

Performance of Al-rich Oxidation Resistant Coatings for Fe-Base Alloys

B. A. Pint

Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

Y. Zhang

Tennessee Technological University
Cookeville, TN 38505-0001

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

Acknowledgments

ORNL

I. Wright, P. Tortorelli

A. Haynes, K. Cooley - CVD coating fabrication

G. Garner, J. Moser, T. Brummett - oxidation experiments

H. Longmire, K. Thomas - metallography

L. Walker - EPMA

B. Bates (TTU) - SEM

This research was sponsored by the U. S. Department of Energy, Fossil Energy Advanced Materials Research Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

Coatings for Power Generation

Next generation power plants

Ultra-supercritical steam - up to 760°C from ~590°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 previously)
- 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

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 $\approx 12 \times 20$ specimens, 2 per run

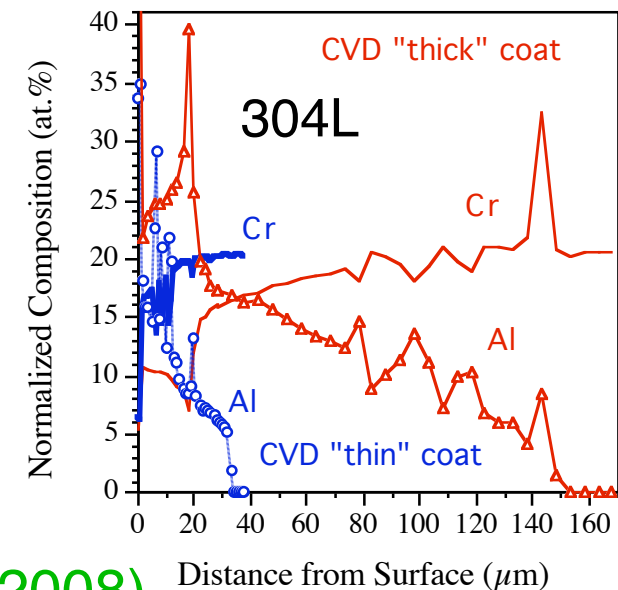
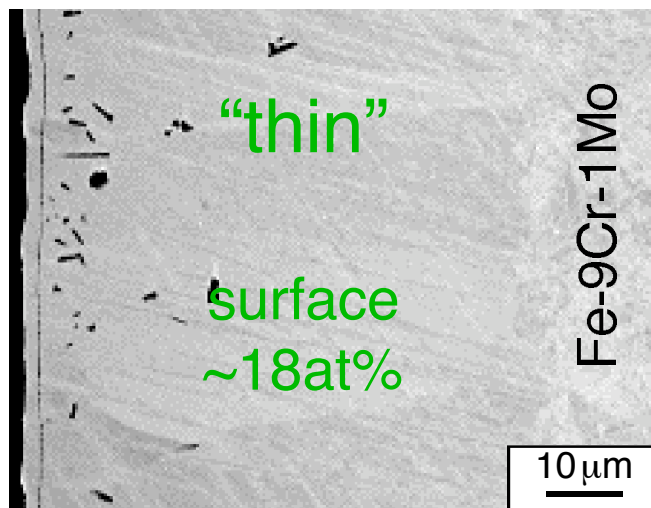
austenitic 304L (Fe-18Cr-8Ni) & ferritic T91 (Fe-9Cr-1Mo)

ORNL laboratory scale reactor

flowing $\text{H}_2\text{-AlCl}_x$, 100 Torr, 6h, 900°C or 4h, 1050°C +2h anneal

increase Al activity by adding Cr-Al or Fe-Al alloy in reactor

“Thick” coatings $\approx 40\mu\text{m}$ Al-rich outer layer, “Thin” $\approx 5\mu\text{m}$ Al-rich outer layer

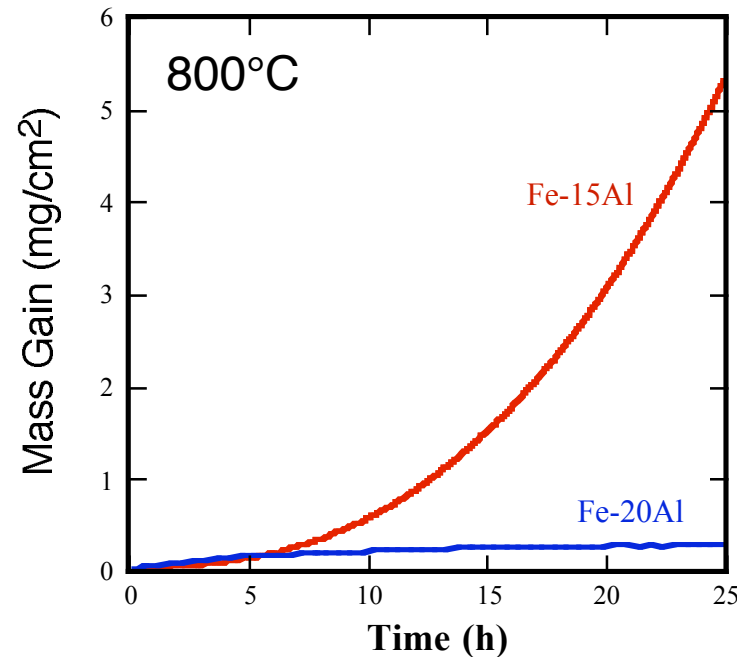


Details in Zhang et al., Surf. Coat. Tech. (2008)

Thin vs. Thick Coatings: Sulfidation

Model Fe-Al alloys at 800°C in H₂-H₂O-H₂S-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

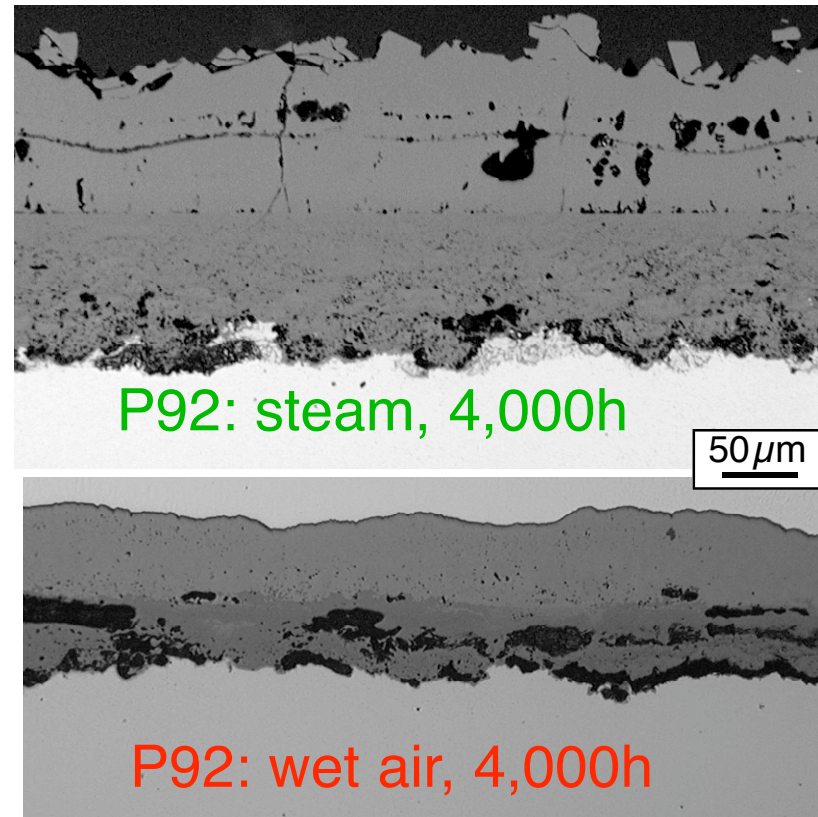
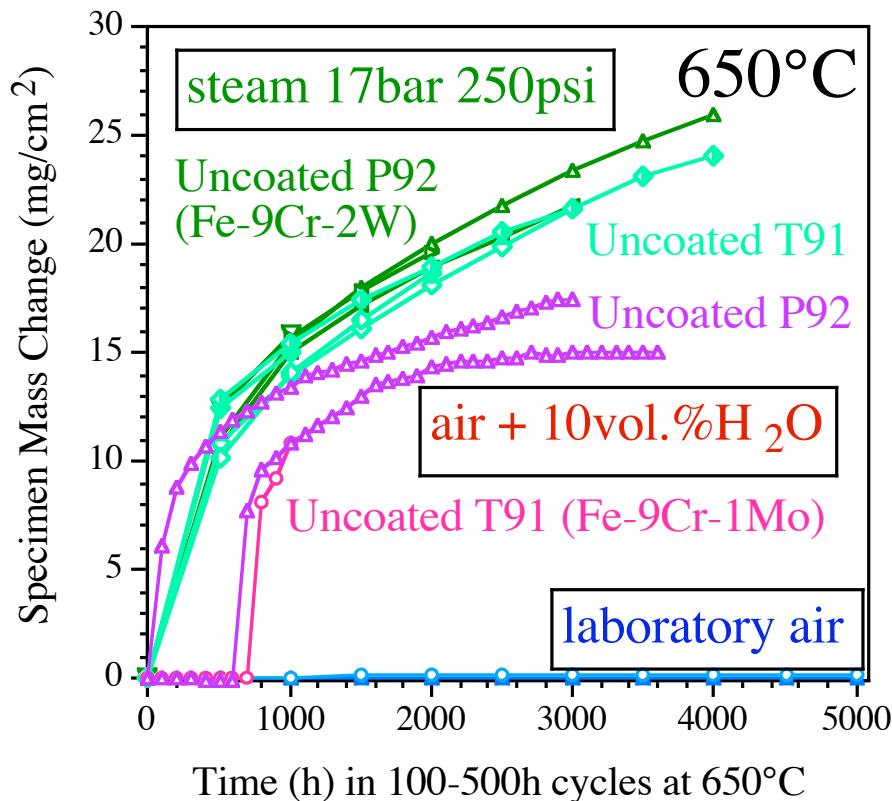
Previous work by DeVan and Tortorelli found 18at%Al needed

Higher Al content (“thick”) needed for sulfidation resistance

Fe-9Cr in Steam vs. Humid Air

comparison of mass gain and reaction products

650°C, 1202°F

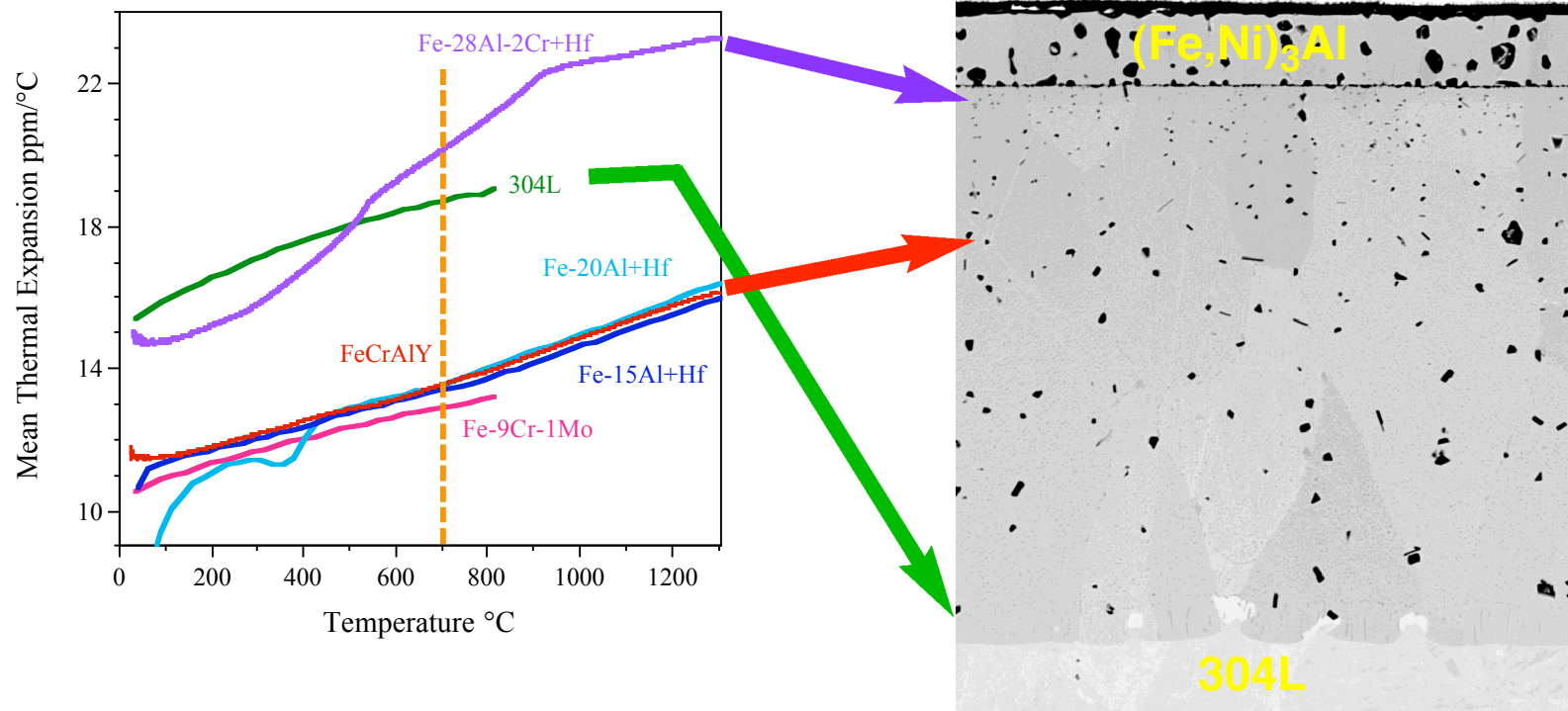


P92 - Fe-9Cr-2W (like T91 with W) Cr-rich scale in air
Thick Fe-rich scale with H₂O addition (steam or humid air)
(Thicker scale in steam: P effect or pO₂ effect ?)

Less expensive for oxidation studies in humid air

Intrinsic Aluminide Coating Problem

Substrate-coating thermal expansion mismatch



For coated **304L**,

Al addition created ferritic inner layer (interdiffusion zone)

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

Mismatch results in stress sufficient to crack coating

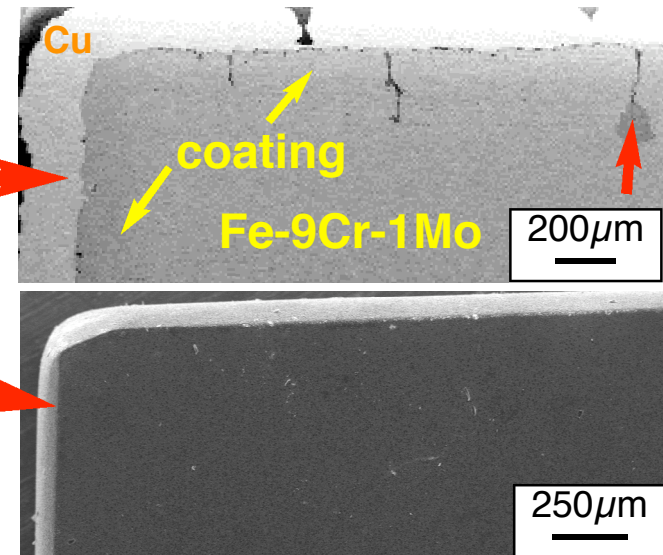
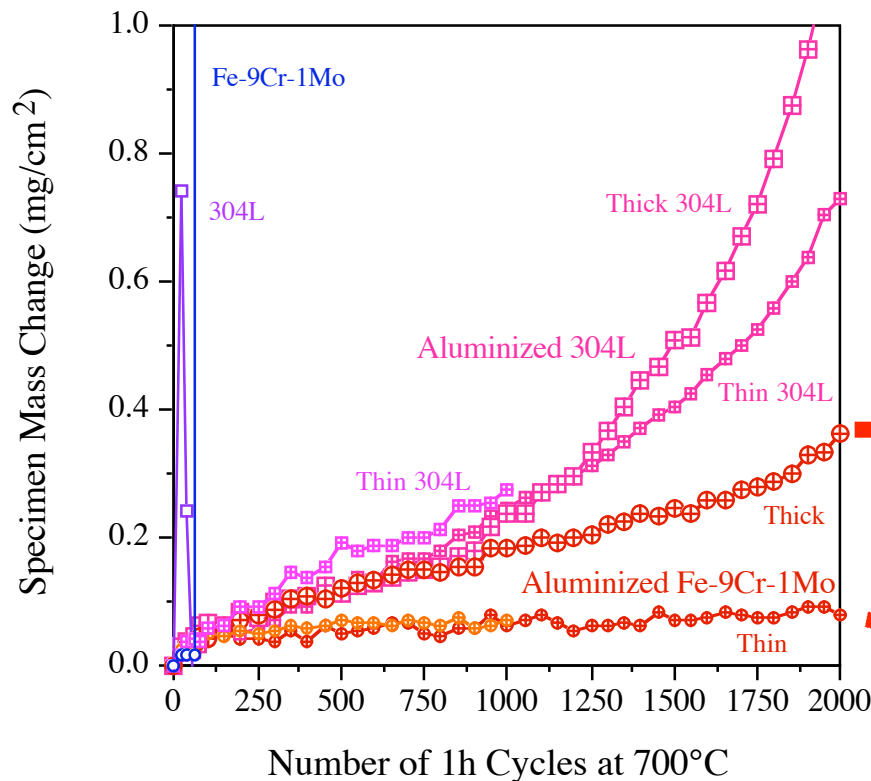
If CTE mismatch is problem, does thickness (δ) affect performance?

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)

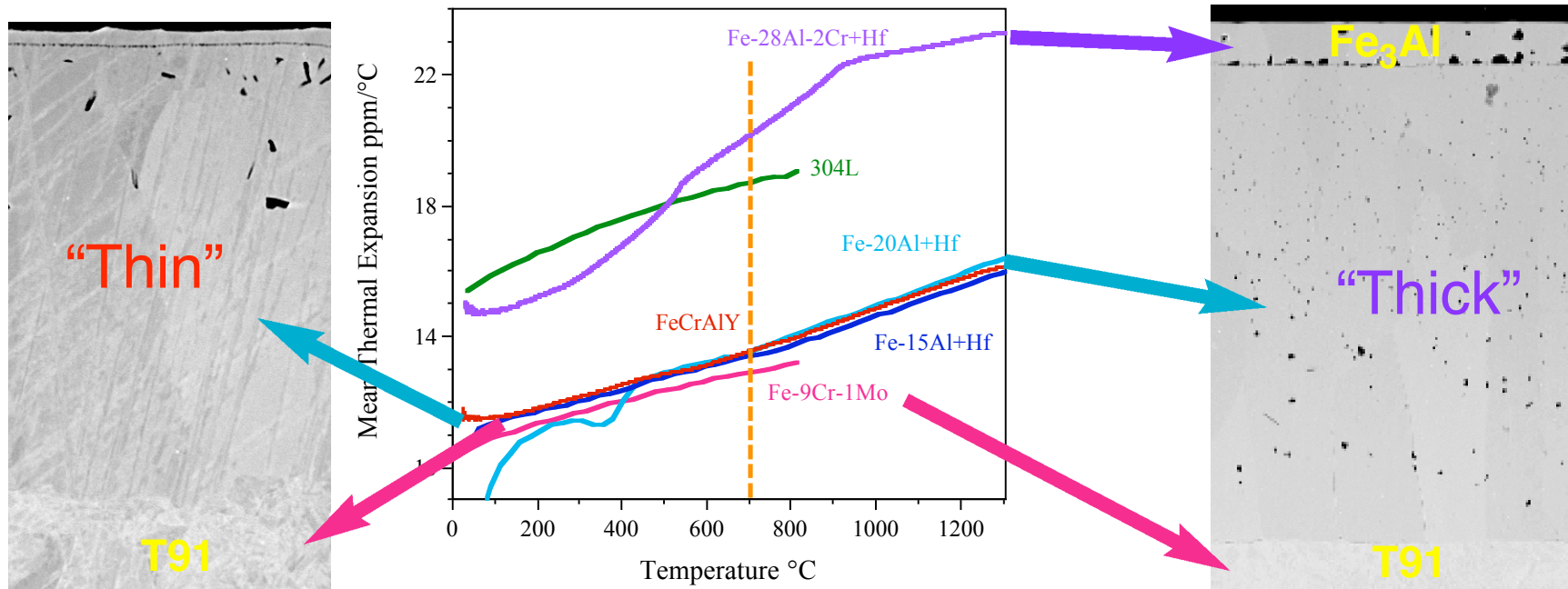


For T91, thinner α -Fe(Al) coating did not show signs of degradation after 2000 cycles at 700°C

For 304L, thin and thick coatings showing similar performance possibly less cracking in thinner coating but still penetrated

Ferritic Alloy Coating Solution

Eliminate CTE mismatch problem



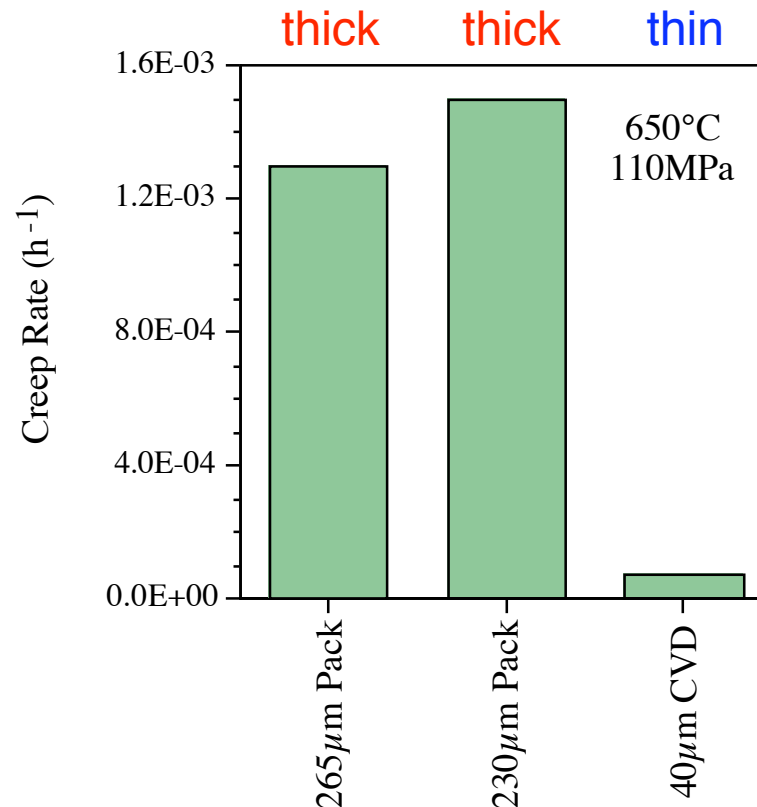
For coated T91:

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

Thin CVD: ~18at.%Al peak surface Al (no aluminide)
only $\alpha\text{-Fe(Al)}$ phase
NO ΔCTE

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

Effect of heat treatment and coating



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

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_0)
- 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, 1 for linear kinetics

$$(C_0 - C_b)/100 \cdot d/2 \cdot \rho = k \cdot t^n \cdot \frac{\text{(mole Al)}}{\text{mole O in Al}_2\text{O}_3}$$

How does this apply to a coating?

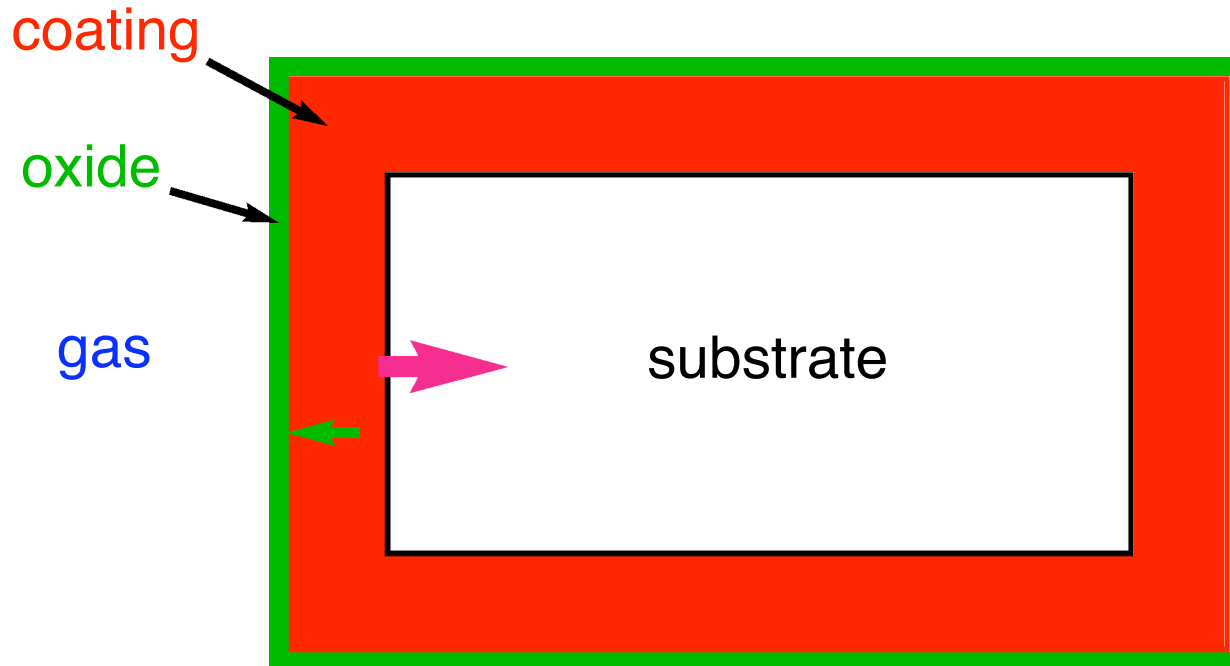
more complex Al “consumption”: **interdiffusion + oxidation**

C_0 becomes a function of the coating thickness

What is C_b for a coating?

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

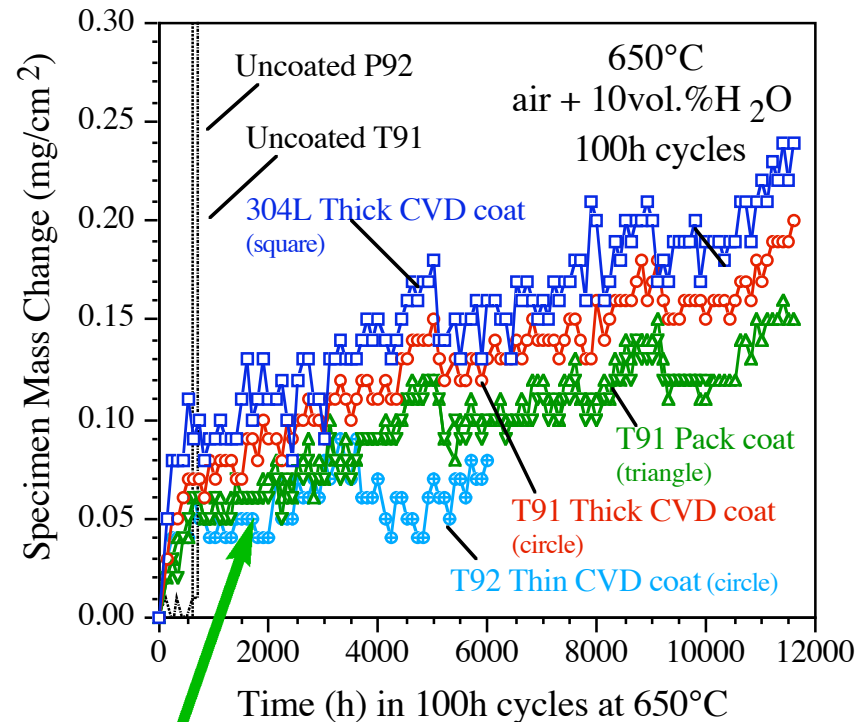
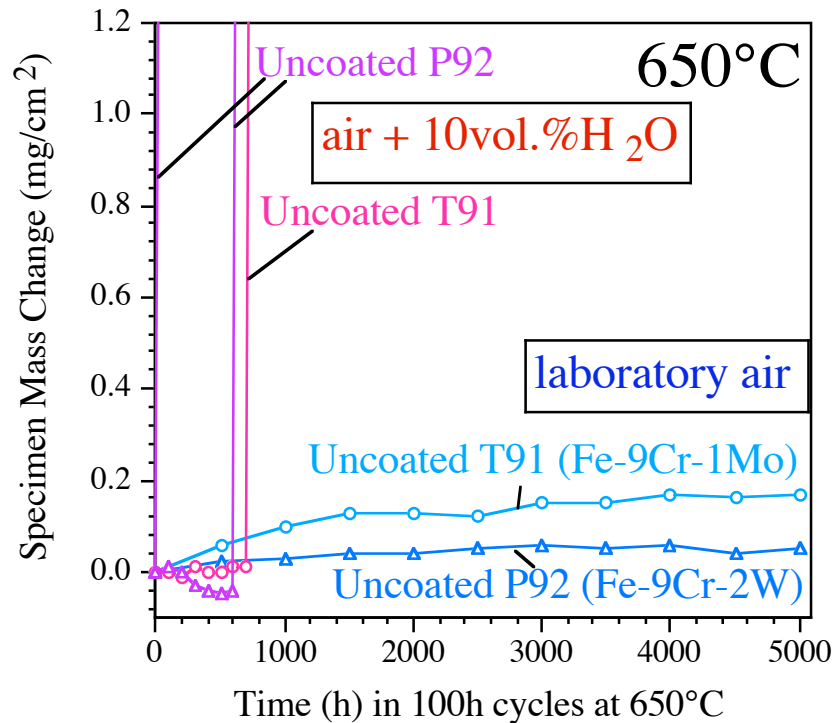
At low temperatures 650-700°C expect loss by (1) \ll loss by (2)

C_b for sulfidation $\sim 20\text{at\%Al}$ similar to cast Fe-Al

How low can Al content drop in steam environment?

Coating Performance: 650°C

CVD or pack cementation coatings



650°C, 1202°F

more commercial coating process

Incubation period before onset of accelerate attack with H₂O

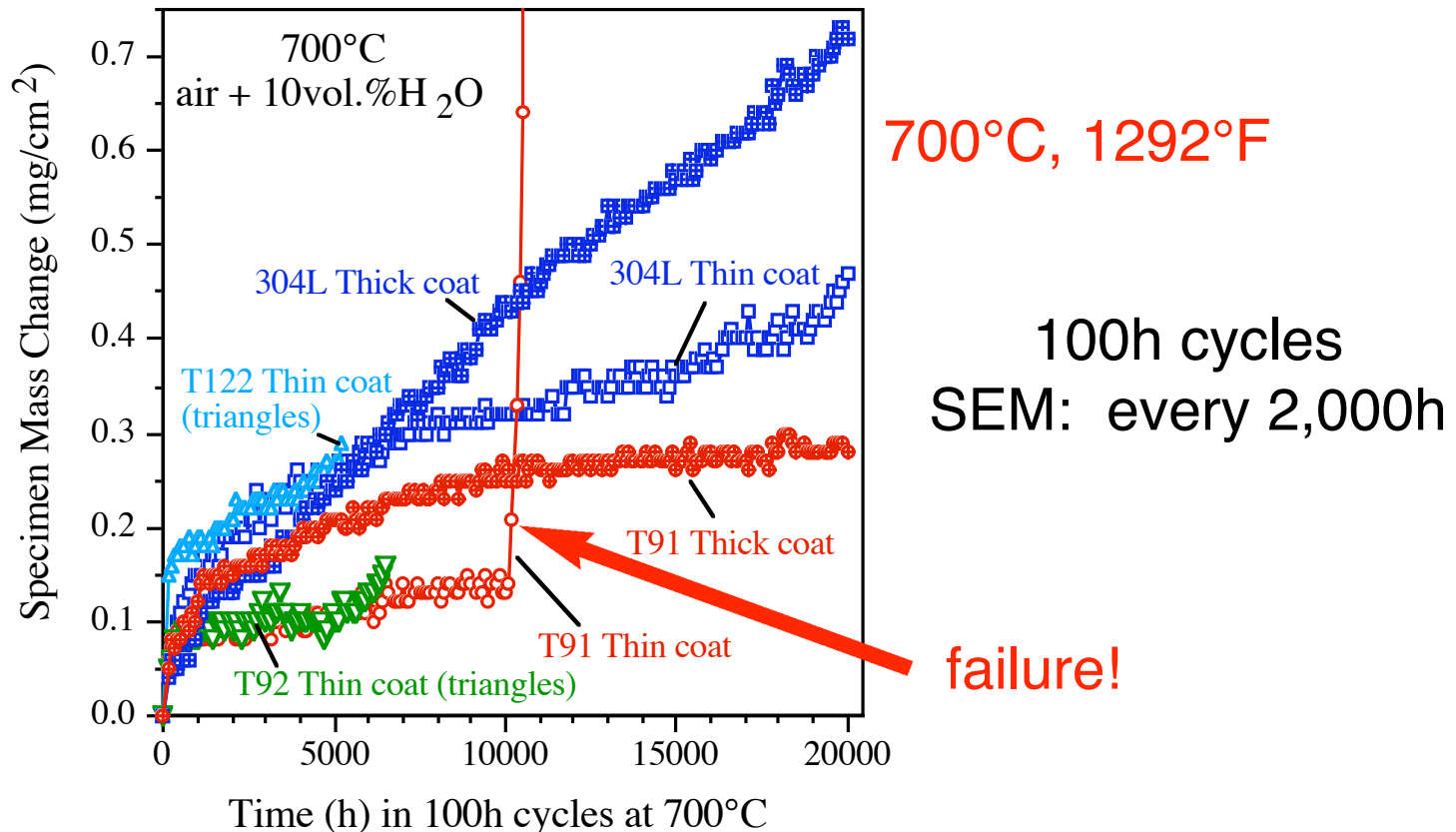
Coatings show low, parabolic-type mass gains to ~8 kh

Limited interdiffusion at this temperature -> long life!

Last year added "thin" coatings to 650°C test

Coating Performance: 700°C

Accelerate failure by increased interdiffusion



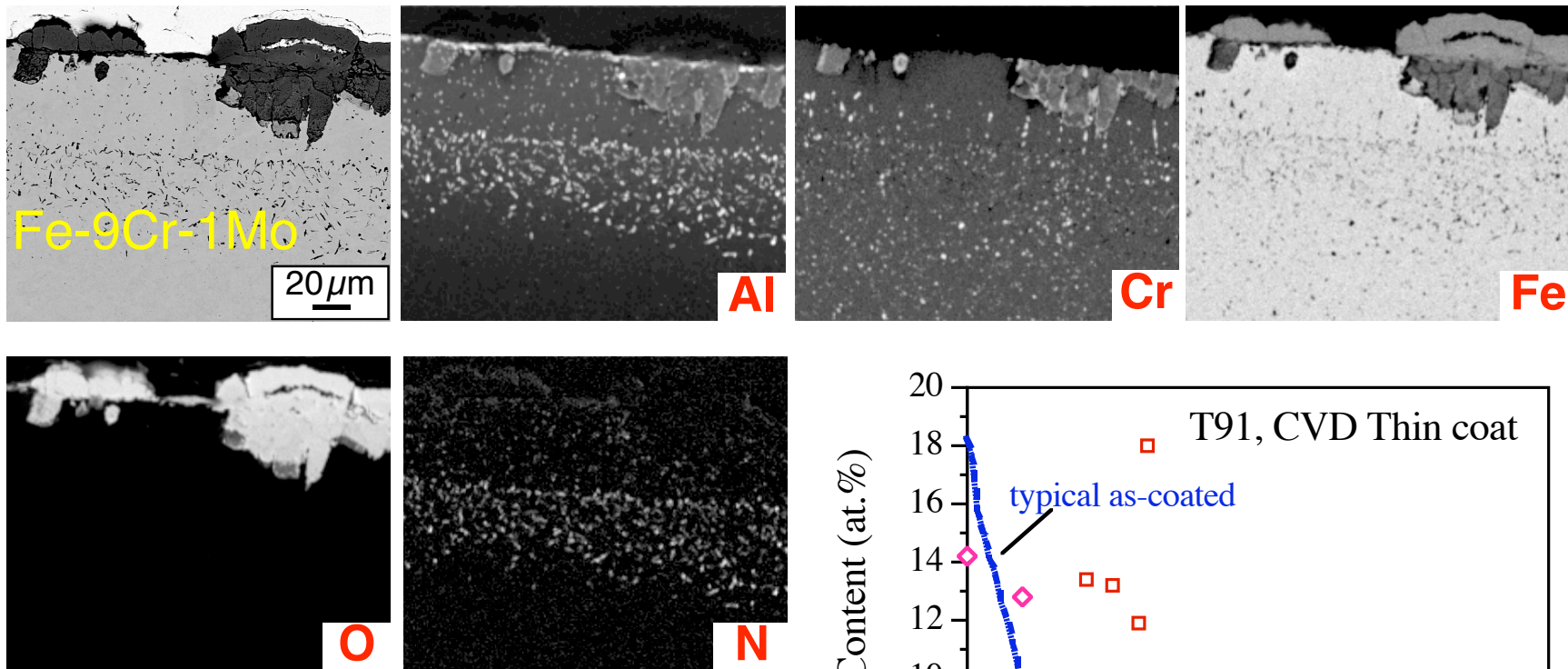
Higher mass gains for thin and thick coatings on 304L

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

Thick coatings stopped at 20kh for sectioning

Failed Coating Characterized

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

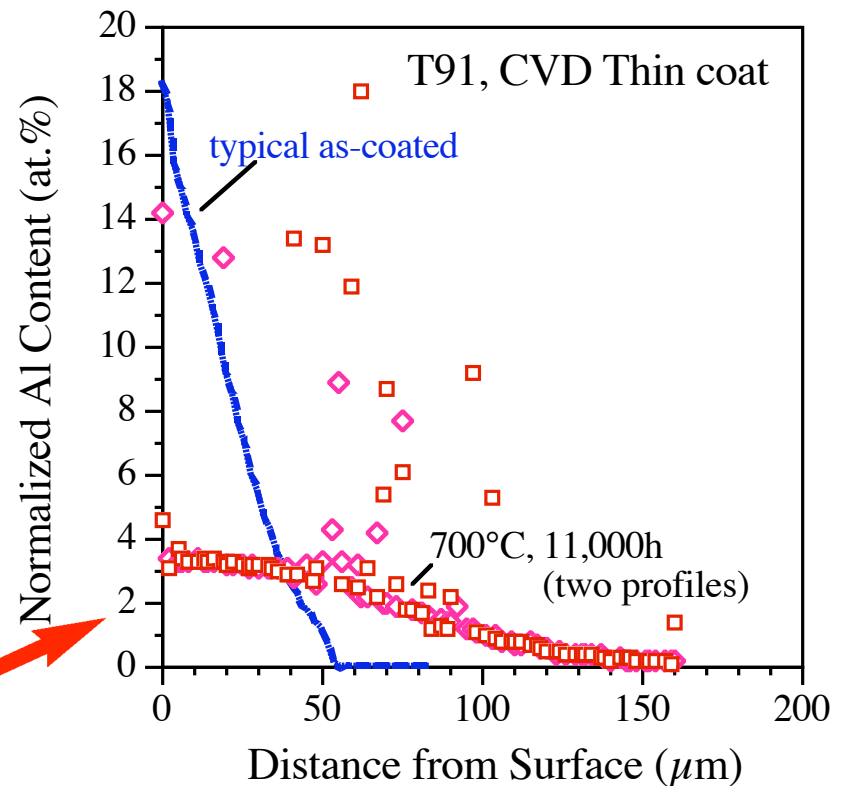


Electron probe analysis:

Typical Fe-rich oxide nodules

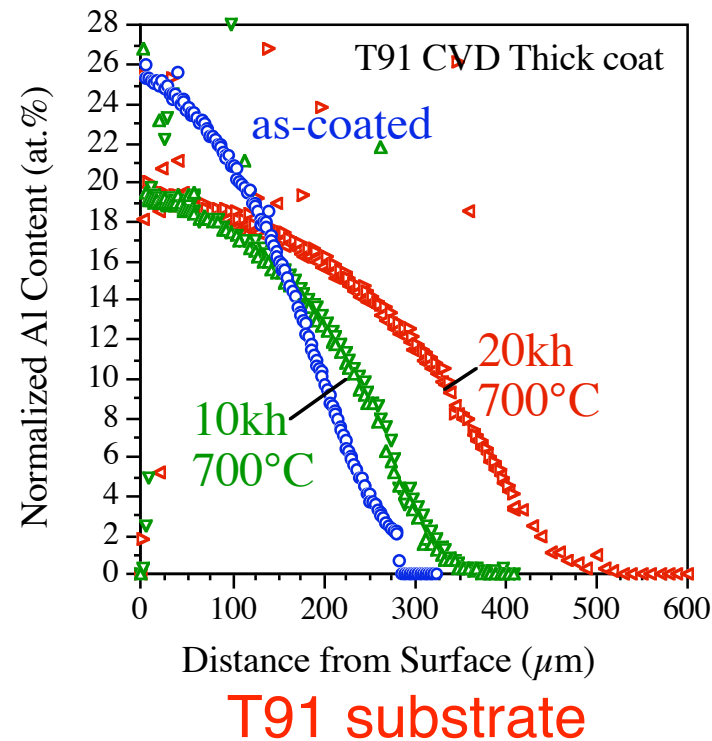
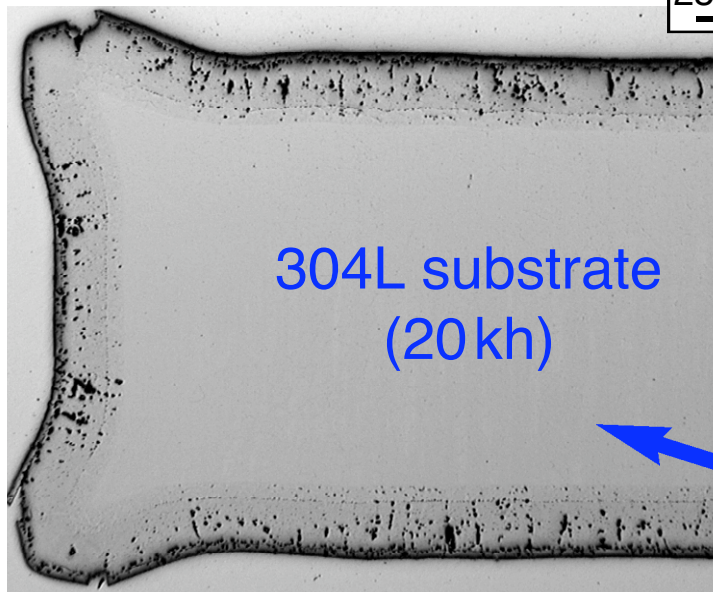
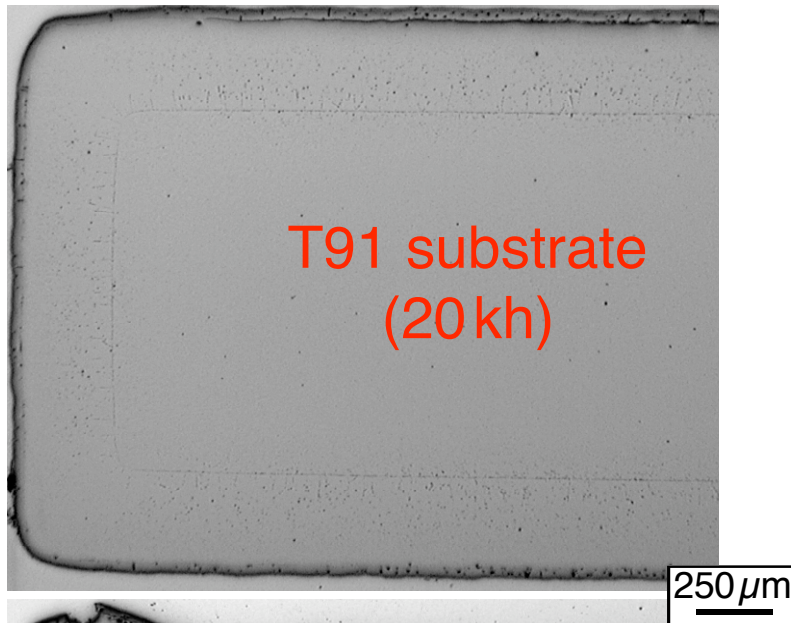
AlN precipitates (0.2at.%N in alloy)

~3.5at%Al at surface (C_b)



700°C Performance of thick coating

Coatings stopped after 10 & 20kh in humid air



Coating Al profiles on T91:

- all for thick coatings
- variations in starting thickness

Deformation difference:

- ΔCTE difference for 304L

Lifetime predictions at 700°C

Using 10kh observations for thick coatings on Fe-Cr

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:					
(sulfidation)					
assuming 20%	6.8 kh	5.0 kh	5.6 kh	7.5 kh	?
(wet air)					
assuming 8%	187	57	66	104	?
assuming 3.5%	639	219	248	592 kh	??

(>2mm depth!)

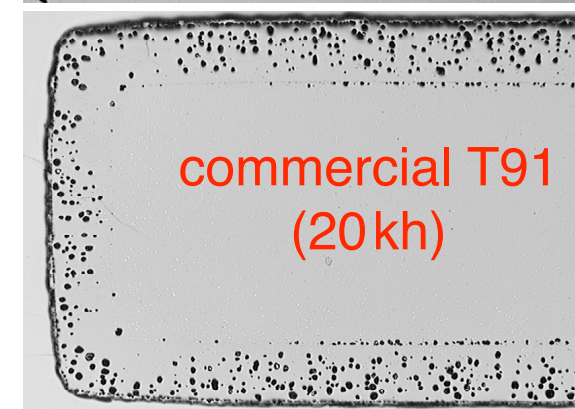
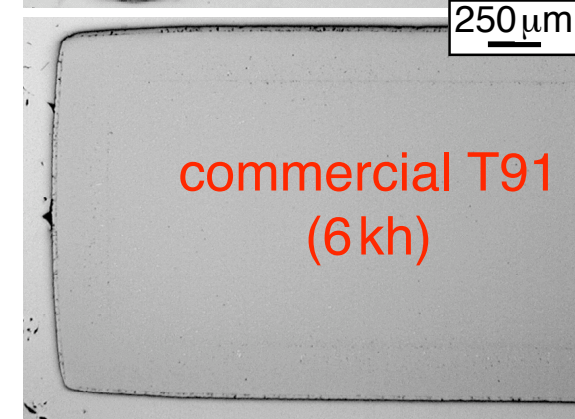
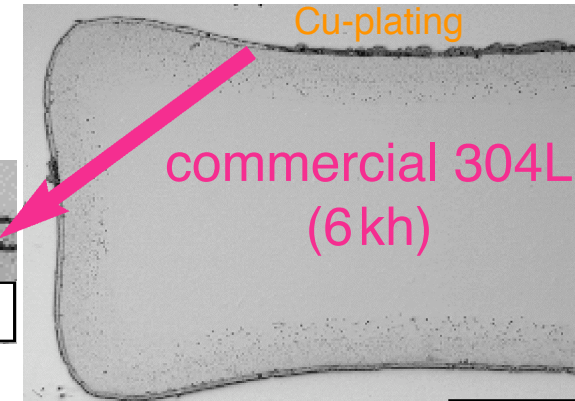
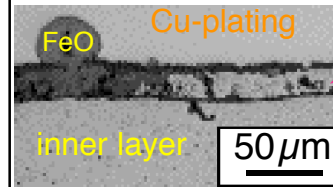
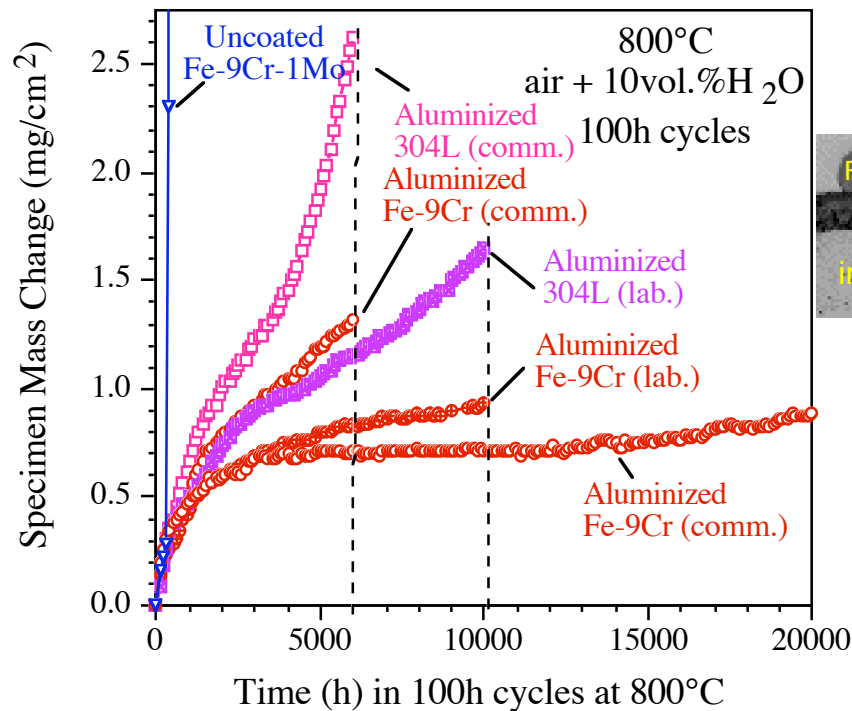
Sulfidation - insufficient life at 700°C, need to drop to ~625°C

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

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

Coating Performance: 800°C

Thick coatings tested to accelerate failure



304L Degradation:

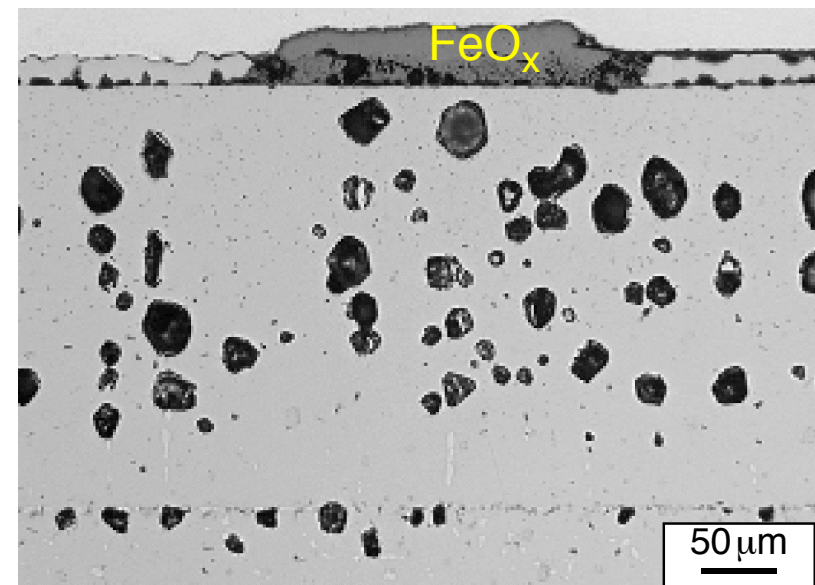
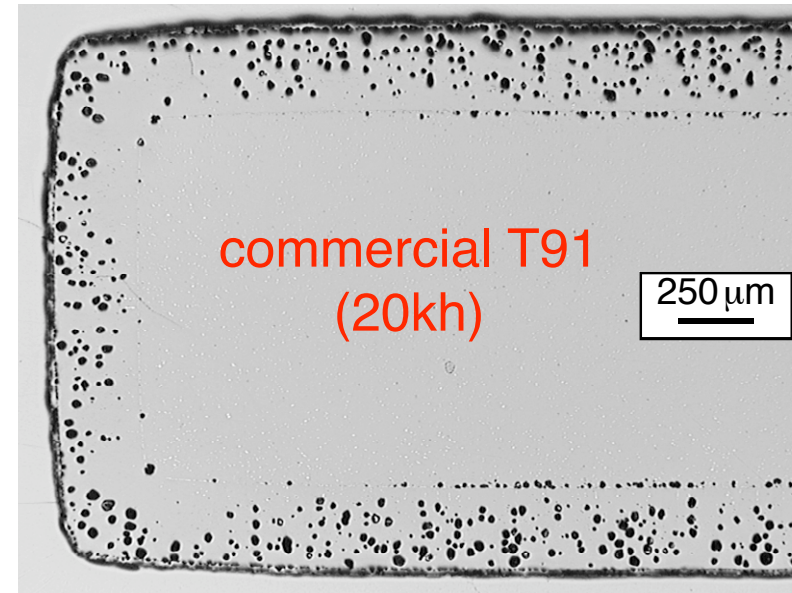
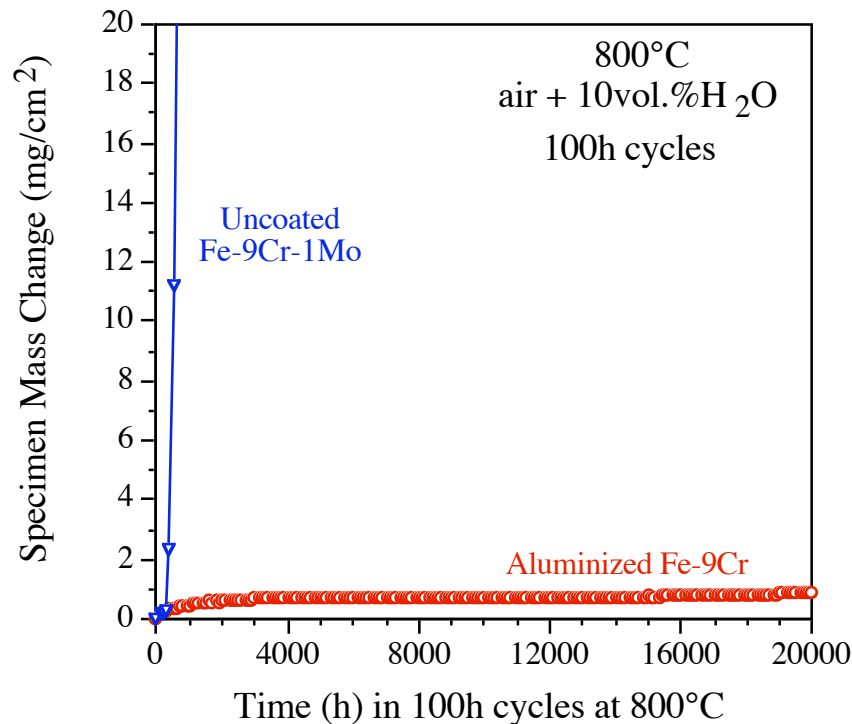
Macroscopic deformation (304L dog bone)
Higher mass gain (consumed outer layer)

T91 specimen completed 6 and 20kh

no coating failure observed
some scale spallation (SEM)

20kh Coating Characterized

Thick coating on T91 in humid air at 800°C



20kh specimen:

No macroscopic deformation

Low mass gain

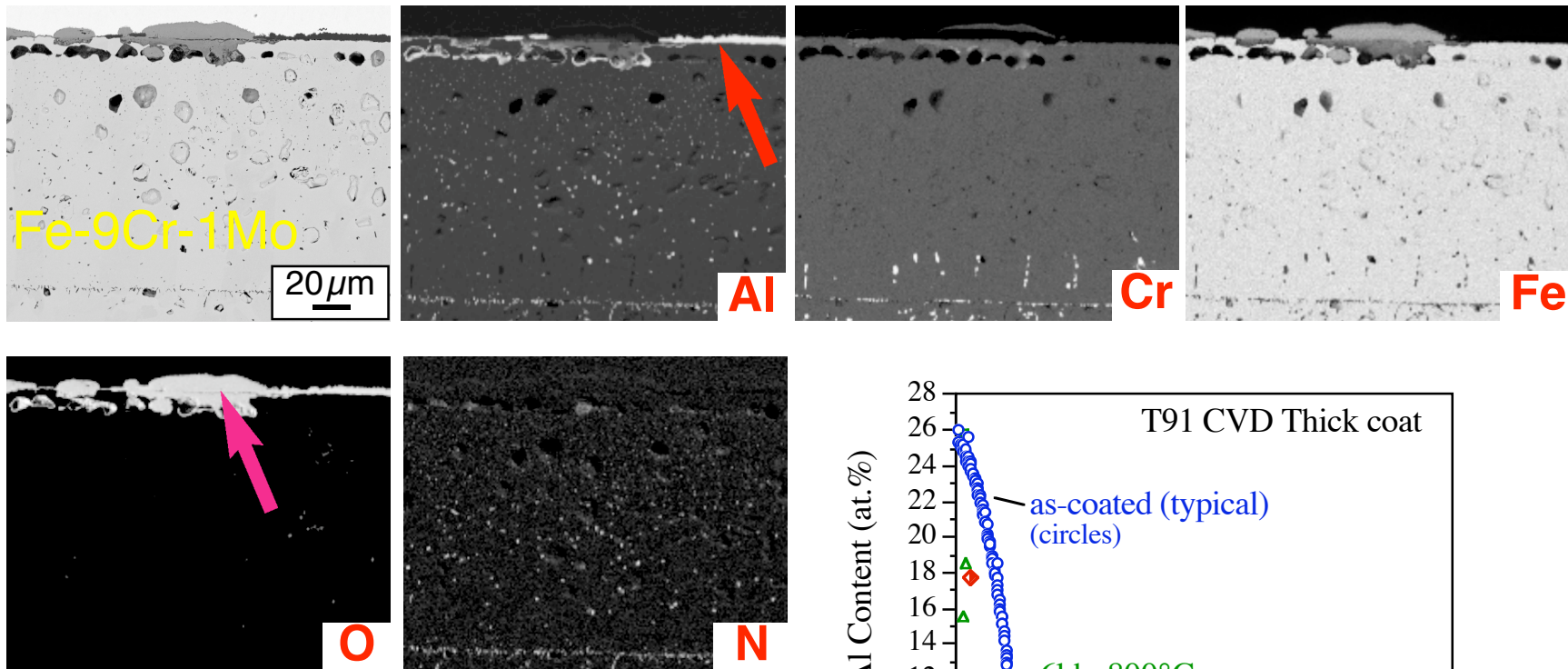
- but outer layer local breach

Porous coating layer

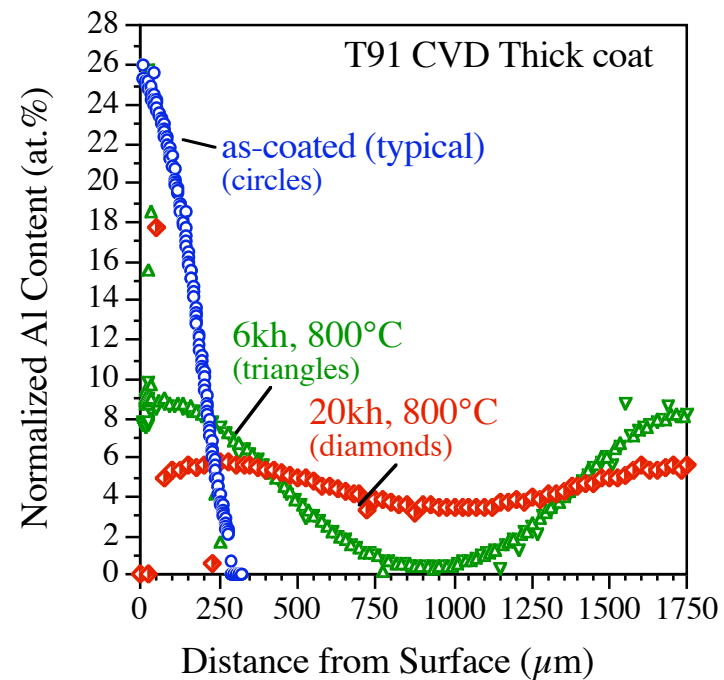
- Al loss due to scale spallation

20kh Coating Characterized

Thick coating on T91 in humid air at 800°C

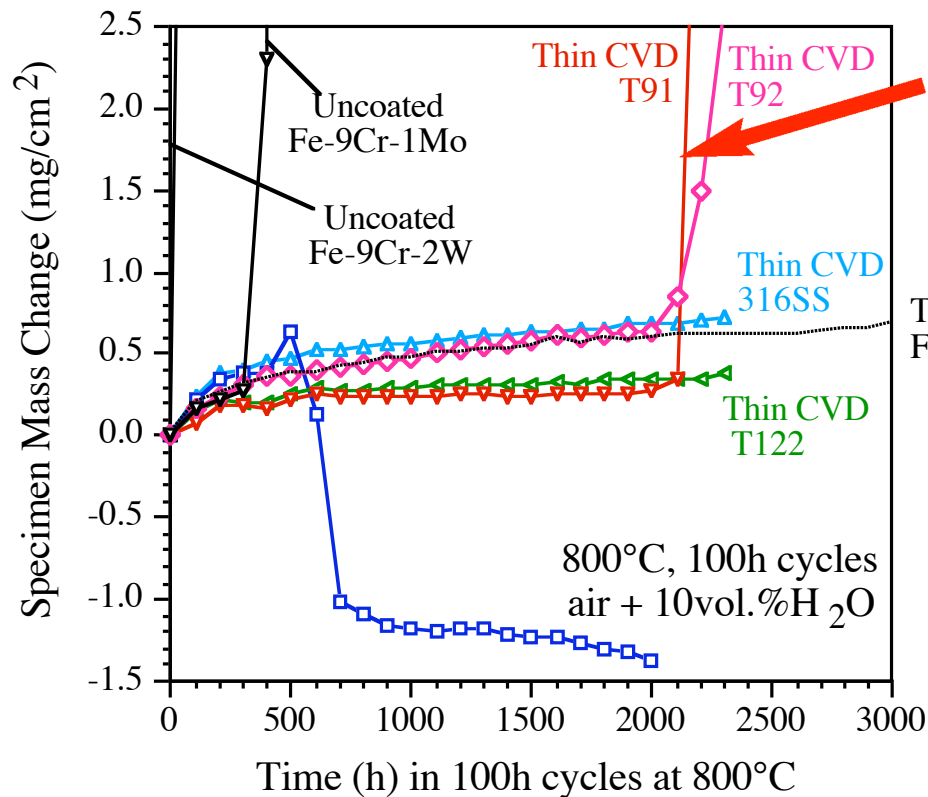


Electron probe analysis:
Typical Fe-rich oxide nodules
Local alumina scale pieces
AlN precipitates (0.2at.%N in alloy)

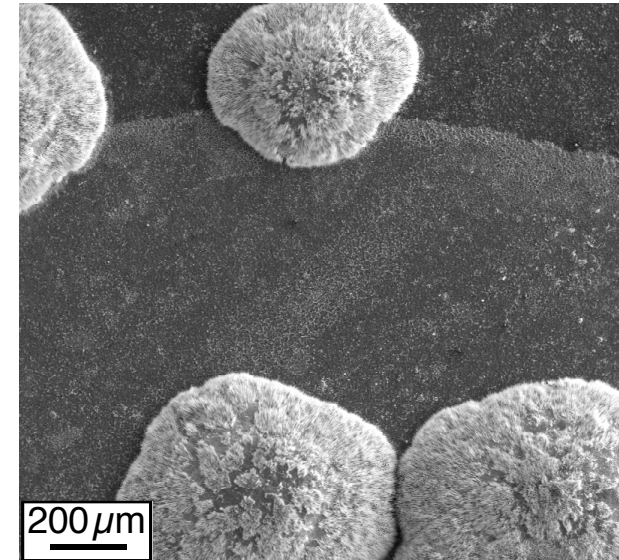


Coating Performance: 800°C

Thin coating testing to failure



failure last week!



SEM plan view

Final series started last year, failures to date:

Thin coating on T92 (2,500h stop last year)

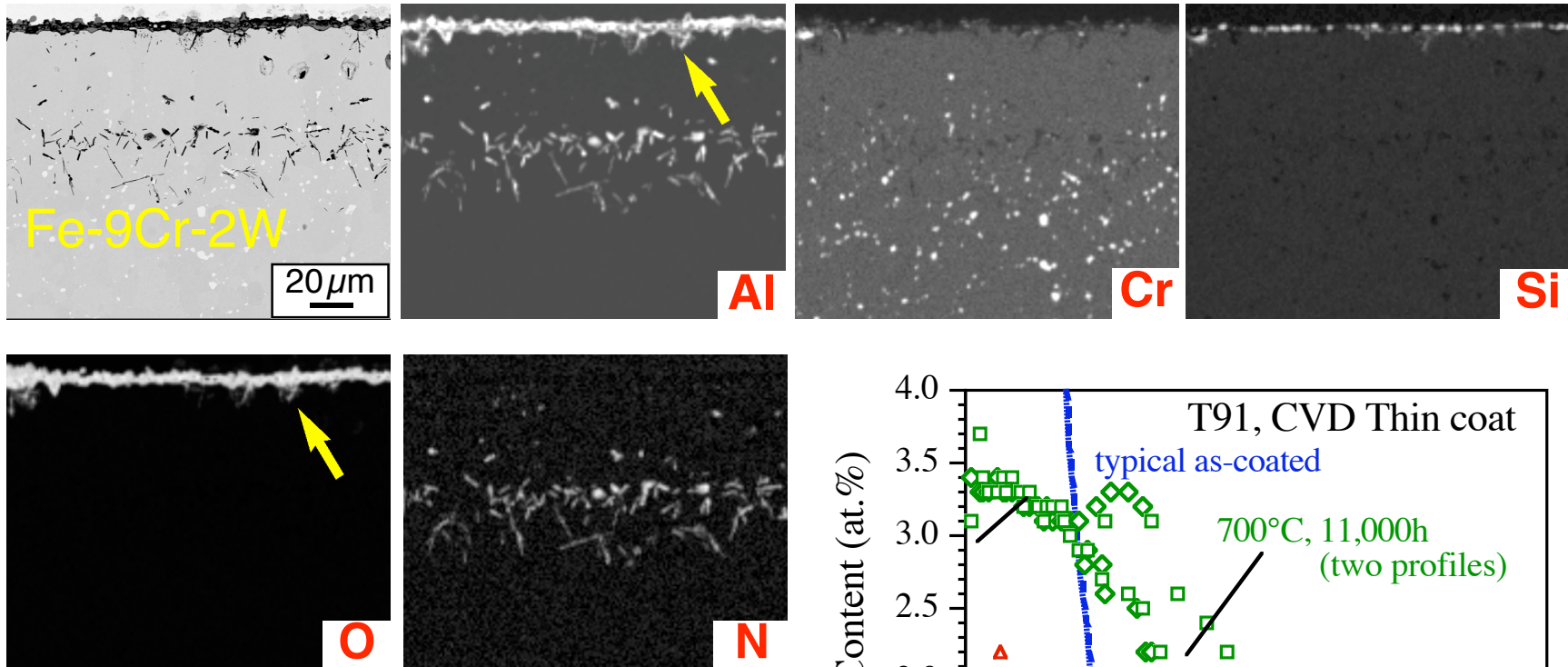
Thin coating on T91 (2,200h stop last week)

Thin coating on 304L (problem at 500h, maybe bad coating)

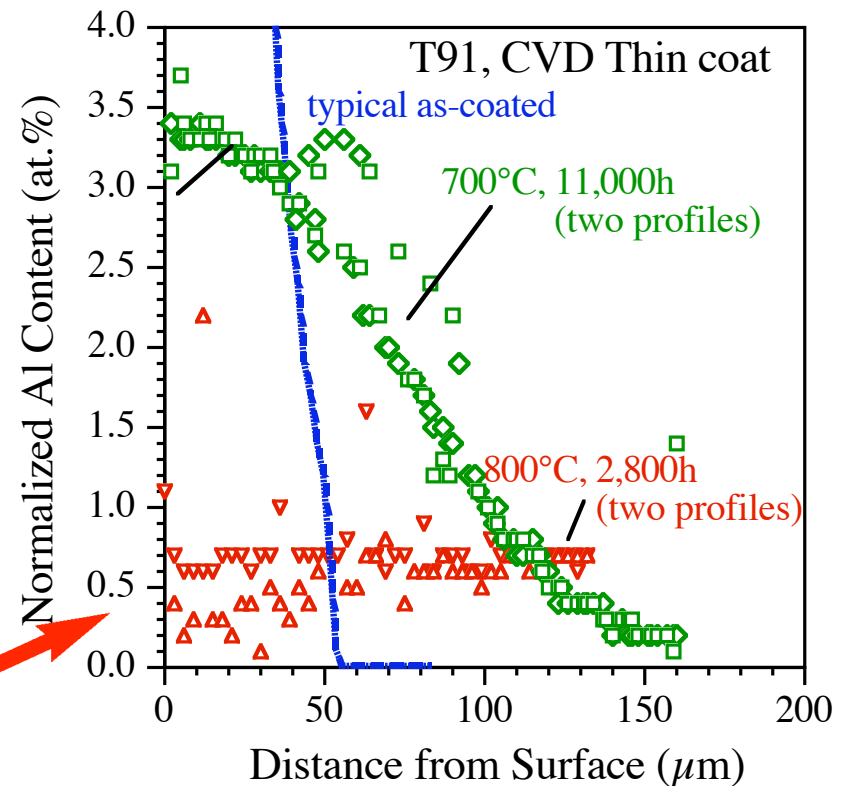
Still running: T122 (higher Cr), 316SS

Failed Coating at 800°C

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

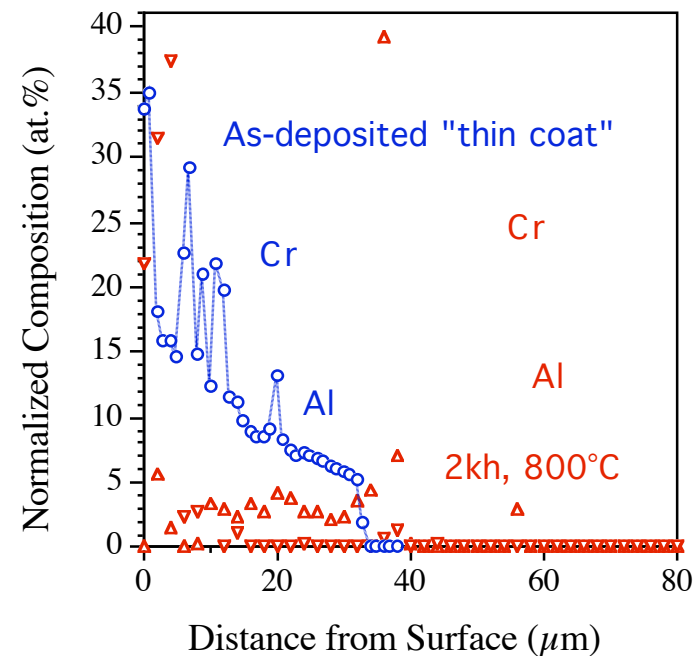
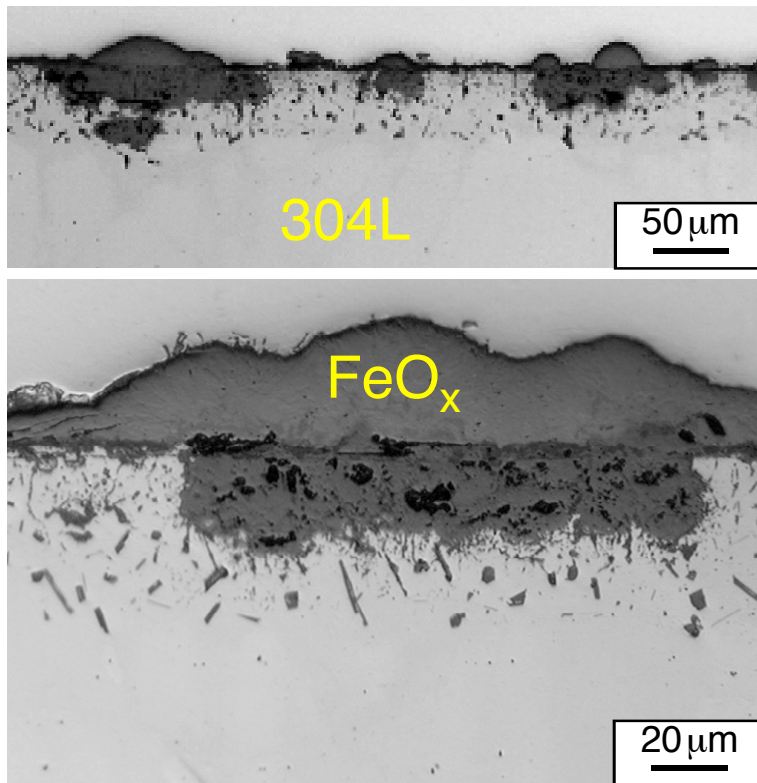


Electron probe analysis:
Area away from FeO nodules
Large AlN precipitates (N in alloy)
~0.7at%Al near surface (C_b)



Failed Coating at 800°C

Thin coating on 304L after 2,000h in humid air



Electron probe analysis:

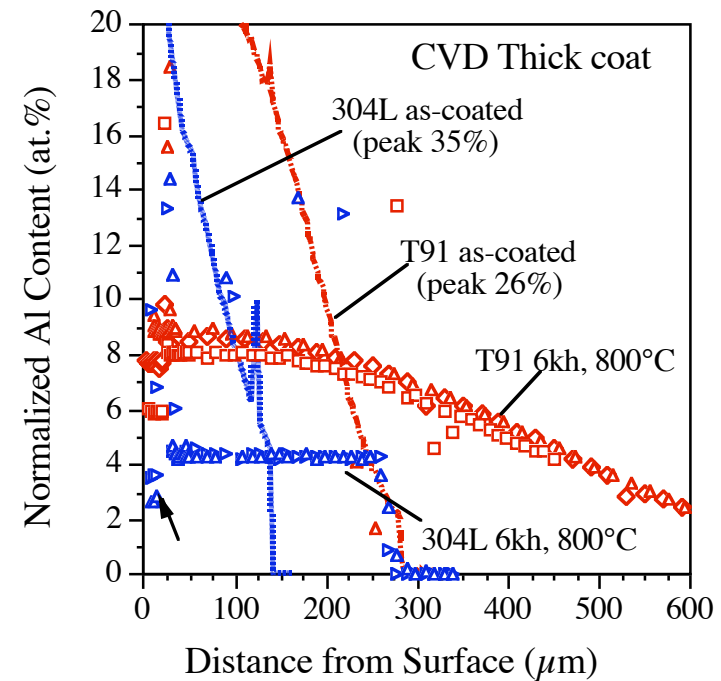
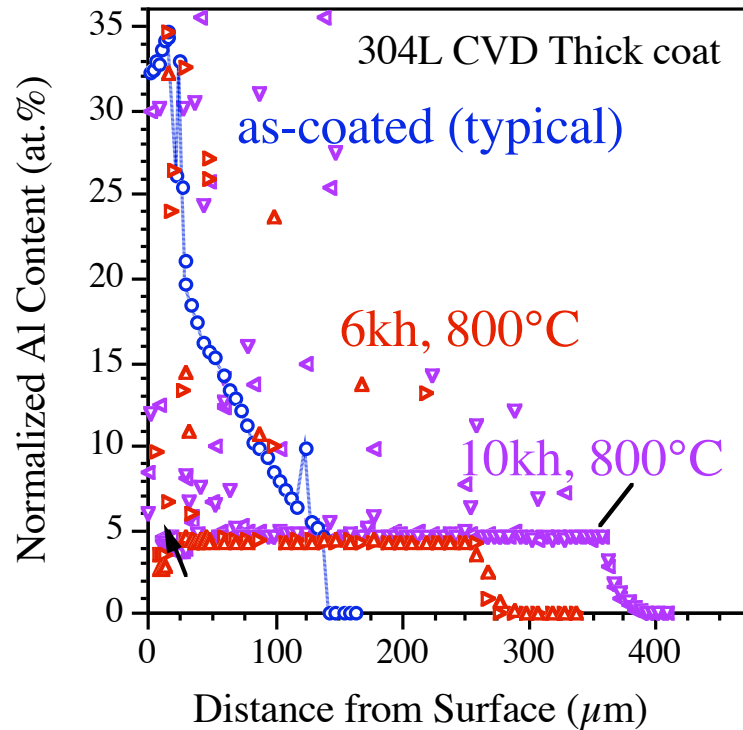
Expected: Large AlN precipitates (N in alloy)

Unexpected: Early failure and little Al remaining in coating

Maybe a poor quality coating (compare to 316SS)

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)

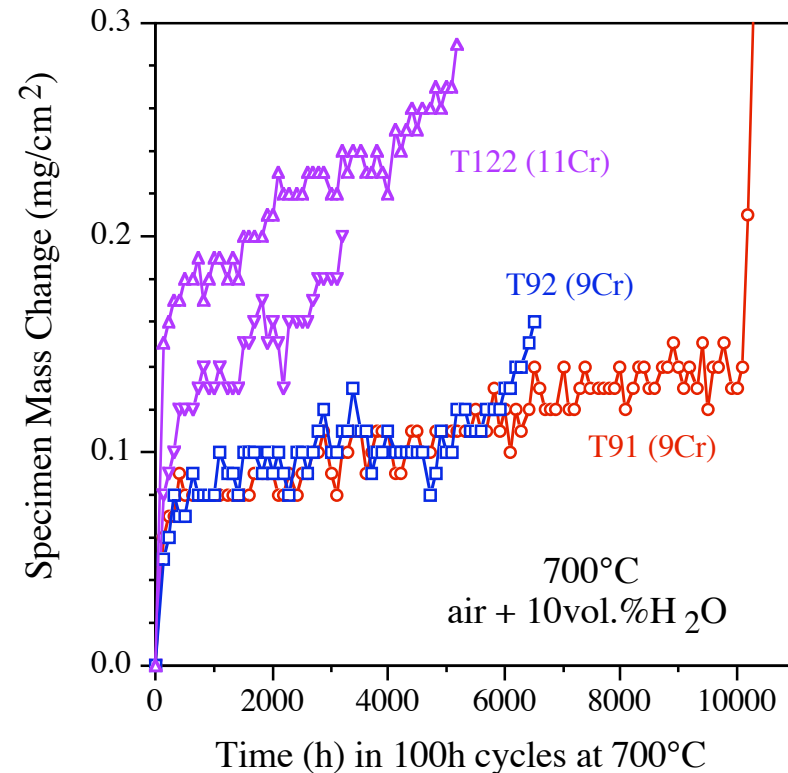
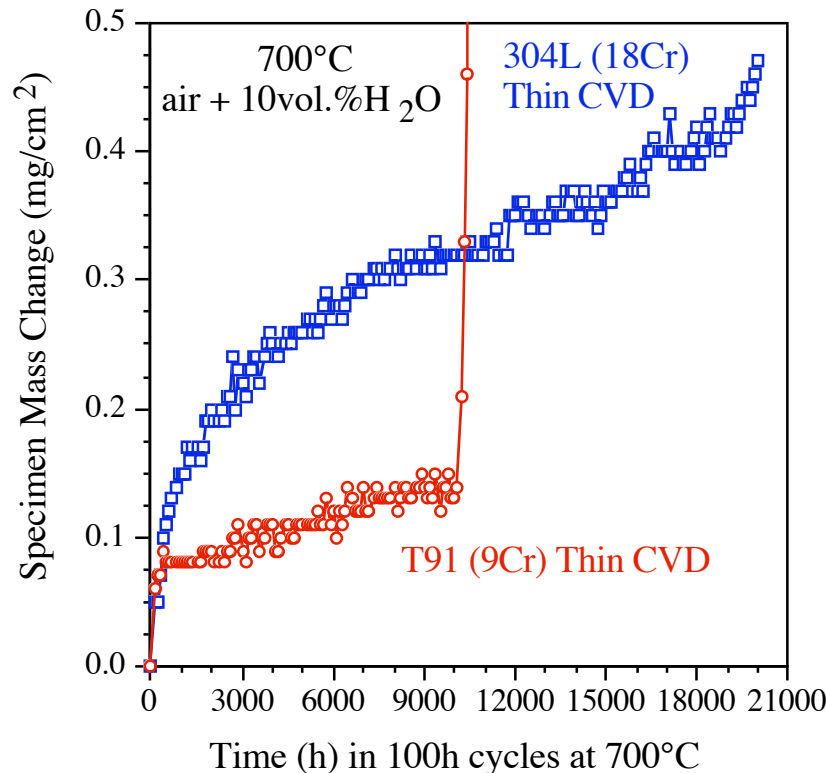
Observations: Thinner starting coating than on T91

Slower Al diffusion: inhibited by phase transformation

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

Incomplete: Effect of C_{Cr} on C_b

Thin coatings at 700°C in humid air



Similar Cr content in coating as in Fe-base substrate

Cr known to improve selective Al oxidation: “third element”

Much longer lifetime for 304L(18Cr) at 700°C (>20kh)

T91(~9Cr) failed at <11 kh

Various Fe-Cr (9-12Cr) substrates being tested

Summary

Oxidation performance of thick and thin CVD aluminide coatings on ferritic (T91) and austenitic (304L) substrates have been evaluated at 650°-800°C in humid air.

CTE mismatch problem

Austenitic alloys: 3 layers aluminide/ferritic/austenitic

- coating deformation and cracking observed on 304L

Ferritic alloys: Fe_3Al /ferritic mismatch can cause cracking

Solution:

“Thin” coatings T91: no high CTE intermetallic Fe-Al phase

Higher temperatures (700°-800°C) used to induce failures.

Failure of thin CVD coating on Fe-9Cr in wet air:

- 700°C: 11 kh $C_b \sim 3.5\text{at}\%$
- 800°C: 2.8 kh $C_b \sim 0.7\text{at}\%$

Accurate C_b needed for lifetime model

- determine C_b as $f(\text{temperature}, C_{Cr}, \text{steam, etc.})$