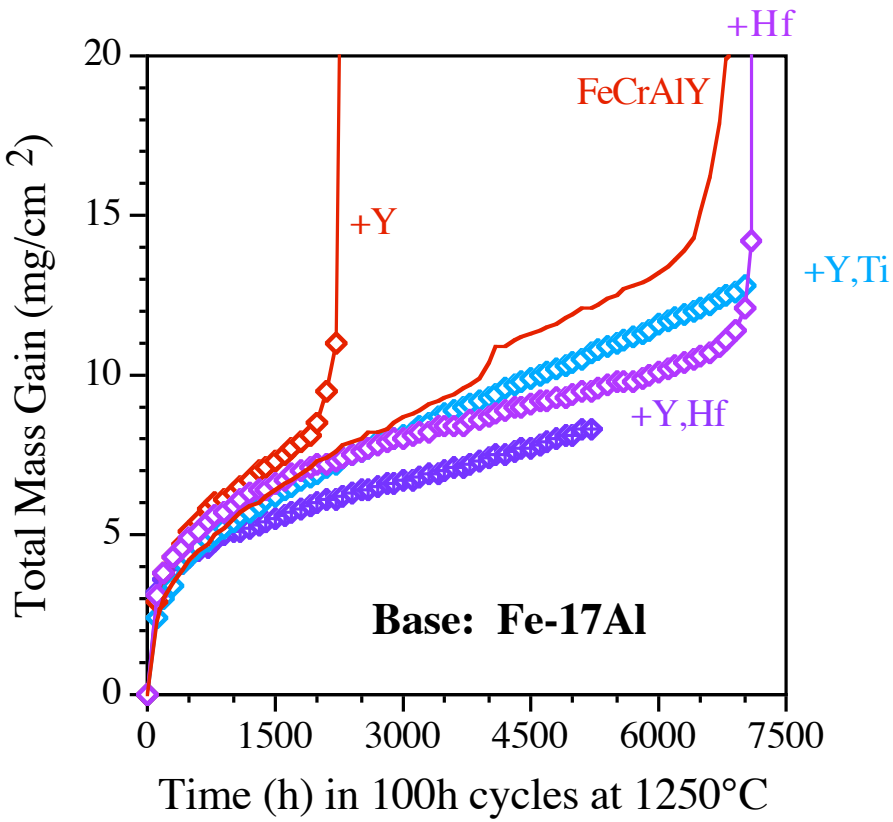
May occur at long times at low T



Successful cures for “broccoli”

Quadakkers: alloys need low C or strong carbide-formers

1250°C, 2282°F



Fe-17Al: adding a second carbide-forming element: Hf, Ti

Testing still in progress, increased life over only Y

For FeCrAl, Y+Hf co-doping more effective than Y alone

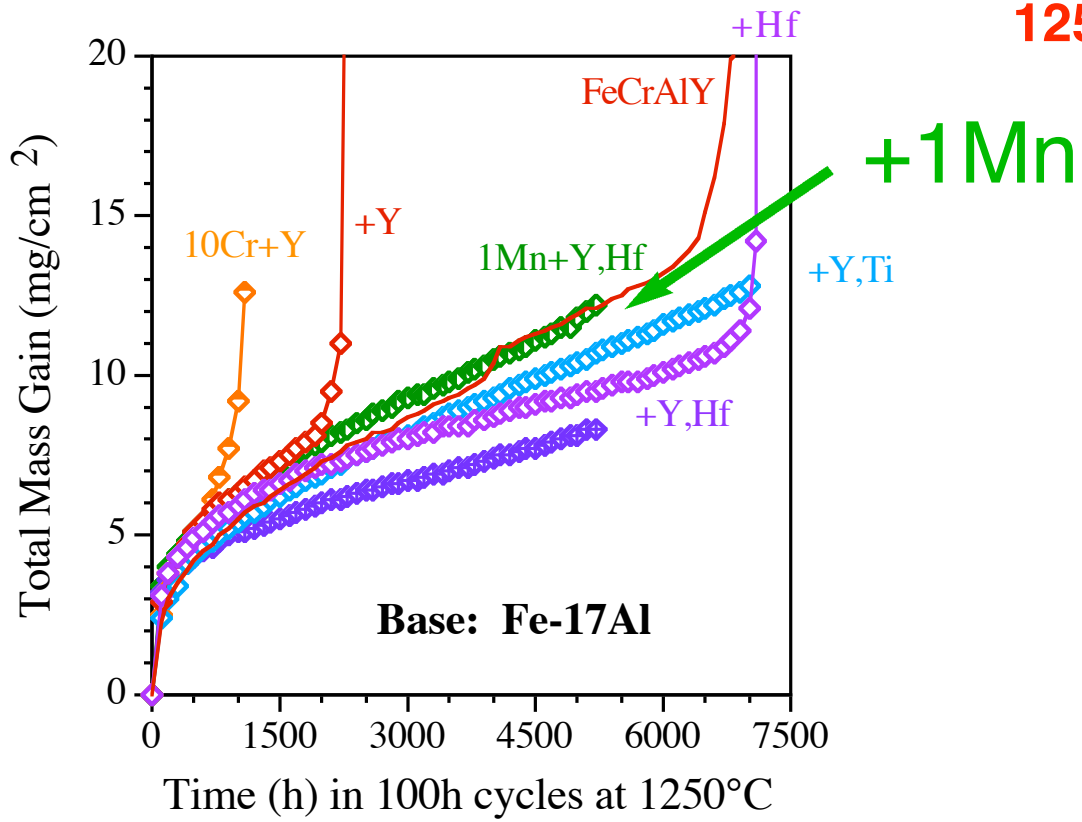
37% increase in lifetime with optimization

Strategies for increasing Al reservoir

Increase lifetime by adding Cr or Mn to lower C_b

1250°C, 2282°F

+10Cr



Could not evaluate 10at%Cr addition due to broccoli attack

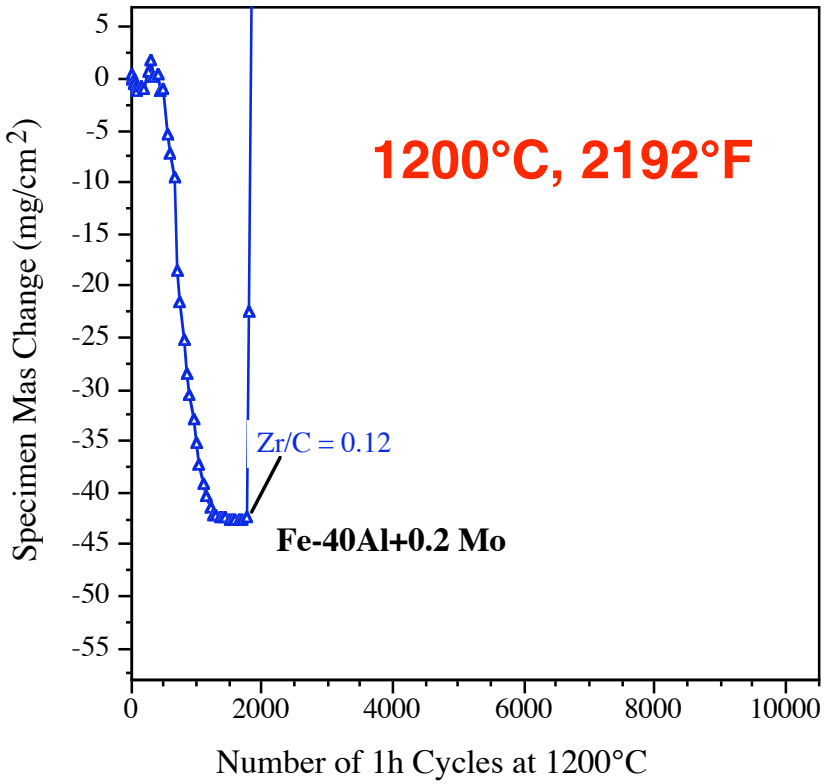
Fe-17Al+1%Mn addition with Y+Hf being evaluated

Castings with 10% Cr or 10%Mn will begin testing soon

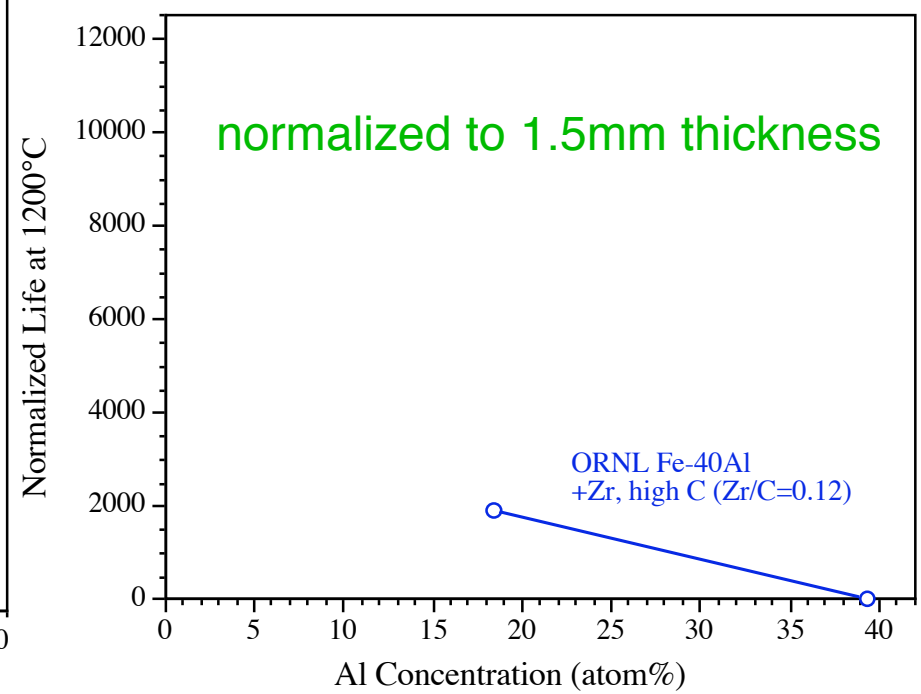
Y+Hf in these castings may slow Al consumption as well

Method for visualizing strategy

Typical mass gain plots don't convey relevant issues well



Life vs. Al: start to finish



Case stud of ORNL base alloy: Fe-40Al-0.2Mo-0.05Zr-0.4C

Despite ~40%Al, only ~2,000h lifetime at 1200°C, 1h cycles

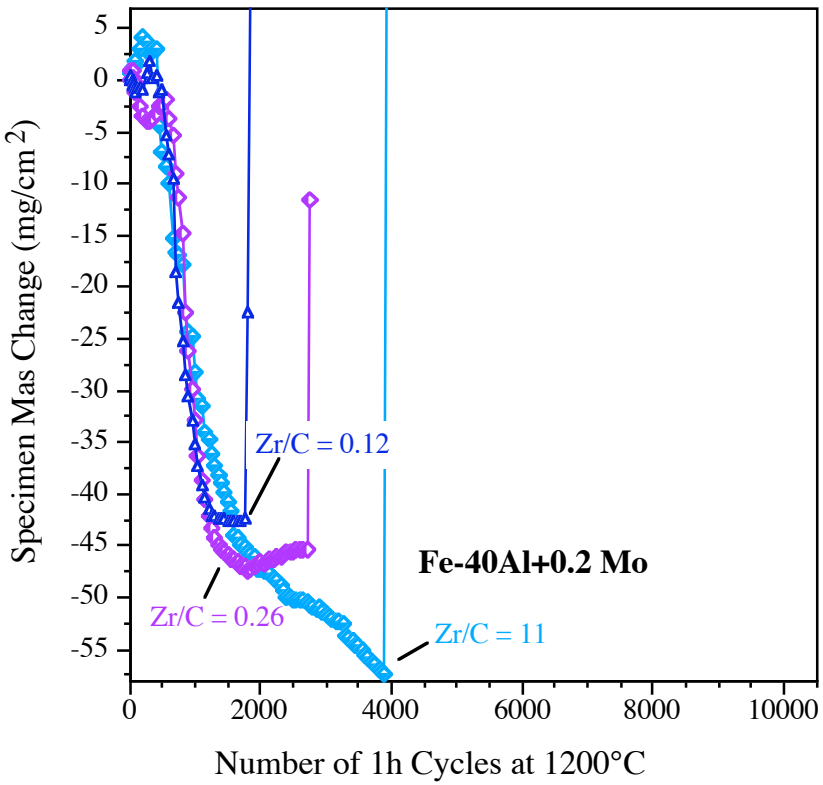
Not surprising based on (1) high CTE FeAl = high spall

(2) high C_C relative to C_{Zr} (Zr/C = 0.12)

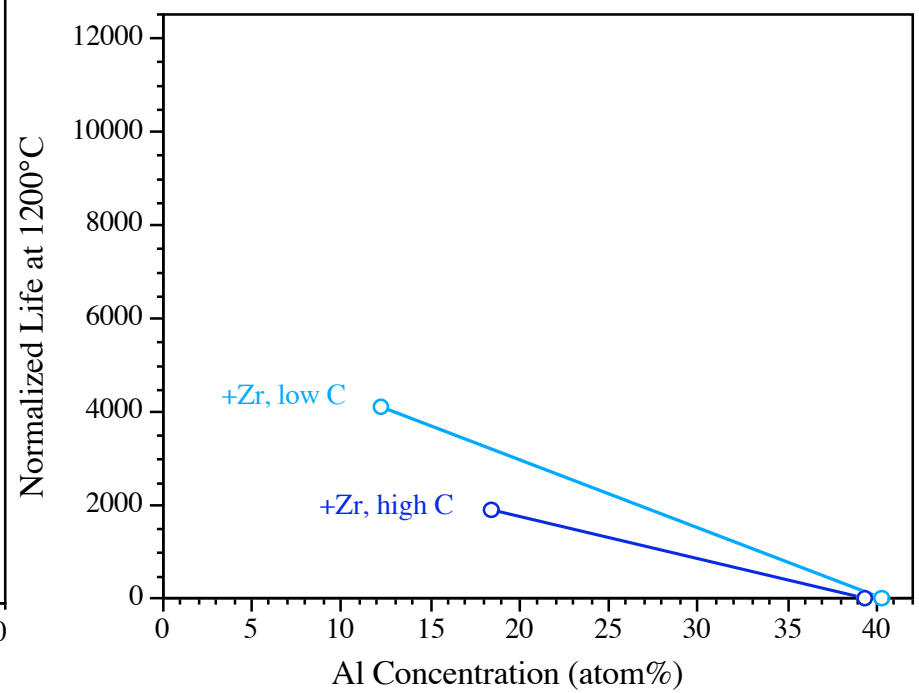
Large Al content gradient observed at failure: C_b ~ 18at%

Changing Zr/C increases life

FeCrAl work: Zr/C, Hf/C, Y/S > 1 is preferable



Life vs. Al: start to finish



Increasing Zr/C (by reducing C_C) increased lifetime

Still initial high spall due to CTE problem, C_{Al} drops to ferritic phase

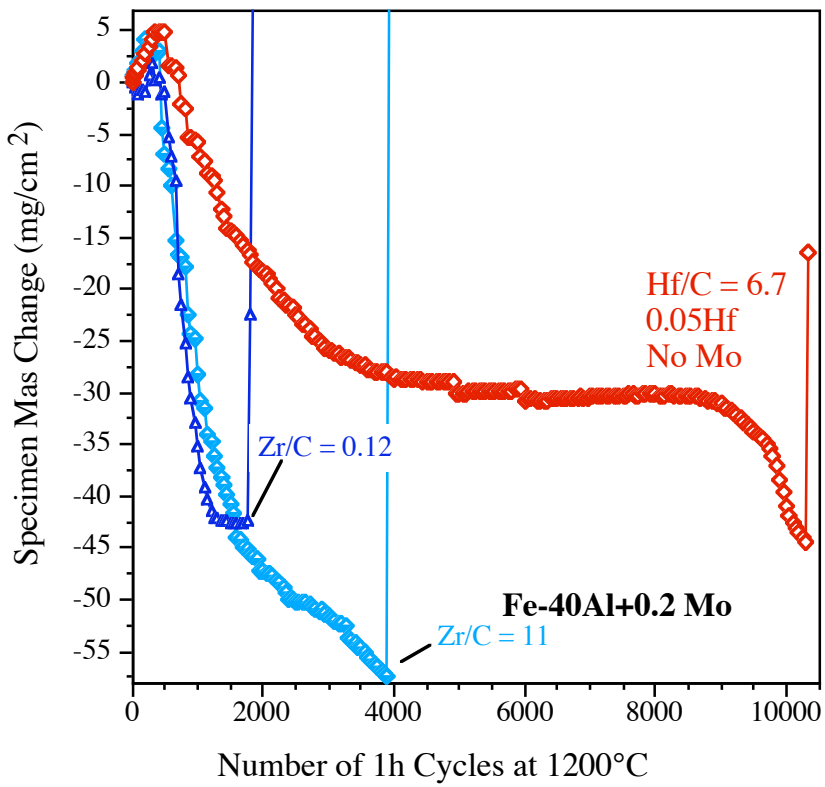
Alloy lifetime increased due to two factors:

(1) decrease in C_b to ~12% Al (larger reservoir, lower gradient)

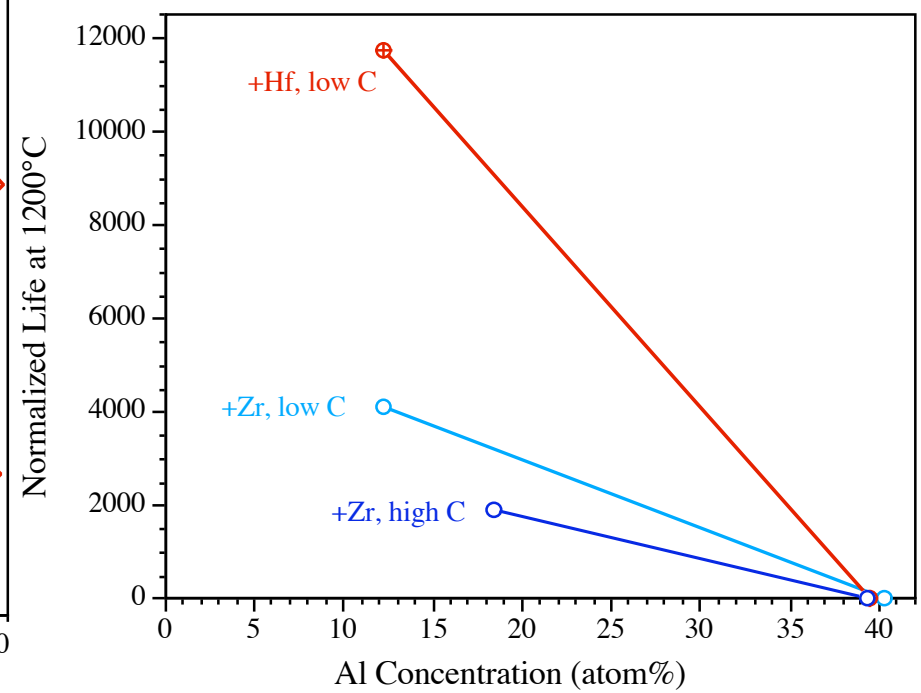
(2) slower Al consumption

6X increase in life with Hf

Fe_3Al work showed Hf more effective than Zr; Hf/C>1



Life vs. Al: start to finish



Little change in C_b with addition of Hf (same reservoir)

Dramatic decrease in the rate of Al consumption

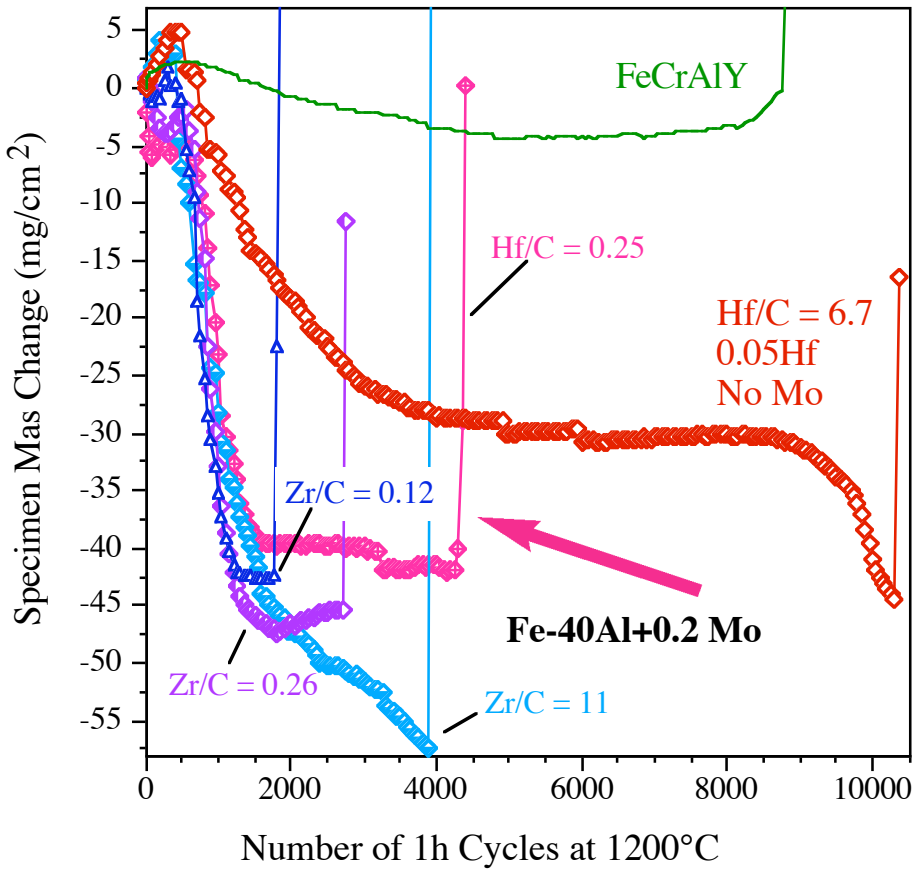
During cycling, FeAl substrate -> Fe_3Al -> Fe(Al)

Hf lowers scale growth rate in Fe_3Al period of life

(Pint and Schneibel, Scripta Mater. 52 (2005) 1199))

Further proof of RE/C effect

Fabricated Fe-40Al+Hf with C to get Hf/C<1



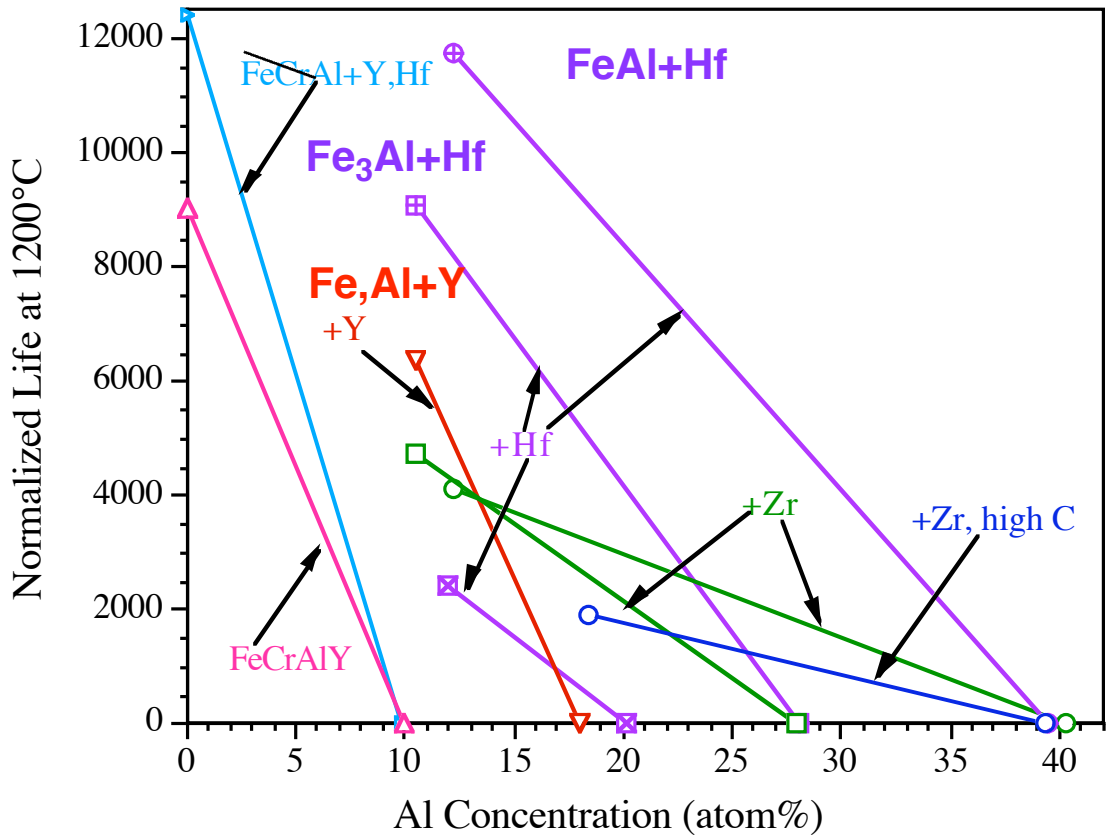
Ruin Hf benefit with addition of C, lifetime reduced by >50%

picked Hf/C=0.25 to compare to Zr-doped FeAl

No analysis of C_b in this material yet

General routes for improvement

Increased oxidation lifetime by slower Al consumption and increased Al reservoir (C_o-C_b)



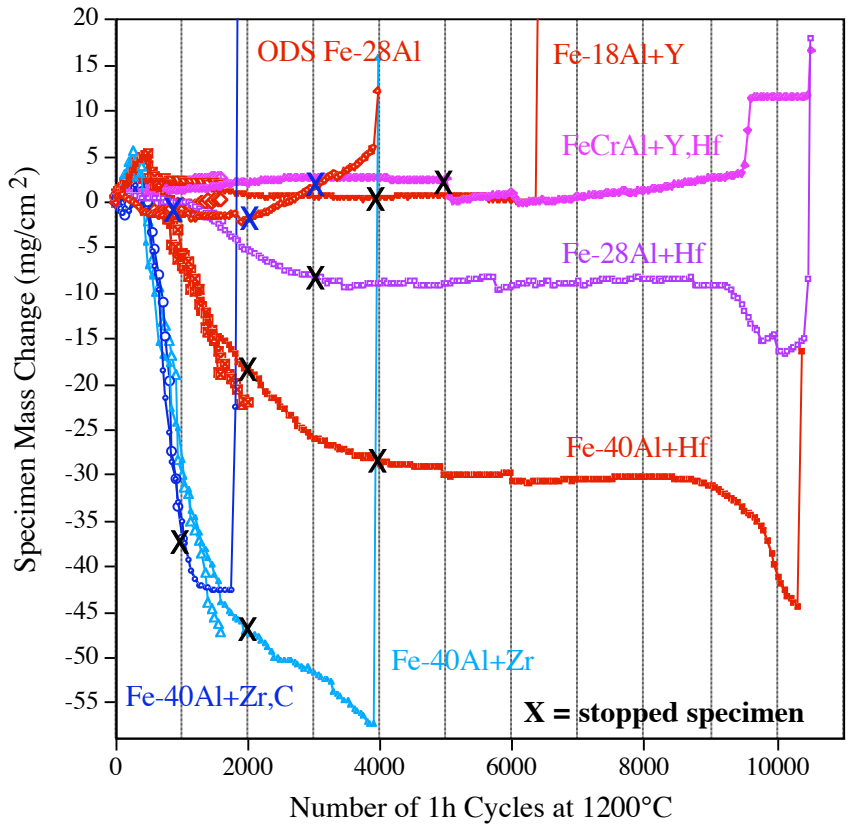
FeCrAlYHf consumption baseline - low reservoir, high life

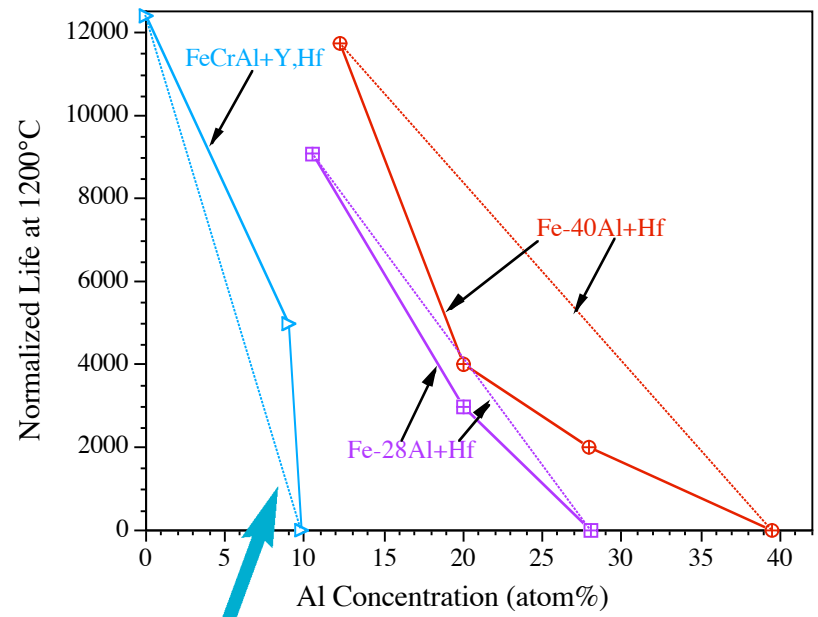
Fe-Al materials - need slower consumption and $C_b < 10\%$

Some limitations due to observation of Al gradients

Improving data on Al loss

Check remaining Al as a function of lifetime





Current C_{Al} vs. lifetime contains only start & finish data (dashed)

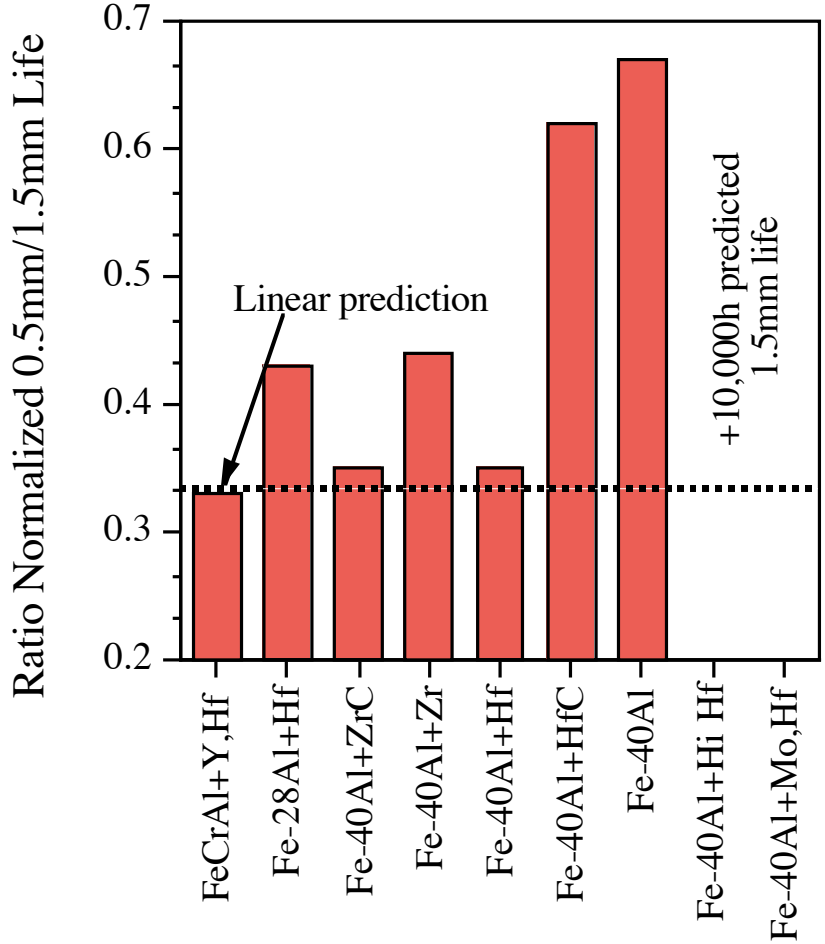
Improved understanding of consumption by knowing more

Accurate mechanistic lifetime model should be able to predict

Shorter experiments could check to see rate of Al consumption

Speeding up the testing

Reduce nominal specimen thickness from 1.5 to 0.5mm



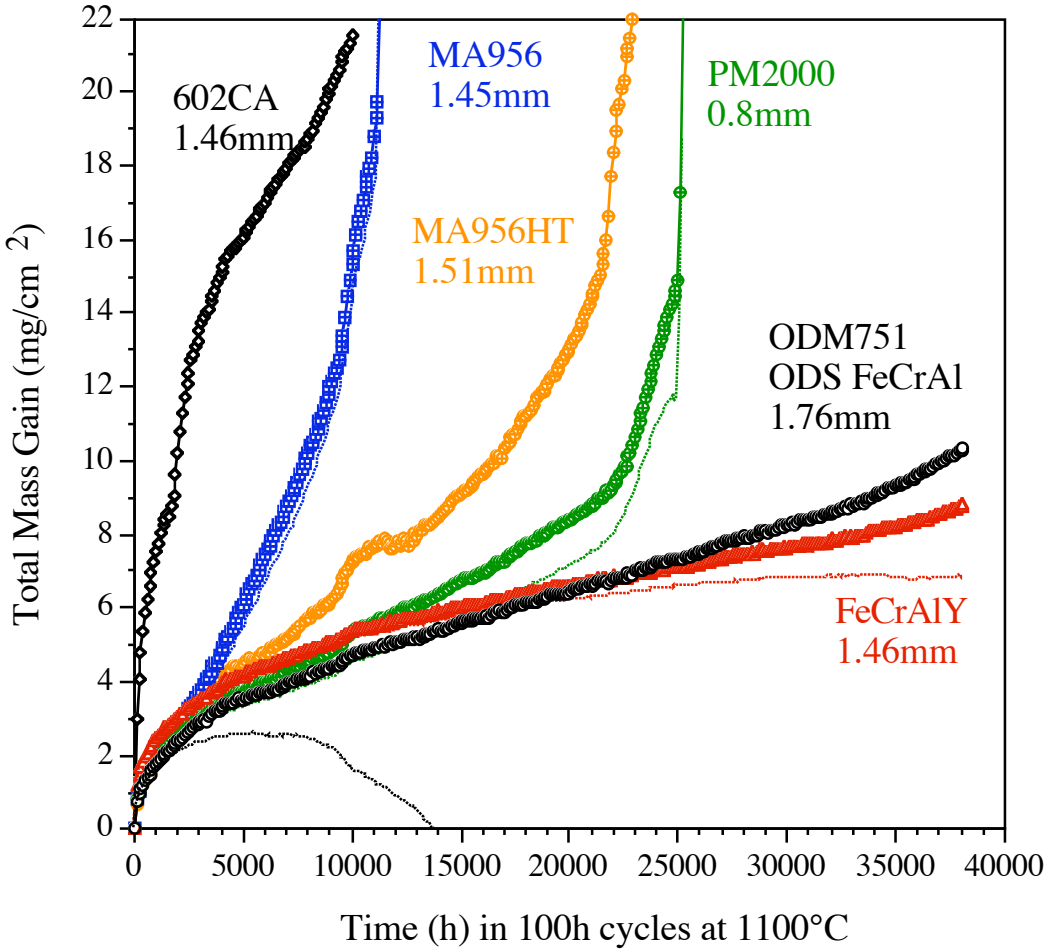
Variety of FeCrAl and Fe-Al specimens tested

Quadakkers model with n~1 would predict 1/3 life in 0.5mm

Some long-life alloys are very close, short-life alloys not!

Al consumption reduction work

Long-term oxidation results in 100h cycles, 1100°C, air



1100°C, 2012°F
laboratory air

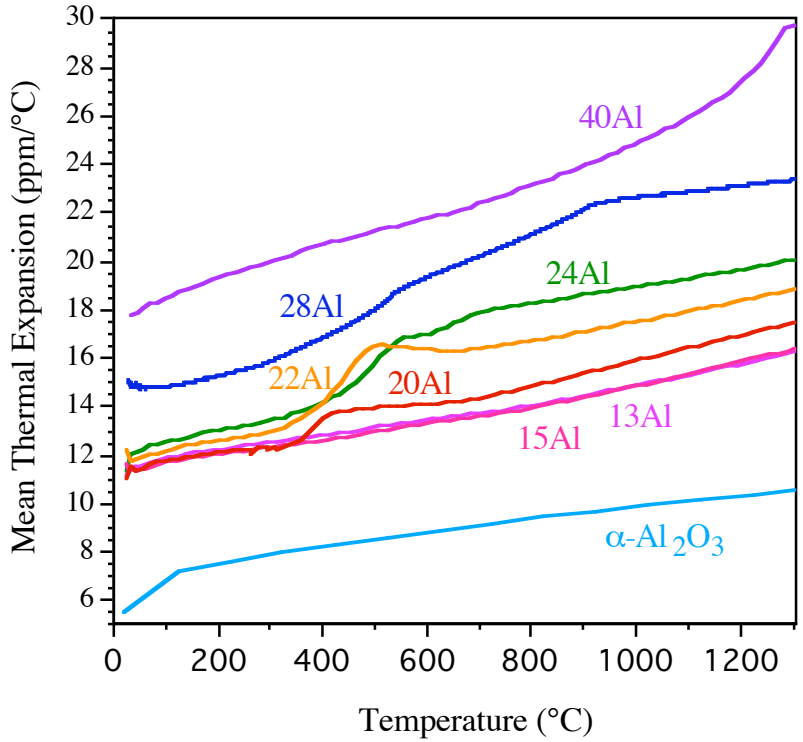
ODM751: Fe-16at%Cr-9.6Al-0.8Mo(1.5wt%)-0.6Ti-0.24Y

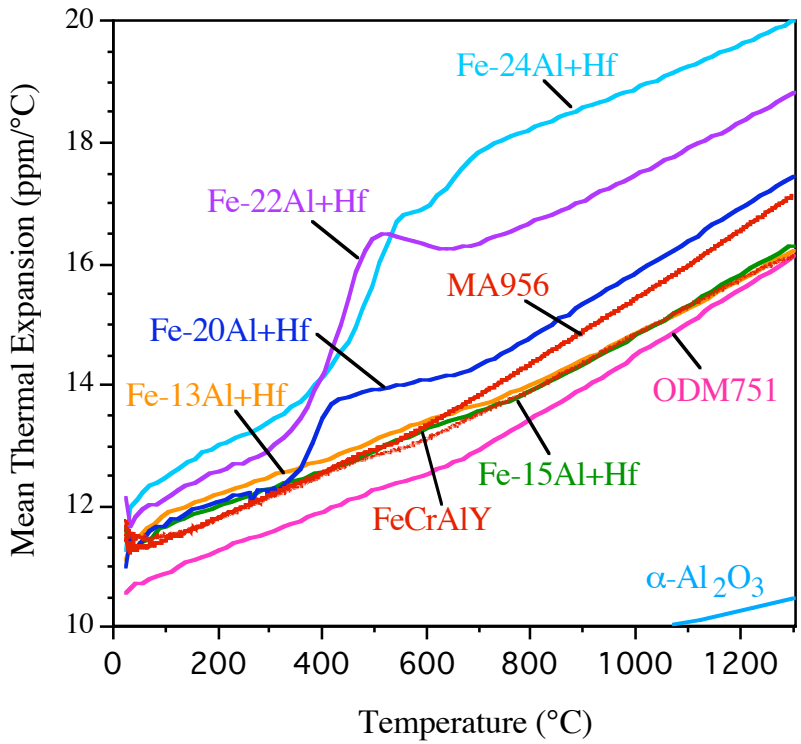
More spall than FeCrAlY (dashed line)

Does Mo provide benefit by reducing alloy CTE?

Measuring CTE of Fe-Al & FeCrAl

Quantify effect of Al in Fe-Al and Mo in FeCrAl





Fe-Al: Clear increase in CTE at 20at%Al

FeCrAlY: similar to Fe-(13-20%)Al

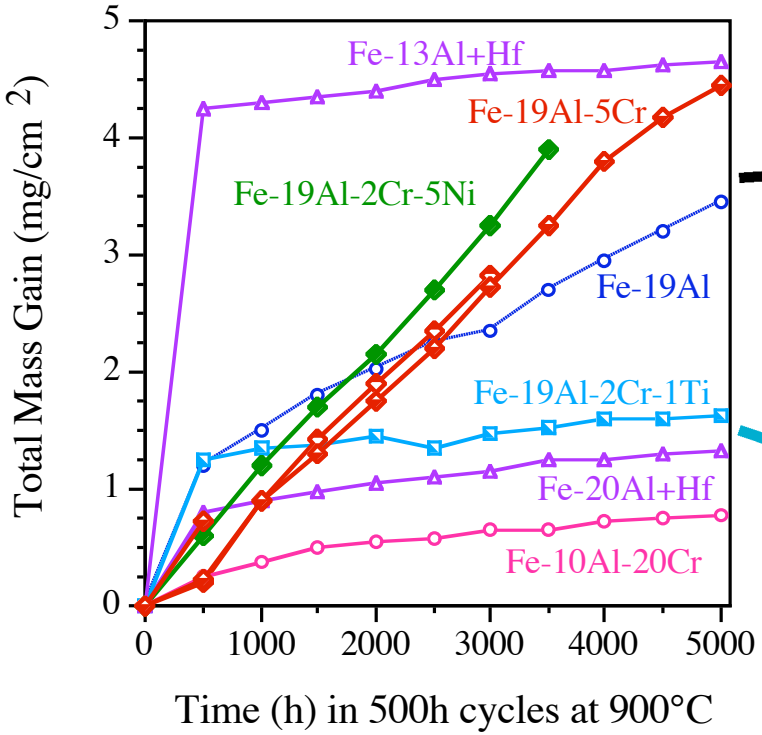
Lowest CTE for ODM751 with 0.8%Mo

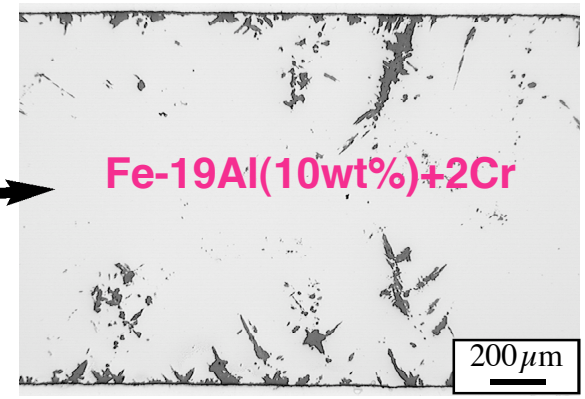
Strategy: lower consumption by reducing ΔCTE, i.e. spall

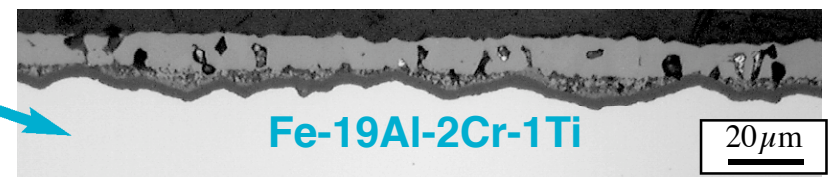
Better understanding of spallation with high T mech. prop. data

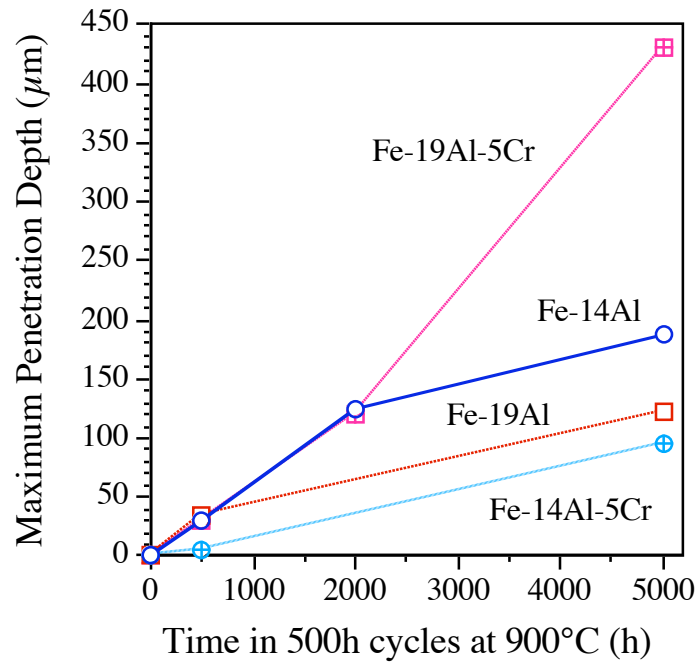
Internal nitridation kinetics of Fe-Al in air

Summer projects of R. Deacon, M. Dwyer (Lehigh)









Fe-Al±Cr±Ti alloys (Lehigh prog.)
EPMA confirmed AlN
Hf, Ti, Zr prevent it, not Ni, Cr
Not seen in undoped FeCrAl

Young: measure reaction kinetics

Future Work

Coatings

- longer times at 700° and 800°C to failure
- duplicates running to 10,000h at 700°C, 5,000h at 800°C
- complete initial creep study of aluminized P92 (Dryepondt)
- TN Tech: developing pack process for larger parts
- ORNL: developing slurry process for evaluation (EU)

Alloy Development

- characterize C_b as f(Al content, temperature, time, etc.)
- lower C_b by Cr or Mn additions
- reduce Al use by lowering CTE (Mo) & optimizing RE (Y,Hf)
- initial study of high temperature creep of Fe-base alloys

Modeling

Have oxidation data and Al back-diffusion data

Need failure criteria: ≈18 at.%Al needed in sulfidation

<10%Al needed for steam/H_2O, depending on C_{Cr}

Summary

Program focus on CVD coatings for laboratory test
- reduced cracking problem with 100h cycles
- protective coating for >14,000h at 700°C
- protective coating with <10at.%Al at 800°C

For lifetime model need critical Al (C_b) at failure
- to estimate lifetime or determine T_{max} at 40kh

Alloy development looking at ferritic Fe-Al
- no CTE problem like Fe-Al intermetallics
- limited by higher C_b (≈10%) than FeCrAl
- improvement in life with Y(+Hf) doping
- solutions for “broccoli” problem
- studying internal nitridation issue

Acknowledgments

K. Cooley - CVD coating fabrication

G. Garner, J. Moser - oxidation experiments

H. Longmire - metallography

L. Walker - EPMA

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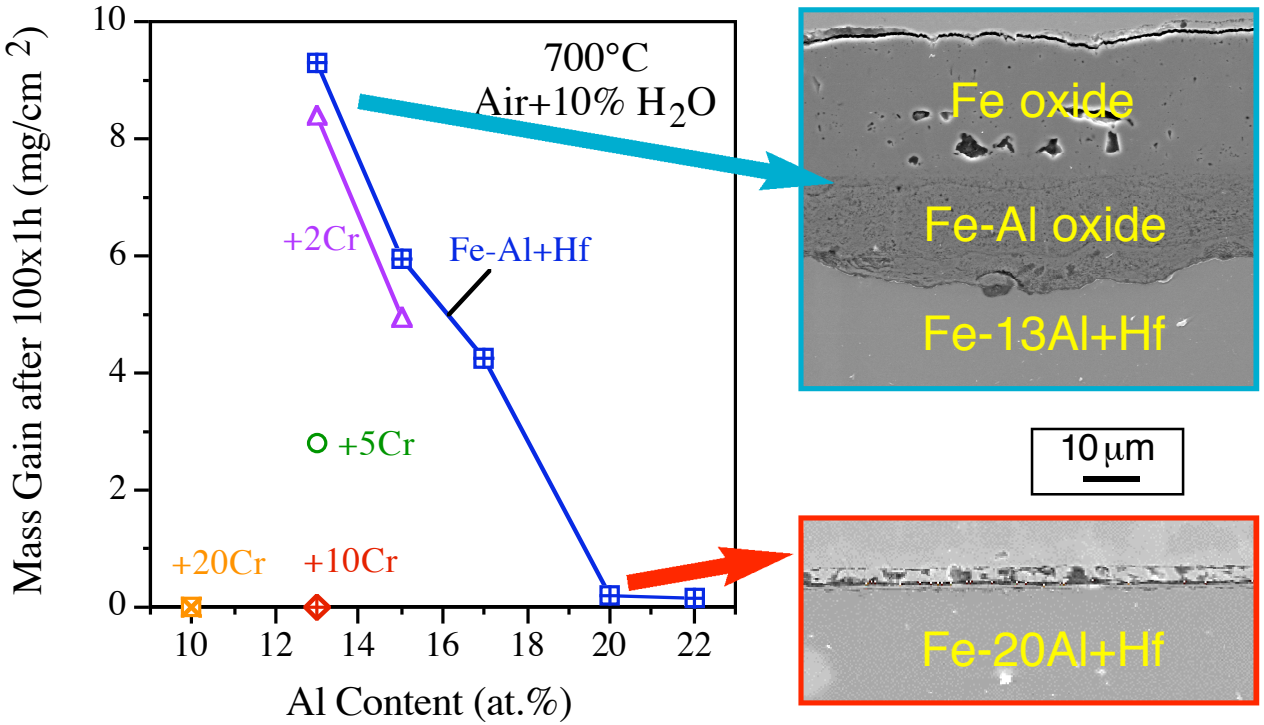
Model Fe-Al-Cr alloy performance

after 100, 1h cycles at 700°C in humid air

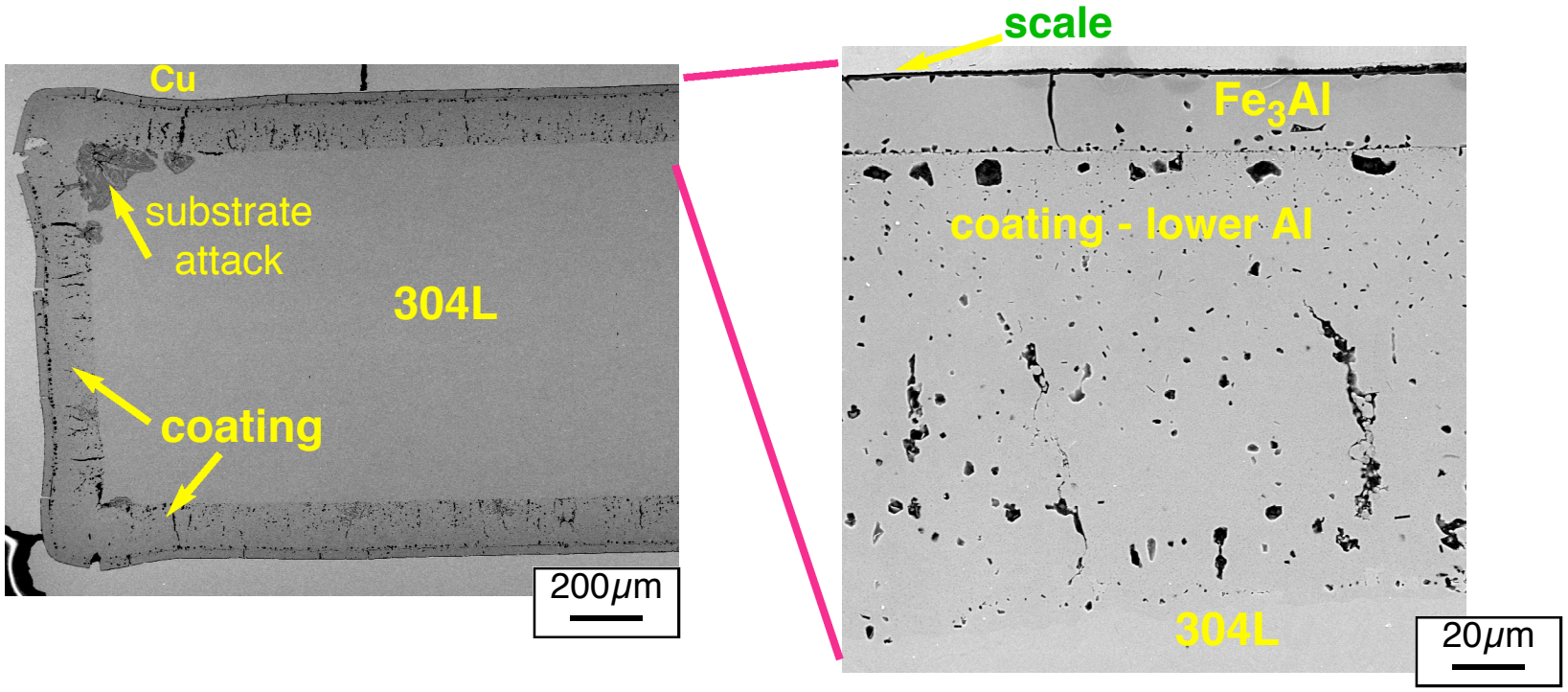


Model alloys indicate with binary Fe-Al, need 20 at.%Al to avoid FeO_x formation

However, when Cr present, critical Al content drops with 10%Cr (≈Fe-9Cr-1Mo), protective with 13%Al with 20%Cr (≈304L) protective with 10%Al (FeCrAl)

Aluminized 304L

Characterized after 2000 x 1h at 700°C in humid air



Cracks mainly observed in outer Al-rich layer

Coating breached in corner

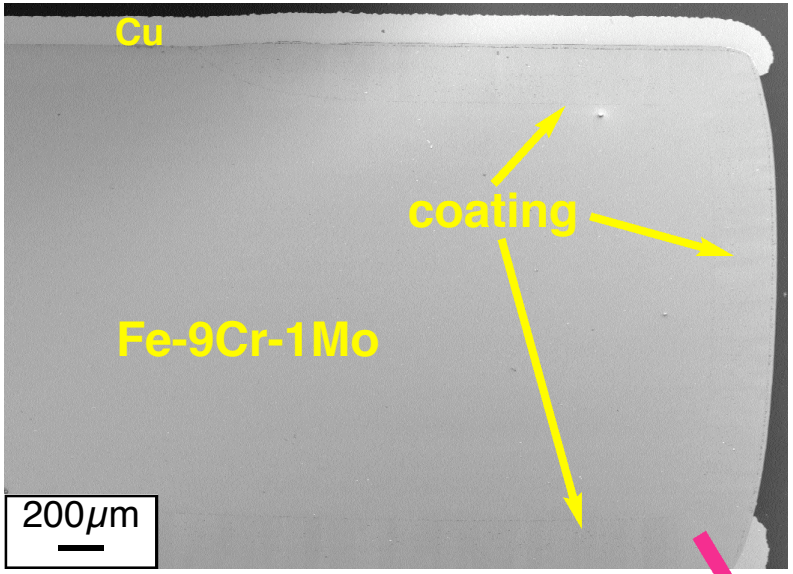
Observed mass gain due to attack of the substrate

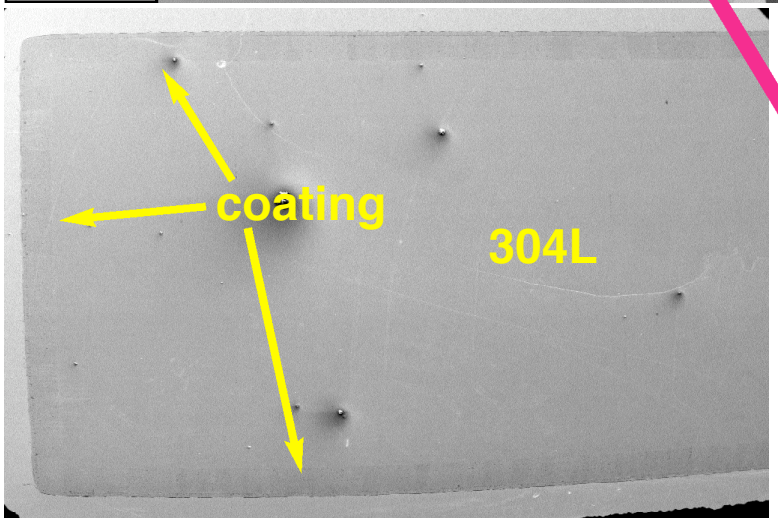
Thin surface scale where coating intact

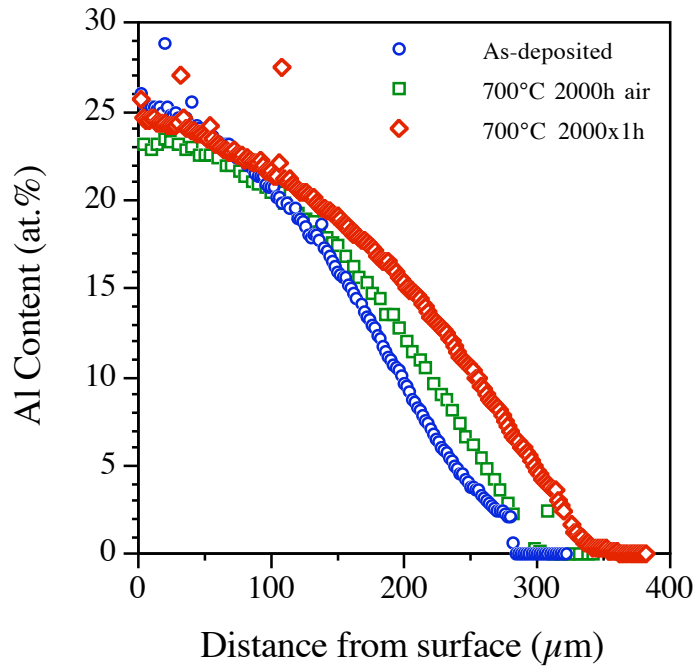
27-30at.%Al remained in outer layer (using EPMA)

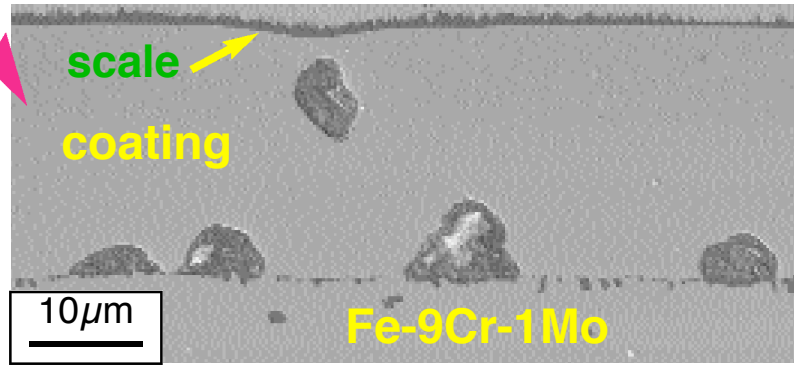
Coatings exposed without cycling

Characterized after 2000h at 700°C in laboratory air









Damage observed after 2000 cycles not due to Al loss

Experimental Procedure

Chemical vapor deposition (CVD) process

selected for controlled laboratory studies, not commercialization

similar to a well-controlled above-pack process

1-2mm x ≈12 x 20 specimens, 2 per run

ORNL laboratory scale reactor

flowing H_2-$AlCl_3$, 100 Torr, 6h, 1050°-1100°C

increase Al activity by adding Cr-Al alloy inside reactor

"Thick" coatings ≈40μm Al-rich outer layer, "Thin" ≈5μm Al-rich outer layer

Environmental testing:

800°C, 20h cycles, H_2-H_2S-H_2O-Ar ($P_{S_2}=10^{-6}$atm; $P_{O_2}=10^{-22}$atm)

800°C, 1h cycles, air+10%H_2O

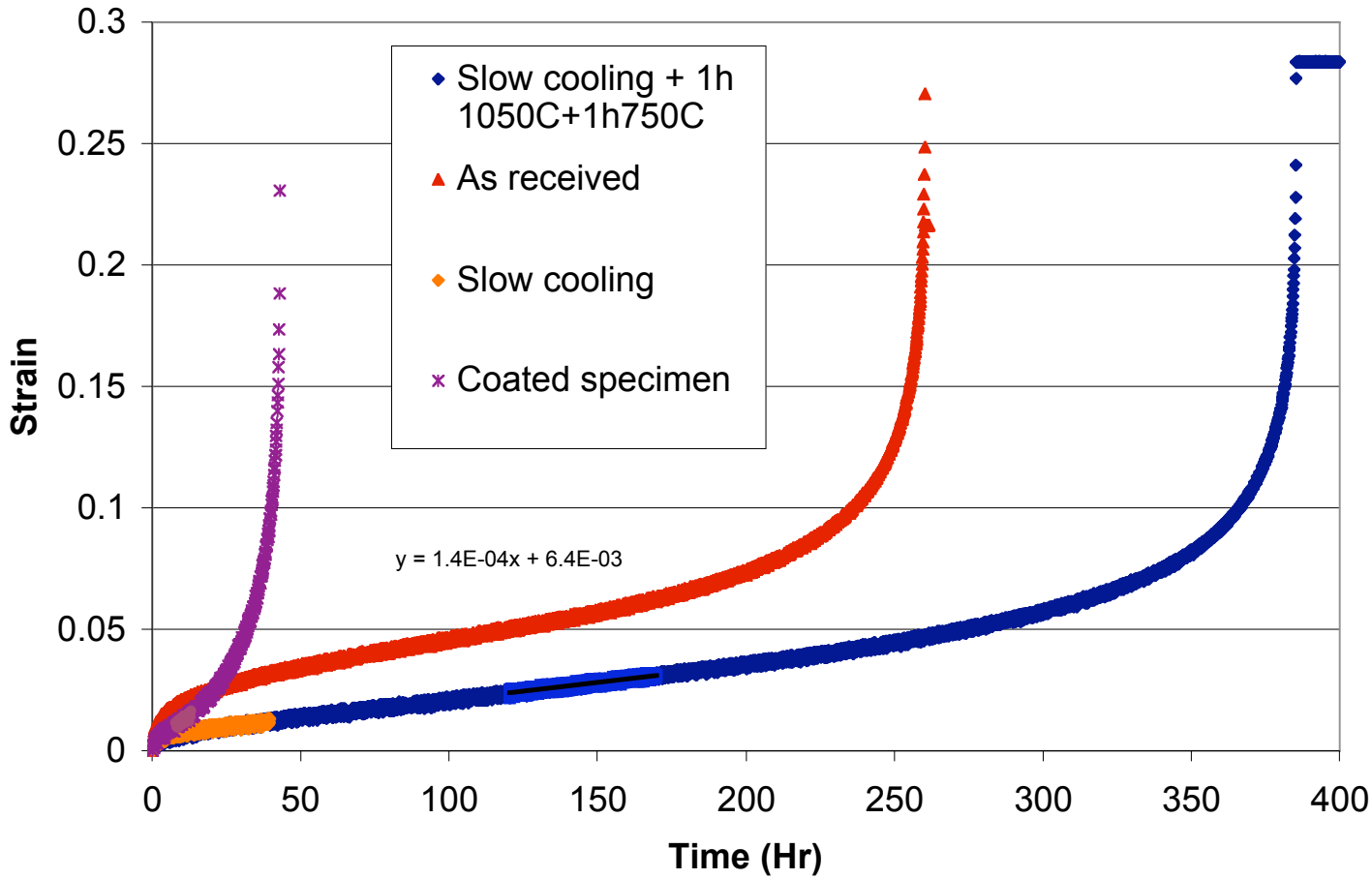
700°C, 1h cycles, air+10%H_2O

700°C, 100h cycles, air+10%H_2O

800°C, 100h cycles, air+10%H_2O

Coating effect on creep

Fe-9Cr-2W at 650°C



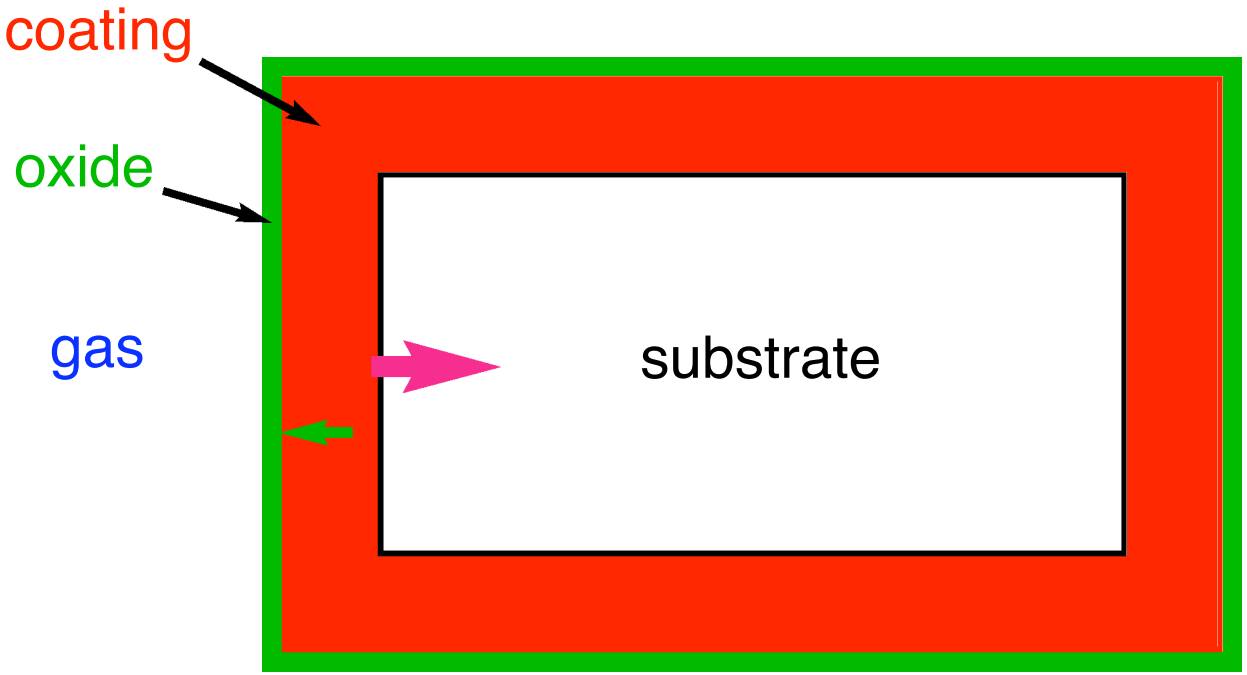
1050°C CVD with slow cooling should lose martensite

Coated specimen reduced creep life as expected

Initially, slow cooling did not weaken specimen (?)

Coating degradation with time

defining the failure criteria



Al supply: coating thickness and starting Al concentration

Coating thickness loss or Al content drop due to:

(1) oxidation/sulfidation: selective formation of reaction product

(2) diffusion into substrate

At low temperatures 650-700°C expect loss by (1) << loss by (2)

How low can coating thickness or Al content drop before coating is no longer effective?

Lifetime predictions at 700°C
using 10,000h parameters

Prediction Method	COSIM dependent	COSIM indep FeAl	COSIM indep FeCrAl	Heckel	Actual
Surface (at.%)	19	16	17	19	18%Al
Thickness	310	438	428	356	320
Lifetime assuming 20% (sulfidation)	6.8	5.0	5.6	7.5	??
assuming 8% (wet air)	187.1	57.2	66.4	104.4	??

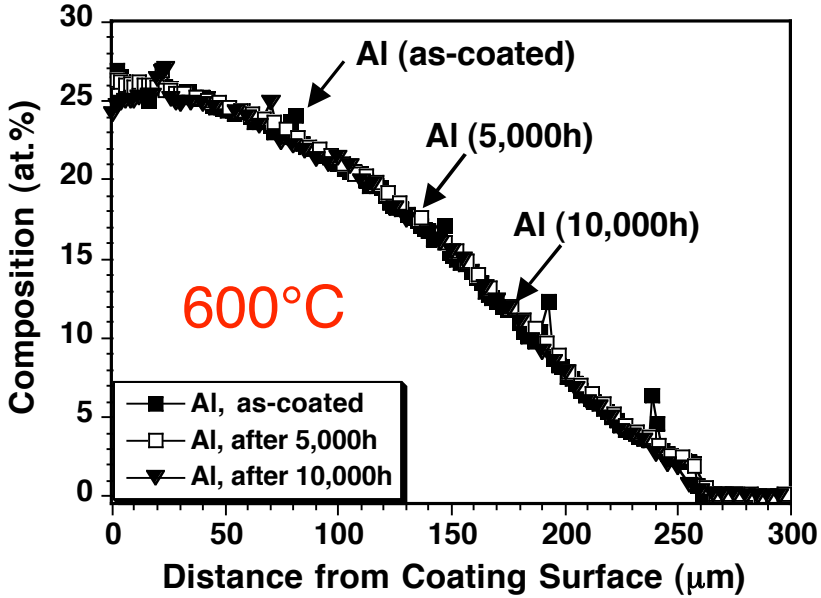
Sulfidation - insufficient life at 700°C, need to drop to 625°C for 40,000h lifetime

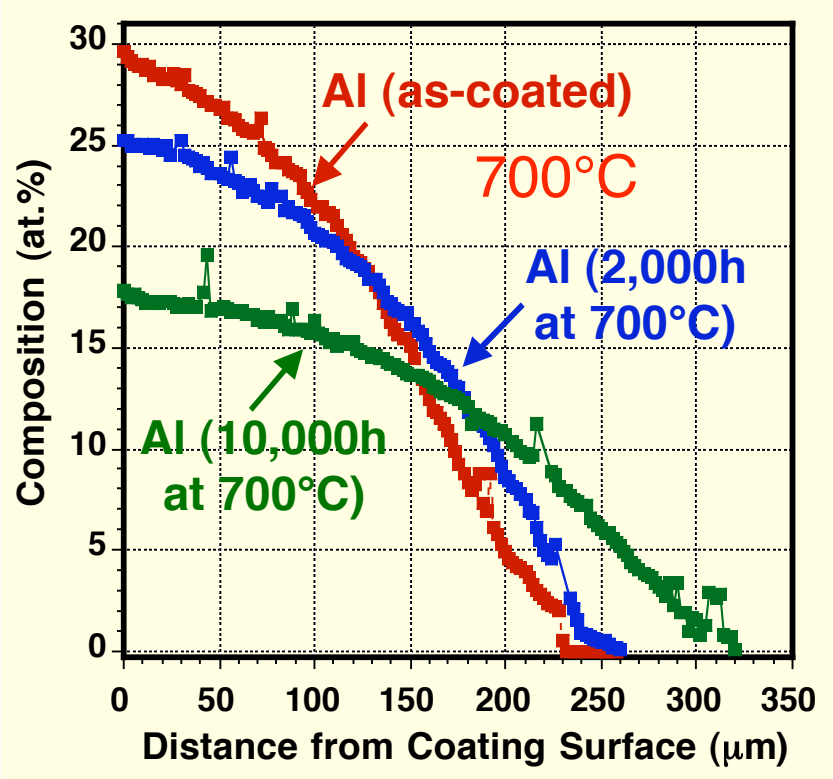
Wet air - high probability of making 40,000h lifetime

"high" assumptions probably over predict lifetime

Diffusion experimental data

isothermal tests in laboratory air





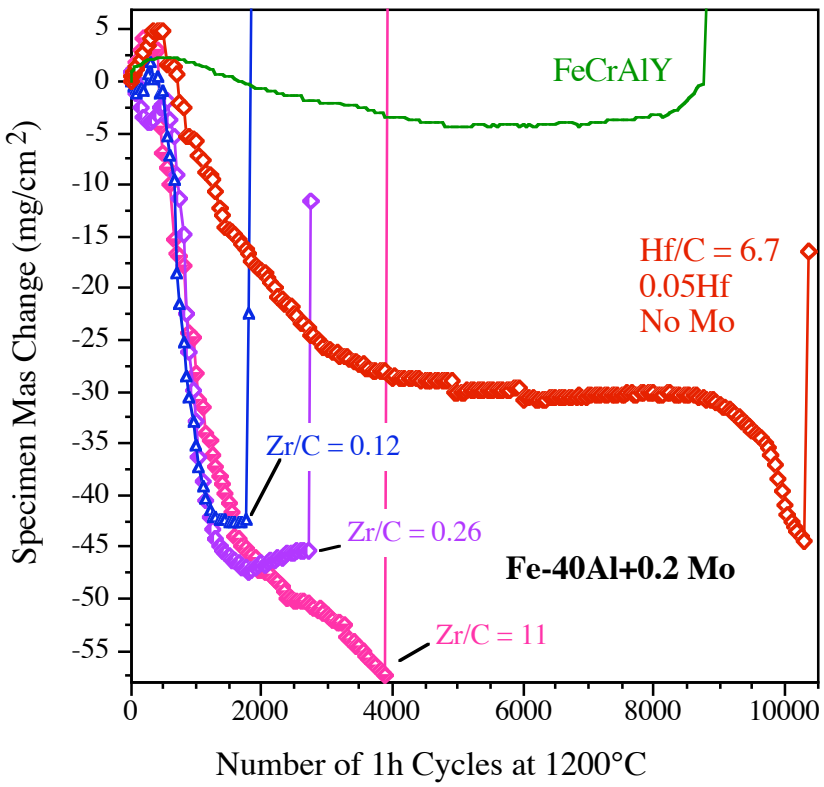
Sectioned coated 304L & Fe9Cr specimens for exposures:

- 500°C, 10,000h (no change)
- 600°C, 5,000 and 10,000h
- 700°C, 2,000, 5,000 and 10,000h
- 800°C, 2,000h (50% drop in surface Al content)

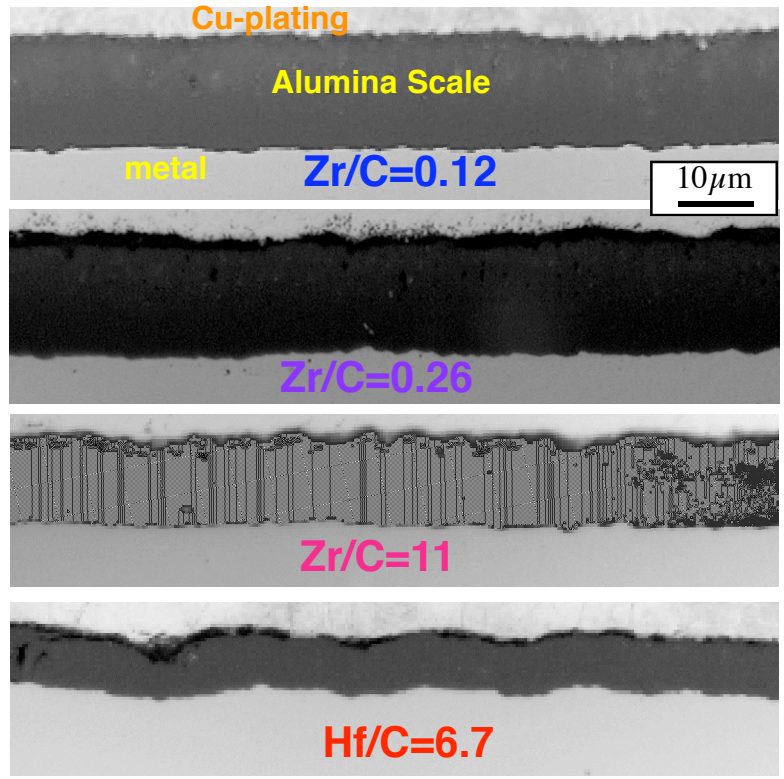
Case study: RE/C effect in FeAl

Relationship between RE dopant and interstitials (C, S, etc.)

ORNL base alloy: Fe-40Al-0.2Mo-0.05Zr-0.4C Zr/C=0.12



200h at 1200°C



Prior work showed RE/C≥1 preferable

Remove C - increased normalized lifetime by 2X

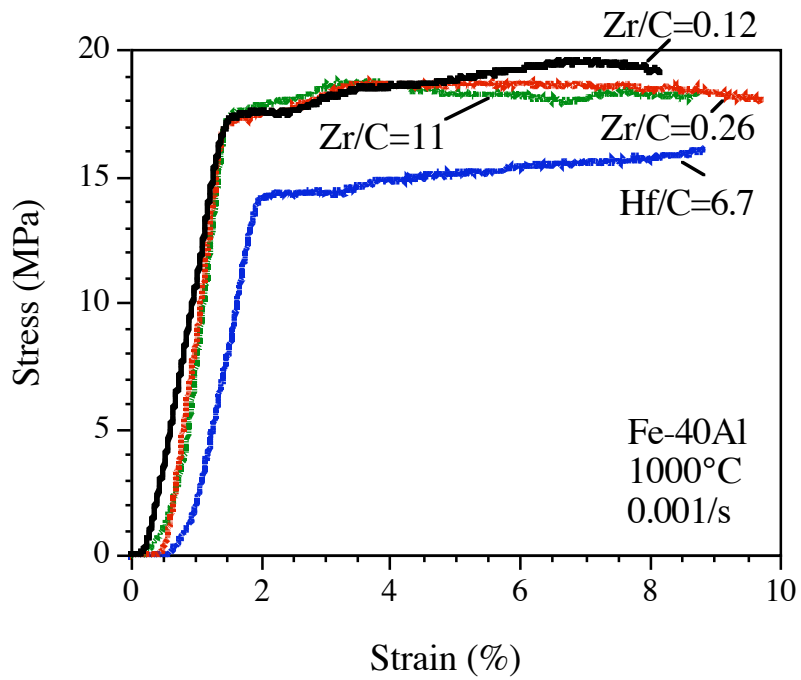
Change Zr to Hf - increased normalized lifetime by 6X

Changes reduce growth rate but not significantly

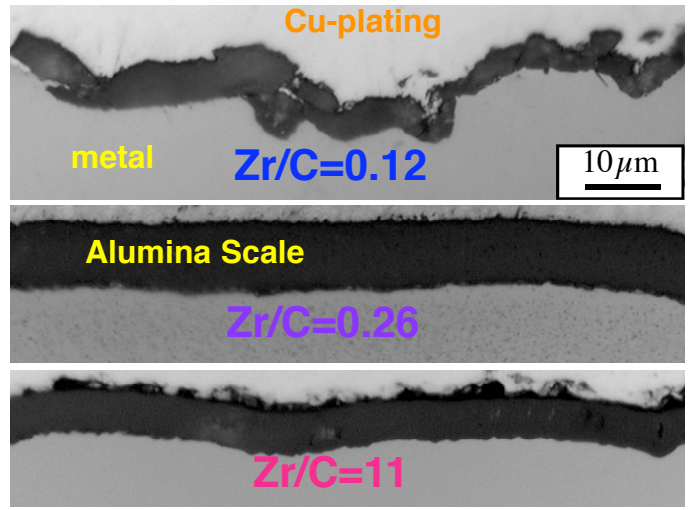
Chemical vs. Mechanical effect?

H. E. Evans et al. view - softer materials have longer life

compressive yield at 1000°C



10 x 500h at 1000°C



Did removing C soften the material? No more ZrC

Compressive yield at 1000°C showed no effect of C

20% lower yield stress for Hf without 0.2Mo

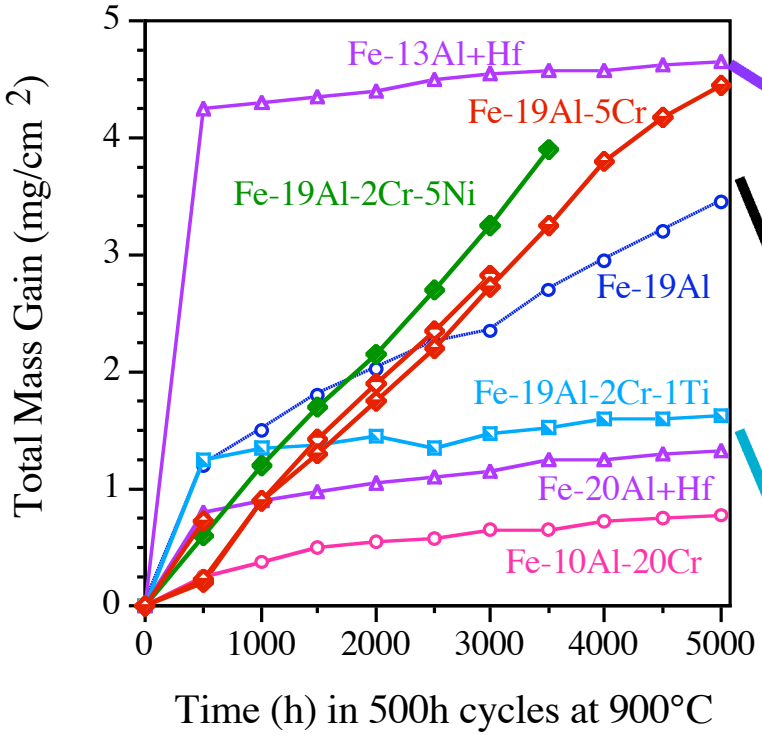
Lifetime would need to be very sensitive to strength

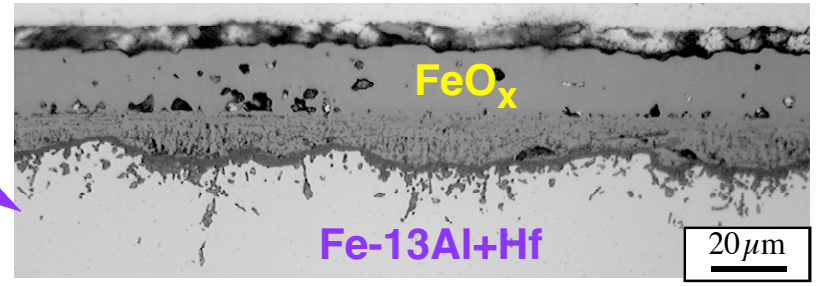
Does not explain surface deformation observed at 1000°C

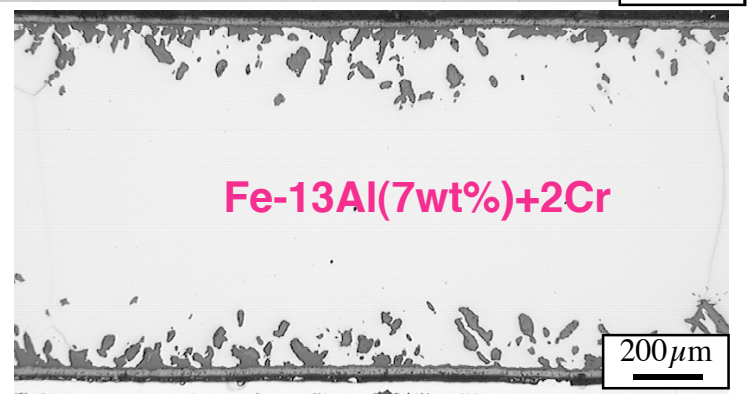
(Details in Pint and Schneibel, Scripta Mater. 52 (2005) 1199)

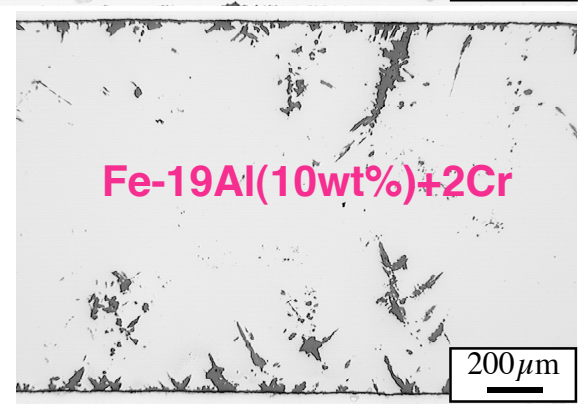
Internal nitridation of Fe-Al in air

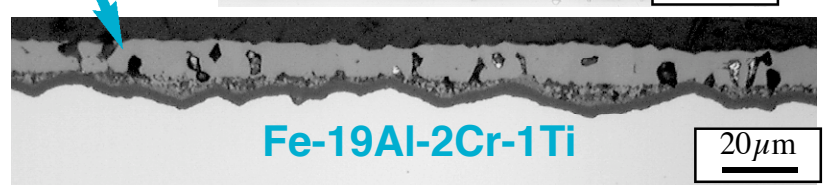
Observed at 900°C, similar to work on Fe_3Al and FeAl











Low Al - form FeO_x at 900°C
Fe-Al±Cr±Ti alloys (Lehigh prog.)
EPMA confirmed AlN
Hf, Ti, Zr prevent it, not Ni, Cr
Not seen in undoped FeCrAl