# High Temperature Oxidation Issues in Fossil Boilers

B. A. Pint, M. A. Bestor, S. Dryepondt
Oak Ridge National Laboratory
Oak Ridge, TN  37831-6156

Y. Zhang
Tennessee Technological University
Cookeville, TN 38505

Research sponsored by the U.S. Dept. of Energy
Fossil Energy Advanced Research Materials Program

# Acknowledgments

ORNL

A. Haynes, K. Cooley - CVD coating fabrication

K. Unocic - characterization

G. Garner, J. Moser, T. Brummett, M. Stephens, M. Howell - oxidation experiments

H. Longmire, K. Thomas - metallography

T. Brummett - SEM

L. Walker - EPMA

Tennessee Tech.

B. Bates - SEM

Research sponsored by the U. S. Department of Energy, Fossil Energy Advanced Materials Research Program

# Outline/Introduction

FY00-FY09: Al-rich (aluminide) coating study
- + Fe-Al alloy optimization study

Oxidation-resistant coating background:
- Al-rich (aluminide) coatings very promising
  - Advanced ultra-supercritical steam - up to 760°C
  - Coal gasification - low $P_{O_2}$, high $P_{S_2}$
- In the US, Al-rich coatings not used in boilers
  - Extensive research by Rapp, ORNL, etc.
  - Field tests in 80's unsuccessful

ORNL objective - define benefits/address issues
- model lifetime (min 40 kh), determine max. T

FY10 Effect of oxy-firing on corrosion
- mechanisms in coal-fired boilers

# Coatings: Last 10 years at ORNL

Fabrication - chemical vapor deposition (CVD)

- not for boilers or commercialization
- make clean, uniform coatings for research
- full control of process, no “black box”

Substrates - representative Fe-base alloys

T91 - Fe-9Cr-1Mo (later T92, T122)

304L - low C Fe-18Cr-8Ni (later 316)

Diffusion - define substrate interaction

exposures at 500°-800°C for 2-10kh

Oxidation - obvious benefit

define failure criteria (critical Al at failure: $C_b$)

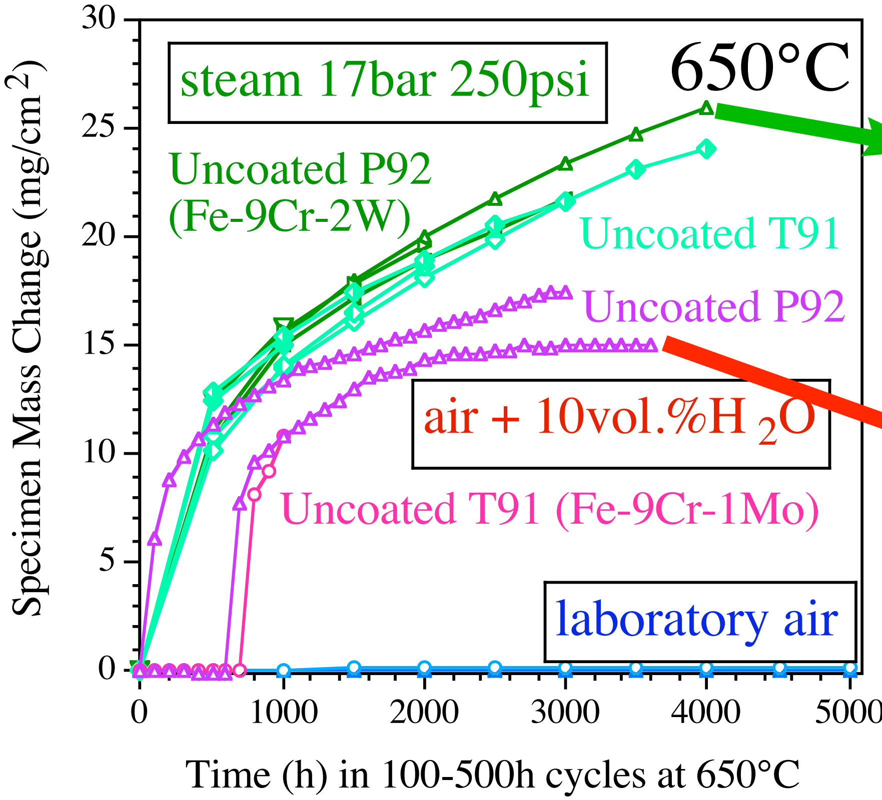
accelerated testing at 700°-800°C

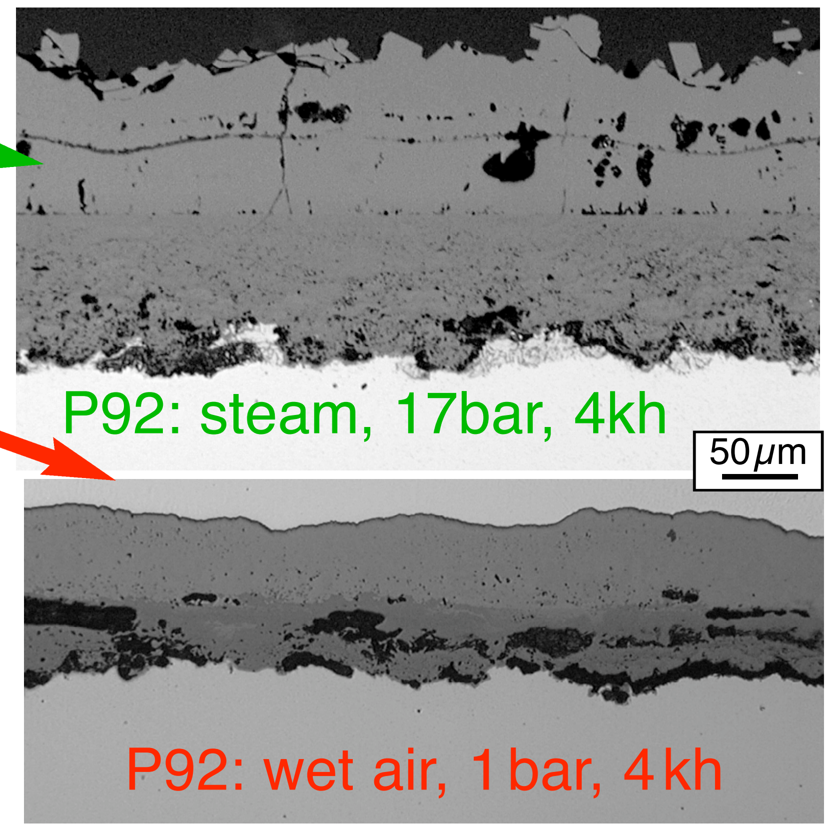
testing: wet air, recently in 17bar steam

# Fe-9Cr in Steam vs. Humid Air

## comparison of mass gain and reaction products

650°C, 1202°F




Similar attack in steam and wet air (10±1 vol.% $H_2O$)

Define failure: must have environment that attacks substrate

Prior work in lab. air could not define coating lifetime

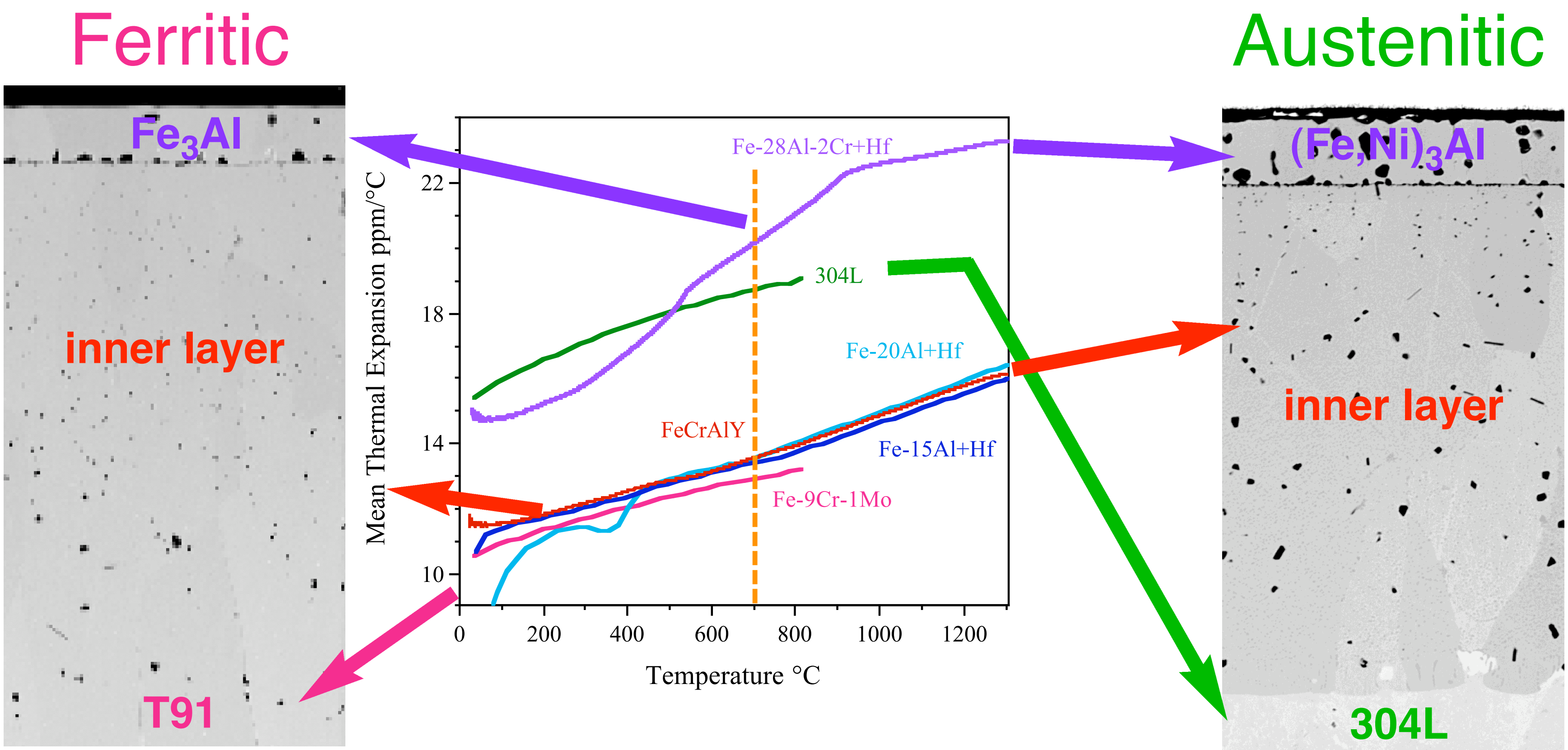
# Key Points

## Normally think that more Al is better

### thermal expansion mismatch problem

# Intrinsic Aluminide Coating Problem

## Substrate-coating thermal expansion mismatch



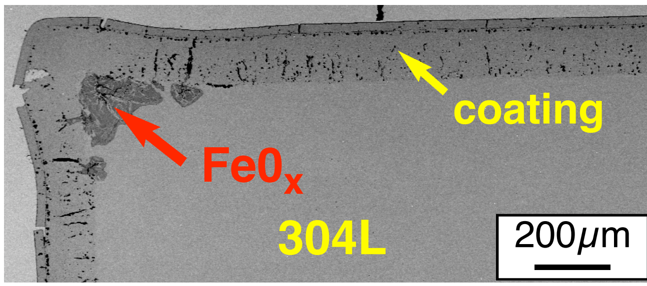

For coated 304L, 3 layers with 3 different CTE

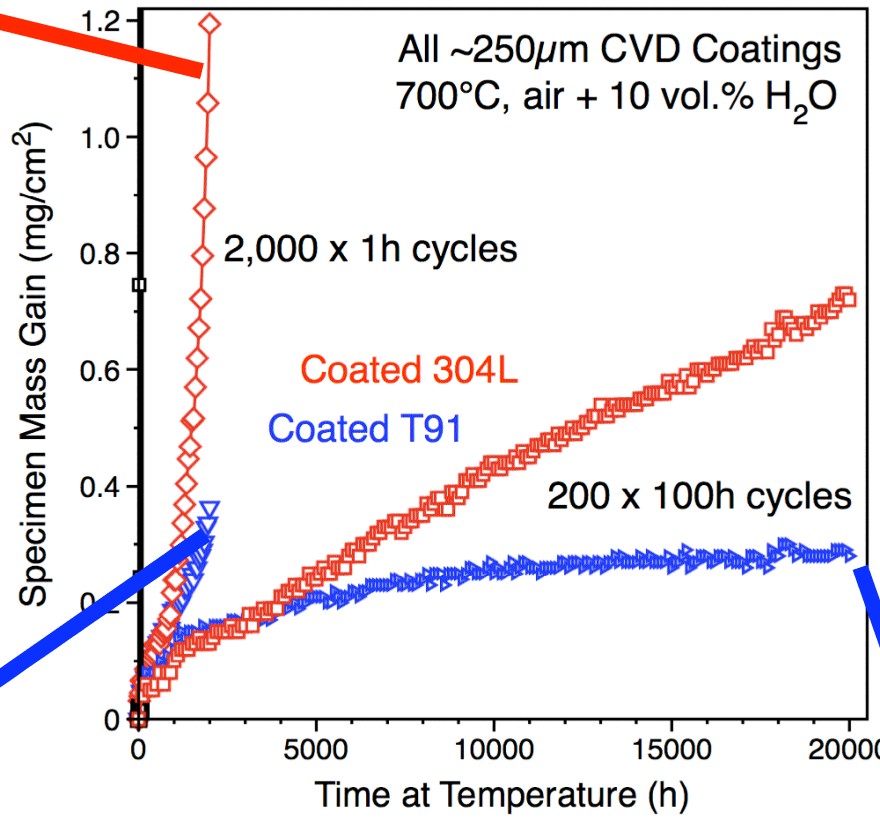
For coated T91, 3 layers with thick (250μm) coat

BUT, "thin" coating (50μm) no $Fe_3Al$ - small ΔCTE

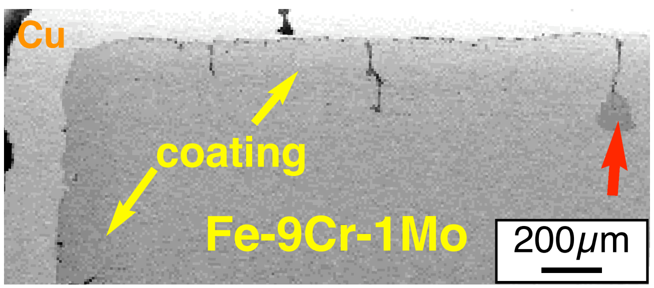
# If CTE mismatch is problem, can thermal cycling crack coating? YES

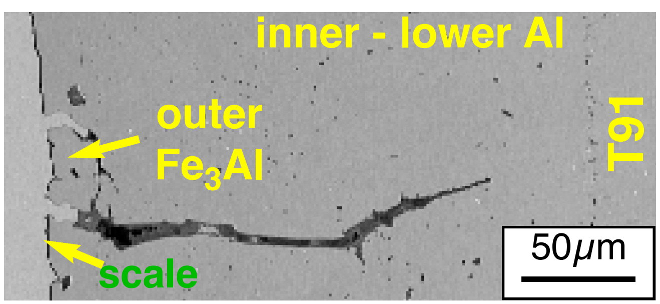
Thick CVD coatings, 1h & 100h cycles, 700°C, humid air




Coating cracking = substrate attack

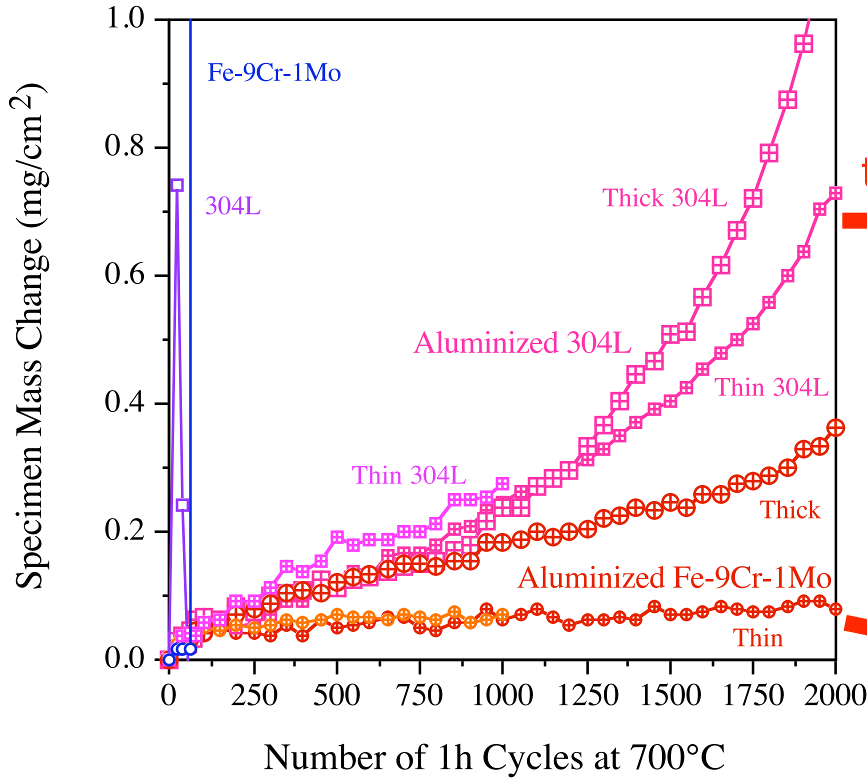


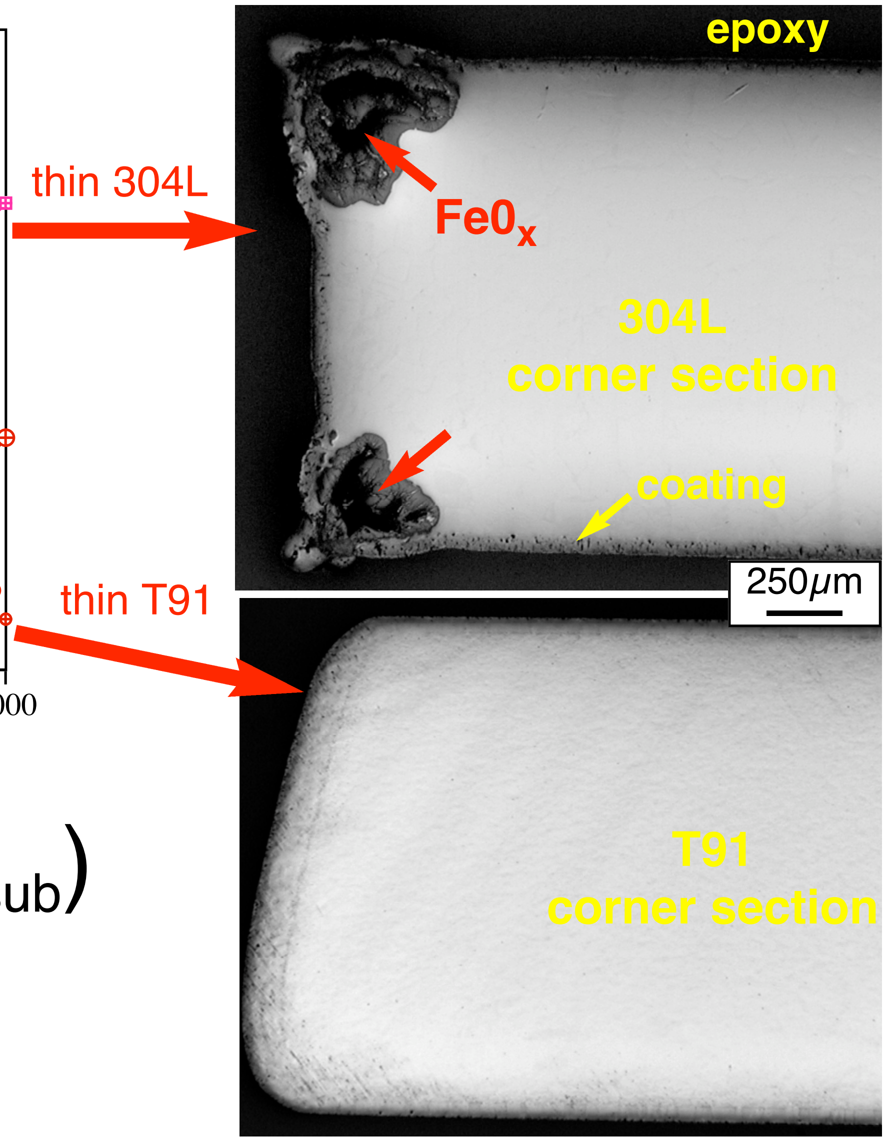




100h cycles stopped at 20kh: no attack

# If CTE mismatch is problem, does thickness (δ) affect performance? Yes

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




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

$$W = f(\delta_{\text{coating}})$$

(strain energy)

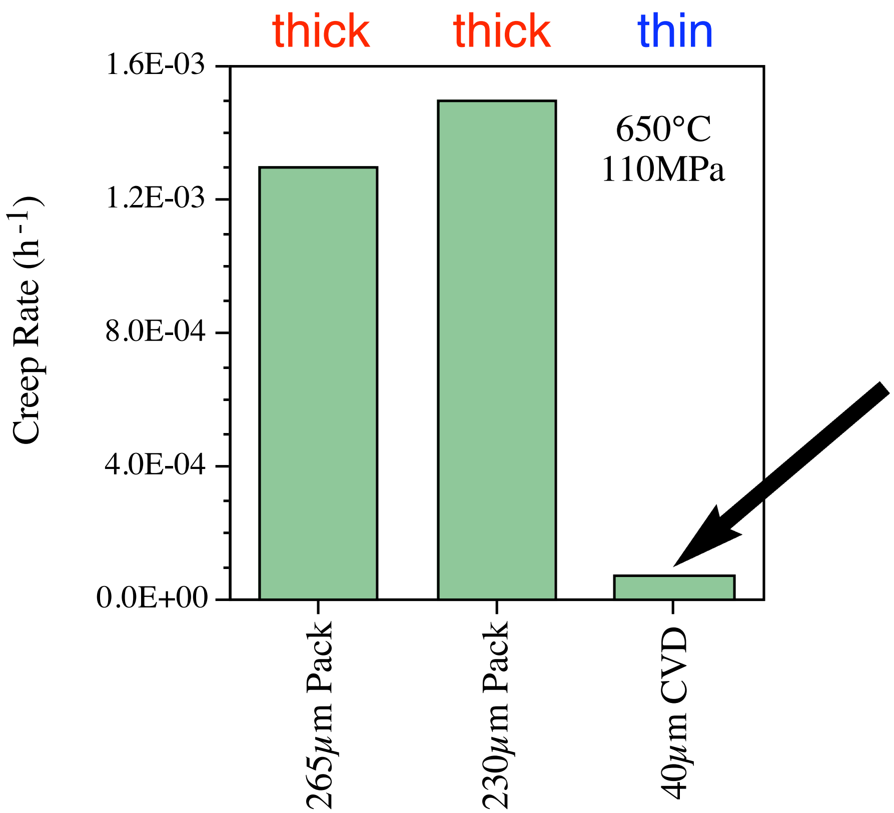
# Key Points

Normally think that more Al is better

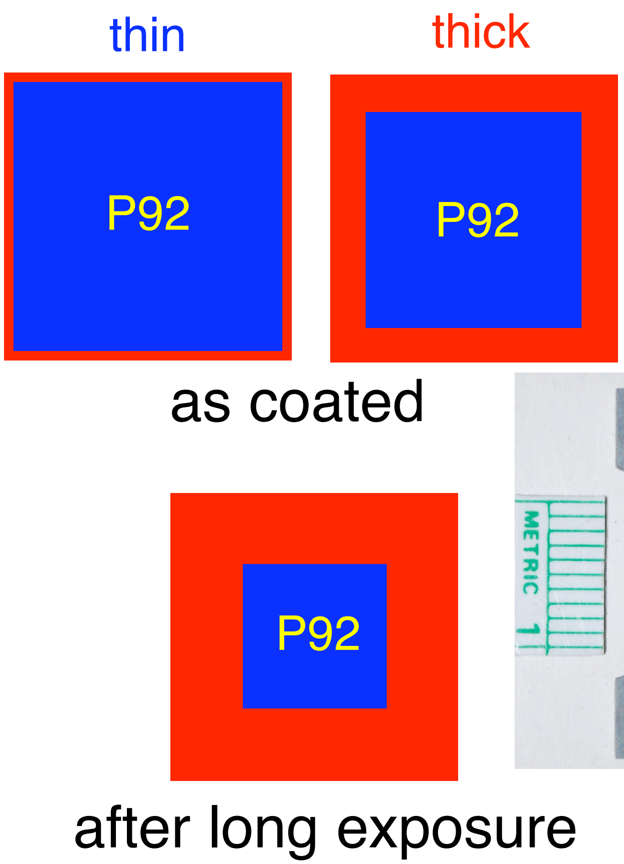
- thermal expansion mismatch problem
- Al loss:  more by interdiffusion than oxidation
  - Al interdiffusion destroys Fe-Cr strength

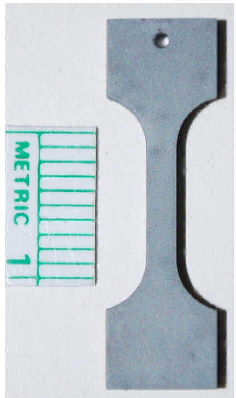
# Creep Testing of P92 (Fe-9Cr-2W)

## Effect of as-deposited coating thickness




650°C, 1202°F; gage: 2 x 2 mm




Specimen with thin coating has better creep resistance

Effect of coating can be modeled as if coated layer absent

Suggests that thin coatings are preferable

Dryepondt et al., Surf. Coat. Tech. (2006)

# Key Points

Normally think that more Al is better

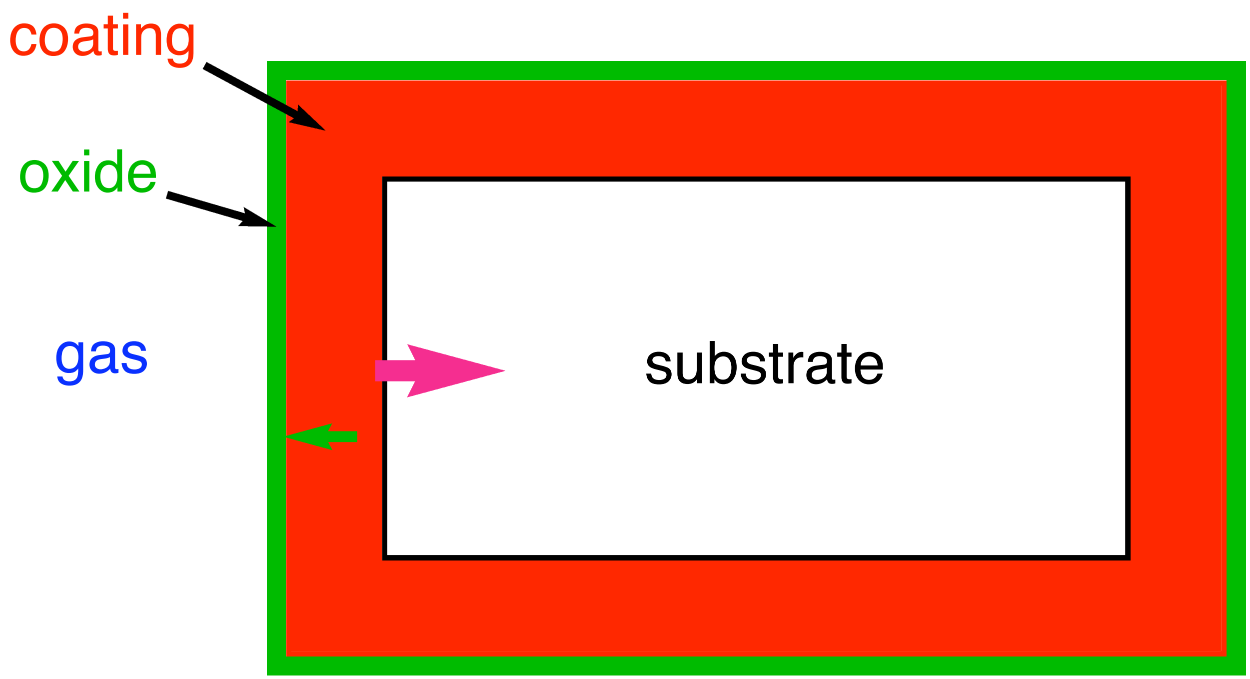
- thermal expansion mismatch problem
- Al loss:  more by interdiffusion than oxidation
  - Al interdiffusion destroys Fe-Cr strength
- less is more:  “thin” ~50$\mu$m coatings better

# Key Points

- Normally think that more Al is better
  - thermal expansion mismatch problem
  - Al loss:  more by interdiffusion than oxidation
    - Al interdiffusion destroys Fe-Cr strength
  - less is more:  "thin" ~50$\mu$m coatings better
- T91 lifetime model developed
  - Based on NASA COSIM model (Nesbitt)
  - Isothermal diffusion experiment data used
  - Need failure criteria to predict life

# Defining a coating failure criteria

## need to determine $C_b$ for coating in steam




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

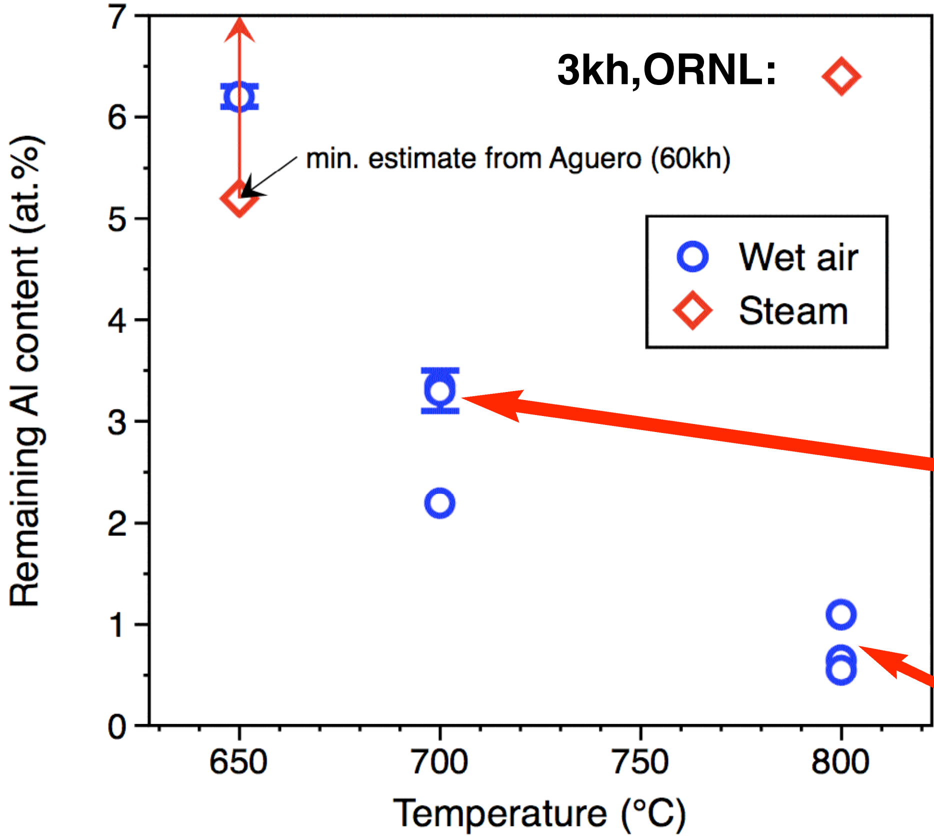
At low temperatures 650-700°C expect loss by (1) << loss by (2)

$C_b$ ~20at%Al for sulfidation

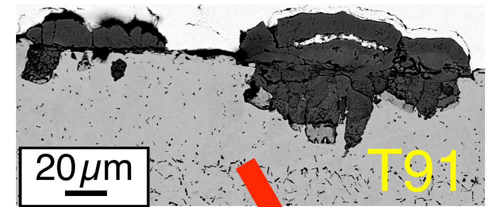
How low can Al content drop in steam environment?

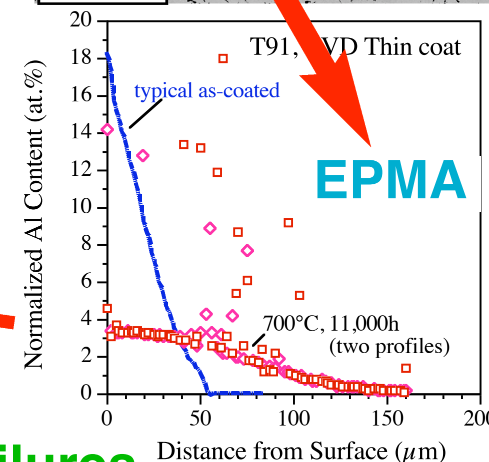
# Effect of temperature on $C_b$

## ~40$\mu$m coatings on Fe-Cr at 650°-800°C in $H_2O$




coating failure




EPMA

3 800°C failures
T91, T92, T122
(Fe-8-11%Cr)

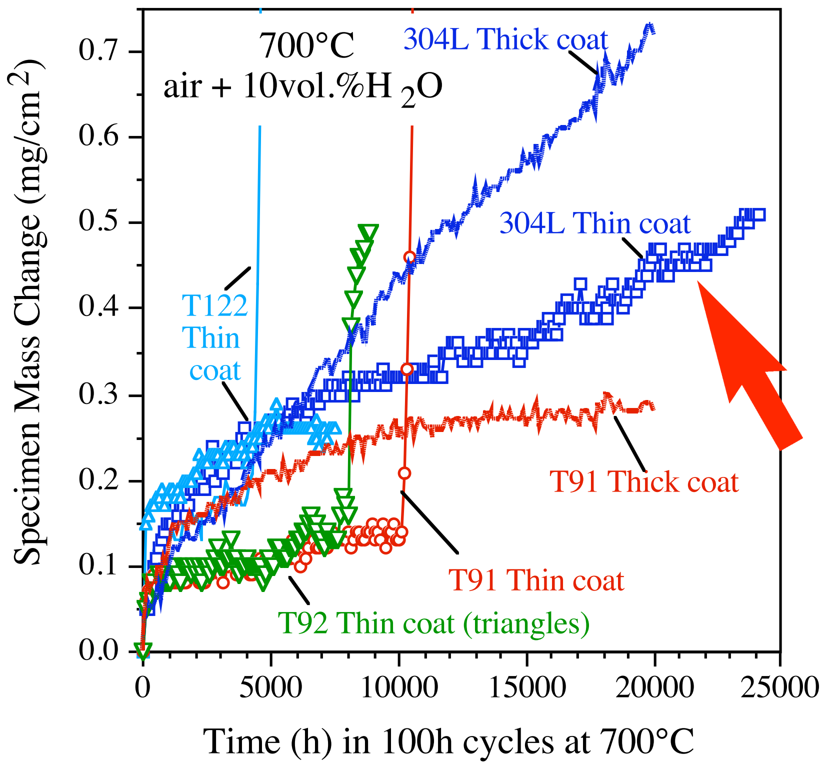
Six failures of thin coatings, one higher Al activity coating

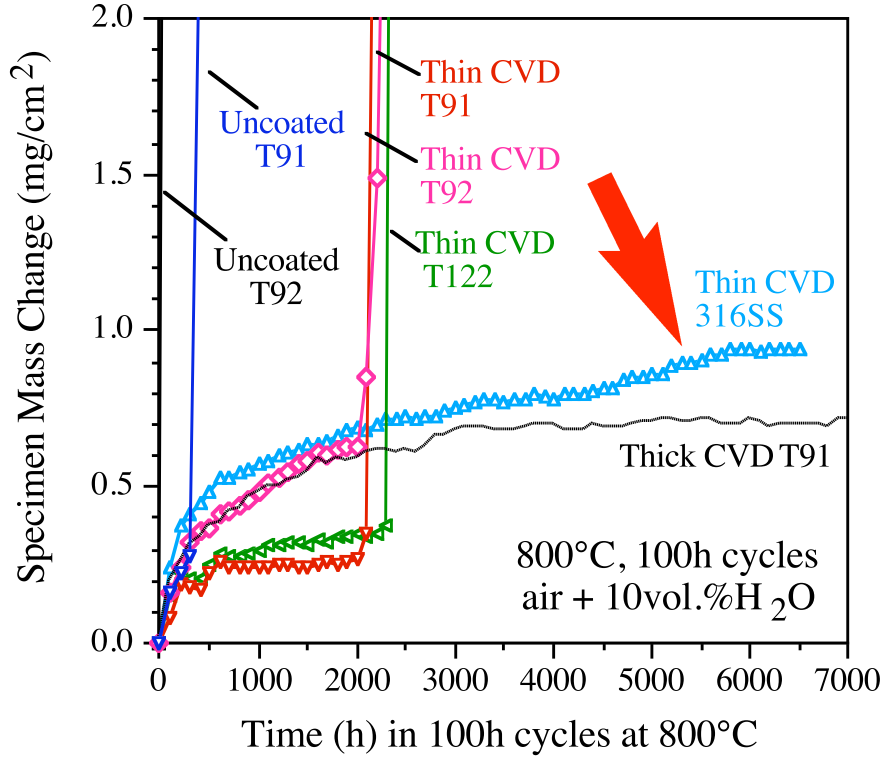
Agüero: 650°C slurry coating failed at ~60kh in steam

If temperature relationship is understood, this data set forms the basis for a comprehensive lifetime model

# No austenitic failures!

## Thin coatings at 700° and 800°C in wet air



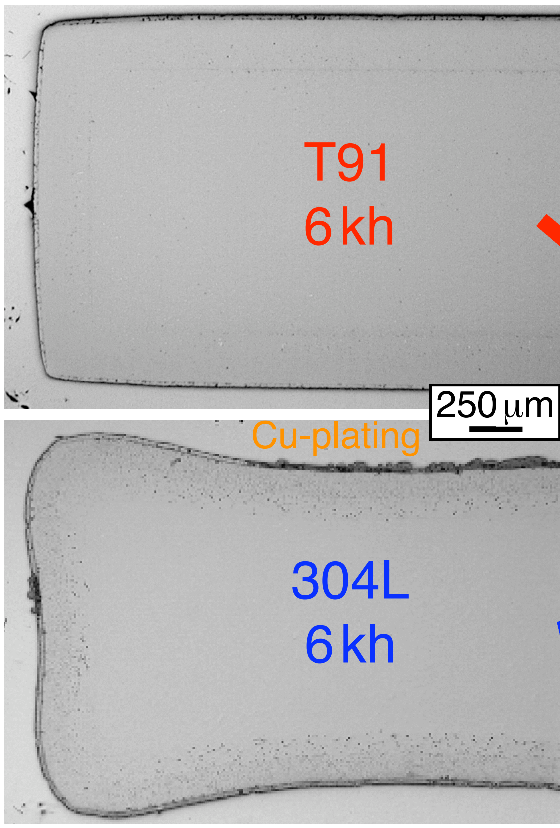

700°C: thin coating on 304L past 24 kh
>2X coating life on T91

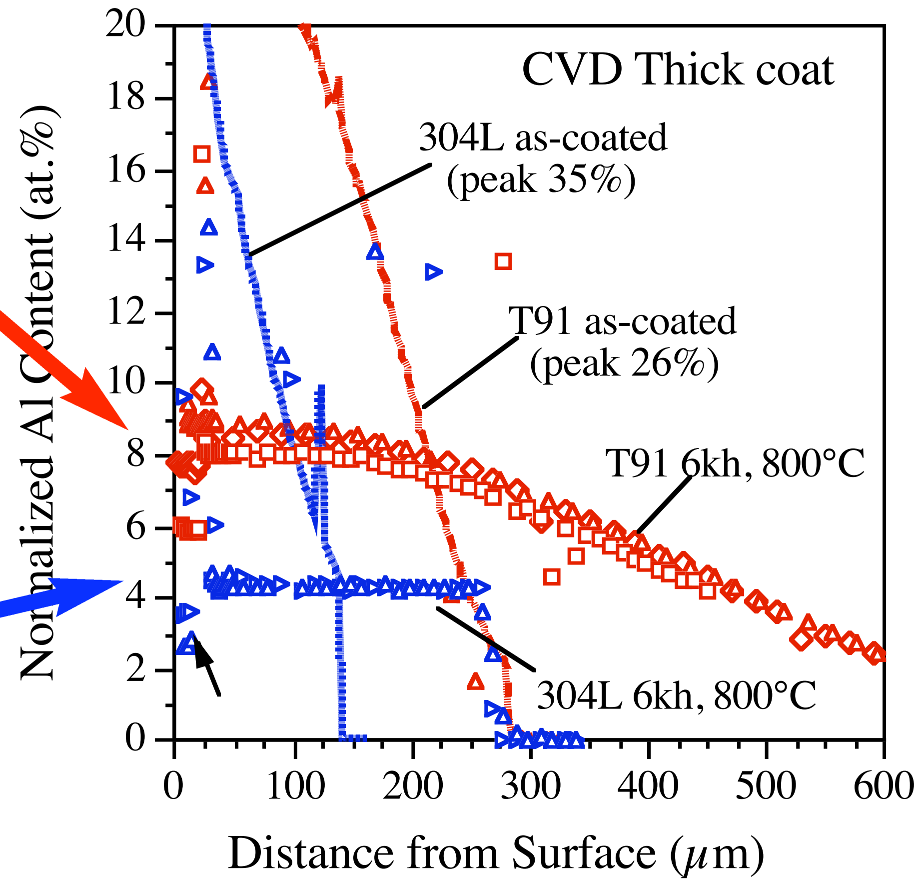
800°C: thin coating on 316SS past 6 kh
almost 3X coating life on T91, T92, T122

Original hypothesis: Higher Cr content in coating (~18%Cr)?

# 800°C interdiffusion difference

## 250$\mu$m coatings stopped 6kh without failure




Austenite-ferrite phase boundary
inhibits Al interdiffusion

# Key Points

- Normally think that more Al is better
  - thermal expansion mismatch problem
  - Al loss:  interdiffusion more than oxidation
  - less is more:  “thin” ~50$\mu$m coatings better
- T91 Lifetime model developed
  - Based on NASA COSIM model (Nesbitt)
  - Isothermal diffusion experiment data used
  - Need failure criteria to predict life
    - 8-10%Cr doesn’t affect lifetime at 800°C
    - $C_b$ decreases with increasing temperature
    - No failures on thin coatings on 304L/316
  - Model still being developed for 304L
    - how account for phase boundary effect?

# Coatings: A path forward

- Coupon tests only of interest if taken to failure
- Reality for T91 (all F/M):
  boiler application ≤600°C - no Al interdiffusion
  Thin coating will minimize mech. problems
- Reality for 304L (347HFG, Super304H, etc.)
  no boiler application above 650°C
  phase boundary will limit interdiffusion
  Will CTE mismatch cause fatigue cracking?
- Fabrication
  How to coat 10m tubes? Thin slurry coating?
  How to coat welds? (Coat before PWHT!)
- Demonstration
  304/347 tube explosions creates need

Now: 2010 EPRI program with ORNL & Praxair

# Milestones

## FY09: Coatings

Done - Complete 800°C testing (9-12Cr failures)

Done - Final report on coatings: presentation at Oct. 09 EFC workshop - 2010 proceedings

Future: EPRI demonstration coating 347H tubes
Tritium permeation barriers

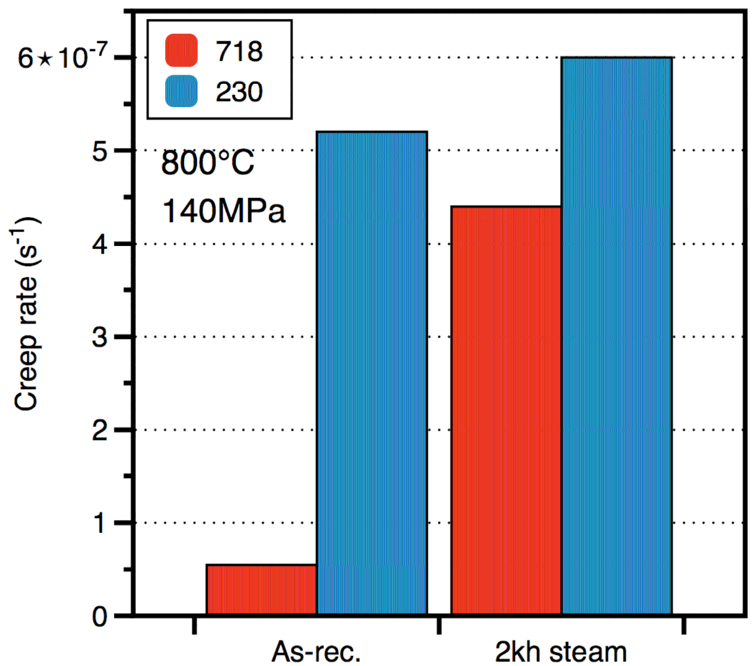
## FY10: Oxy-firing corrosion

- Literature review
- Begin testing in $CO_2$, $H_2O$ (i.e. no ash) (piggy-backing on USC: 800°C, 17bar steam)
- Begin testing in fireside corrosion (done)
- Build in-situ rig for creep testing in steam

# What is effect of steam on creep?

## Little experience with new alloys in steam

ex-situ (in air)





in-situ

Untested: C617, 740

also 4 kh steam, 2 kh anneal

under construction

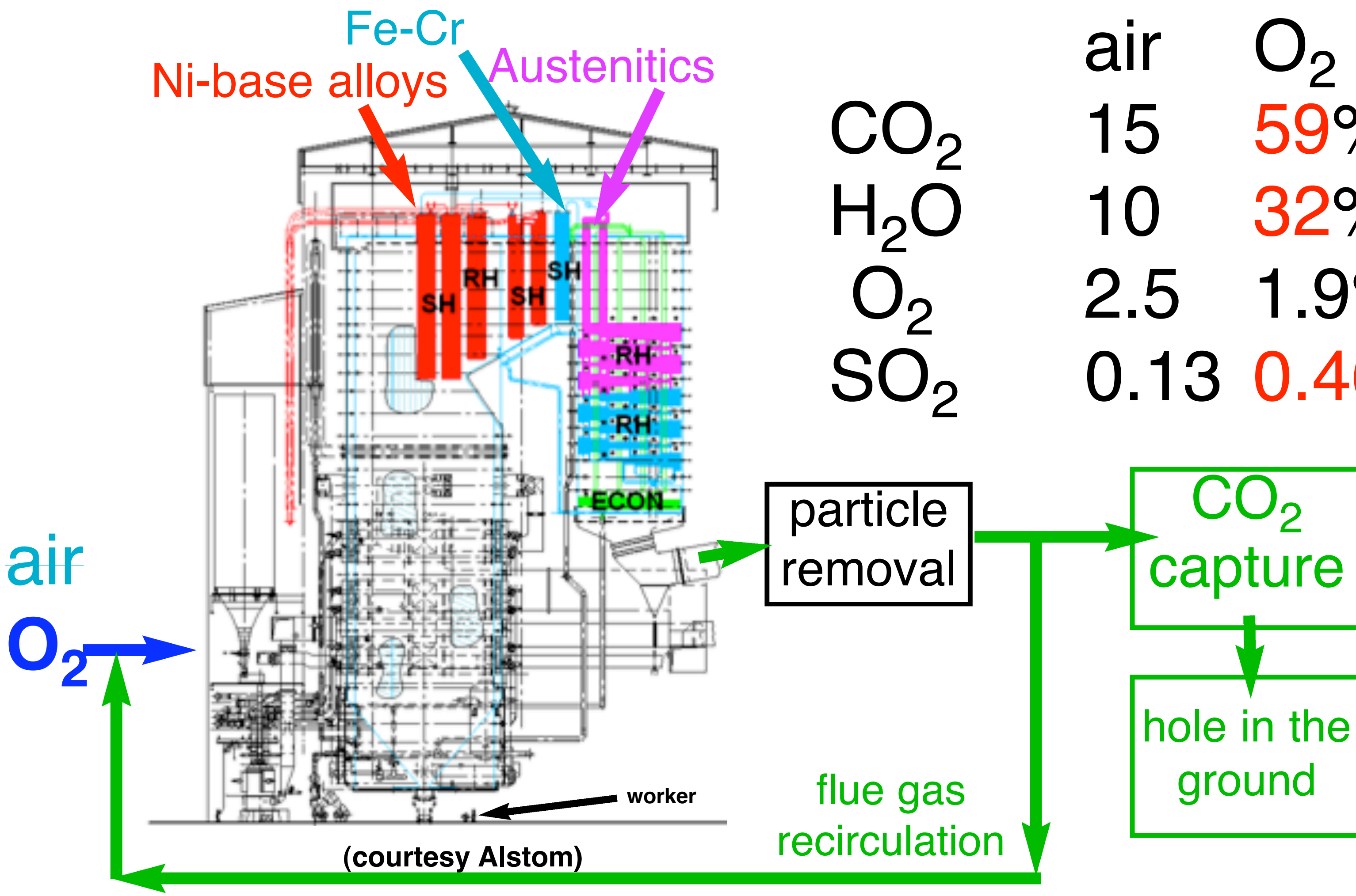
In $H_2O$, well-known that H injected into metal: effect?

Better comparison: coating debit vs. corrosion debit

# Introduction - Oxy-fired Coal Boilers

Several studies published by Alstom (Bordenet)

| | air | $O_2$ |
|---|---|---|
| $CO_2$ | 15 | 59% |
| $H_2O$ | 10 | 32% |
| $O_2$ | 2.5 | 1.9% |
| $SO_2$ | 0.13 | 0.46% |

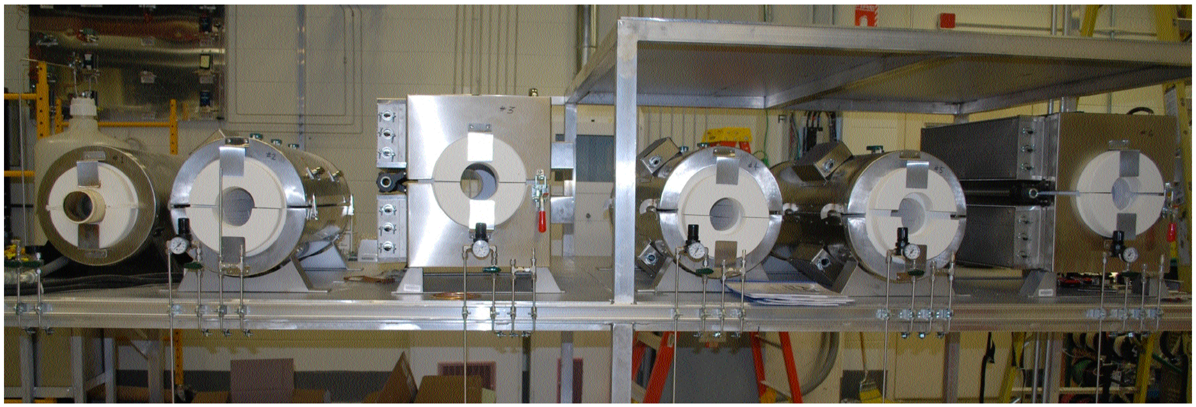



Germany: 30MW oxy-fired pilot plant (Alstom)

U.S. utilities: no oxy-firing without $CO_2$ legislation

# Corrosion testing

## Determine effect of higher $CO_2$, $H_2O$, $SO_2$...



gas only, no ash
- $H_2O$ only
- $CO_2$ only
- $H_2O$-$CO_2$

(under construction)


Synthetic ash: 30%$Fe_2O_3$-30%$Al_2O_3$-30%$SiO_2$-5%$Na_2SO_4$-5%$K_2SO_4$

Gas: $N_2$-15%$CO_2$-3.5%$O_2$-0.25$SO_2$

Temperature: 600°C

Time: 500 h (1 cycle)

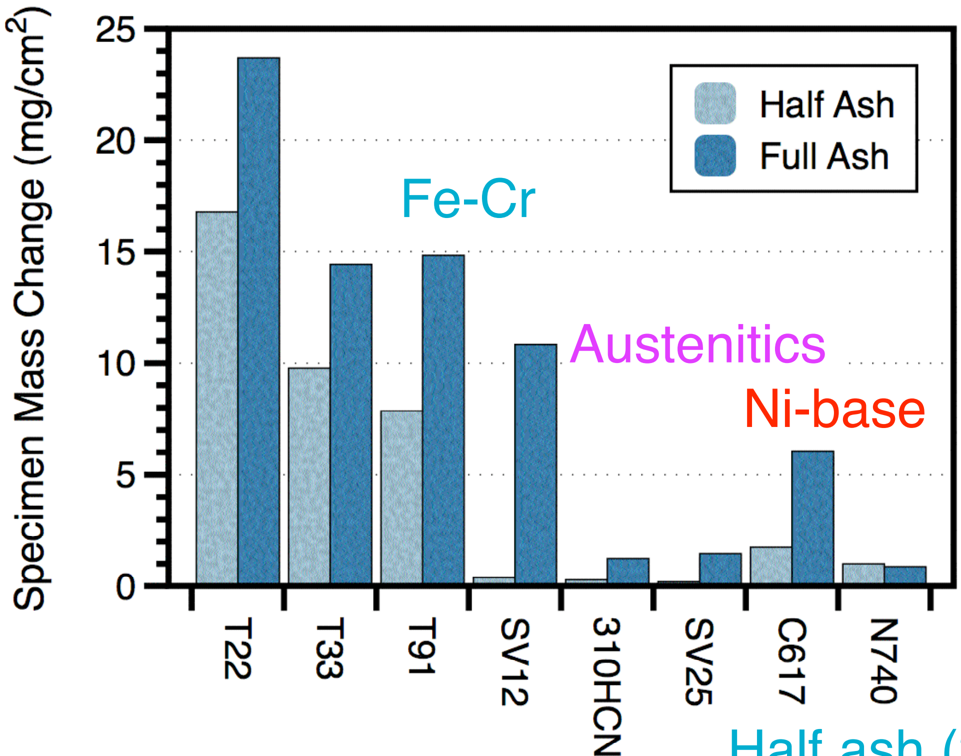
Porous alumina

Get started: establish methodology + safety/health

make specimens, work out experimental issues

# Half ash vs. full coverage

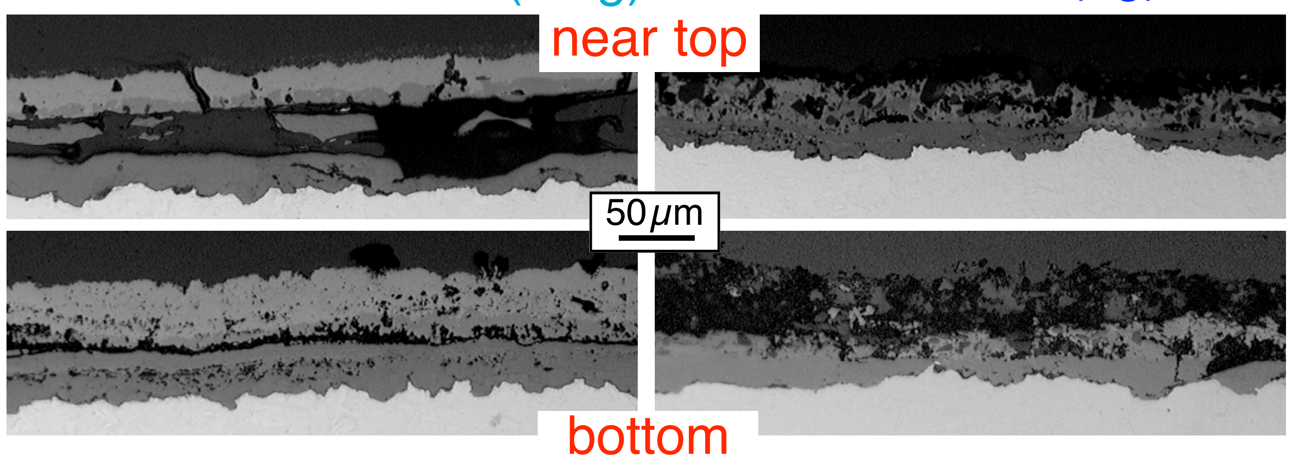
## Different procedures reported in literature





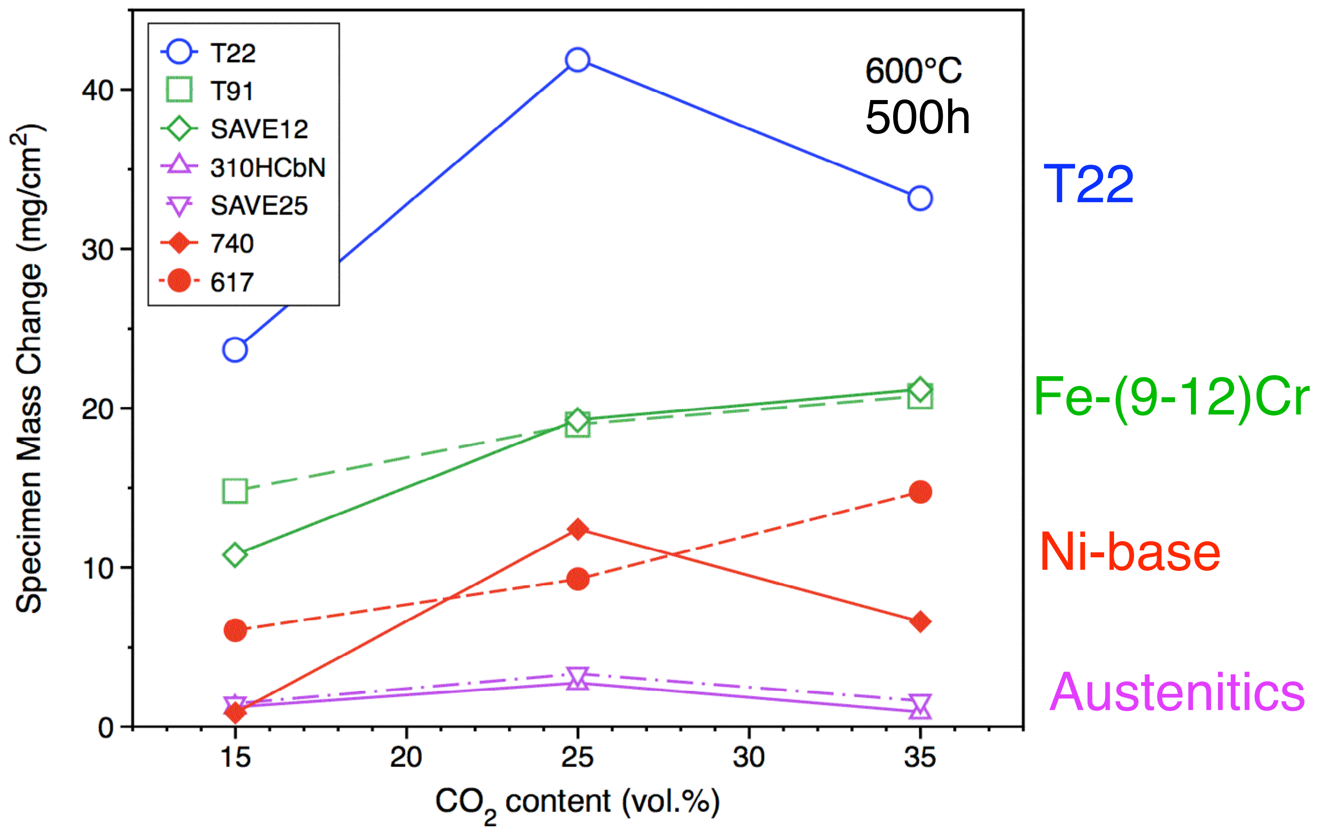

Half ash (3.8g)

Full ash (9g)



# Preliminary results: $\Delta CO_2$

## Increased $CO_2$ concentration in base gas




Mass change data only - need metal loss

Qualitatively similar to 700°C Bordenet data

(austenitics better than Ni-base)

# Not just commercial alloys

## Model alloys: better composition understanding

| Cr Content (wt.%) \ Ni Content (wt.%) | 0 | 25 | 35 | 45 |
|---|---|---|---|---|
| 15 | X | | | |
| 20 | X | | | |
| 25 | | X | X | X |
| 35 | | X | X | X |

Alloy 33

622,625

chromizing

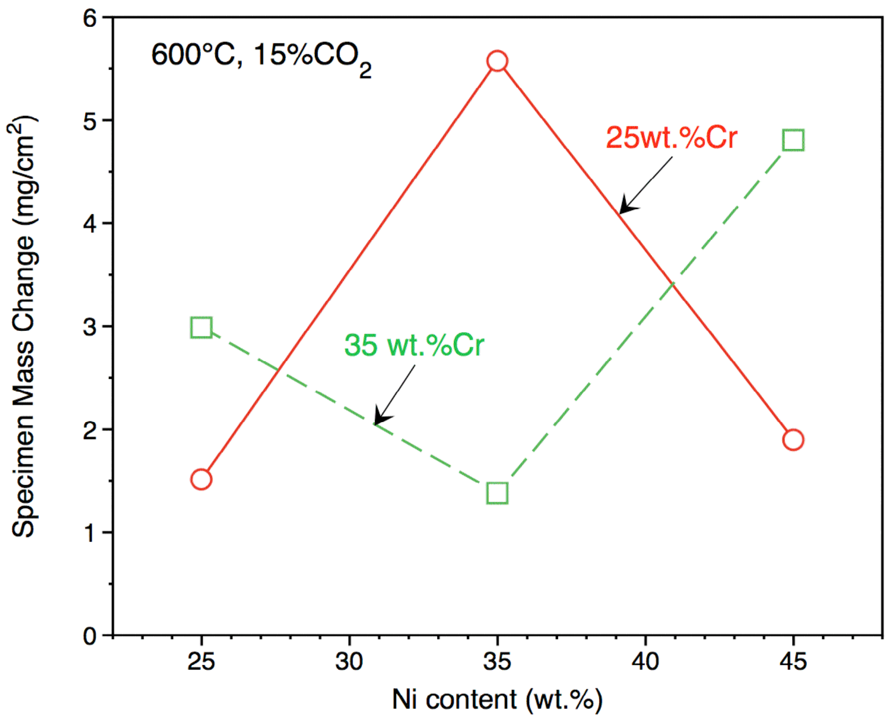
Cast, hot-rolled to 8mm: cut coupons and rods

- Potential coating compositions
- Information for alloy development
- Future: quaternary additions, etc.

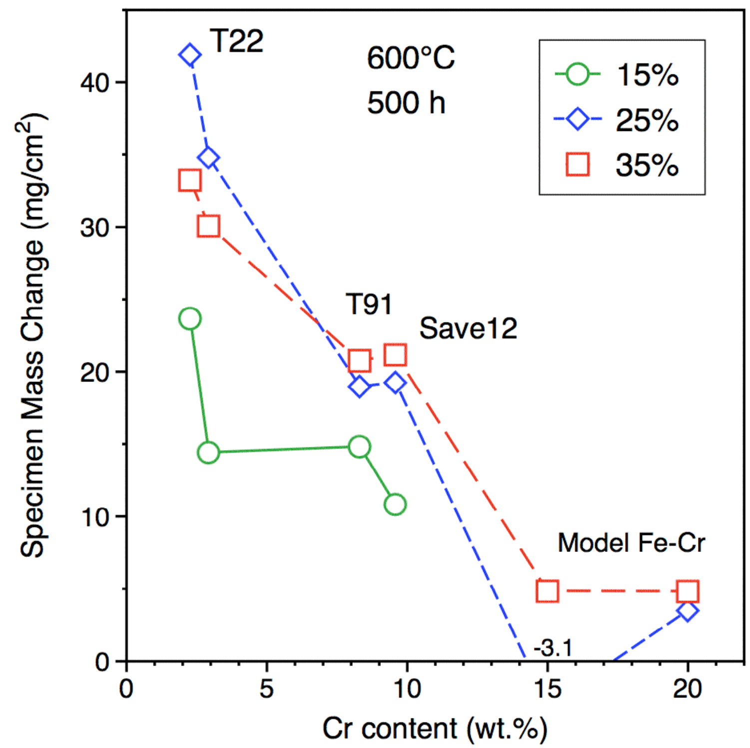
# Initial model alloy results

## Ash tests, 500h 600°C

### FeCrNi alloys




### Fe-Cr alloys




Mass change data only - need metal loss

35%Cr alloys significantly less pitting than 25%Cr

# Long-term plan

## FY10: Setup

- Literature review
- Begin testing in $CO_2$, $H_2O$ (i.e. no ash)
- Begin testing in fireside corrosion (done)
- Build in-situ rig for creep testing in steam

## FY11: Complete work on Fe-Cr

## FY12: Austenitics

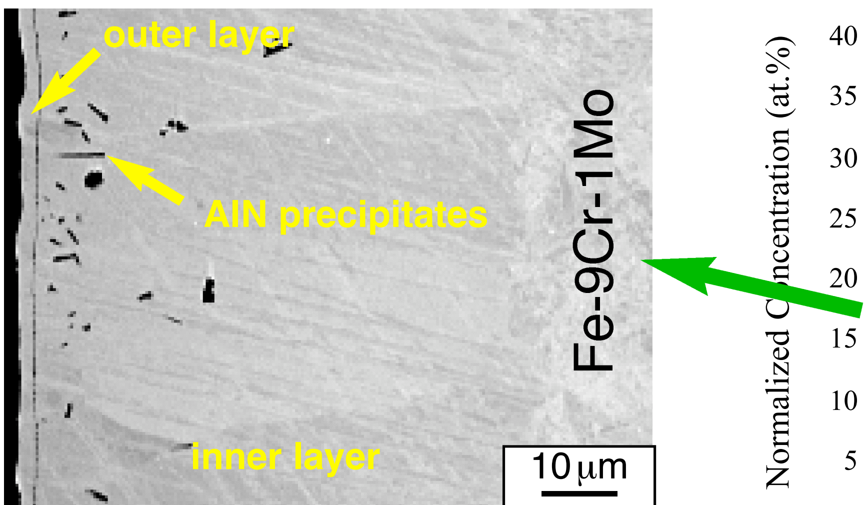
## FY13: Ni-base alloys

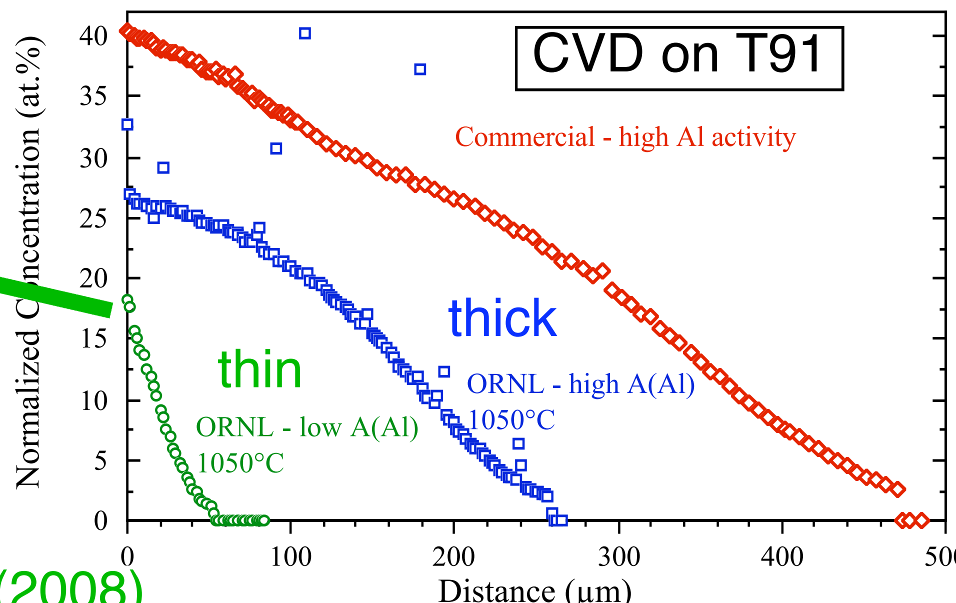
backups

# High-purity well-controlled process

## Chemical vapor deposition (CVD) coatings

- similar to a well-controlled above-pack coating process
- ORNL laboratory scale reactor with 2-4, 2x1 cm specimens
  - austenitic 304L (Fe-18Cr-8Ni)
  - ferritic-martensitic T91 (Fe-9Cr-1Mo)
- flowing $H_2$-$AlCl_x$, 100 Torr, 6h, 900°C or 4-6h at 1050°C
- Two types: "Thick" coatings ≈40μm Al-rich outer layer, 150μm total
  "Thin" ≈5μm Al-rich outer layer, 35μm total thickness

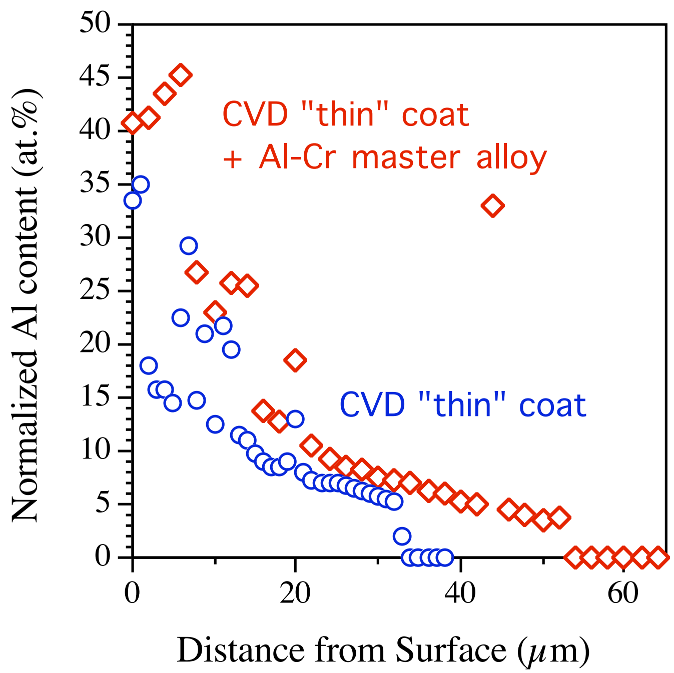


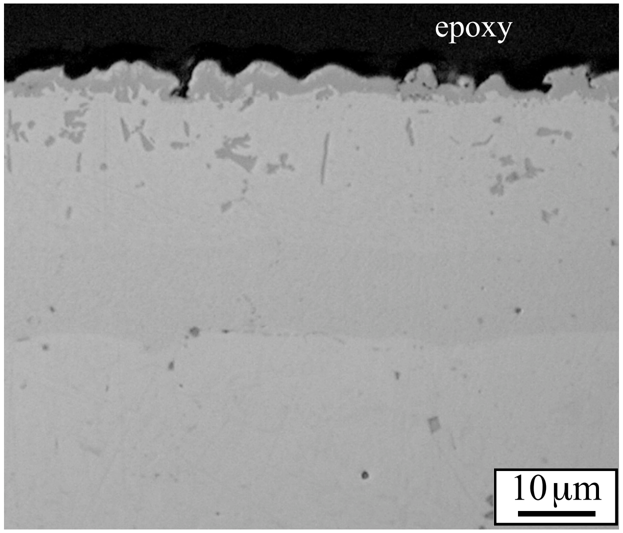



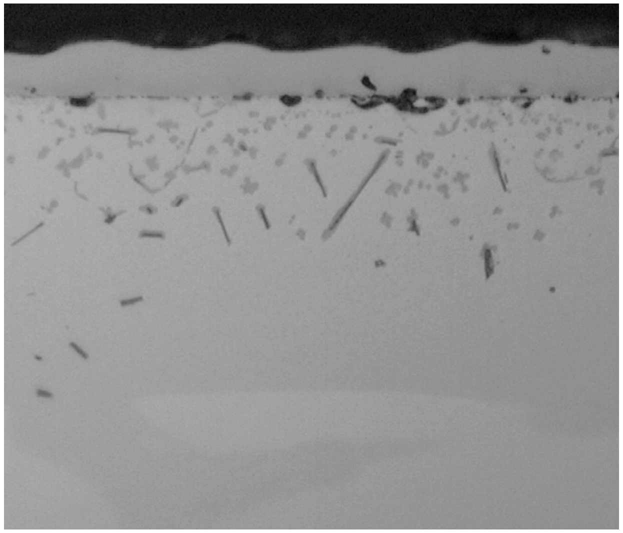

Zhang et al., Surf. Coat. Tech. (2008)

# Less thin coatings

## Modify CVD process by adding Al-Cr powder



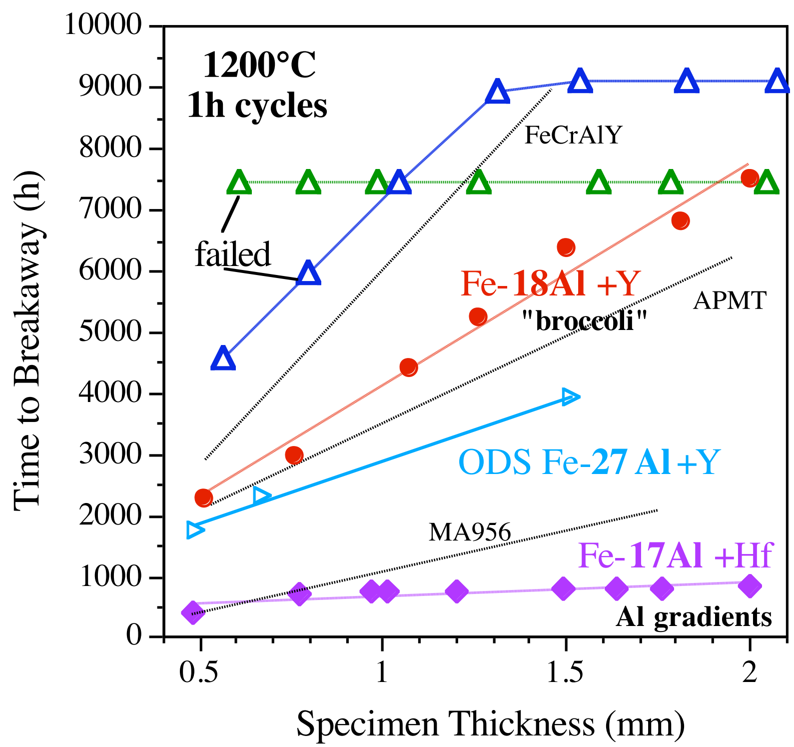



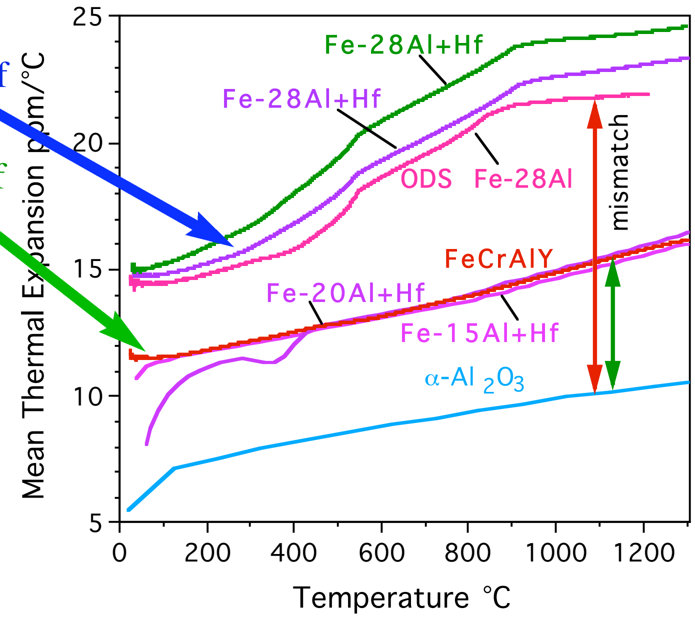



## Improved processing for H permeation barriers

# Final work: Fe-Al alloys + Y,Hf

## Academic exercise to see comparison




$DO_3$-> <- B2 -> <- α

**Phase change with T**

Fe-17Al+Hf: Al gradients reduce life

Fe-18Al+Y: broccoli failure (shorter life than FeCrAlY)

Fe-19Al+Y/Hf: Optimized dopant, highest Fe(Al)

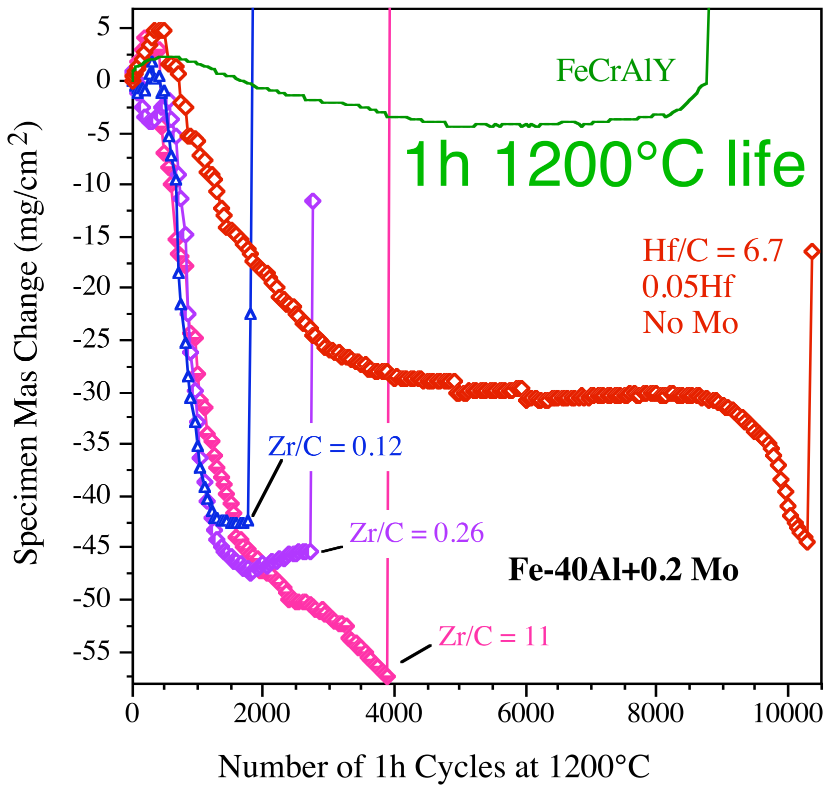
Fe-28Al-2Cr+Y/Hf: $Fe_3Al$ (high CTE)

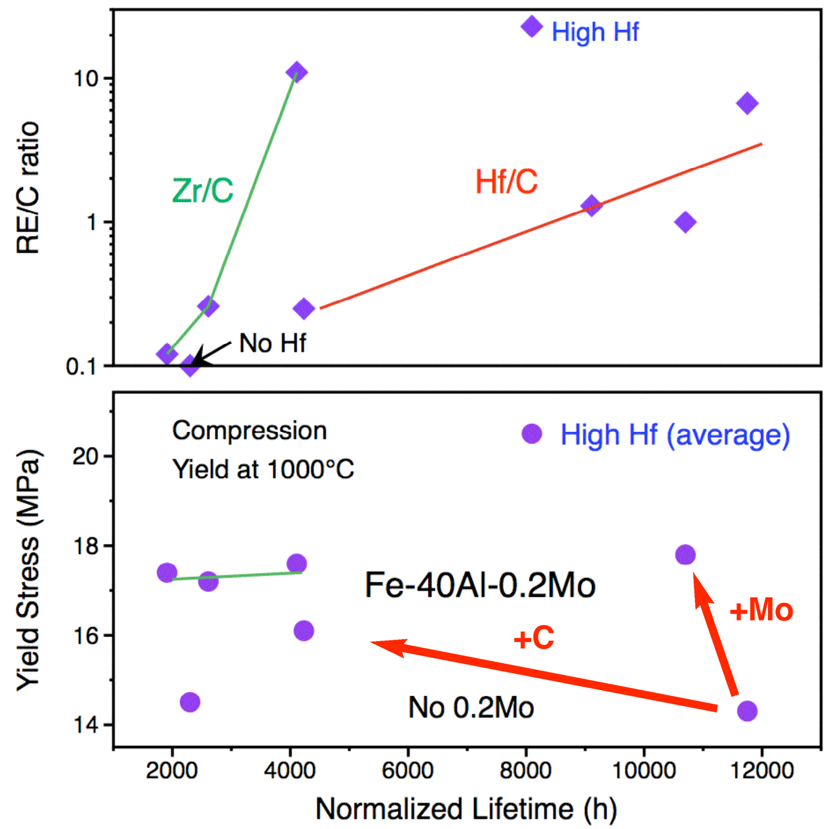
5kh/yr: taking a long time to complete!

# Case study: Fe-40Al doping

## 10+ year argument on RE strengthening

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



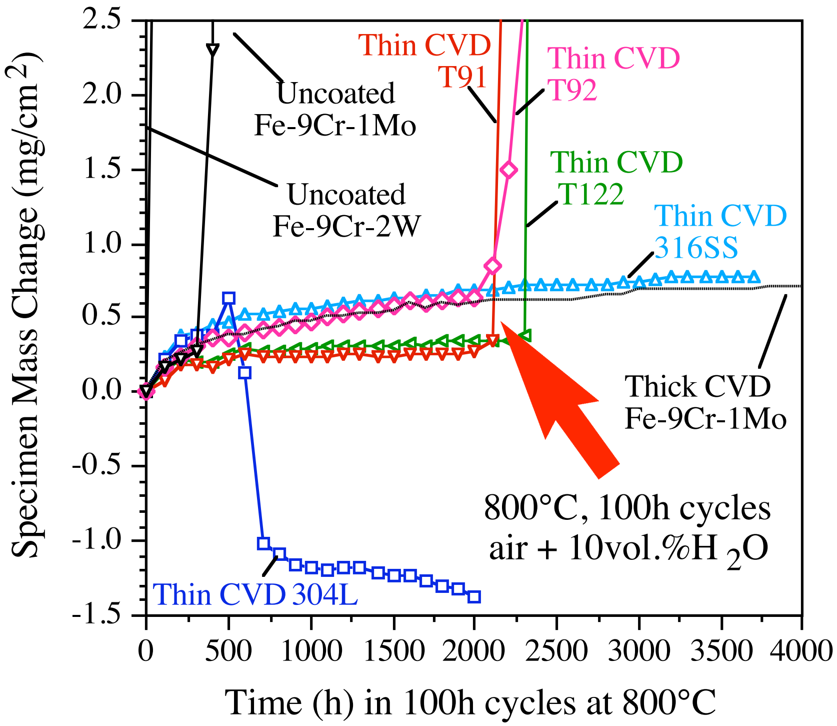

Whittenberger: in NiAl, Zr strengthening gone by 1100K

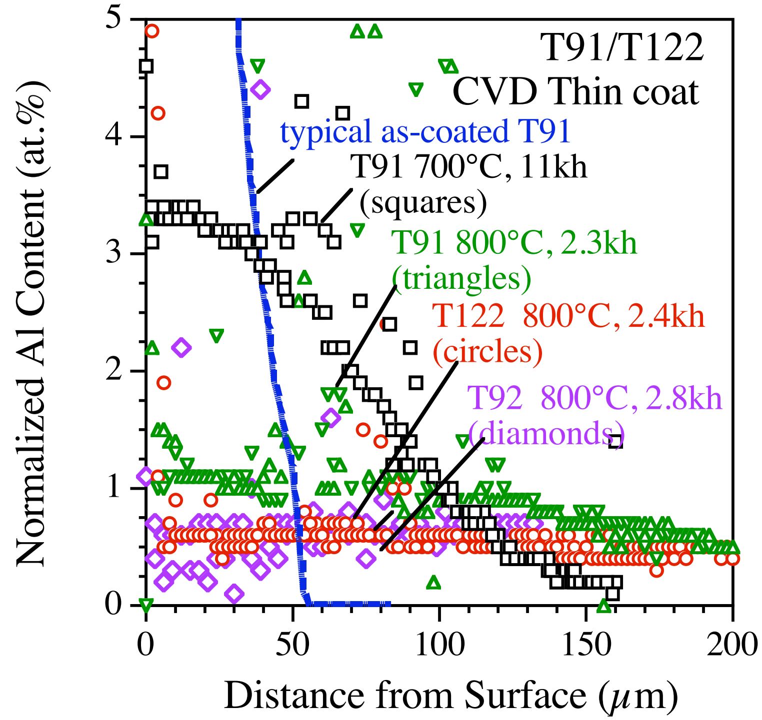
Only 1000°C compression yield data (Schneibel,Dryepondt)

Fe-Al: RE/C predicts life better than yield strength

# Effect of $C_{Cr}$ on $C_b$

## Thin coatings at 800°C in wet air




T91, T92, T122 (10.5%Cr) all failed within 10% of life

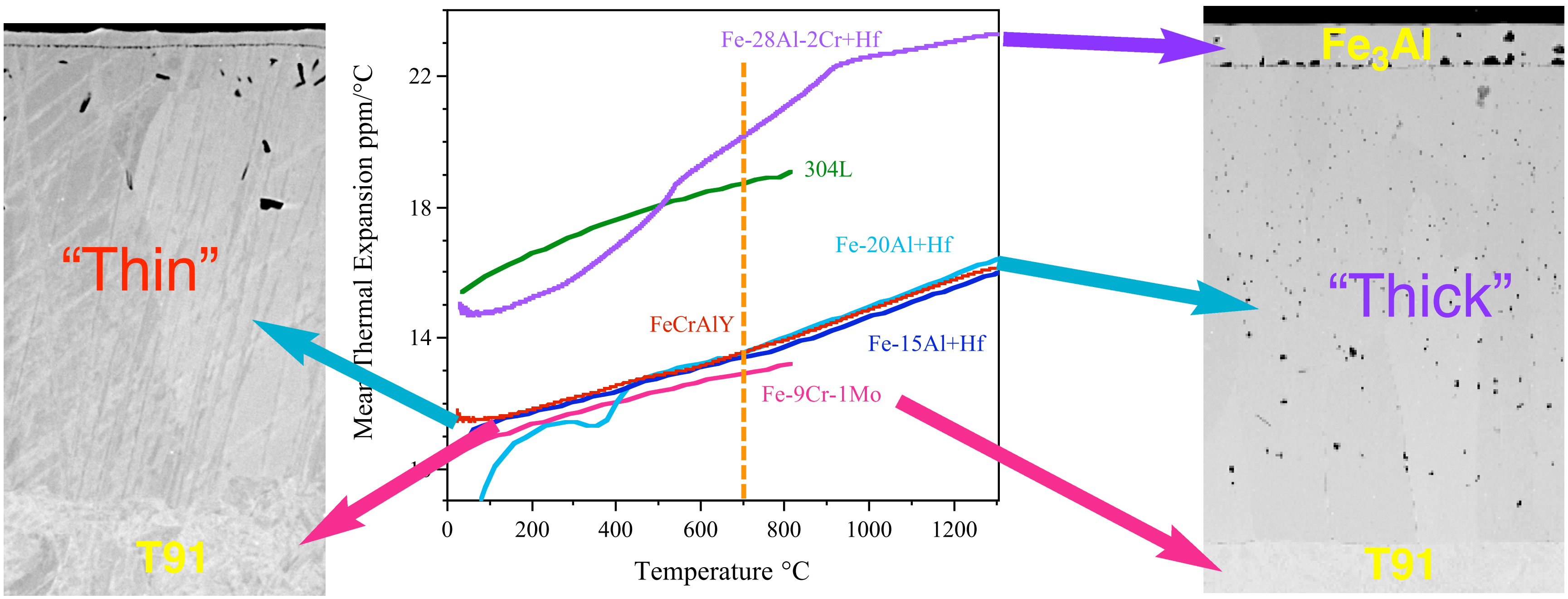
- $C_b$ at failure was <1.1 at% Al
- Kvernes (Fe-13Cr-xAl) said more Al required with T!

304L: bad coating

316SS: no failure at 4kh!

# Fe-Cr Coating Solution

## Eliminate CTE mismatch problem



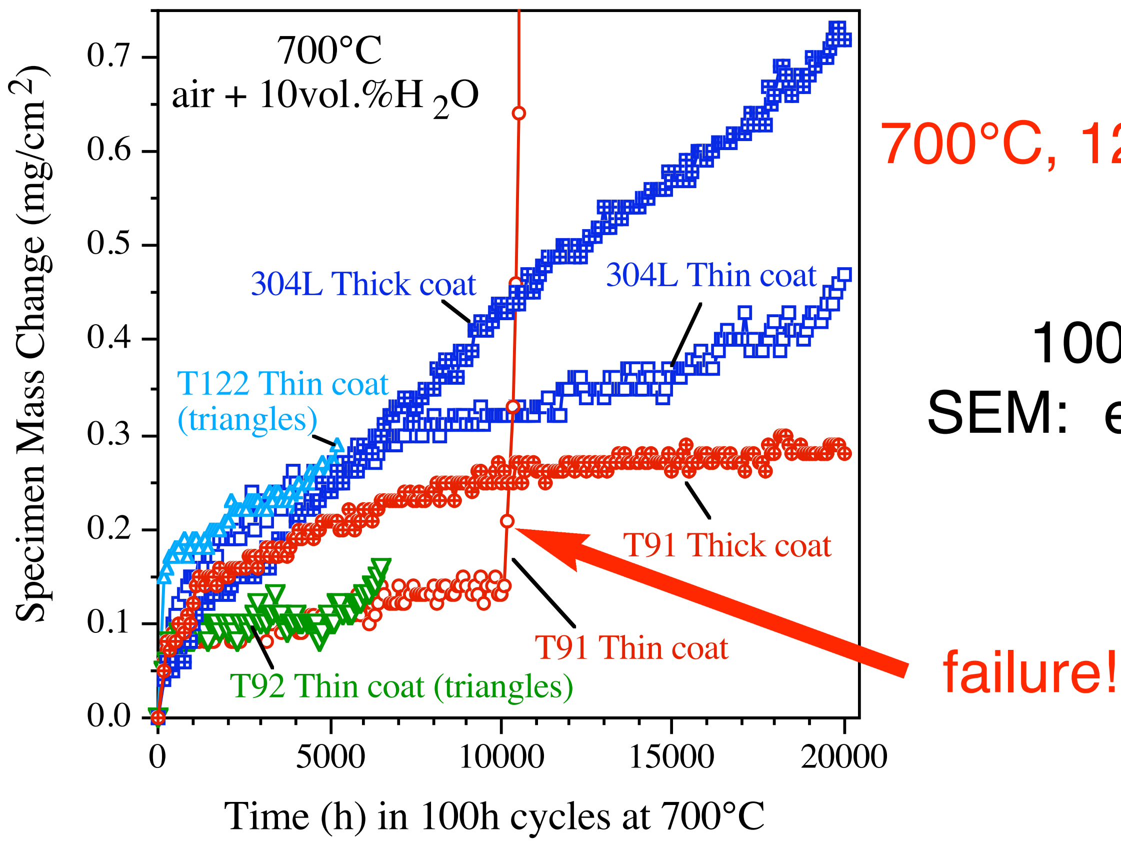

For coated T91:

Thick CVD: Outer $Fe_3Al$ layer
inner coating & substrate are ferritic

Thin CVD: ~18at.%Al peak surface Al (no aluminide)
only α-Fe(Al) phase
NO ΔCTE

# Coating Performance: 700°C

## Accelerate failure by increased interdiffusion




700°C, 1292°F

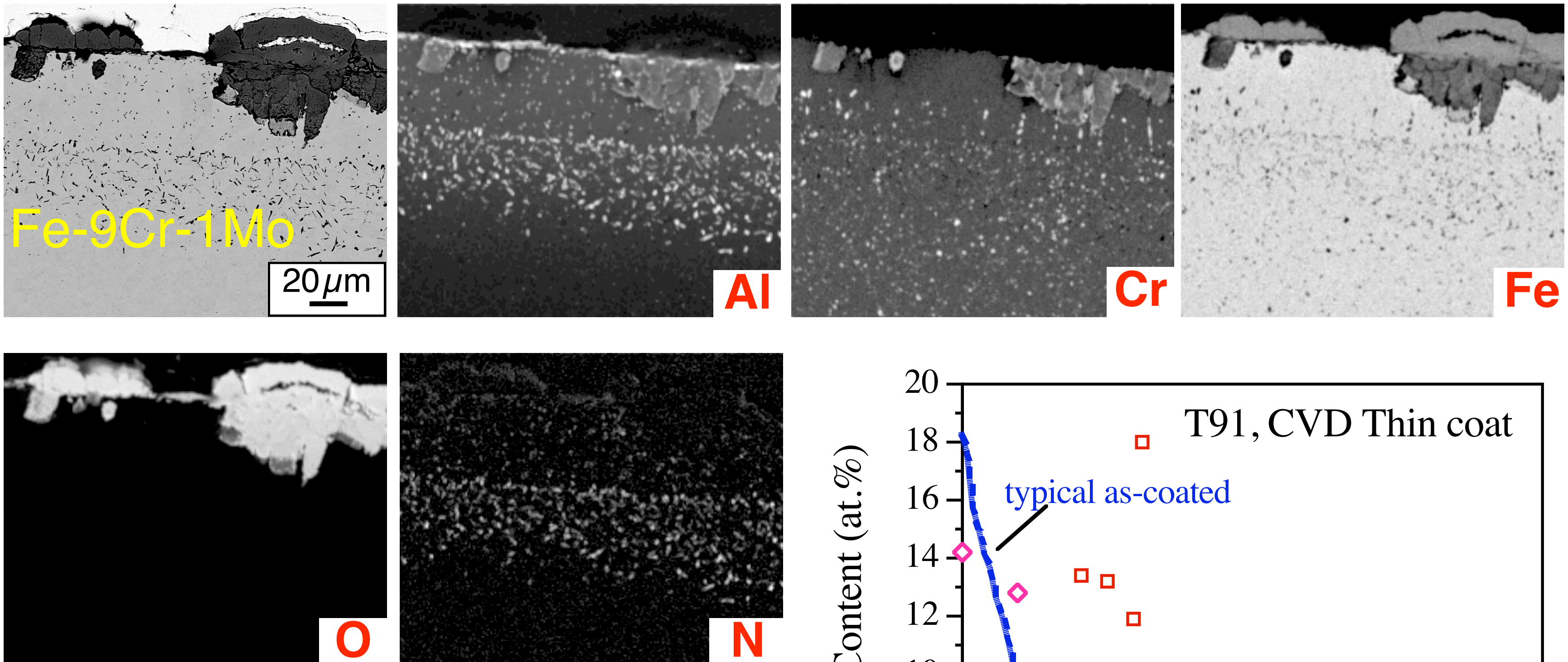
100h cycles
SEM: every 2,000h

Thick coatings had a longer lifetime on T91 and 304L

Breakaway oxidation for thin coating on T91 at ~10,500h

# Failed Coating Characterized

## Thin coating after 11,000h in humid air at 700°C

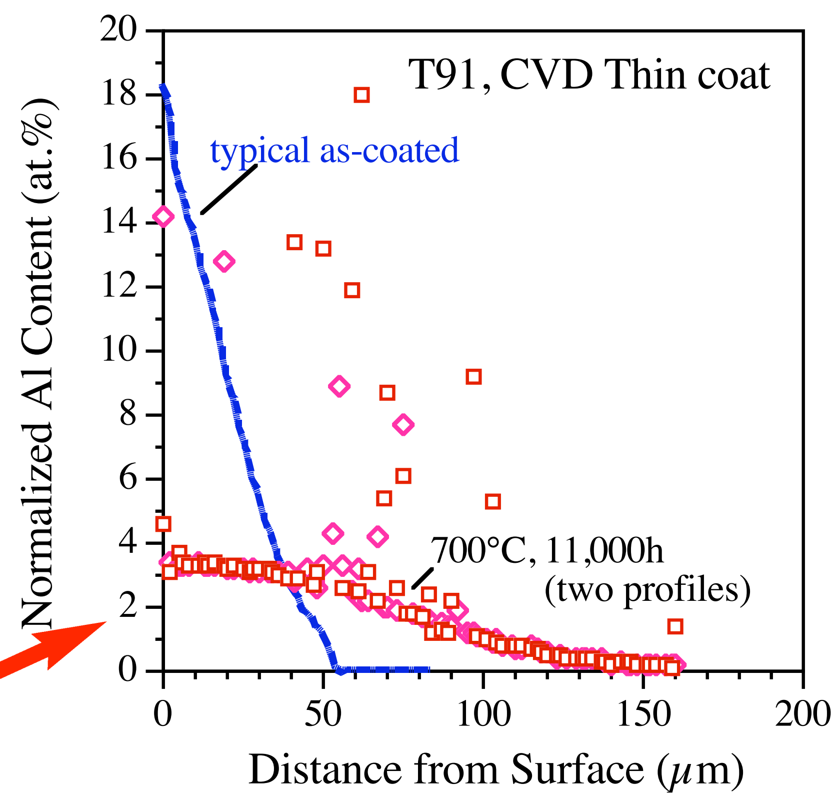



Electron probe analysis:

Typical Fe-rich oxide nodules

AlN precipitates (0.2at.%N in alloy)

~3.4 at%Al at surface ($C_b$)



# Diffusion predictions at 700°C

## Using 10kh observations for ~250$\mu$m coatings on T91

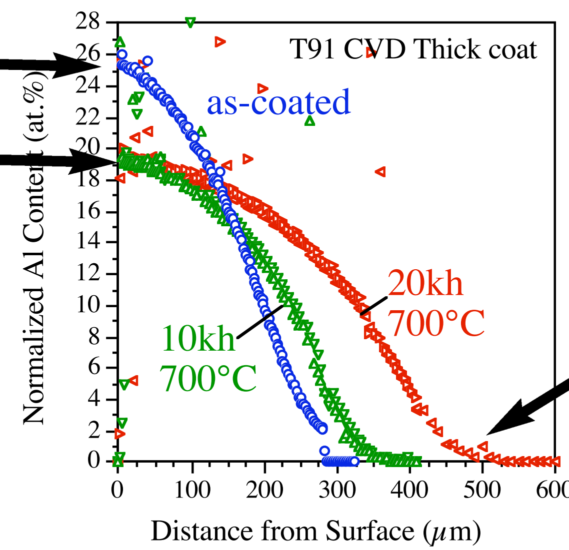
| Prediction Method | COSIM dependent | COSIM indep. FeAl | COSIM indep. FeCrAl | Heckel | Actual (diffusion test) |
|---|---|---|---|---|---|
| Surface (at.%) | 19 | 16 | 17 | 19 | 18%Al |
| Thickness ($\mu$m) | 310 | 438 | 428 | 356 | 320 $\mu$m |

COSIM - NASA (Nesbitt) developed model - missing key $D_{xy}$ terms

Heckel - simple parabolic rate constant from 2,000h data

starting Al surface content

after 10kh diffusion at 700°C

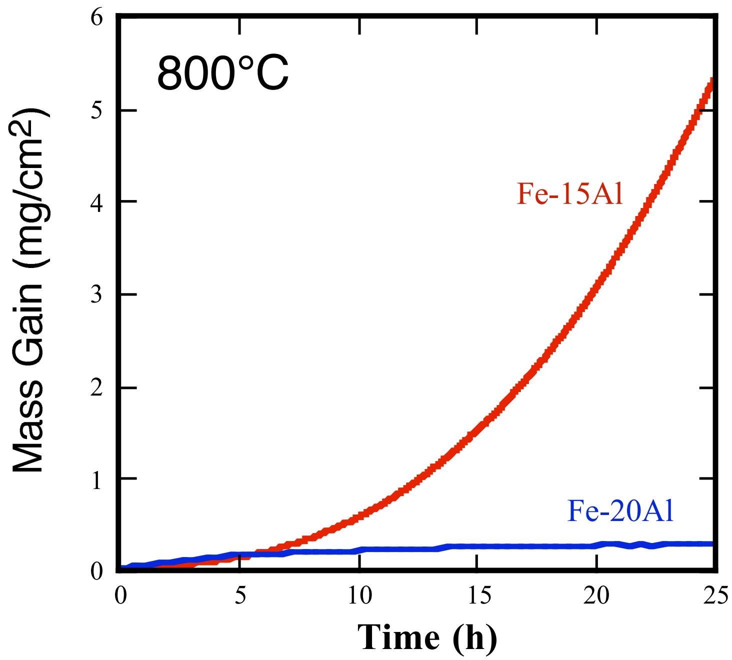



diffusion depth increases with t

# Thin vs. Thick Coatings: Sulfidation

## Model Fe-Al alloys at 800°C in $H_2$-$H_2O$-$H_2S$-Ar

800°C, 1472°F




For comparison to coatings, cast Fe-15at%(8wt%)Al & Fe-20%(11wt%)Al

Fe-15at%Al showed accelerated mass gain in test similar to thin coatings

Low mass gain for Fe-20%Al

Previous work by DeVan and Tortorelli found 18at%Al needed in Fe-Al

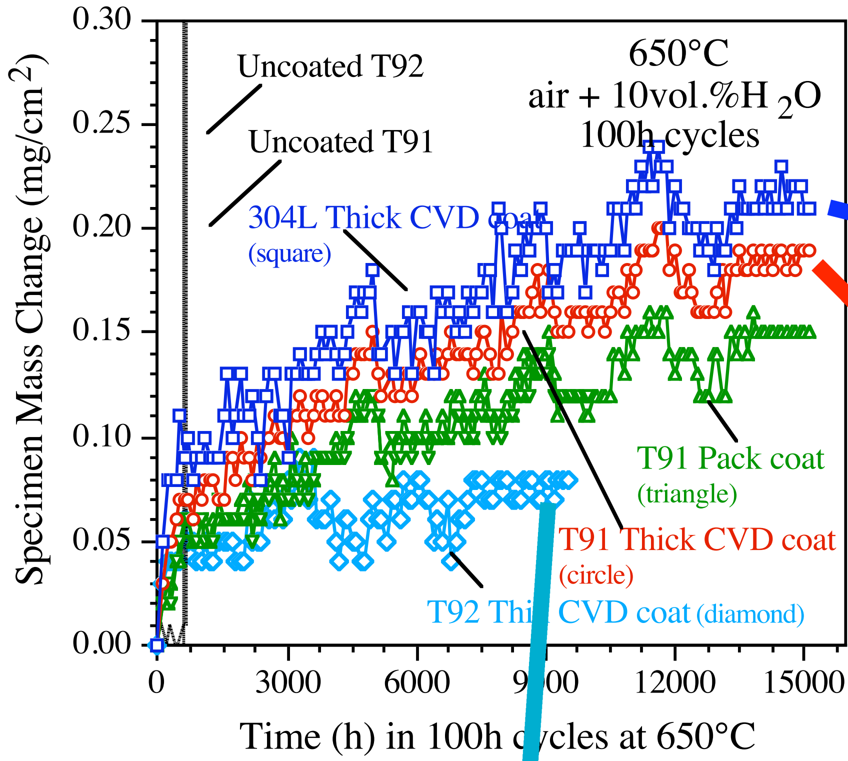
Higher Al content ("thick") needed for sulfidation resistance

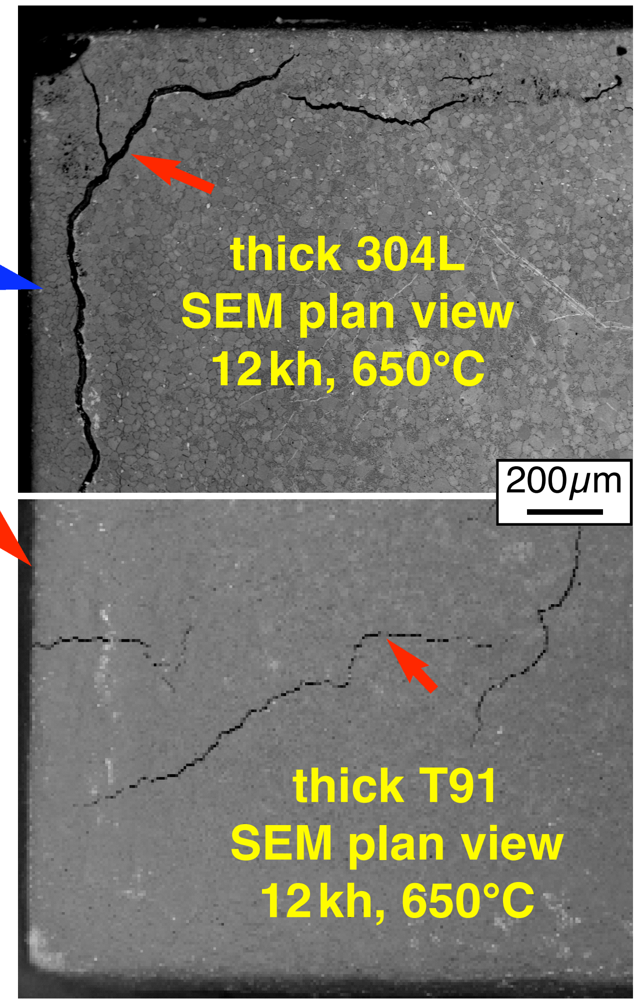
# Summary

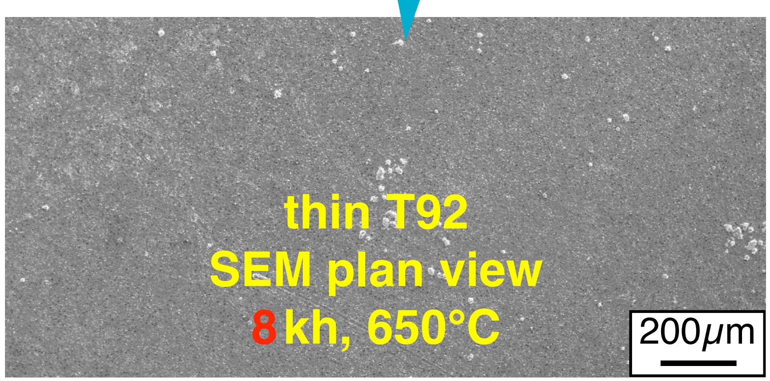
| | Fe-9Cr | 304L |
|---|---|---|
| CTE/cracking | ⇑ | ⇓ |
| Cr content | ⇓ | ⇑ |
| Phase boundary | ⇓ | ⇑ |

# Coating Performance: 650°C

## CVD or pack cementation coatings, 100h cycles



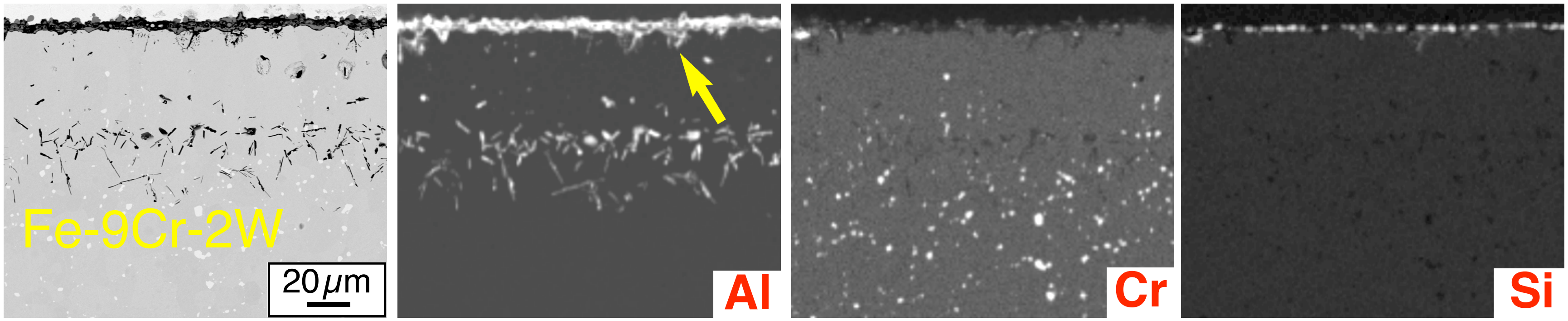



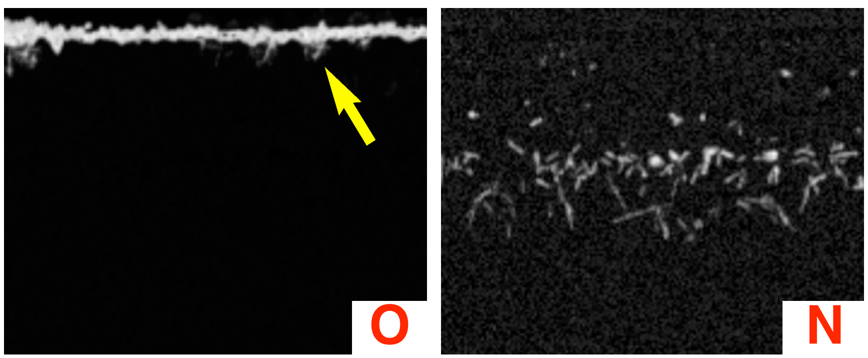

Not a fair comparison

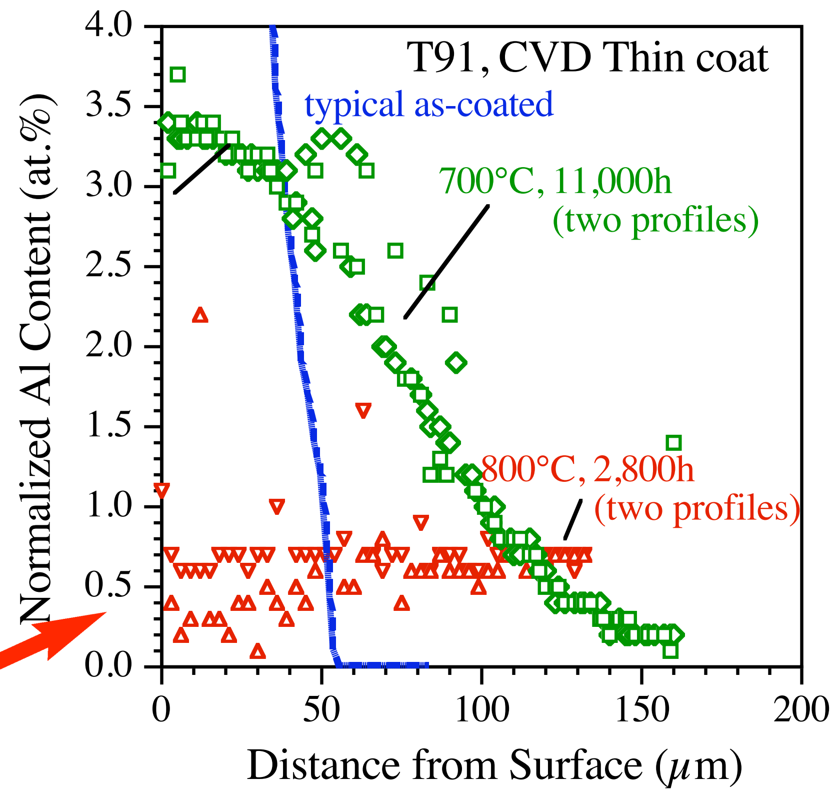
Cracks appeared at ~10kh

# Failed Coating at 800°C

## Thin coating on P92 after 2,800 h in humid air




Electron probe analysis:

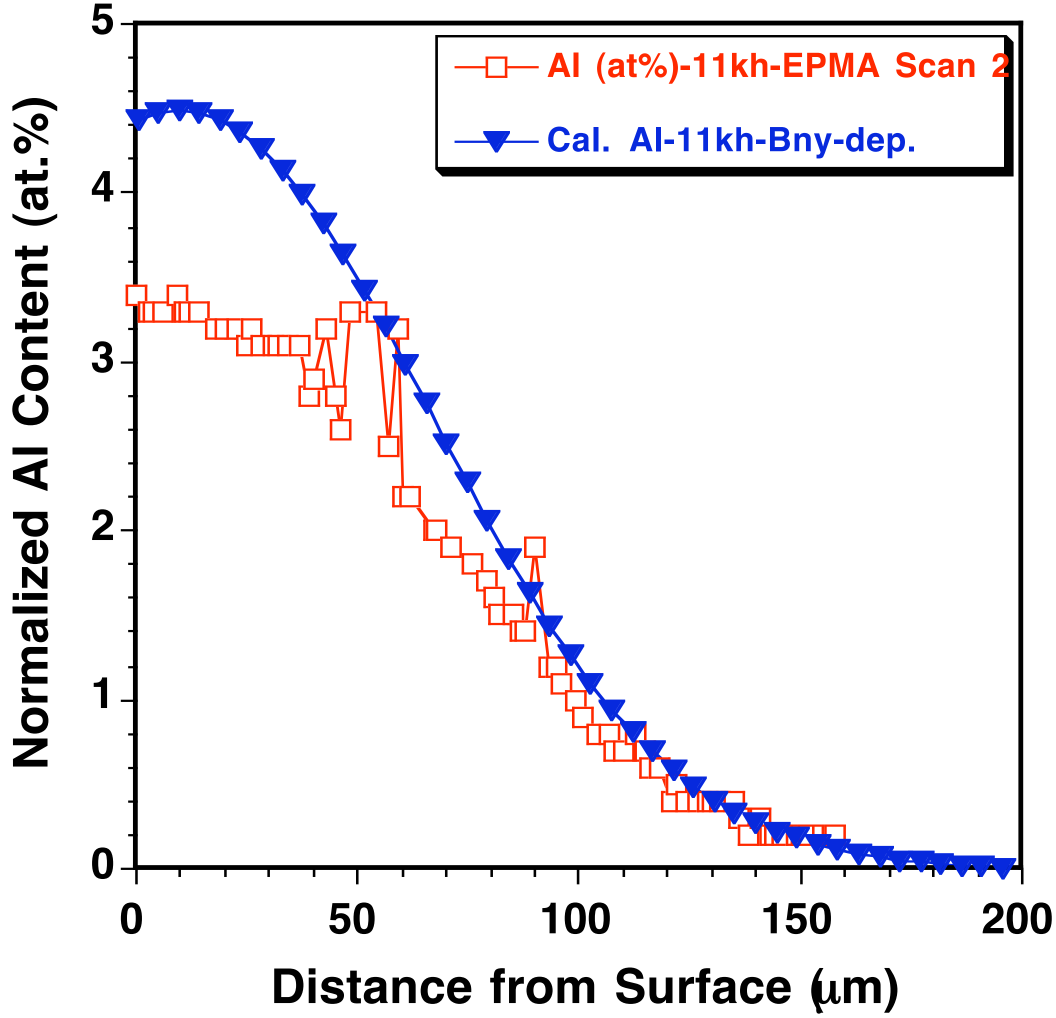
Area away from FeO nodules

Large AlN precipitates (N in alloy)

~0.7at%Al near surface ($C_b$)

# T91 model for thin coatings

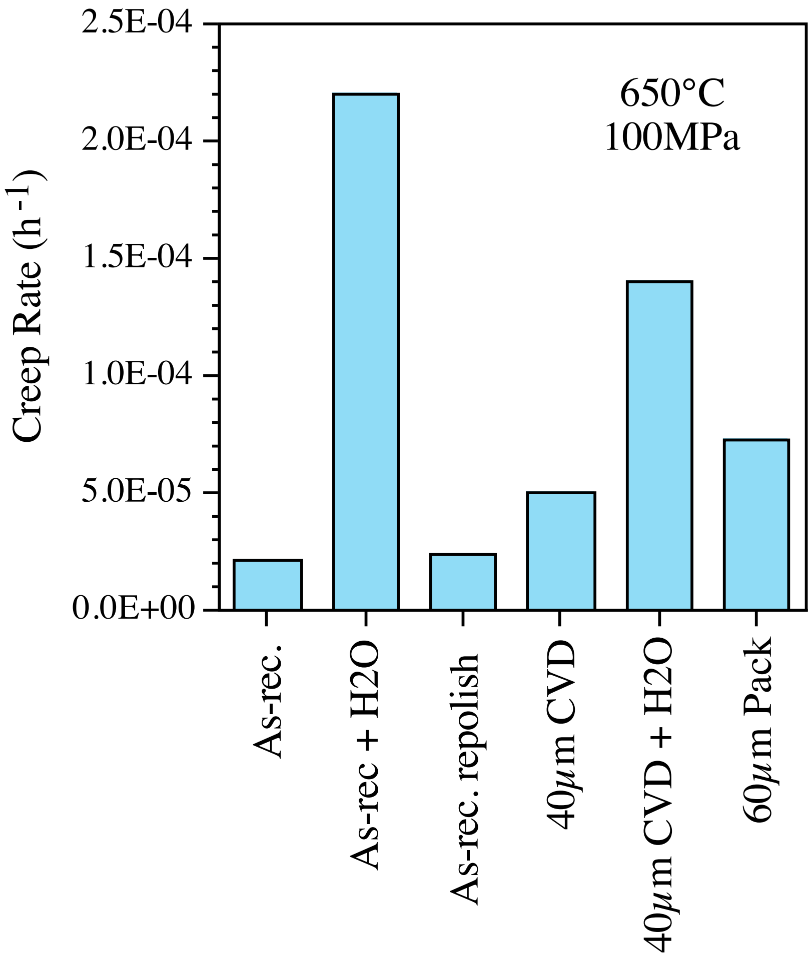
## COSIM prediction based on 11kh failure




Need to refine Al consumption term to match profile

# Combined Creep/Corrosion Testing

## P92: alternating wet air & creep in dry air 650°C




650°C, 1202°F
100MPa, 14.5ksi

Ideally wanted to compare:
- loss of strength (coating)
  40μm CVD, 60μm Pack
- uncoated loss (oxidation)

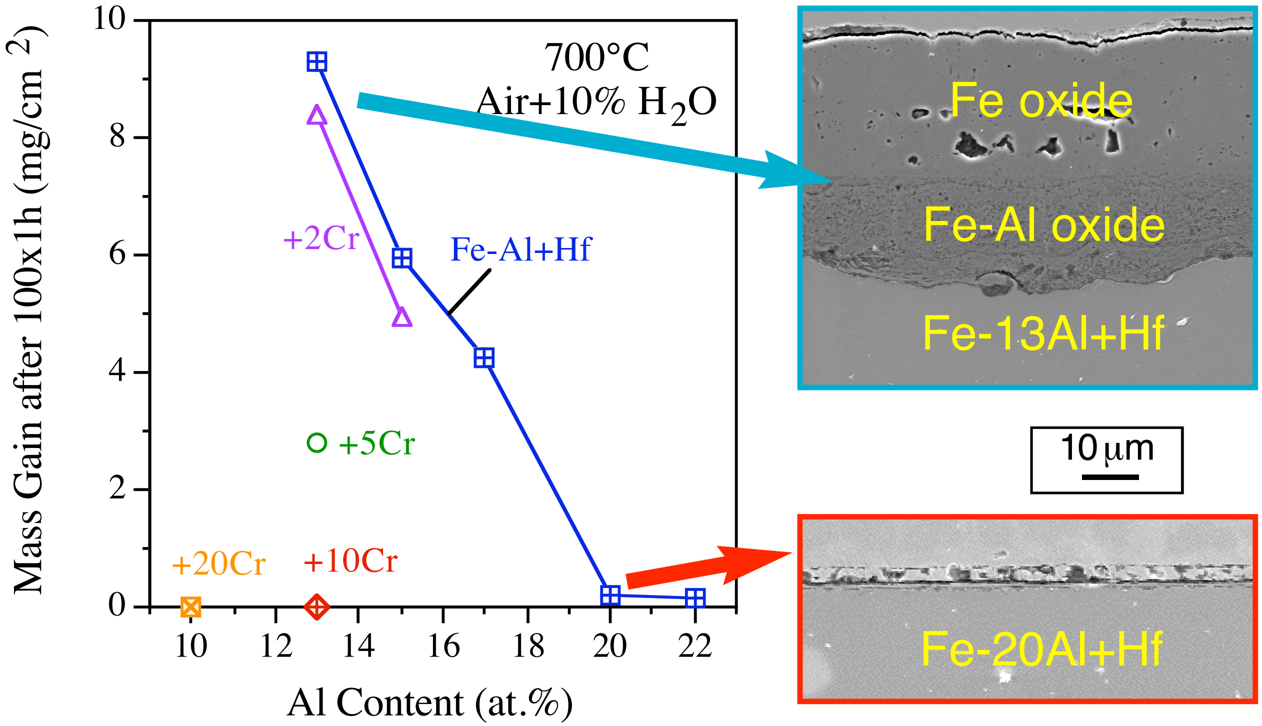
Order of testing effect:
creep test first - low rate
wet air test first -
higher creep rate

Observations: uncoated specimen did not lose strength
>7% deformation did not breach coating (true for $Fe_2Al_5$?)

Creep testing in steam (or wet air) needed

# 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)

# Standard Oxidation Lifetime Model

Lifetime model developed by Quadakkers, Bennett, et al. for ODS FeCrAl alloys 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 ($\rho$)
- Al consumption rate (e.g. **$kt^n$**), **t** is time,
  **n**=0.5 for parabolic, 1 for linear kinetics

$$(C_0 - C_b)/100 \cdot d/2 \cdot \rho = k \cdot t^n \cdot \frac{\text{(mole Al)}}{\text{mole O in } Al_2O_3}$$

## How does this apply to a coating?

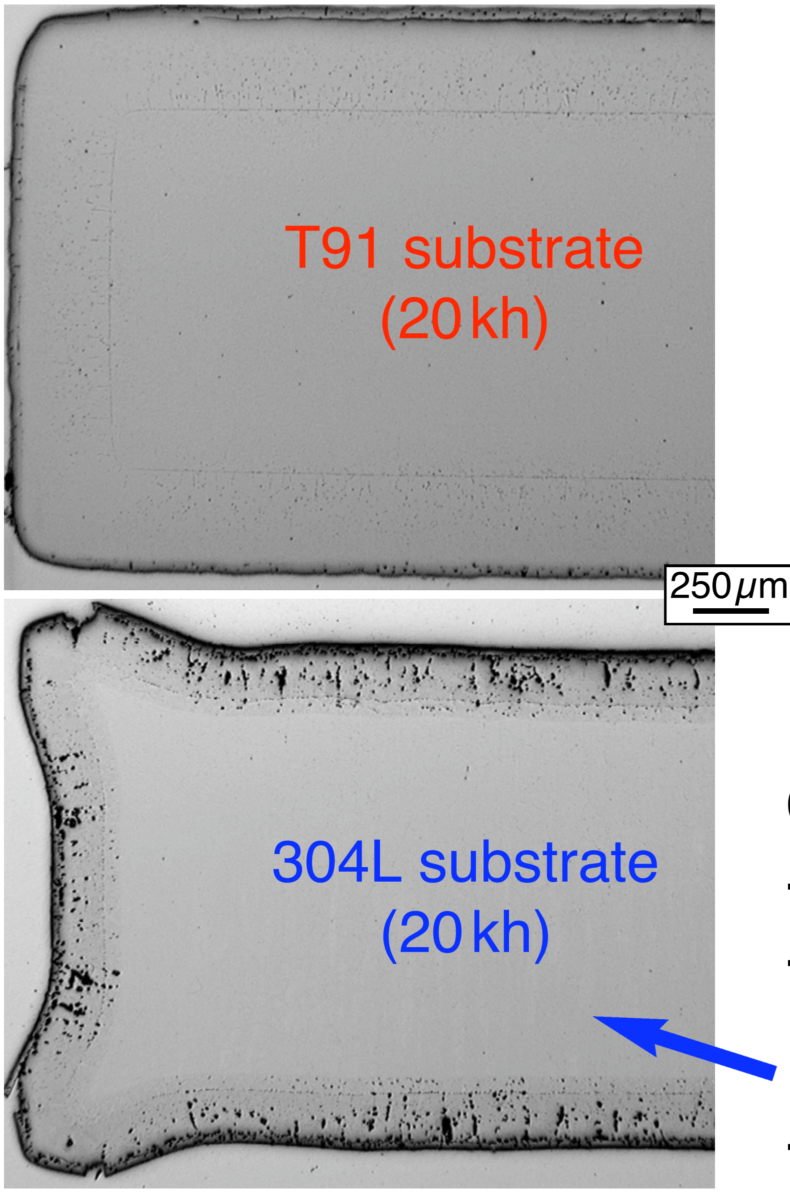
more complex Al "consumption": interdiffusion + oxidation

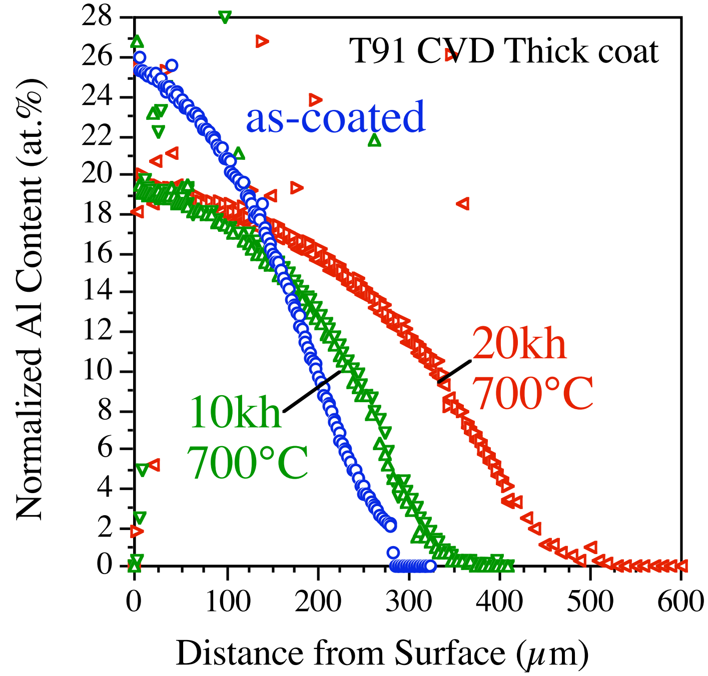
$C_0$ becomes a function of the coating thickness

What is $C_b$ for a coating?

# 700°C Performance of thick coating

## Coatings stopped after 10 & 20kh in humid air



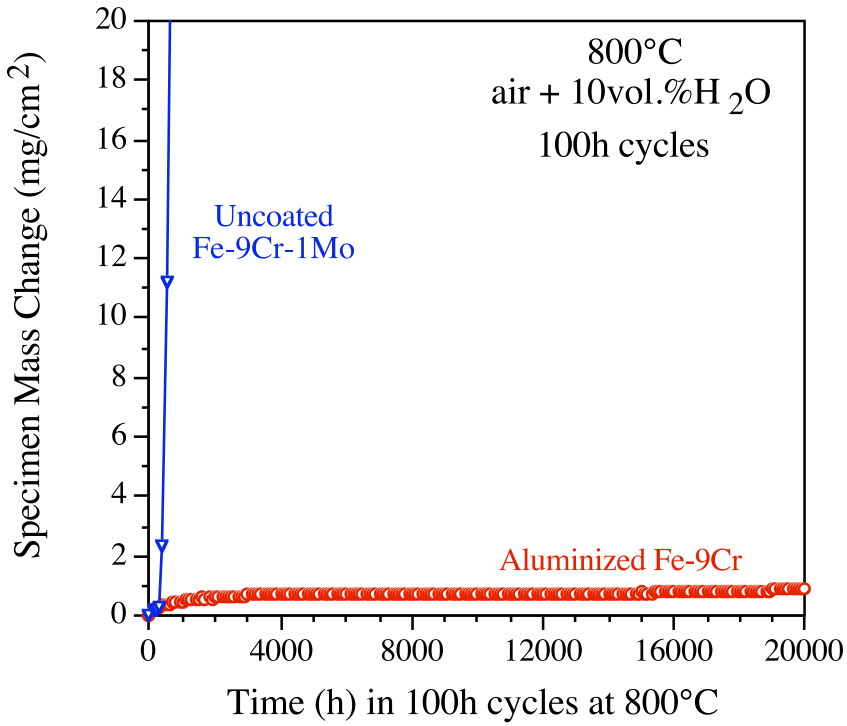

T91 substrate

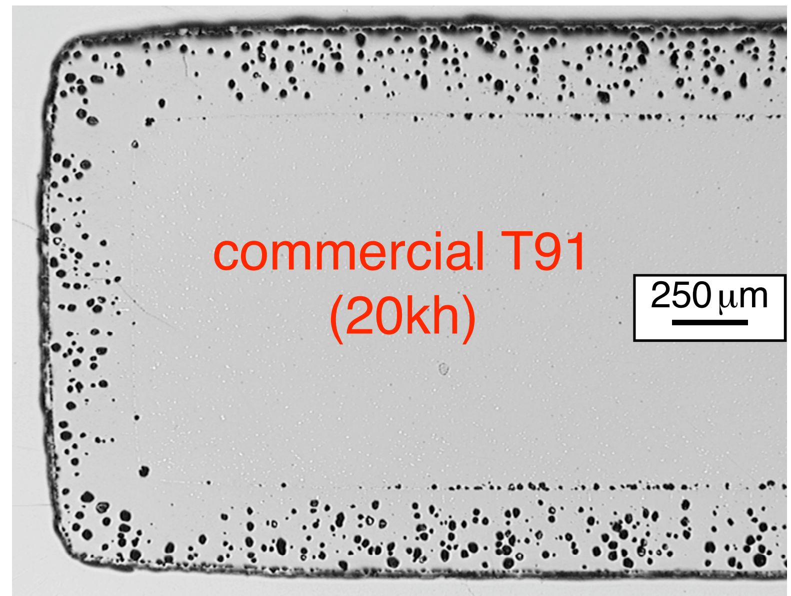
Coating Al profiles on T91:
- all for thick coatings
- variations in starting thickness

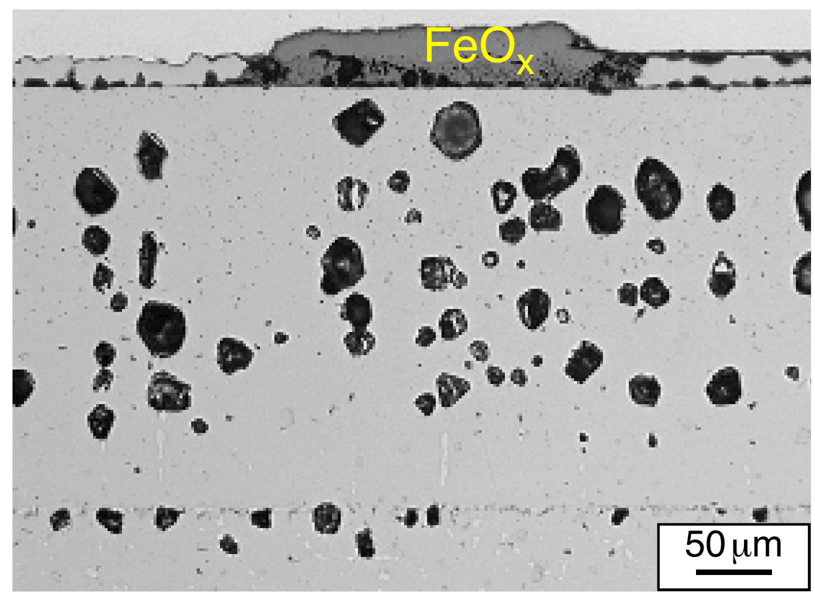
Deformation difference:
- ΔCTE difference for 304L

# 20kh Coating Characterized

## Thick coating on T91 in humid air at 800°C




20kh specimen:

No macroscopic deformation

Low mass gain

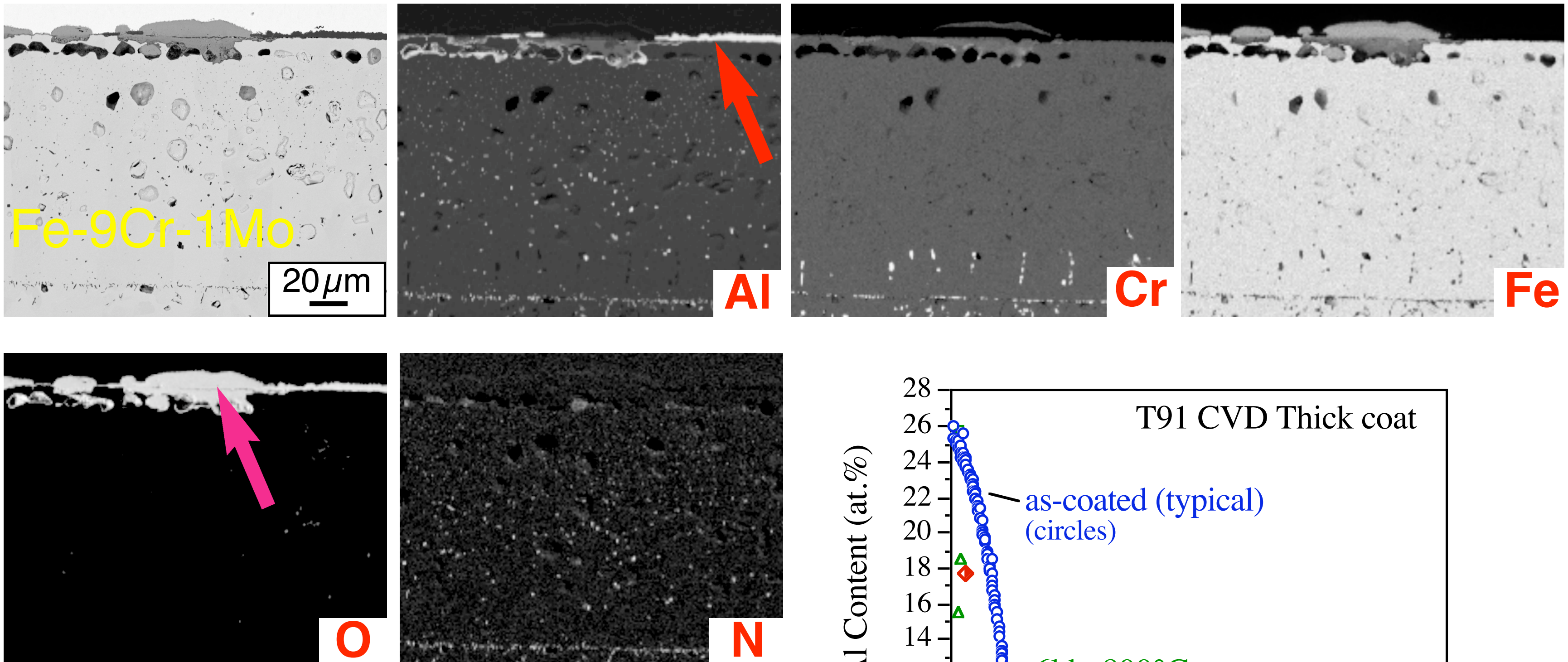
- but outer layer local breach

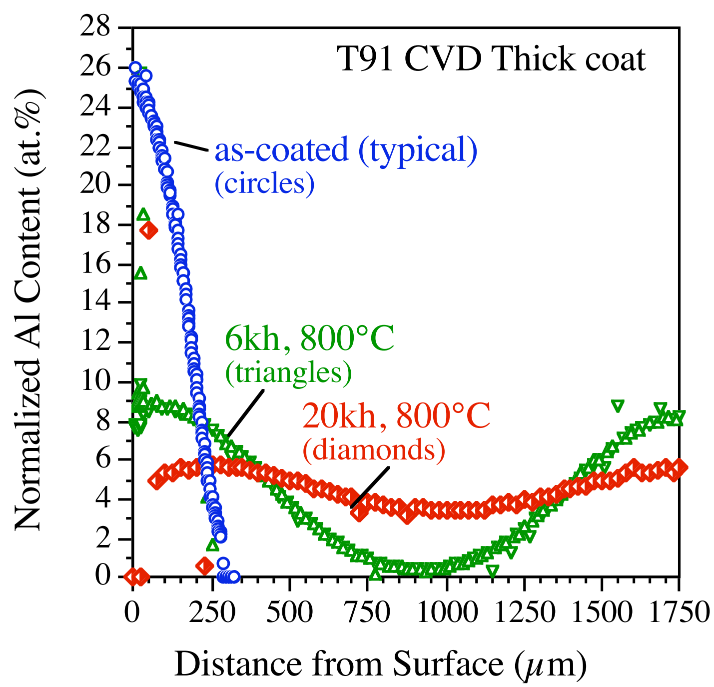
Porous coating layer

- Al loss due to scale spallation

# 20kh Coating Characterized

## Thick coating on T91 in humid air at 800°C




Electron probe analysis:

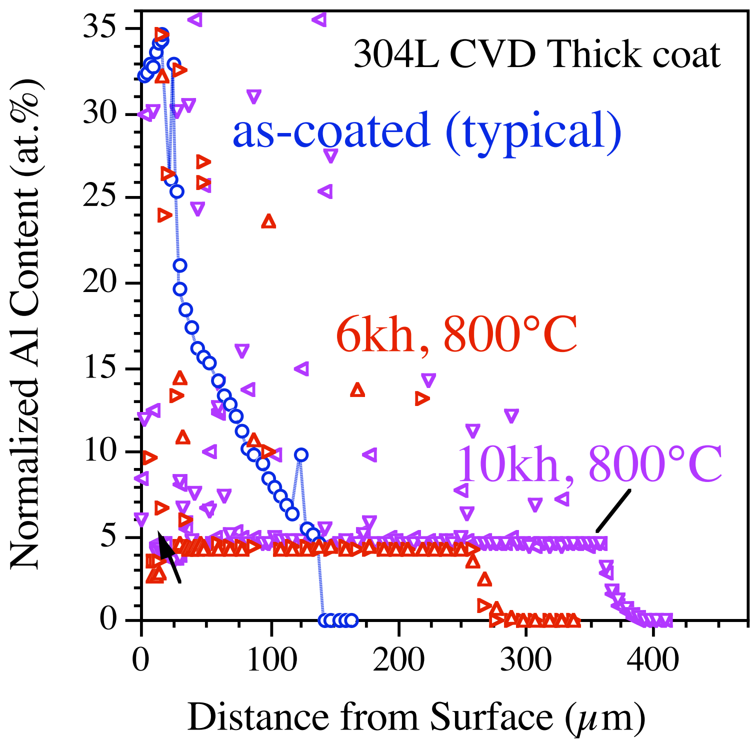
Typical Fe-rich oxide nodules

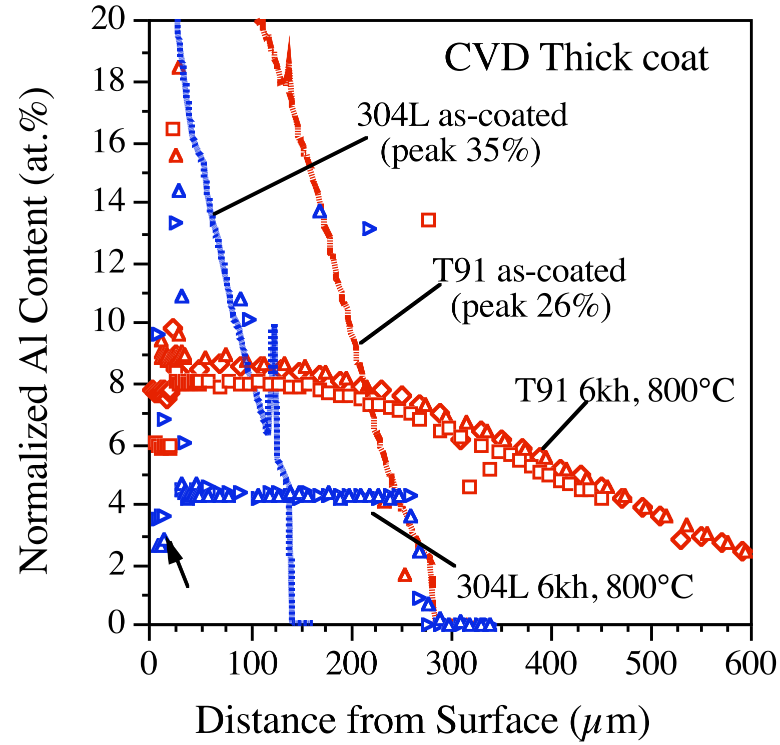
Local alumina scale pieces

AlN precipitates (0.2at.%N in alloy)

# Future work: austenitic model

## Four component system (Fe, Ni, Cr, Al) + two phase




304L: COSIM model missing diffusion terms

Three phase system (β-(Fe,Ni)Al+ ferrite + substrate)

Observations: Thinner starting coating than on T91

Slower Al diffusion: inhibited by phase transformation

~4.5at%Al remained in inner layer (+ ~18%Cr) - equilibrium?

# Lifetime predictions at 700°C

## Calculations for ~250μm thick coatings on T91

| Prediction Method | COSIM dependent | COSIM indep. FeAl | COSIM indep. FeCrAl | Heckel | Actual (diffusion test) |
|---|---|---|---|---|---|
| Surface (at.%) | 19 | 16 | 17 | 19 | 18%Al |
| Thickness (μm) | 310 | 438 | 428 | 356 | 320 μm |
| Lifetime Predictions: | | | | | |
| (sulfidation) | | | | | |
| assuming 20% | 6.8 kh | 5.0 kh | 5.6 kh | 7.5 kh | ? |
| (wet air) | | | | | |
| assuming 3.5% | 639 kh | 219 kh | 248 kh | 592 kh | ?? |
| assuming 8% (conservative) | 187 kh | 57 | 66 | 104 kh | ? |

Sulfidation - insufficient life at 700°C, need to drop to ~625°C

Wet air - high probability of thick coating making 100 kh lifetime

Model details in Zhang et al., Mater. Corr. 58 (2007)

# Lifetime predictions at 700°C

## Calculations for ~250μm thick coatings on T91

| Prediction Method | COSIM dependent | COSIM indep. FeAl | COSIM indep. FeCrAl | Heckel | Actual (diffusion test) |
|---|---|---|---|---|---|
| Surface (at.%) | 19 | 16 | 17 | 19 | 18%Al |
| Thickness (μm) | 310 | 438 | 428 | 356 | 320 μm |
| Lifetime Predictions: | | | | | |
| (sulfidation) | | | | | |
| assuming 20% | 6.8 kh | 5.0 kh | 5.6 kh | 7.5 kh | ? |
| (wet air) | | | | | |
| assuming 3.5% | 639 kh | 219 kh | 248 kh | 592 kh | ?? |

Sulfidation - insufficient life at 700°C, need to drop to ~625°C

Wet air - high probability of thick coating making 100 kh lifetime

- thick coatings will never fail on 1.7 mm substrate!