Materials Issues for Advanced Supercritical CO_2 Cycles and High Efficency Gas Turbines

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Acknowledgments

TBC Task leaders: J. A. Haynes - coating procurement
K. A. Unocic - characterization (TEM)
S. Sampath, Stonybrook U. - processing

M. Lance - PSLS, 3D LM
H. Aldridge, U. Florida PhD student - lifetime modeling
G. Garner, M. Stephens - oxidation experiments

sCO_2: Jim Keiser - autoclave design
Mike Howell - construction and operations
T. Lowe - characterization
D. W. Coffey - TEM specimen preparation, FIB
T. Jordan - metallography
D. Leonard - EPMA

Superalloys: Howmet, Siemens,Capstone Turbines
Alloys: Haynes, Special Metals, ATI, Sumitomo, Sandvik...

Research sponsored by: U. S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy

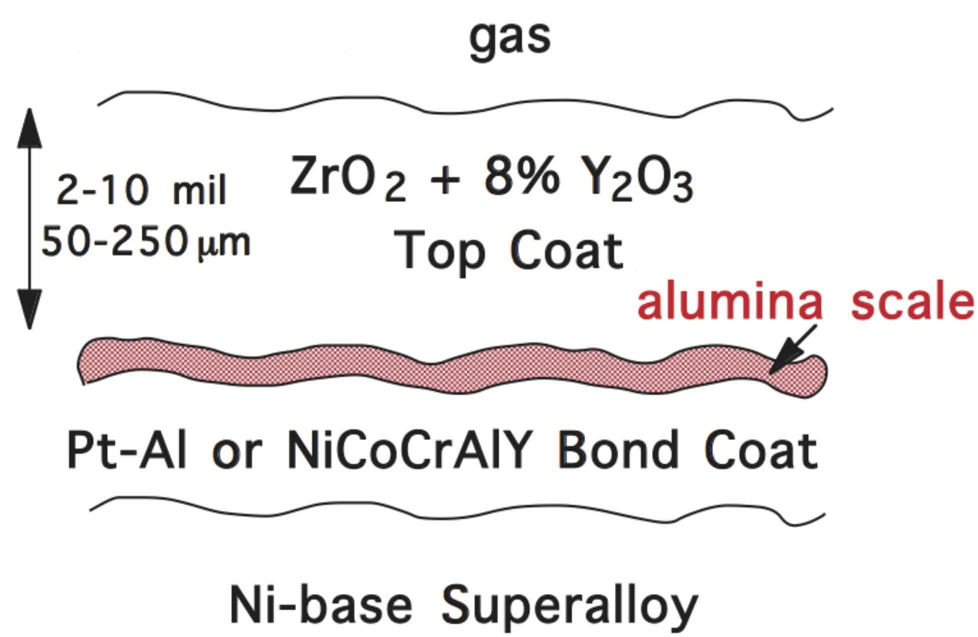
Looking for coating solutions

New environments (higher H_2O, CO_2, SO_2)

CTSR: new top coat

New bond coatings?

Different substrates



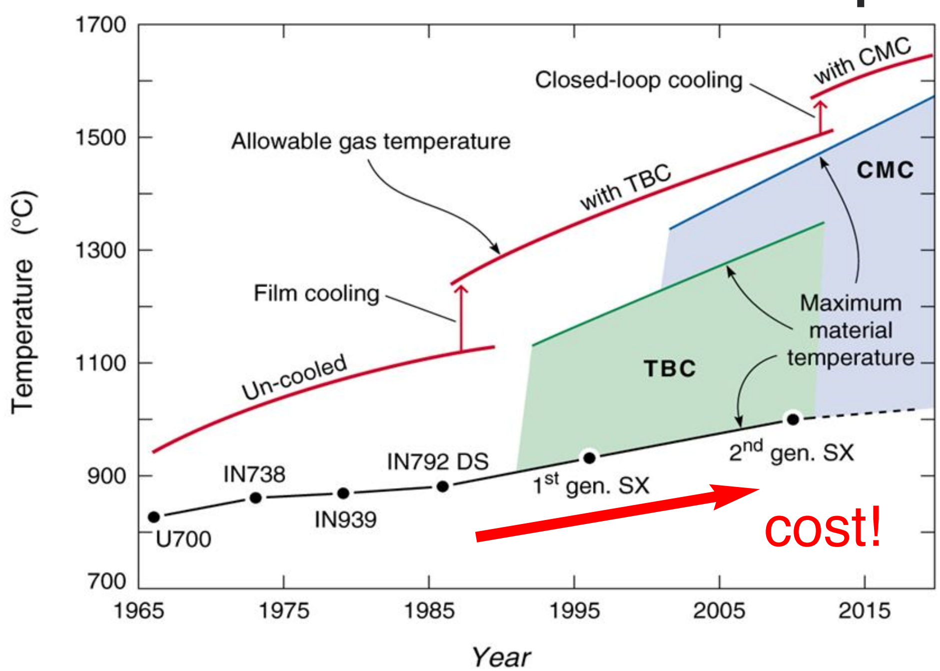
#1 More durable coatings will benefit IGCC and NGCC

#2 Focus on alumina scale as "weak link"

Coatings for Syngas-H_2 Turbines completed in 2015

Used furnace cycle testing to evaluate:

- Effect of H_2O, CO_2, etc. on TBC lifetime
- 1-h vs. 100-h cycles
- NiCoCrAlYHfSi bond coatings vs. Ti-B additions
- effect of substrate composition (de-evolution):



MarM247 <- PWA1483 <- CMSX4

8Cr+1Hf 12Cr+4Ti 6Cr+3Re

Standardized coating procedures

16mm disks: superalloy substrates (all at.%):

X4: 13.0Al 1.2Ti 6.4Cr **0.9Re** 0.03Hf 17ppmaS

1483: **7.3Al 4.9Ti 13.6Cr** 0Re <0.001Hf <3ppmaS

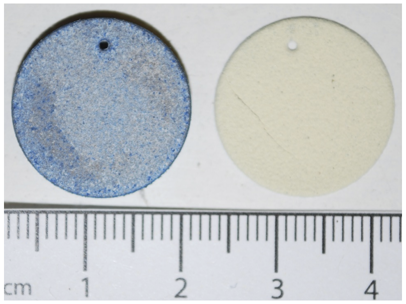
247: 12.6Al 1.3Ti 9.7Cr 0Re **0.47Hf** <3ppmaS

High Velocity Oxygen Fuel (HVOF) bond coating:

Ni-18Co-16Cr-23Al-0.4Y-0.07Hf-0.65Si

Roughness: final coarse powder spray

16mm diameter coupon



APS top coating: ZrO_2-Y_2O_3 (1 side)

Oxidation: 1-h and 100-hcycles

900° and 1100°C: air + 10% H_2O

Characterization: Metallographic cross-sections

SEM/EDS/EBSD

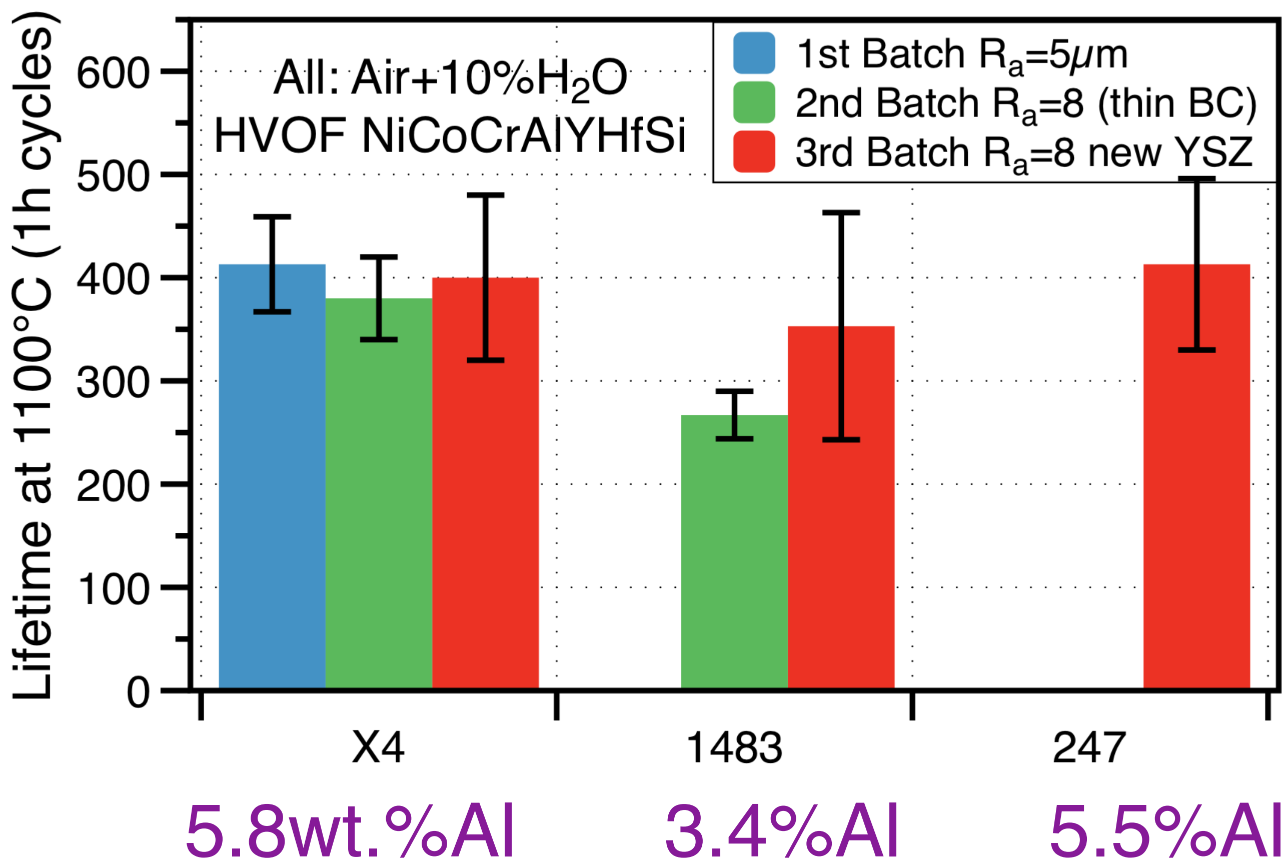
EPMA (WDS)

PSLS, 3D LM

FIB/TEM

1-h cycles: DS 247 similar to X4

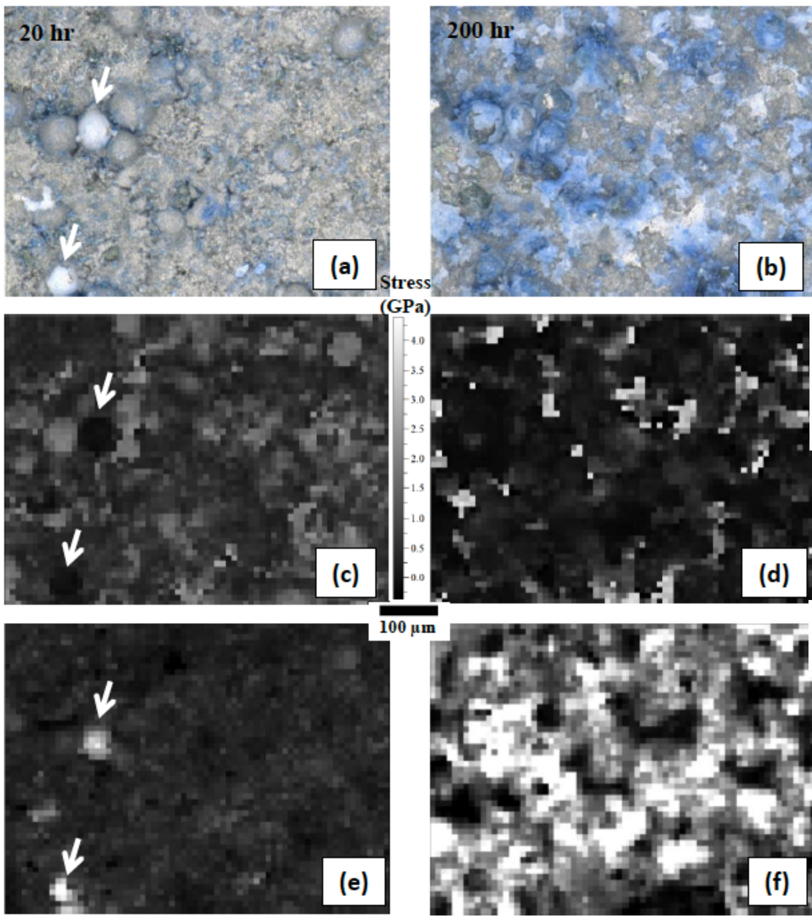
HVOF NiCoCrAlYHfSi/APS YSZ coatings



1100°C average lifetime of 3 similarly coated specimens

No parameter effect #1

3D image + PSLS: maps & histograms
1483: 1100°C, dry air, 1h cycles

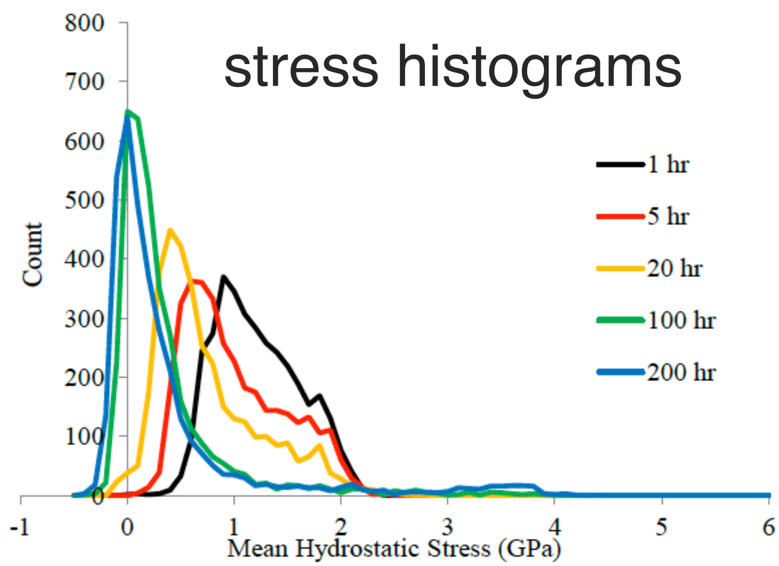


3D Light microscopy (Keyence)

Photo-Stimulated Luminescence Spectroscopy: mean stress

PSLS: total R-line area

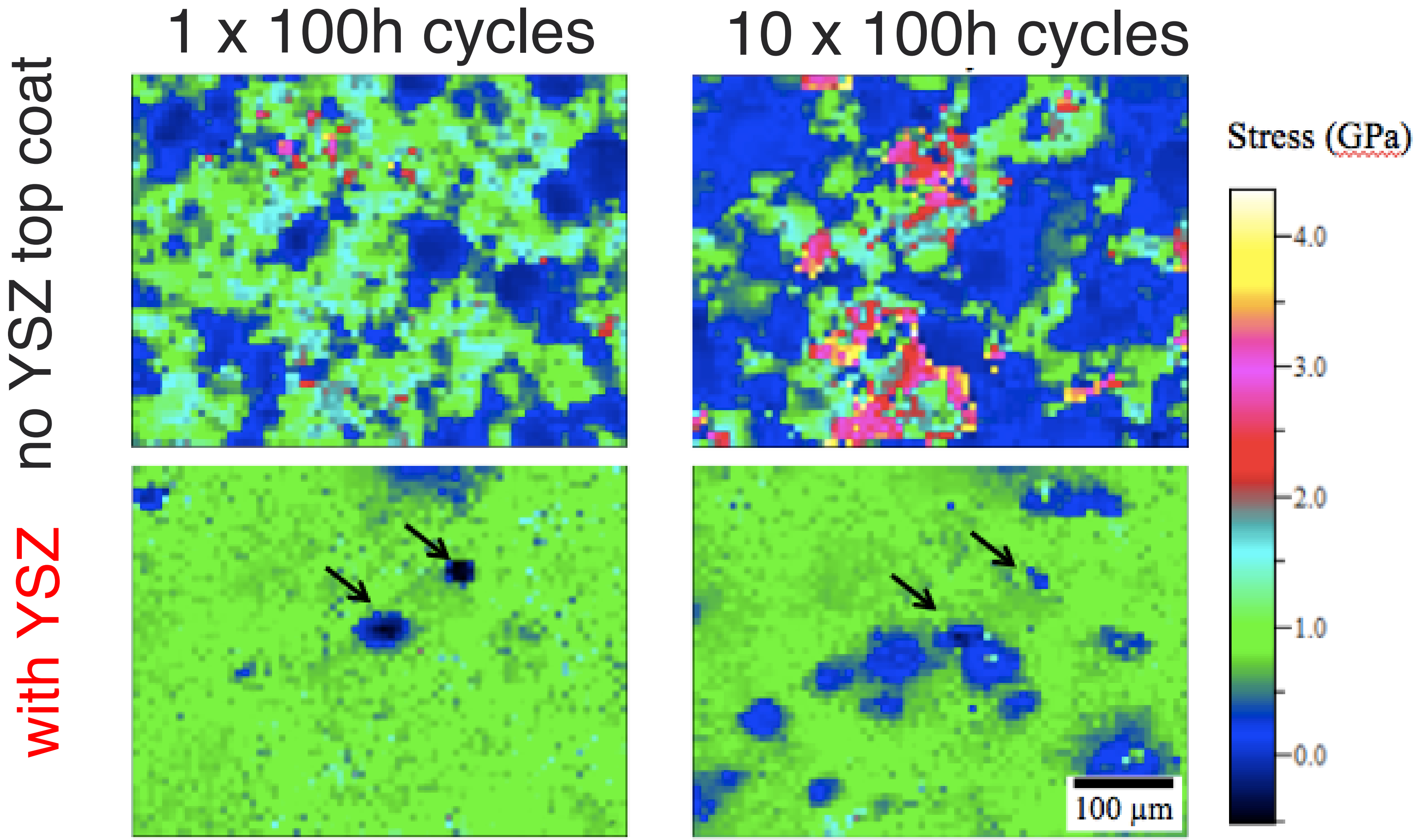
20 cycles　　200 cycles



No YSZ top coat:
nothing to constrain spallation

Able to measure stress under YSZ

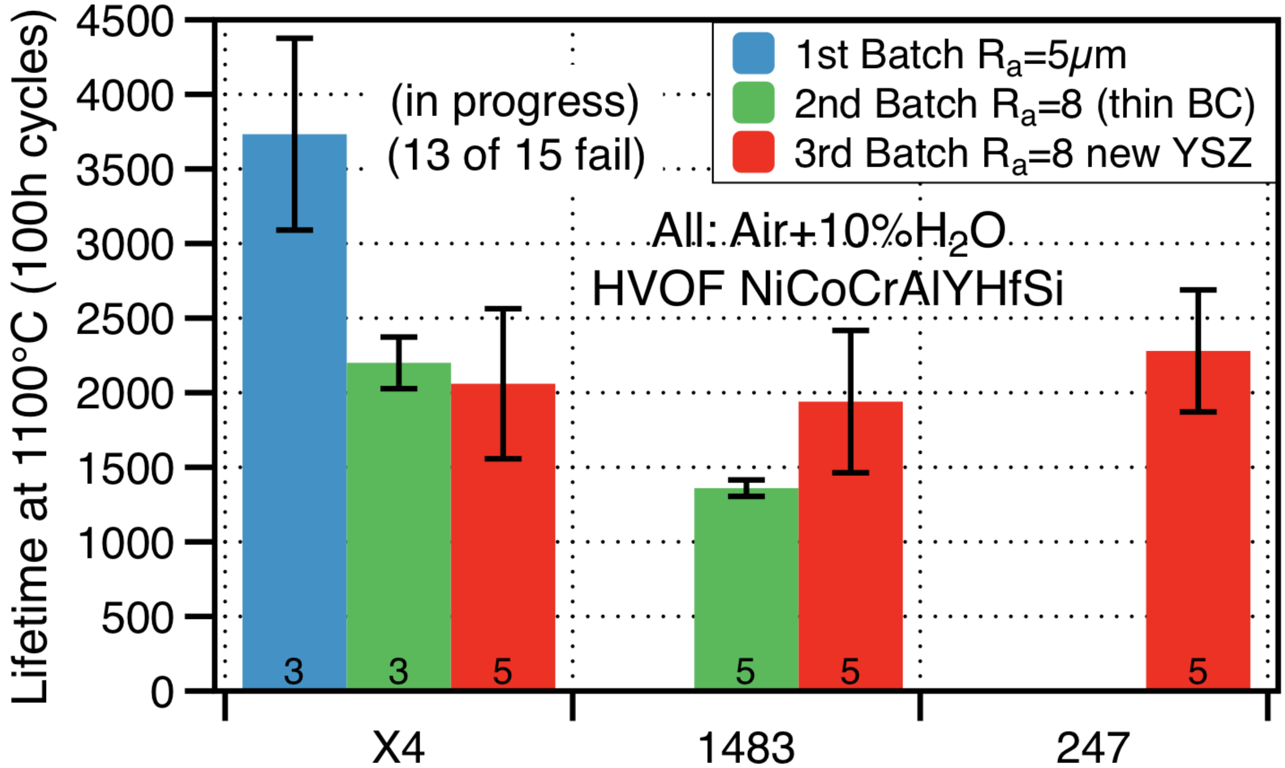
HVOF MCrAlYHfSi/APS YSZ on 1483 in 50%H_2O



Stress in alumina scale measured by PSLS or PLPS

Also similar lifetime with 100h cycle

HVOF NiCoCrAlYHfSi/APS YSZ coatings



5.8wt.%Al 3.4%Al 5.5%Al

1100°C
2012°F

10%H_2O
simulated
exhaust

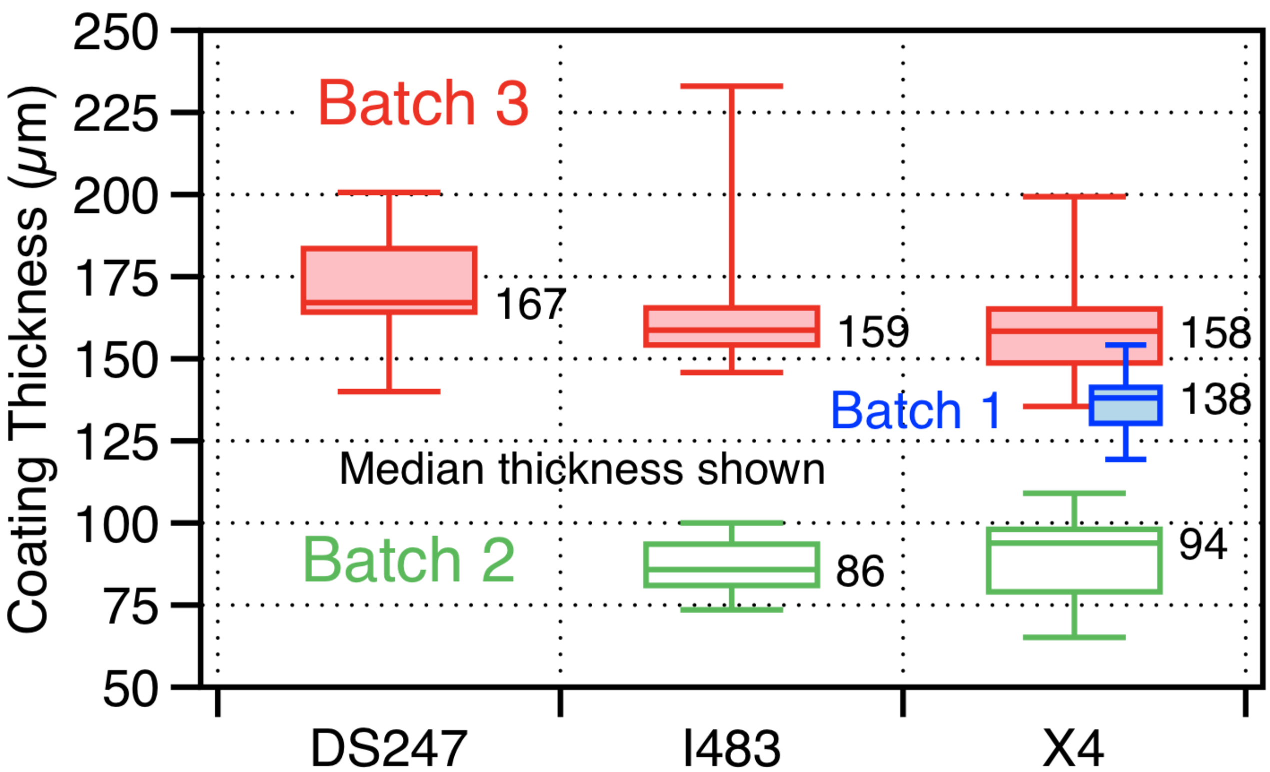
5 similarly coated specimens with each substrate

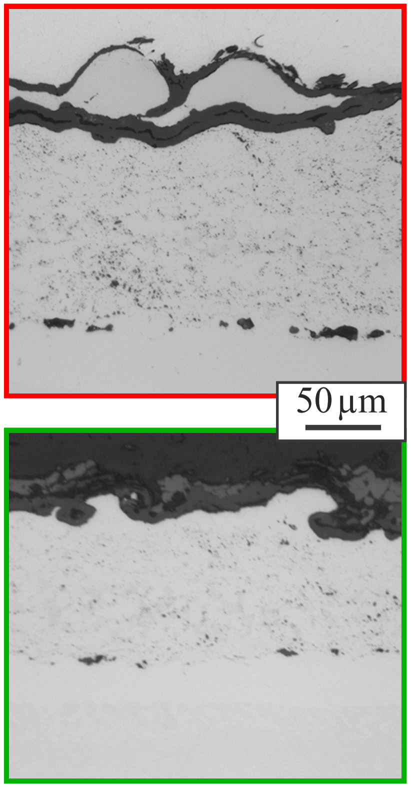
100h cycles more relevant to baseload generation

No parameter effect #2

Thicker bond coating appeared to eliminate substrate effect

3 batches of HVOF NiCoCrAlYHfSi coatings



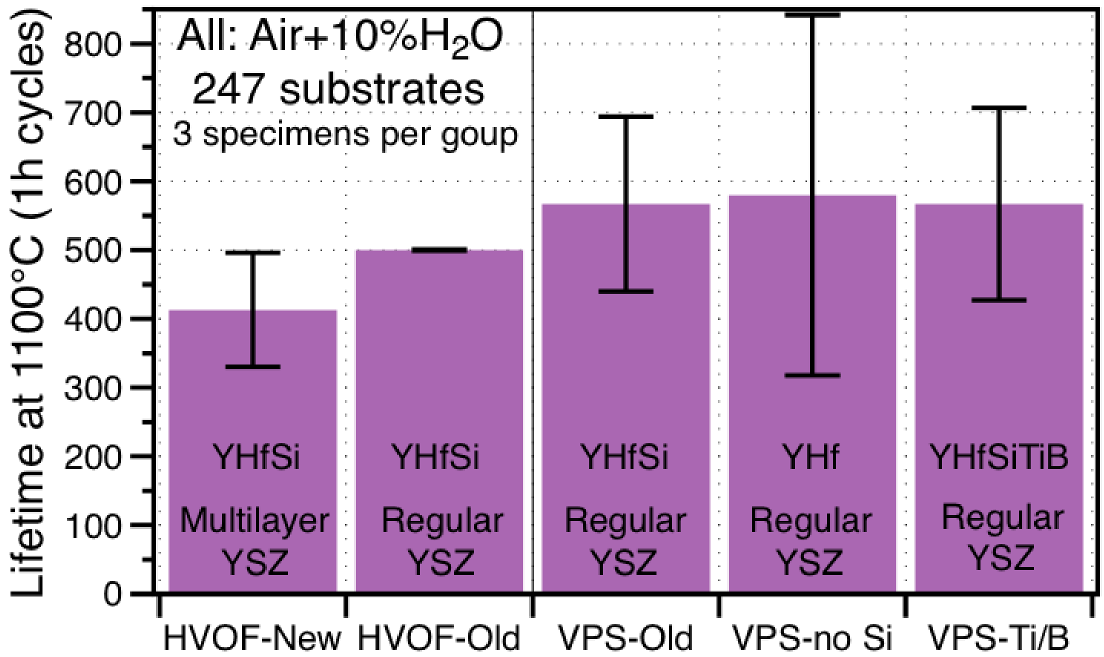


Batch 2 - saw lower lifetime for 1483 substrates

Batch 3 - no substrate effect observed

Last set of coupons: similar lifetimes

1-h cycles, 1100°C, air + 10%H_2O



1100°C, 2012°F
247 substrates
3 specimen average

Bars 1-2: single vs. CTSR double layer YSZ
Bars 2-3: HVOF vs. VPS NiCoCrAlYHfSi
Bars 3-4: VPS YHfSi vs. YHf (effect of Si)
Bars 3-5: VPS YHfSi vs. YHfSiTiB (effect of Ti,B)

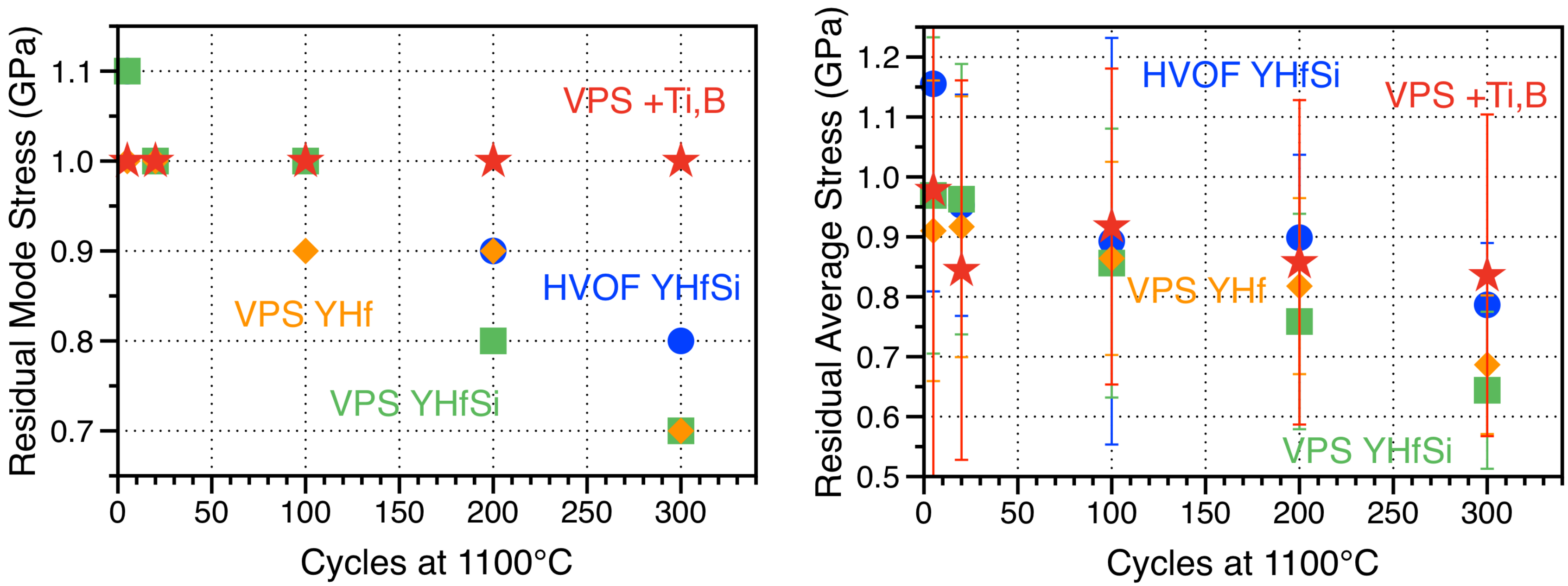
No parameter effects #3, #4, #5, #6

Different stress with Ti-B addition

PSLS measurements during 1-h cycles at 1100°C

mode stress

average stress

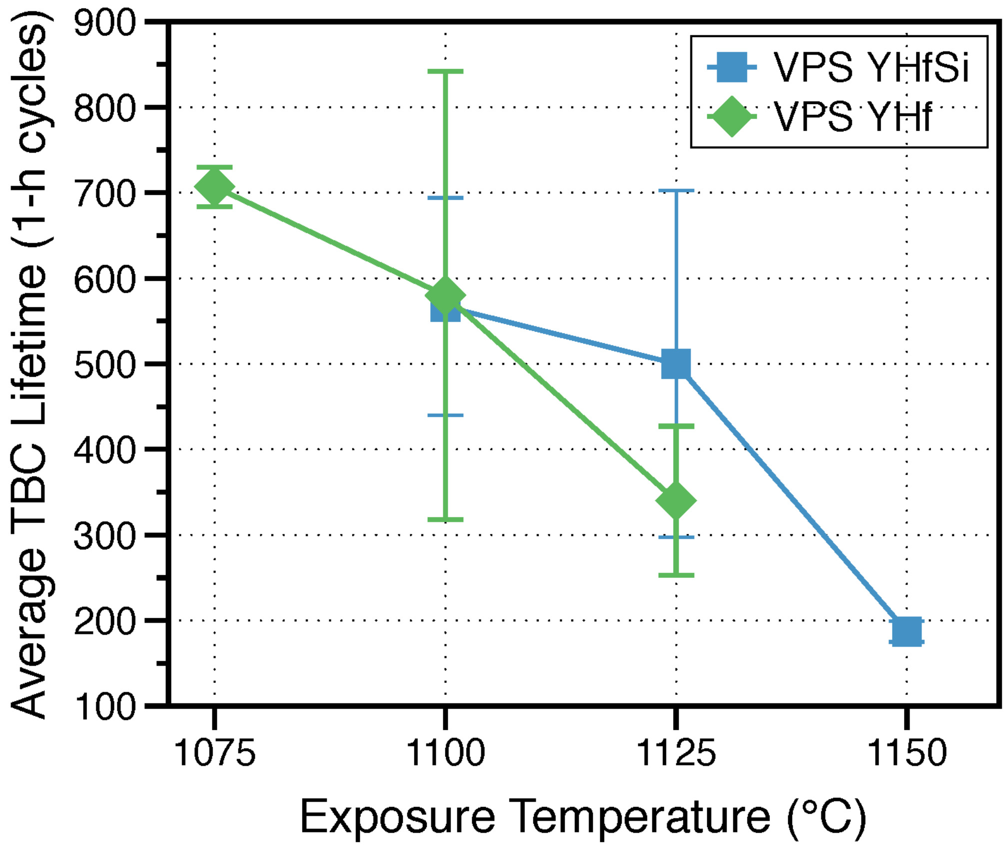


Mode stress - peak of stress histogram

Higher residual stress with VPS NiCoCrAlYHfSiTiB

- average stress: not significant difference
- did not result in increased lifetime

Temperature showed lifetime effect
VPS NiCoCrAlYHf±Si/APS YSZ coatings



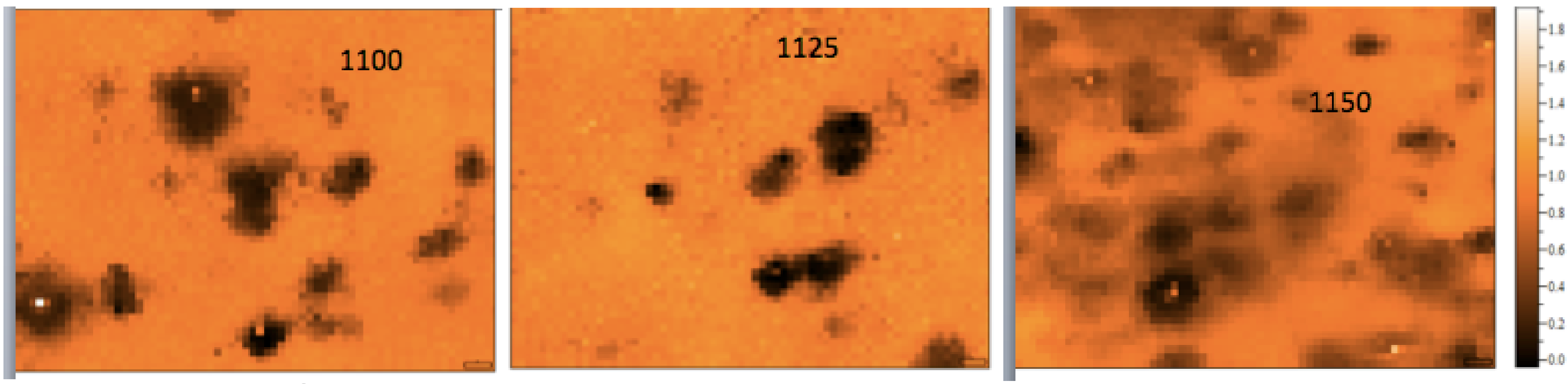
air+10%H_2O
simulated exhaust
3 samples/group

No change in lifetime w/o Si addition

PSLS: lower stress at 1150°C

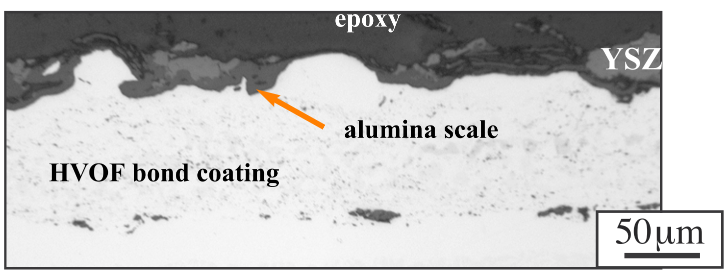
All 100 1-h cycles in air+10%H_2O

1100°C | 1125°C | 1150°C



Average lifetime:

567 cycles | 500 cycles | 187 cycles

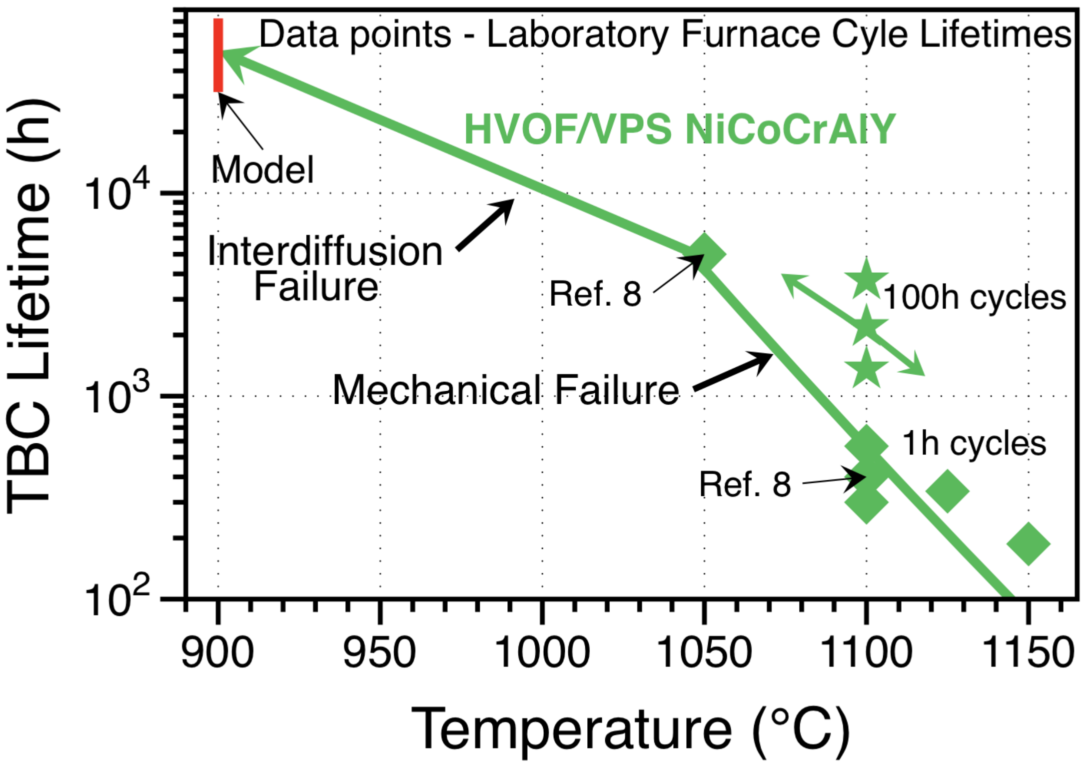


Low stress areas due to asperities in bond coating

- areas growing after 100 cycles at 1150°C

Initial model work focused on 900°C

Model inputs based on 900°C 5-20 kh samples



Failure map from Schütze et al.

Lifetime modeling:

1. Beta depletion

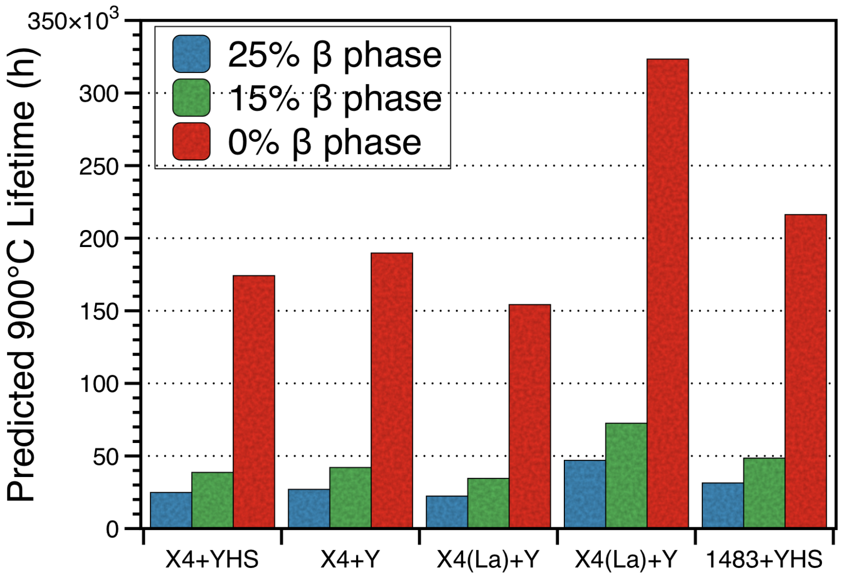
2a. NASA COSIM model with D_{eff} from EPMA

2b. COSIM model with extrapolated D

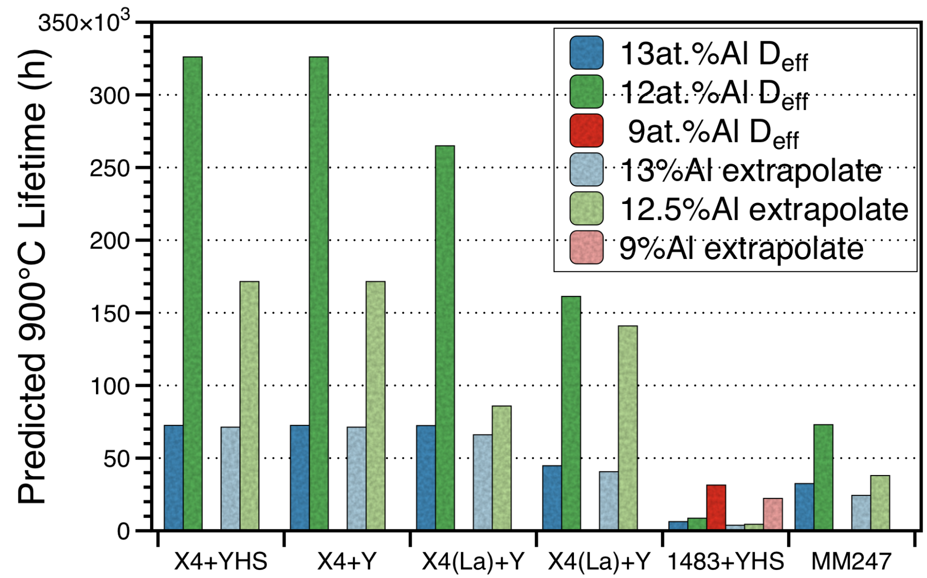
Wide range of lifetimes predicted

Highly dependent on parameter inputs at 900°C

β phase depletion



COSIM



HVOF bond coating

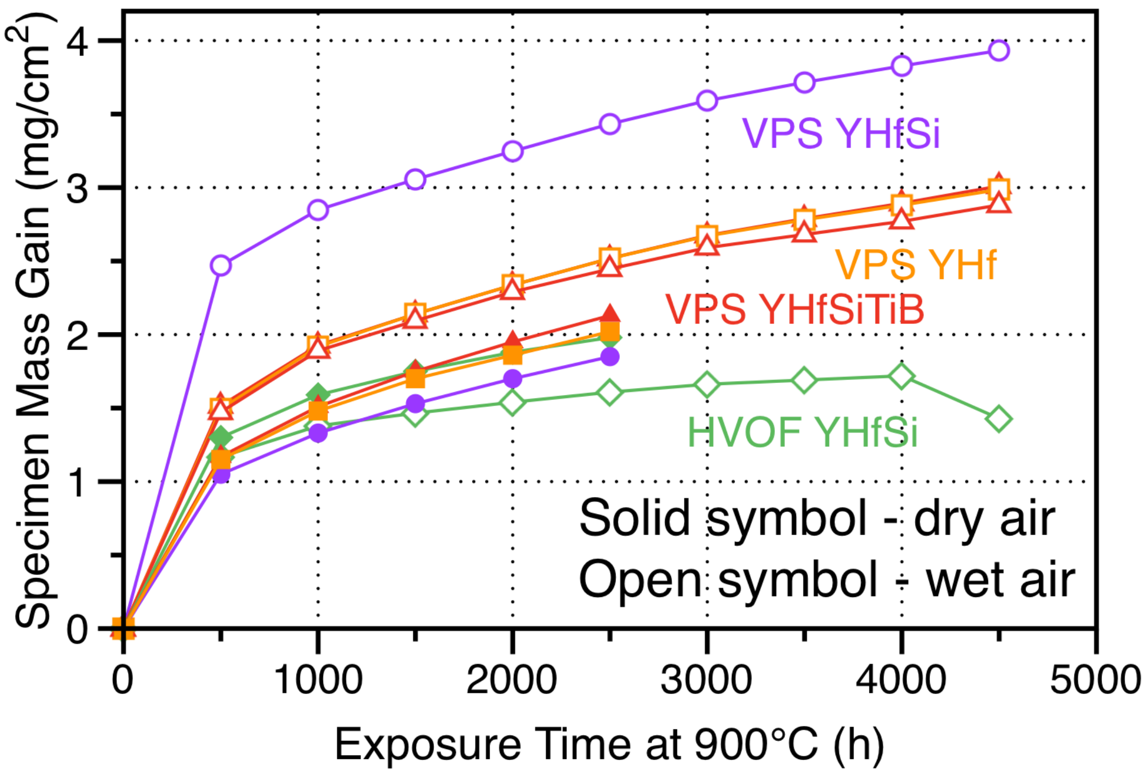
Coating on 1483 (low Al): low life by COSIM

Little effect of YHfSi compared to Y alone

Next phase: collect data between 900°-1100°C

What is effect of H_2O at 900°C?

500-h cycles in wet air and laboratory air



Slight change in rate constants with H_2O

Stop specimens at 5,000h for metallography

- compare change in oxide thickness

2015 focus areas

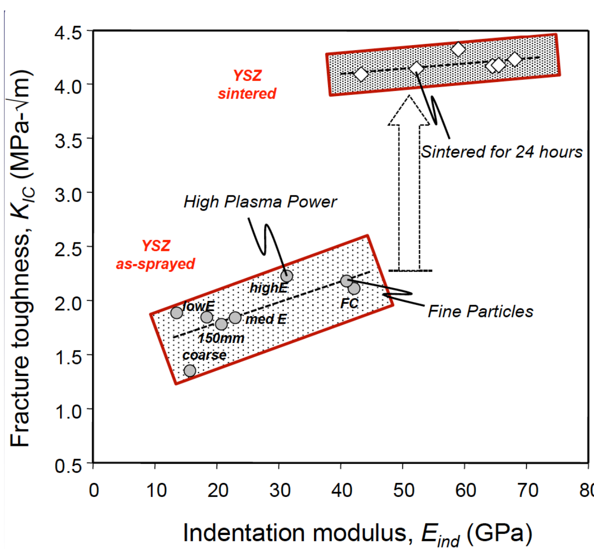
1. Use CTSR/ORNL experience for best TBC
2. Get away from testing flat coupons

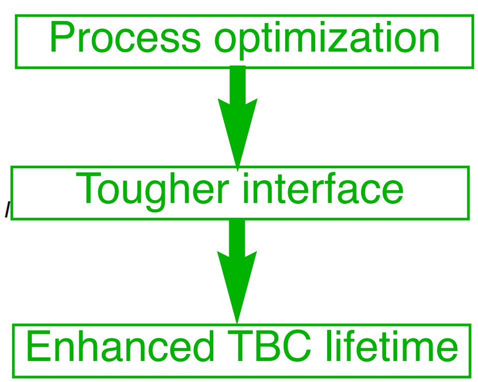
Cranfield/Jülich coat more complex shapes

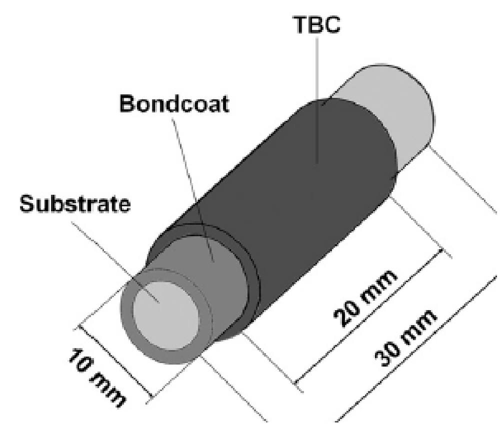
~4 specimens from each rod/tube: 100h cycles

- measure lifetime, alumina stress...

Optimize coating process for rod (CTSR)



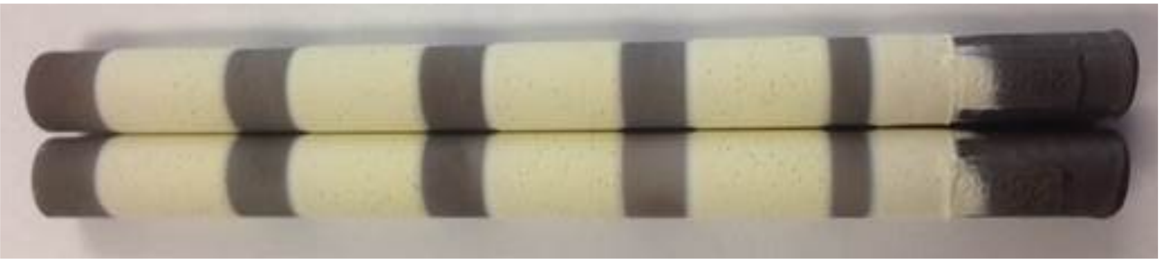




Jülich specimen design

Rod specimens begun testing

Wet air at 900°, 1100° and 1150°C



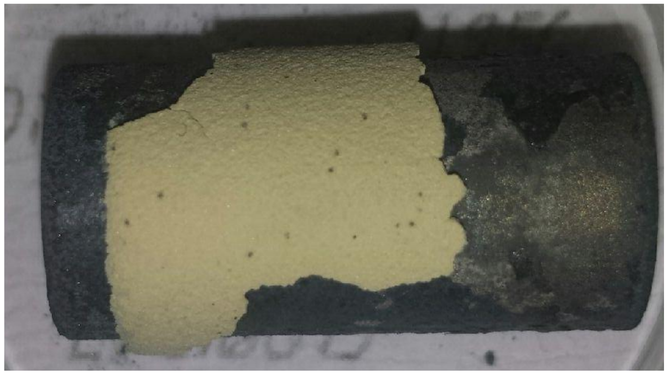
APS YSZ top coating; NiCoCrAlYHfSi APS + HVOF

Exposures:

500-h cycle at 900°C (in progress)	run to 5 kh
100-h exposure at 1100°C	run to fail
100-h exposure at 1150°C	run to fail

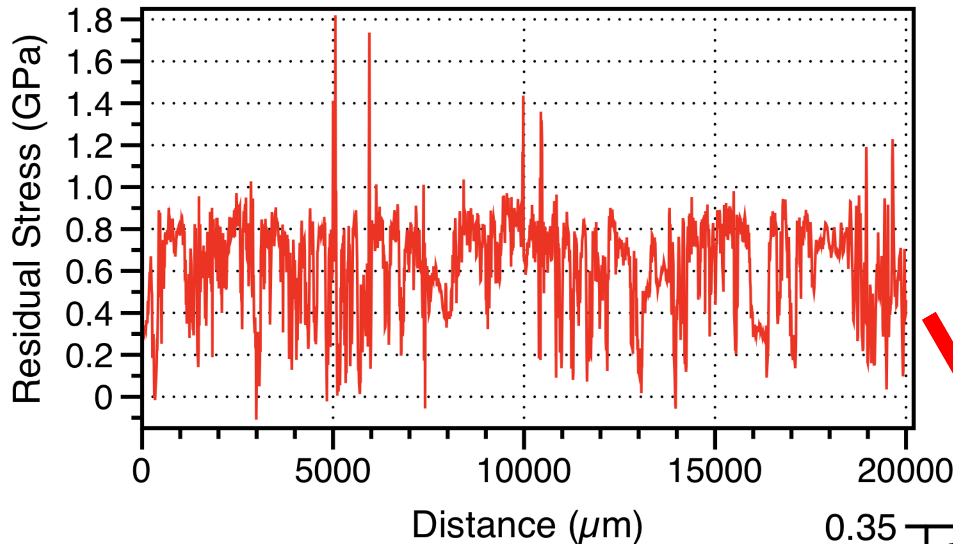
APS MCrAlYHfSi bond coating
After 100h at 1100°C

APS MCrAlYHfSi bond coating
Failure after 100h at 1150°C

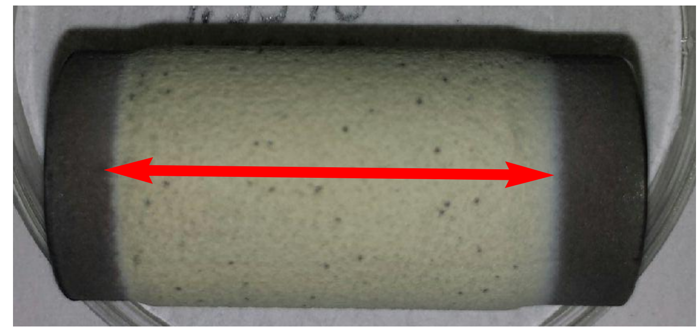


Initial stress measurements

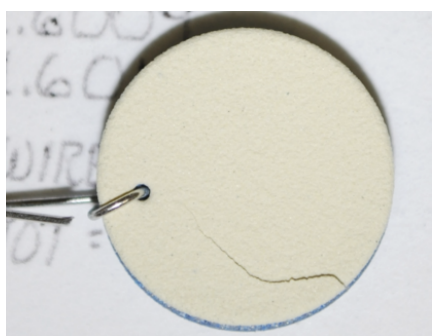
One 100-h cycle at 1100°C in air+10%H_2O

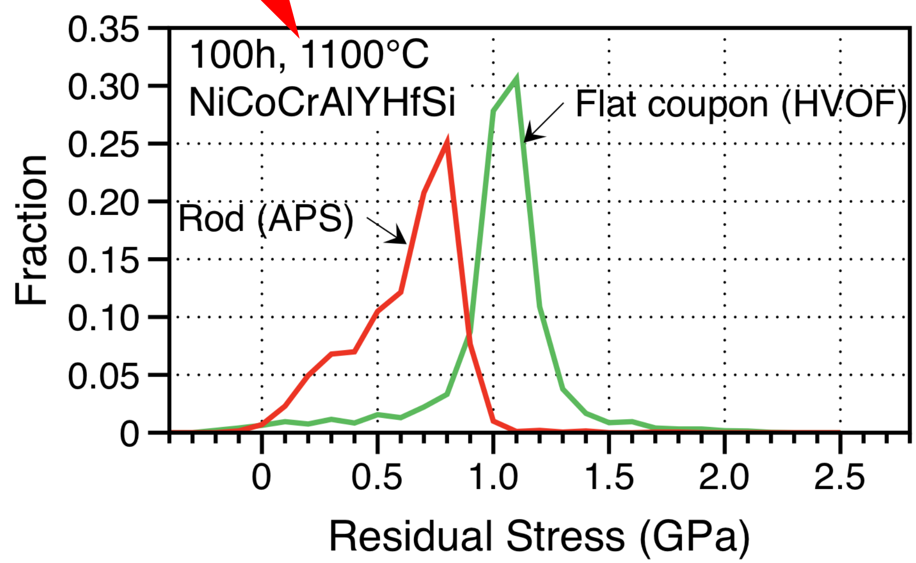


PSLS measurement along length of rod



Next measurement at 500 h





Lower mode stress in APS rod specimen after 1 cycle

TBC Summary

2014-15 work concluded multi-year investigation:

- Effect of environment (H_2O, CO_2...)
- Effect of bond coating chemistry
- Effect of superalloy chemistry
- Effect of cycle frequency
- Lifetime at 900°C (NASA COSIM model)

Furnace cycle testing on 16mm disk specimens

1. 100h cycles at 1100°C failed by interdiffusion
2. Suspect early edge failures on coupons

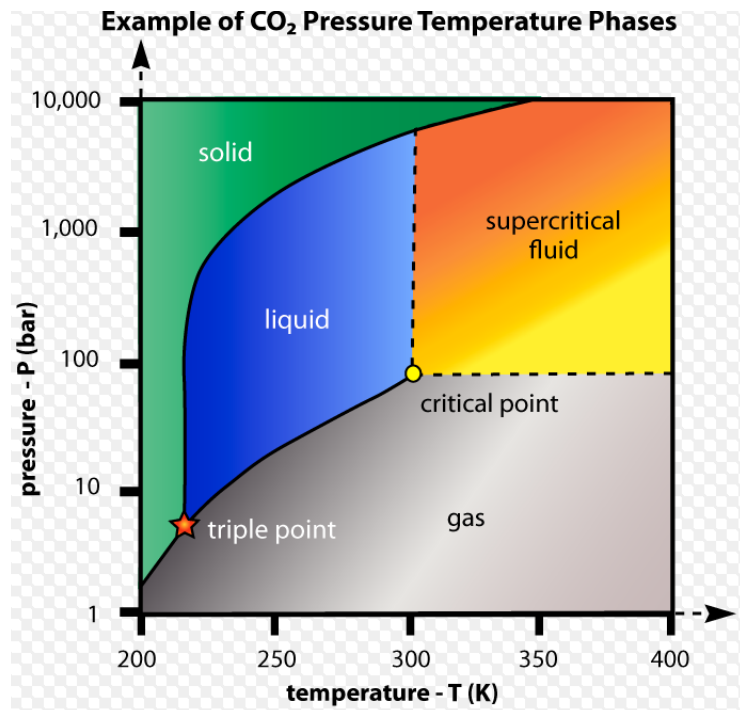
2015 project

- coating 12.5mm diameter rod specimens (247)
- initial exposures started at 900°,1100°, 1150°C
- Focus on lifetime modeling at <1100°C

Why use supercritical CO_2?

Potential supercritical CO_2 (sCO_2) advantages:

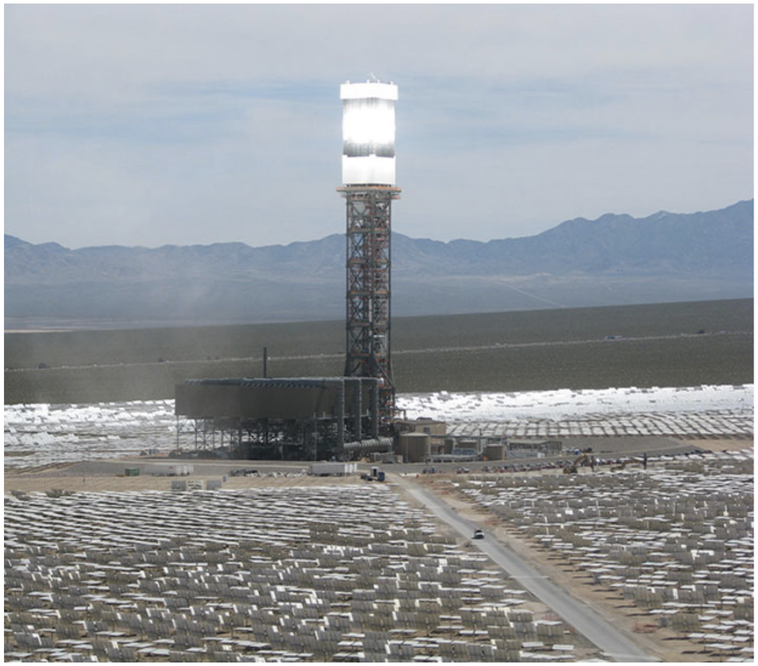
- no phase changes
- high efficiency
- more compact turbine
- short heat up
- less complex
- lower cost (?)



Direct- and indirect-fired sCO_2 Brayton cycles for:

- fossil energy (coal or natural gas) FY13- ?
- concentrated solar power FY16-FY18
- nuclear (paired with sodium for safety)
- waste heat recovery/bottoming cycle

Many possible applications

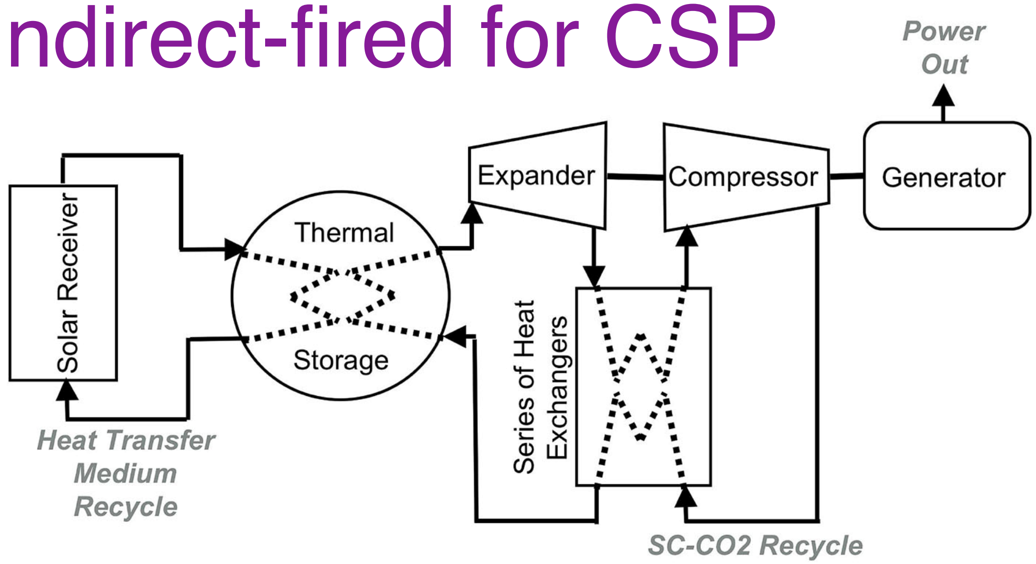


Smaller fossil fuel turbines

7MW Echogen (WHR)

Indirect & direct-fired systems of interest

Indirect-fired for CSP



Closed loop of relatively pure CO_2
- primary HX (>700°C)
- recuperators (<600°C)

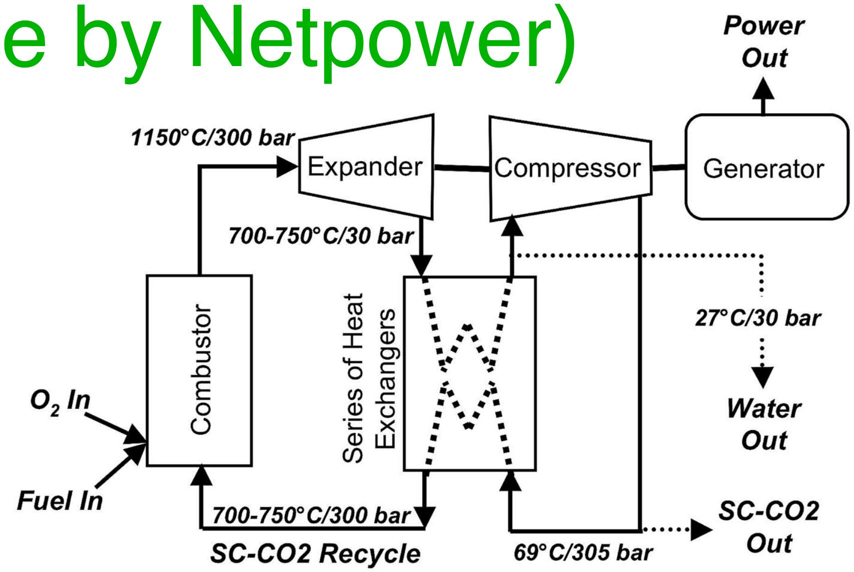
Also, waste heat recovery, bottoming cycle

Direct-fired (Allam cycle by Netpower)

In: natural gas + O_2

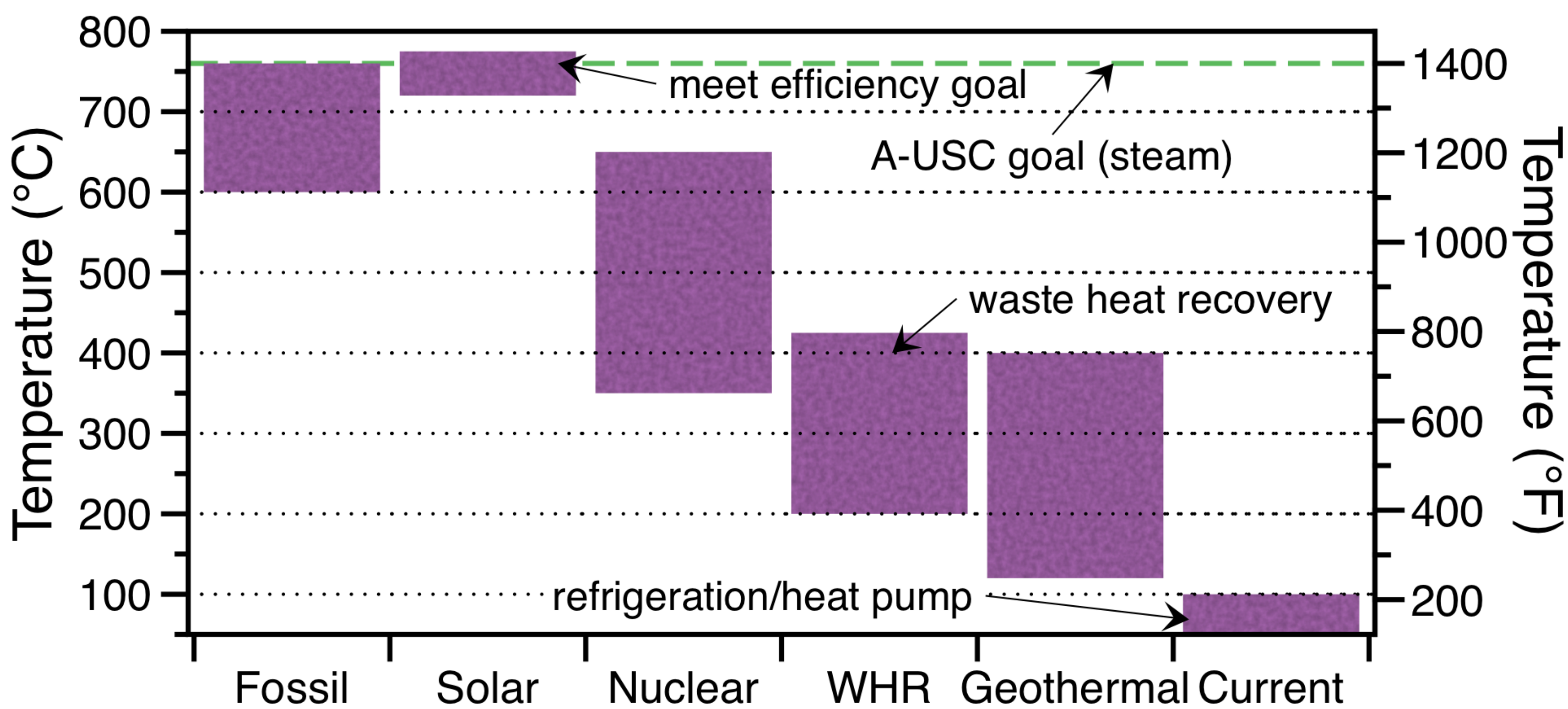
Impurities: ~10%H_2O
~1%O_2, CH_4?

Out: CO_2 for EOR
(enhanced oil recovery)



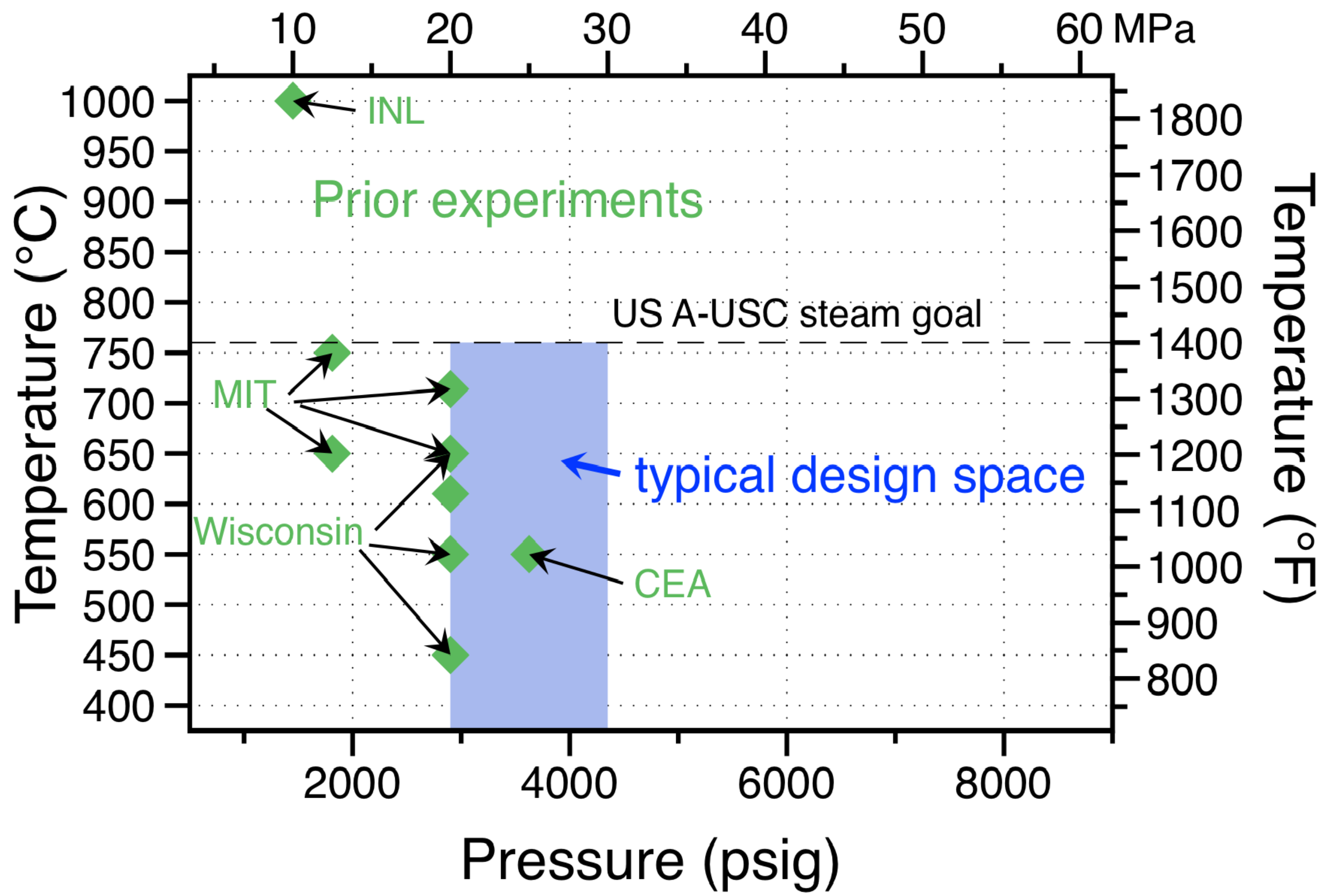
Different temperature targets

- Uncertainty about ranges for sCO_2 applications
- Fossil energy interest for power generation
  coal/natural gas: replace steam with closed cycle



Relatively little prior sCO_2 work

Especially at >650°C and 300 bar



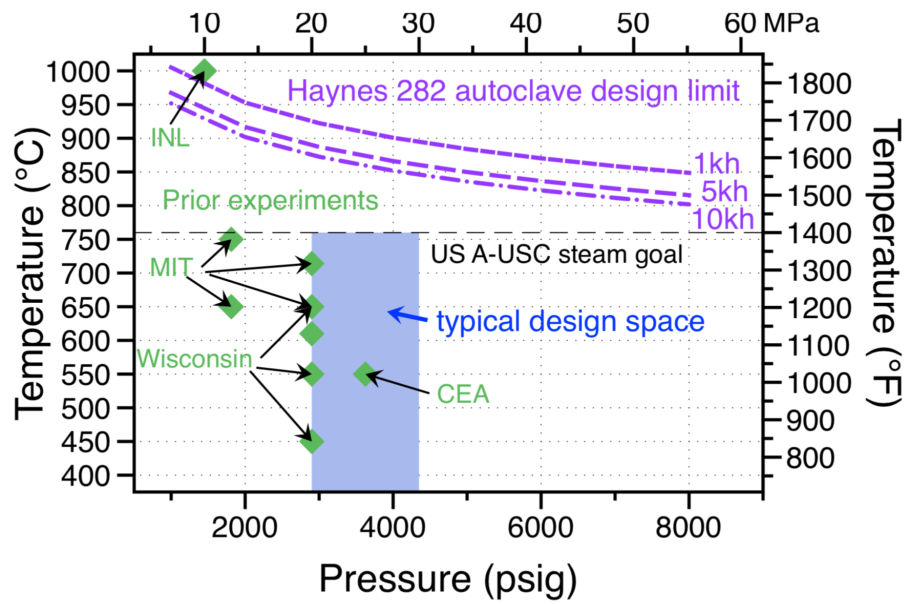
Several groups active in the past 10 years

U. Wisconsin group has published the most results

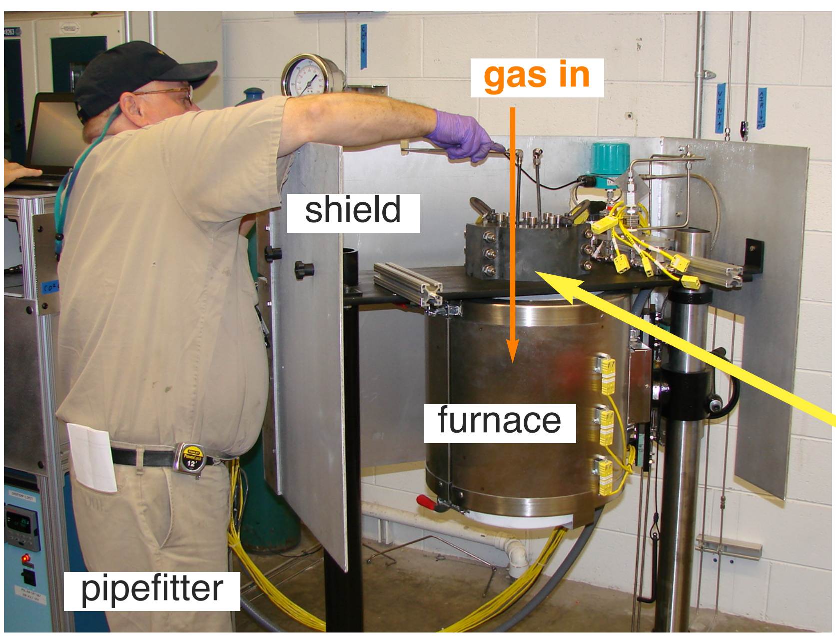
Temperature/pressure limited by autoclave design

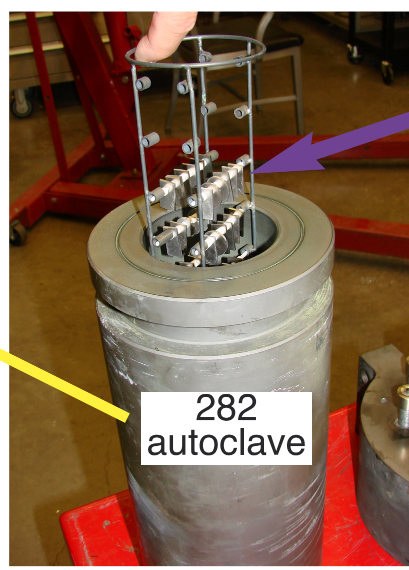
ORNL sCO_2 rig finished in 2014

- ORNL design team: 100+ years of experience
- Haynes 282 autoclave
  - 152mm (6”) dia.
  - 1ml/min flow

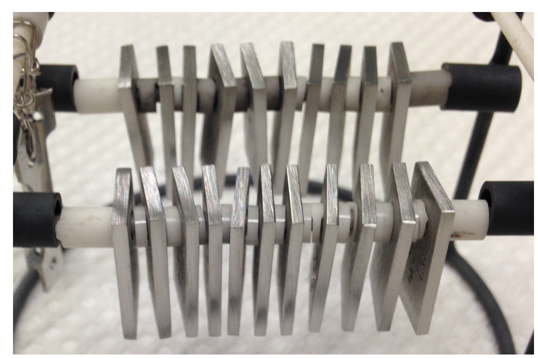


ORNL sCO_2 rig:



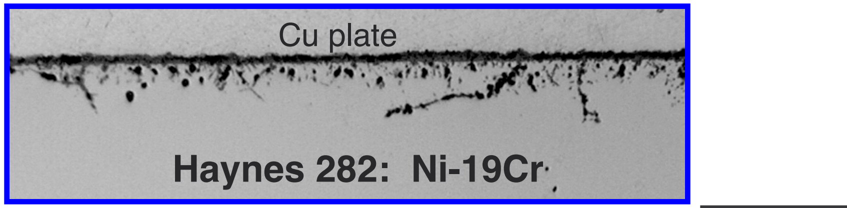


specimen holder

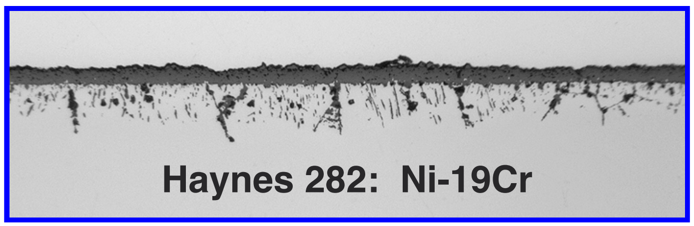


Why worry about 740/282?

5-10kh at 800°C still form thin reaction product in air

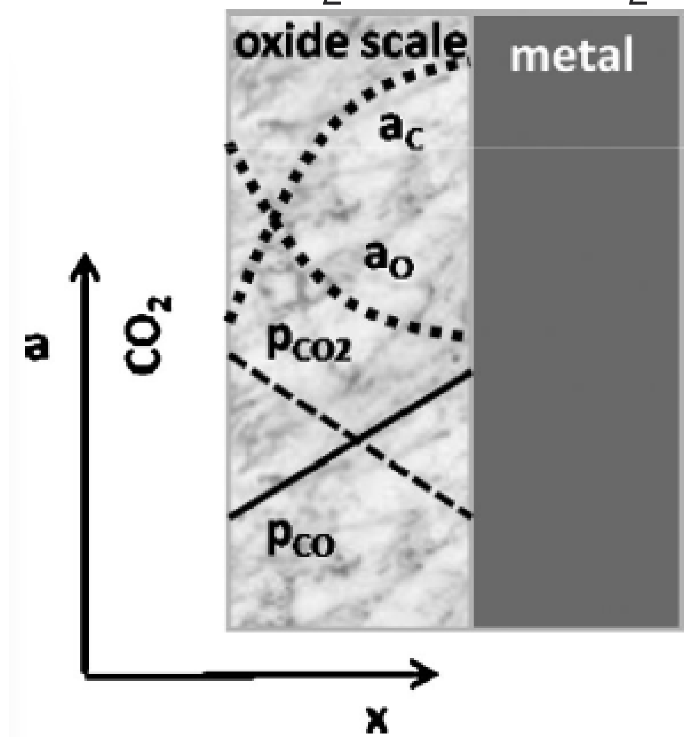


800°C, 5,000h in wet air



800°C, 10,000h in dry air
both exposures: 500h cycles
Al+Ti internally oxidize beneath
Cr_2O_3 oxide scale

$CO_2 = CO + 1/2O_2$



from Young, et al. 2011

General: C activity (a_C) relatively low, favors oxidation

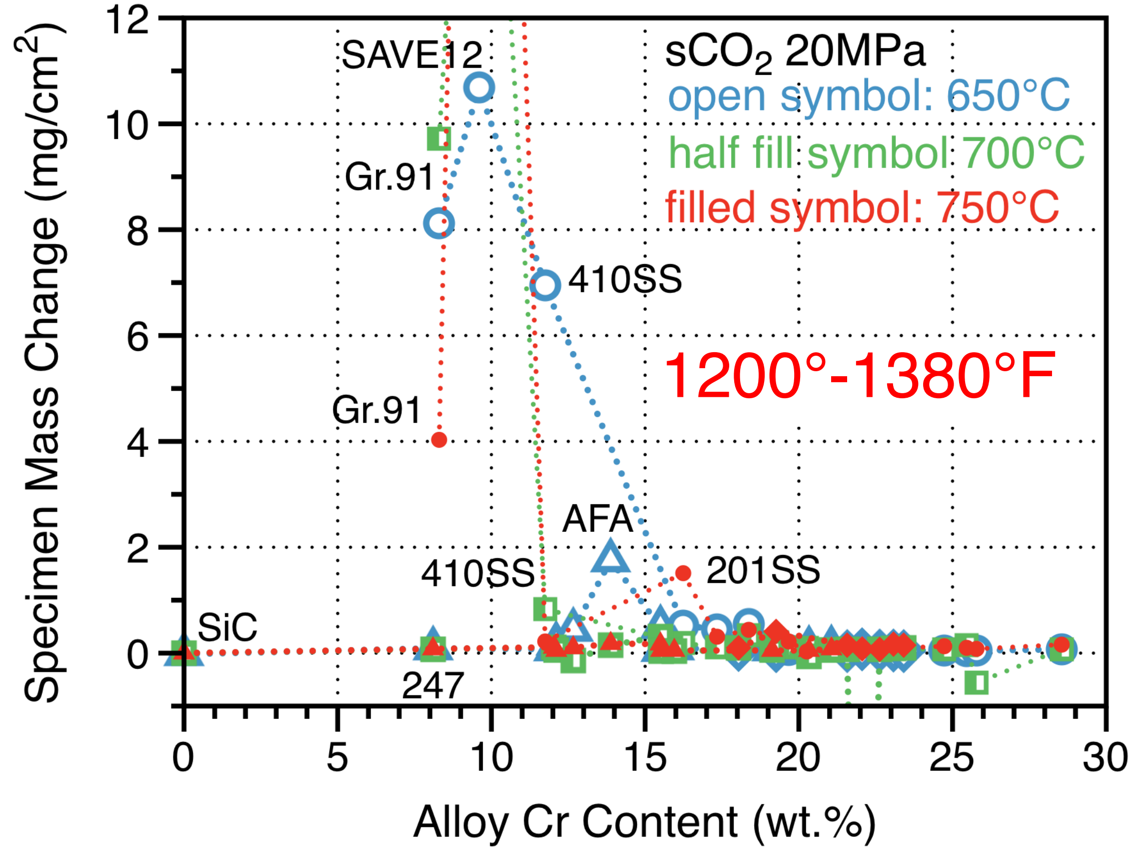
McCoy 1965: 18Cr-8Ni steel internally carburized in 1bar CO_2

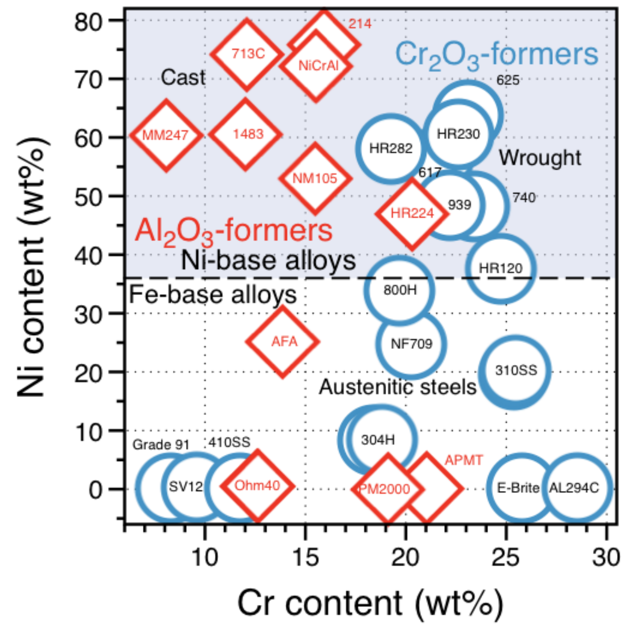
High a_C predicted - what about NiCr in sCO_2 after 10 years?

Many alloys exposed 650°-750°C

~30 alloy coupons exposed 500h at 200 bar (20 MPa)

Most Ni-base alloys did fine



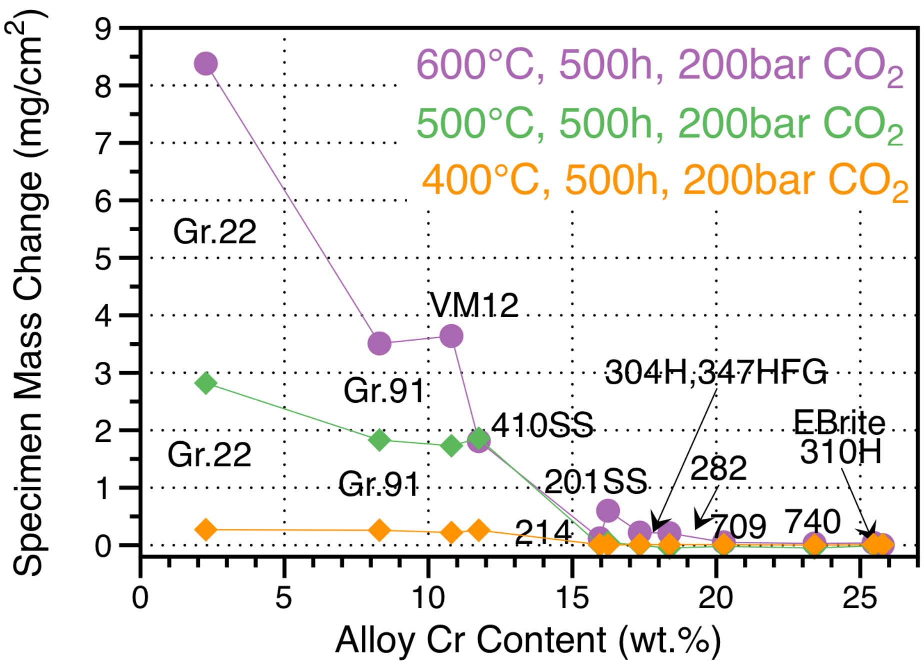


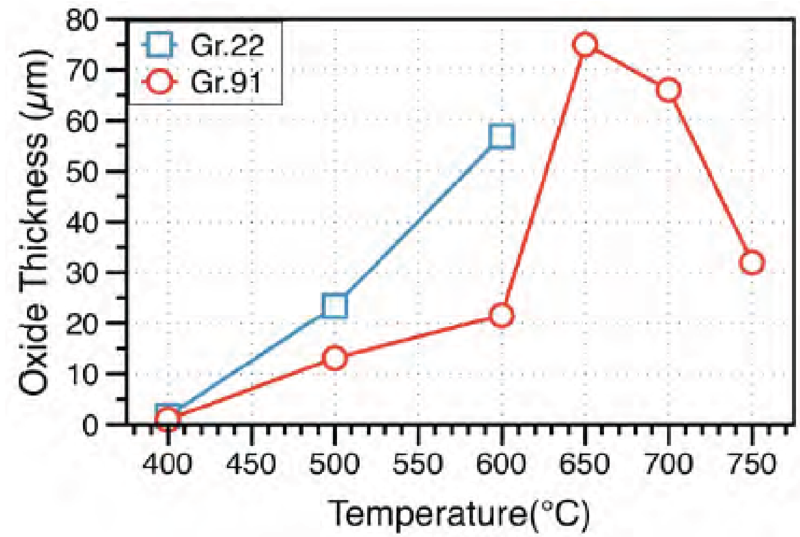
Fe-9Cr-1Mo (Gr91):
- similar to other studies

BUT, only 500h

Steels exposed at 400°-600°C

500h exposures in 20 MPa CO_2

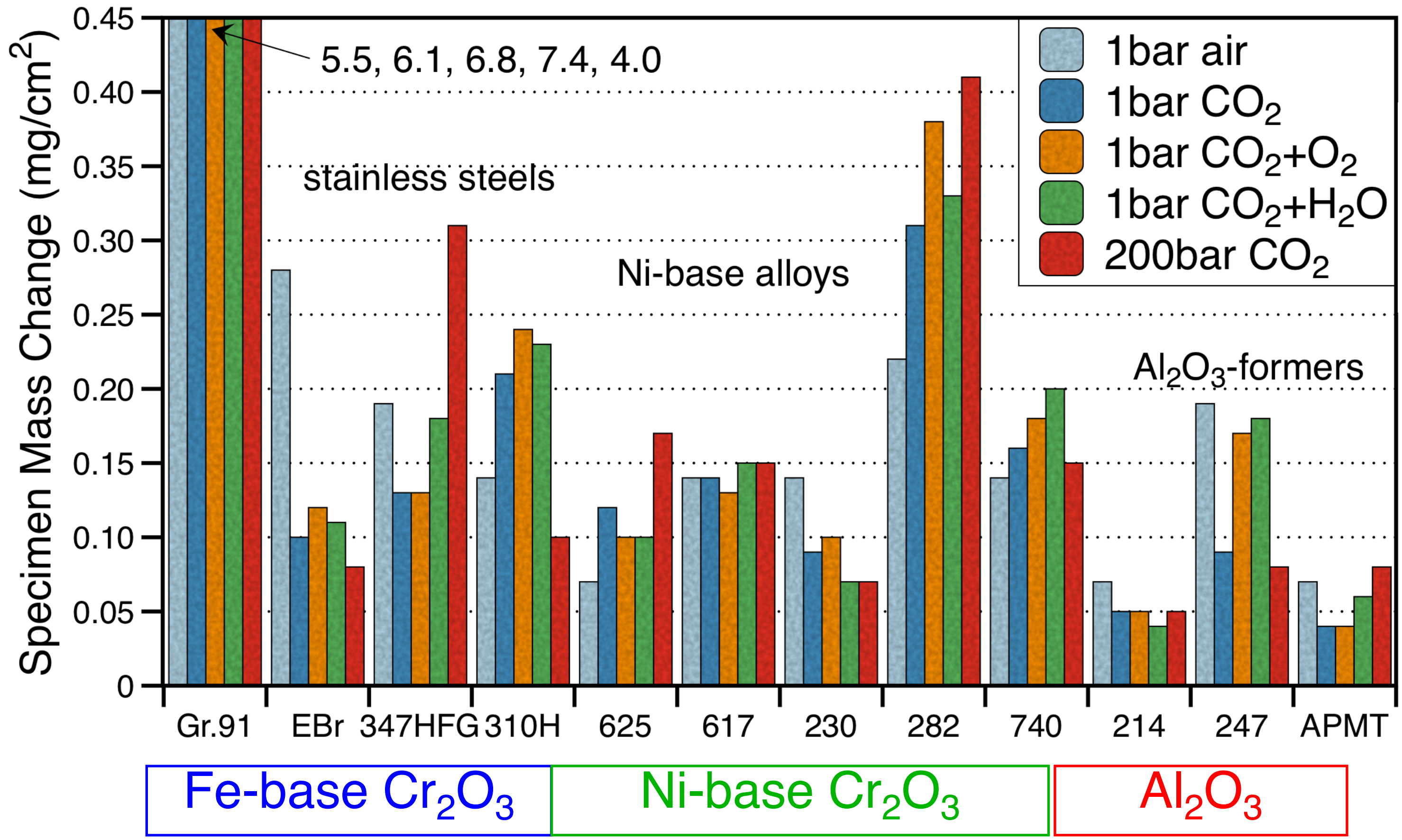




Industry interested in where low-cost alloys can be used

Baseline created at 750°C 1bar

Core 12 alloys, 1bar: dry air, CO_2, CO_2+10%H_2O



All 500h tests

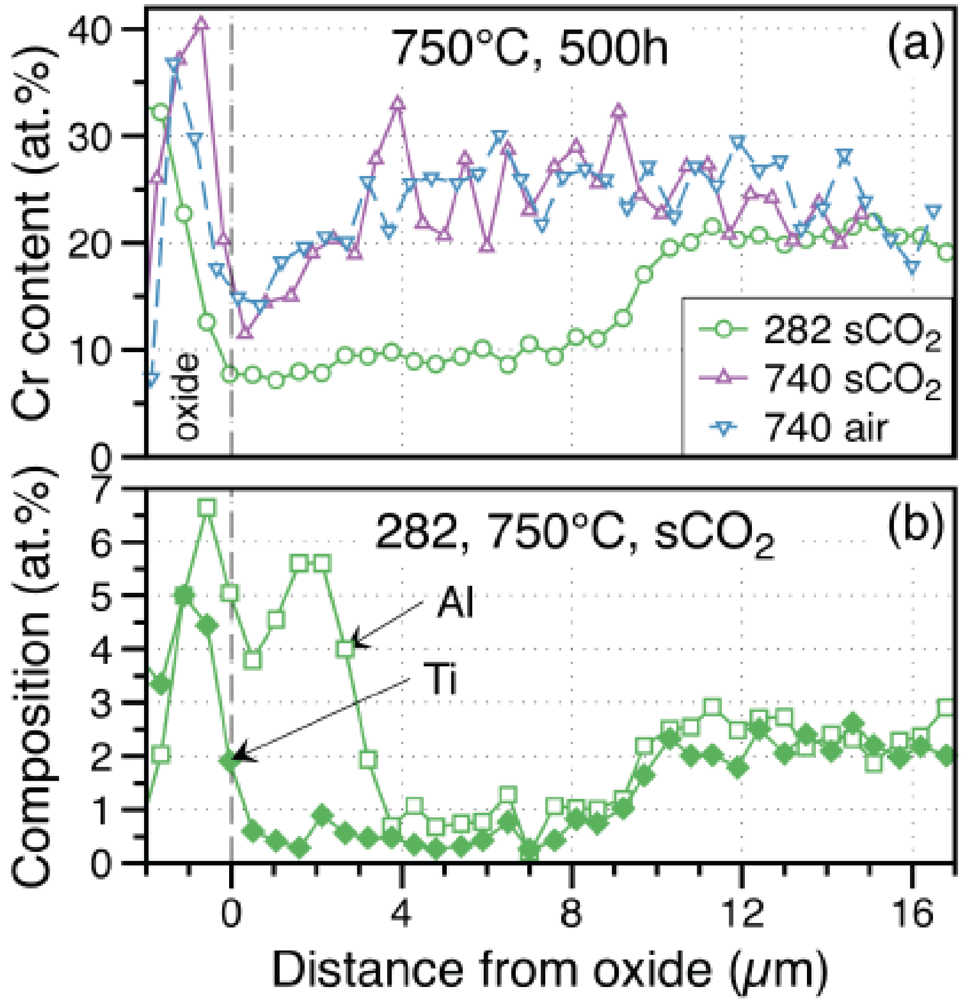
0.1 mg/cm² ~ 0.5 μm surface oxide

10 mg/cm² ~ 50 μm (2 mils)

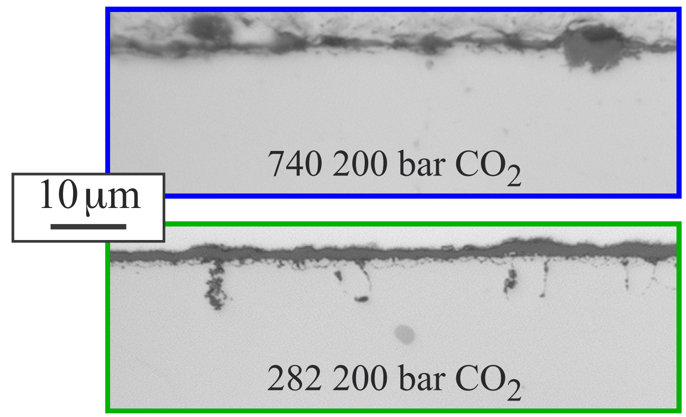
Consistently higher mass gains for alloy 282

282 deeper Cr depletion than 740

EPMA depth profiles beneath scale at 750°C



1 bar air vs. 200bar CO_2



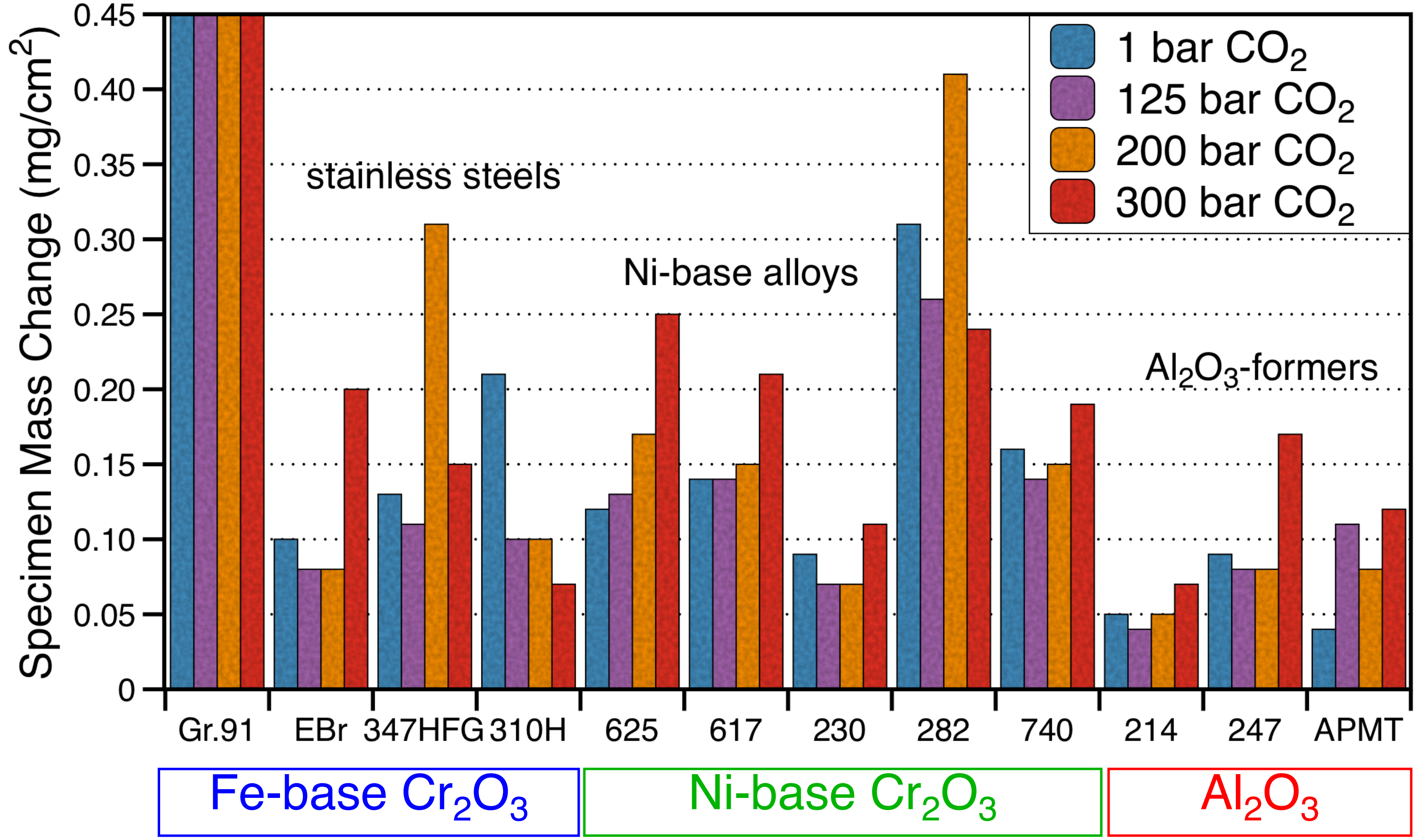
282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

740: 49Ni-24.6Cr-20Co-0.5Mo-1.3Al-1.5Ti

Little effect of pressure observed

500h exposures at 750°C

Core group of 12 alloys evaluated



All 500h tests

0.1 mg/cm² ~ 0.5 μm surface oxide

10 mg/cm² ~ 50 μm (2 mils)

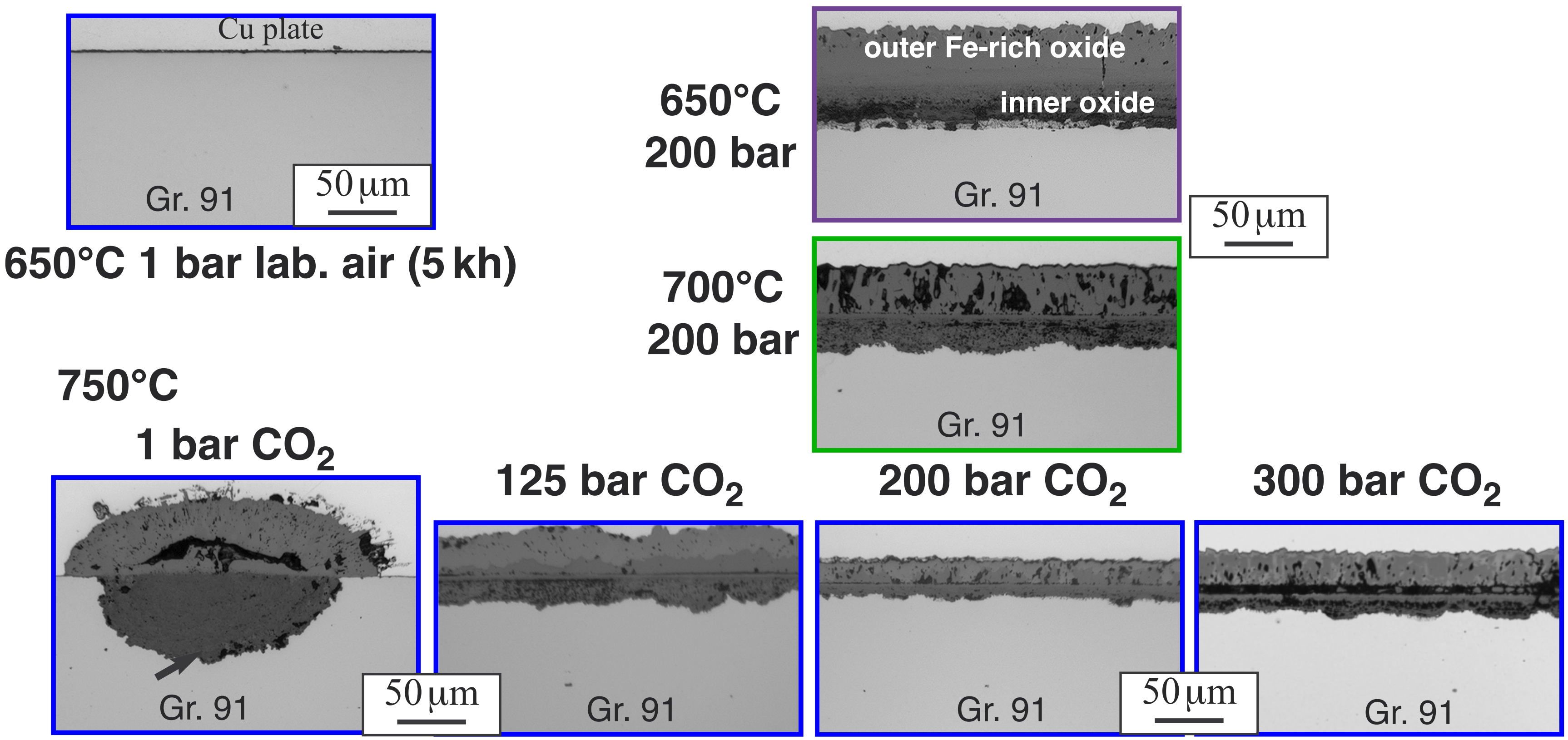
Typical Fe-rich oxide on Gr.91

However, inner/outer ratio appears to change with P

- Outer Fe_2O_3/Fe_3O_4 layer
- Inner $(Fe,Cr)_3O_4$ layer

Grade 91: Fe-9Cr-1Mo

Some thin-protective Cr-rich scale at 1bar

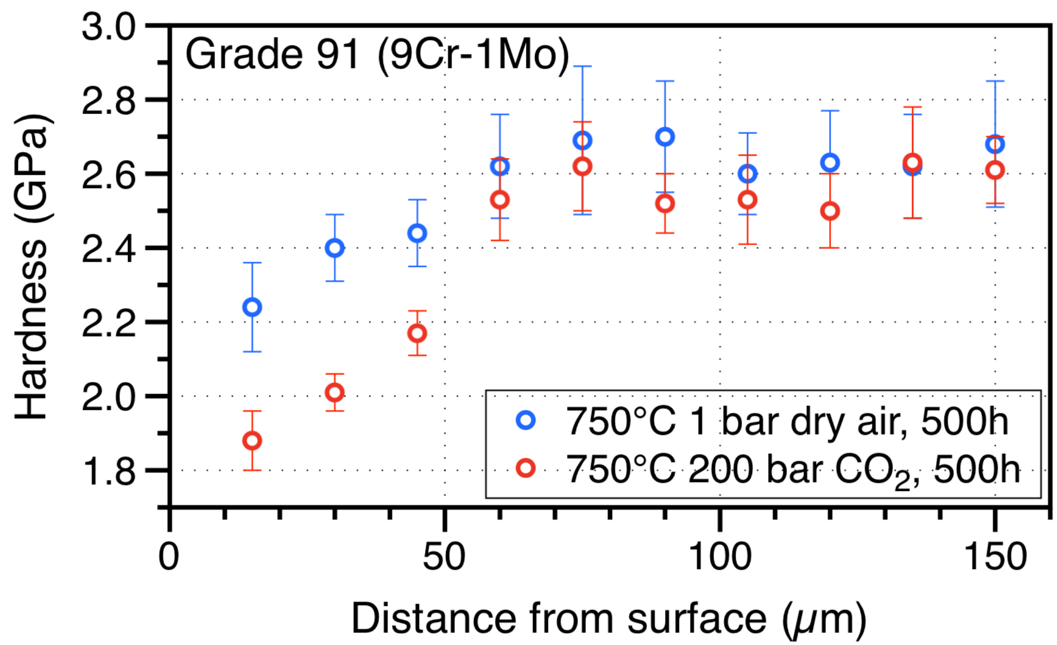


light microscopy of polished cross-sections

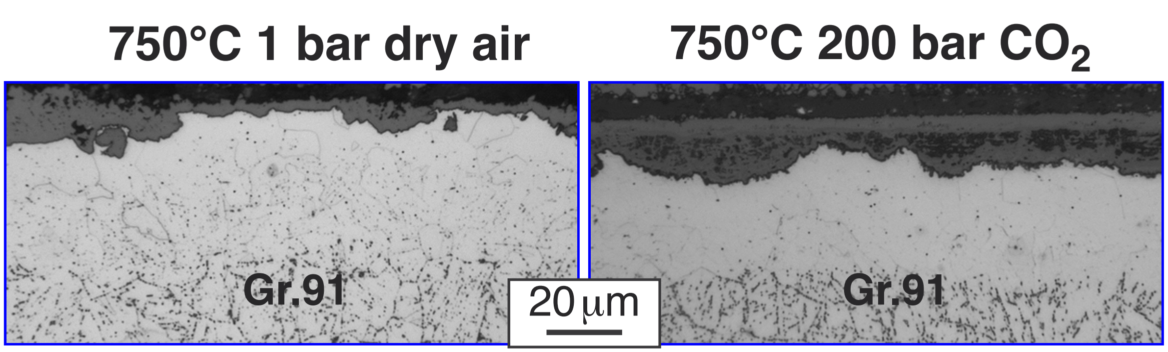
Looking for internal carburization

High a_c predicted, McCoy (1965) observed in 1bar CO_2

microhardness of Gr.91



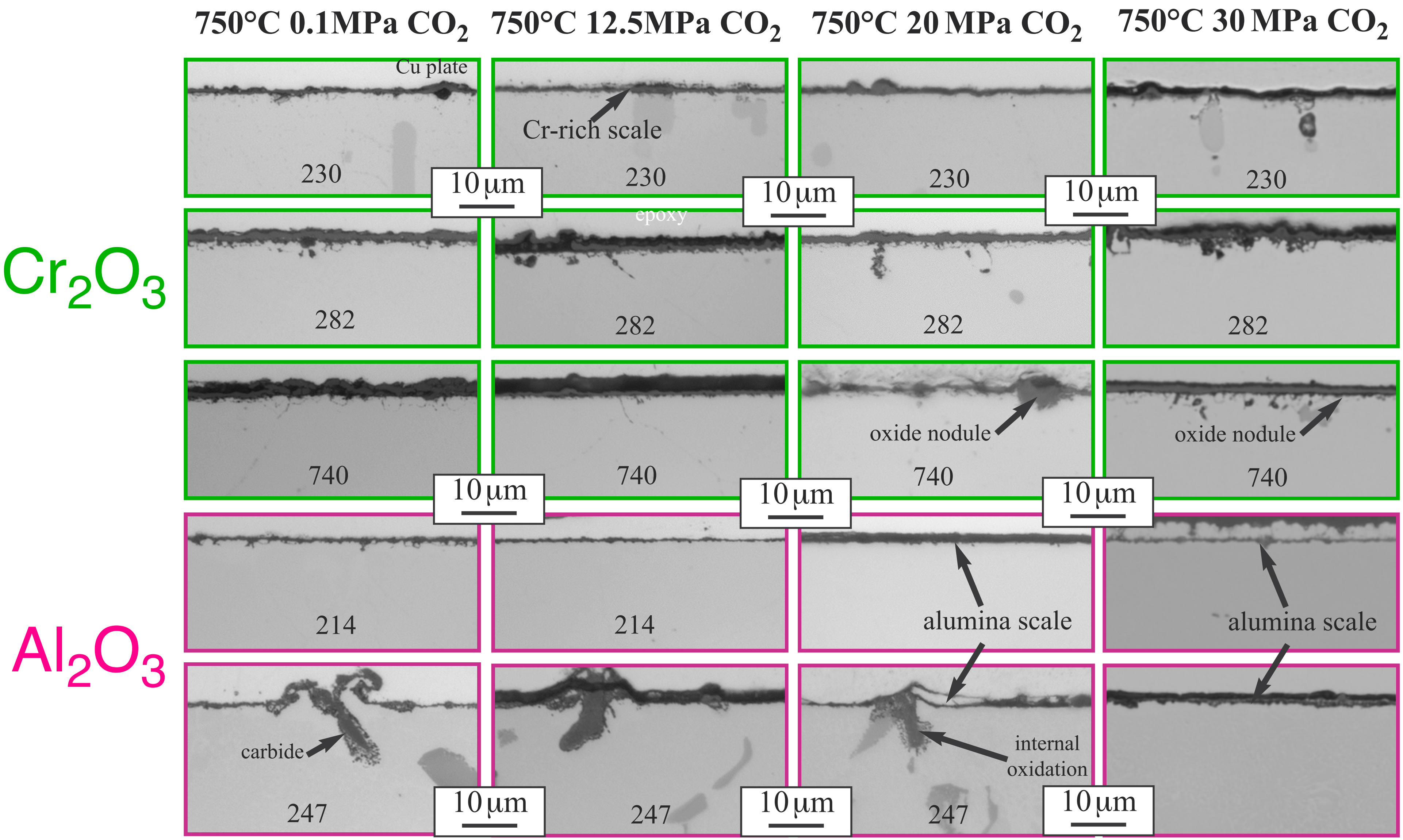
oxalic acid etch



Did Cr depletion dissolve the carbides at 750°C?

Ni-base alloys: thin scales

All thin Cr-rich or Al-rich scales at 750°C in CO_2

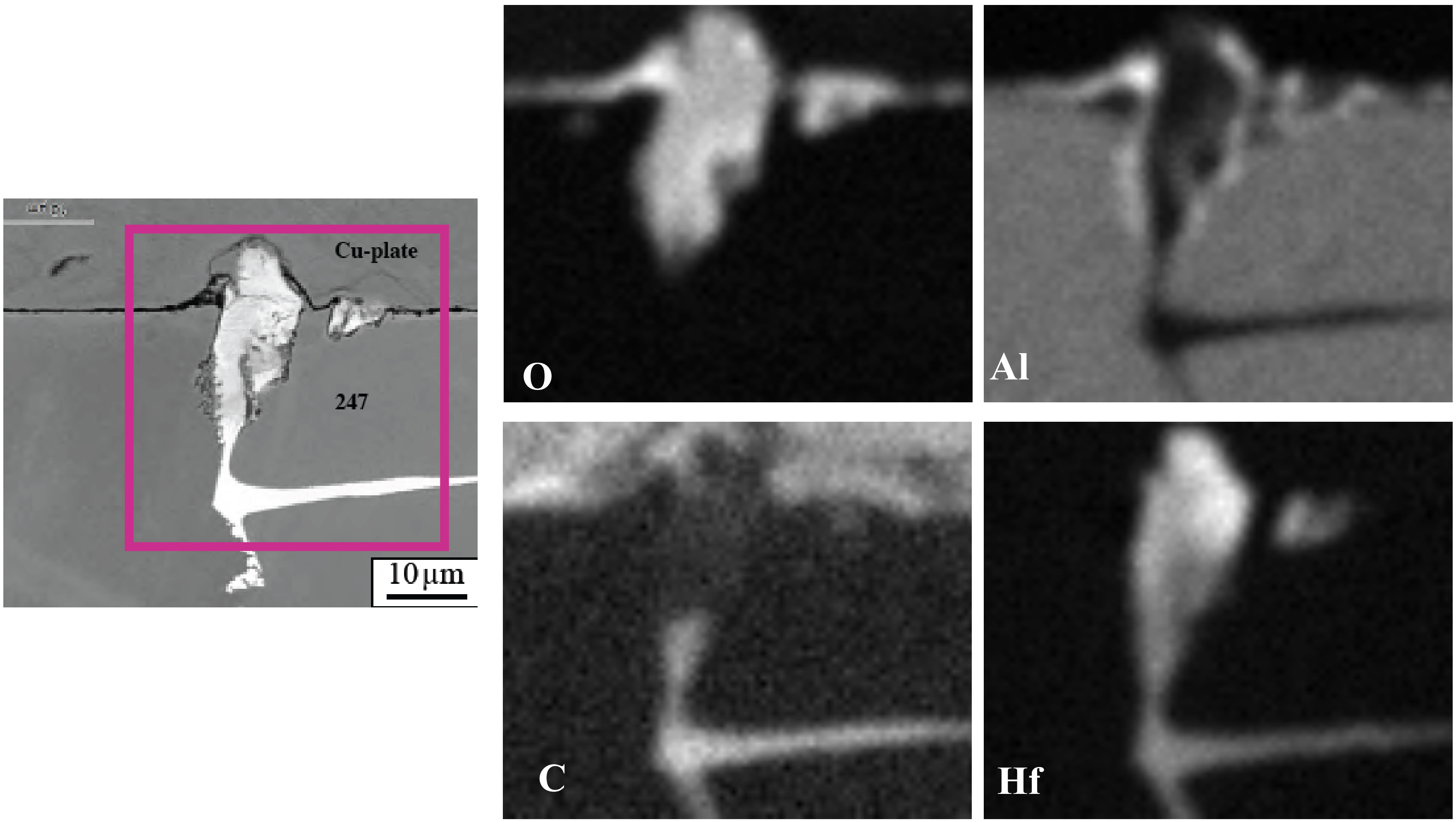


light microscopy of polished cross-sections

Hf-rich carbide oxidized in sCO_2

EPMA: carbide transformed to oxide at 750°C 20MPa

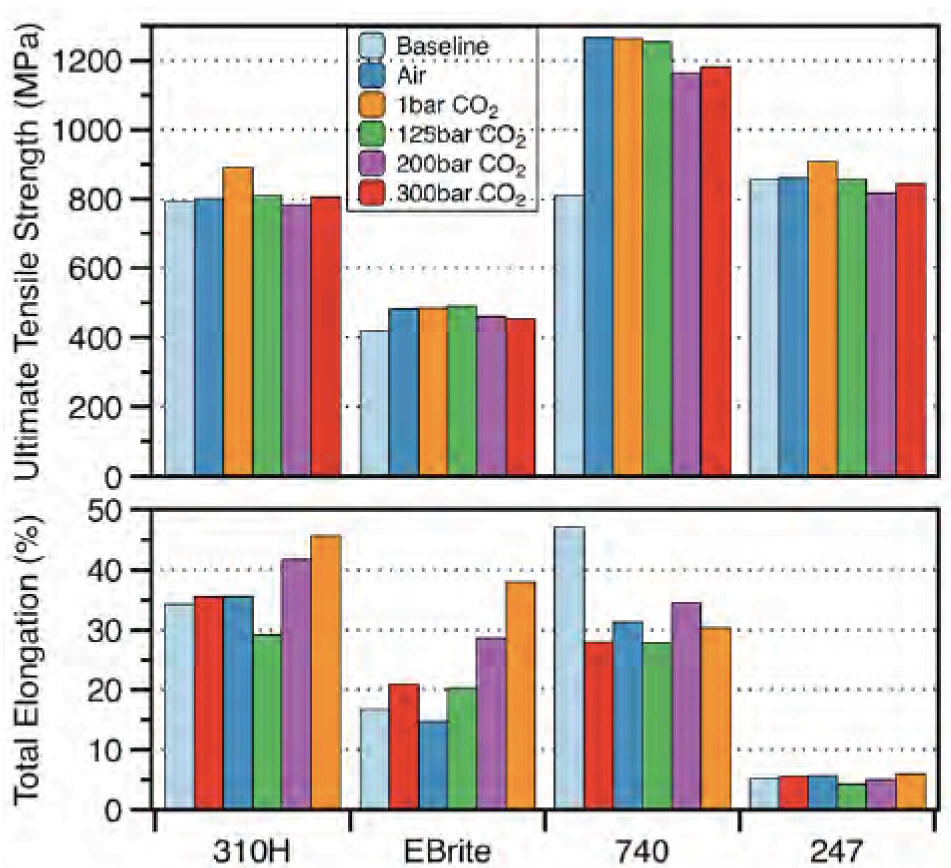
247: Ni-8Cr-6Al-10Co-10W-3Ta-1.4Hf



750°C: initial tensile experiments showed little effect of sCO_2

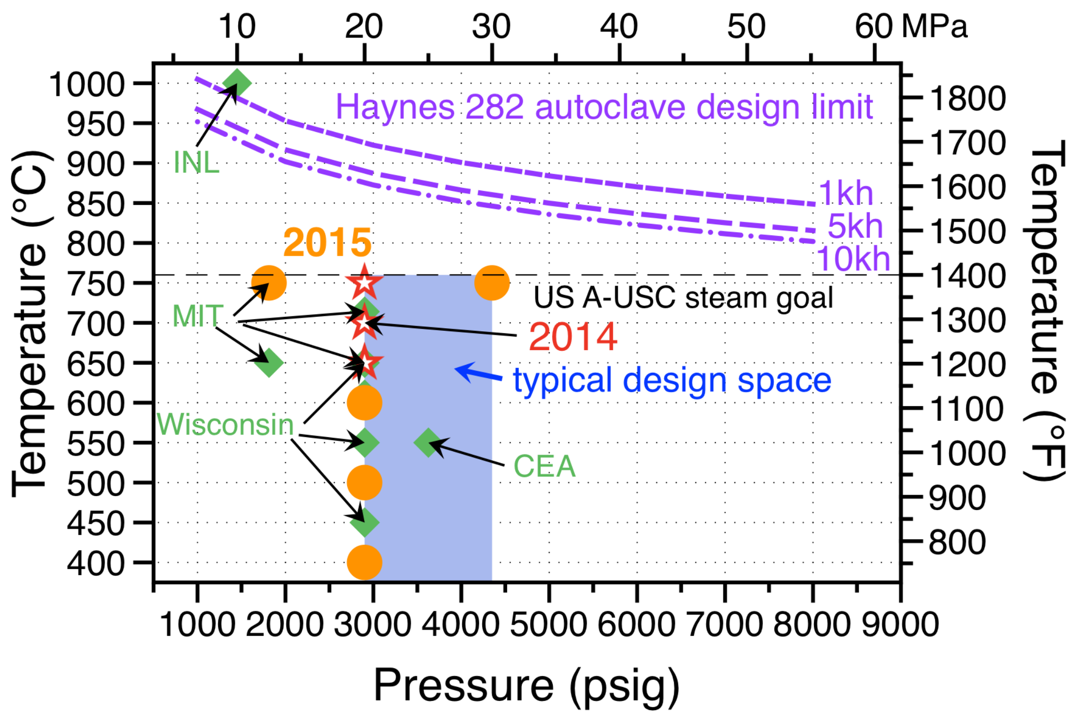
25mm tensile bars exposed at each condition

Tensile test at room temperature: 10^{-3}/s strain rate



sCO_2 Summary

Completed five 500h sCO_2 tests in 2015:



- Wide range of alloys exposed (12)
- Surprisingly little effect of pressure
- Little effect on 25°C tensile properties
  for alloys 740, 310HCbN, E-Brite & 247
- Fe-9Cr formed thick scales, similar to other studies

Future work

TBC project:

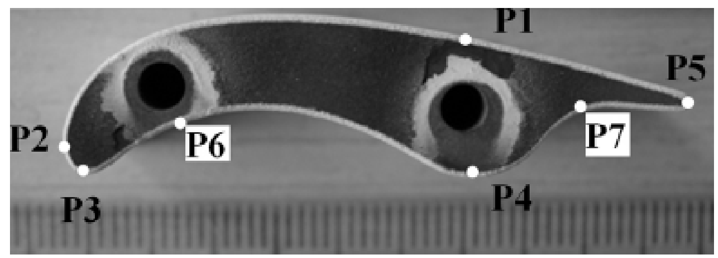
Long-term testing of rod specimens

Develop a path to deployment

- solicit OEM input
- next step: burner rig testing? provide samples
- address issues identified

Specimens with more complex geometry

Cranfield design:



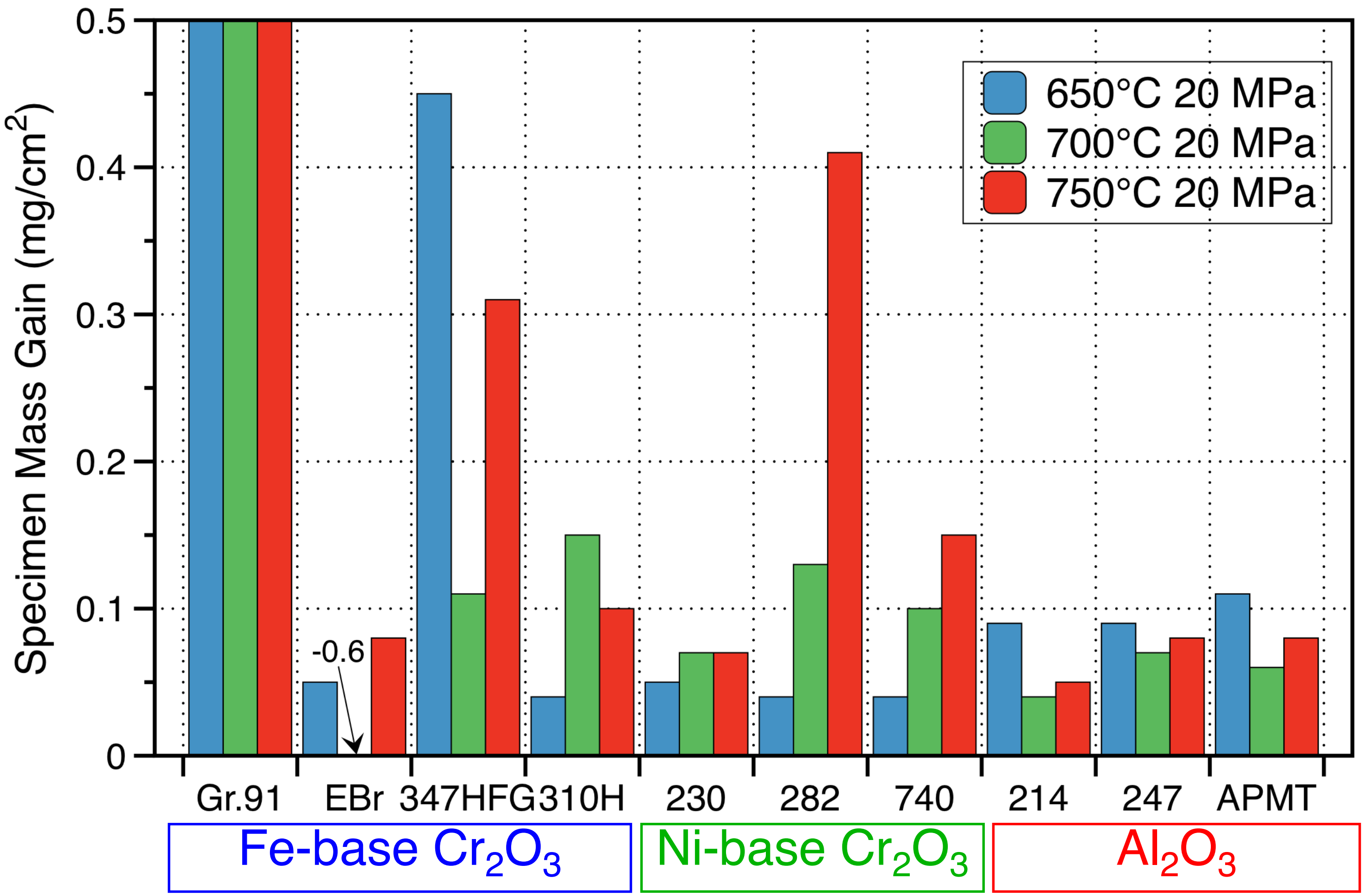
Supercritical CO_2:

- 2nd autoclave for impurity effects (measure in + out)
- developing on-line O_2, H_2O detector at pressure
- long-term exposures at 750°C/300 bar (30 MPa)

backup slides

1st: 20MPa runs, most low gains

10 representative alloys were focus of metallography

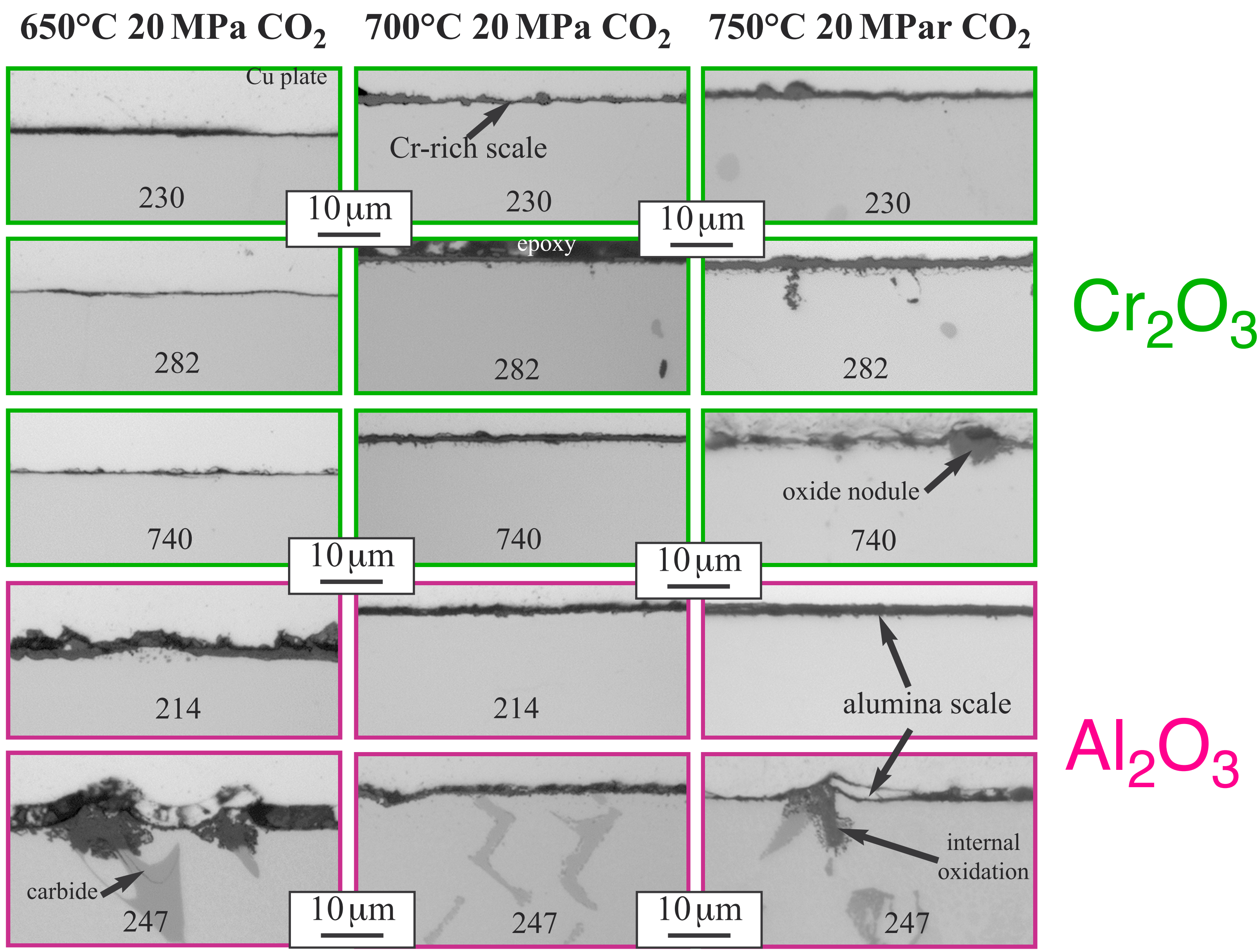


0.1 mg/cm² ~ 0.5 μm surface oxide

10 mg/cm² ~ 50 μm (2 mils)

Ni-base alloys: thin scales

All thin Cr-rich or Al-rich scales in 20 MPa sCO_2

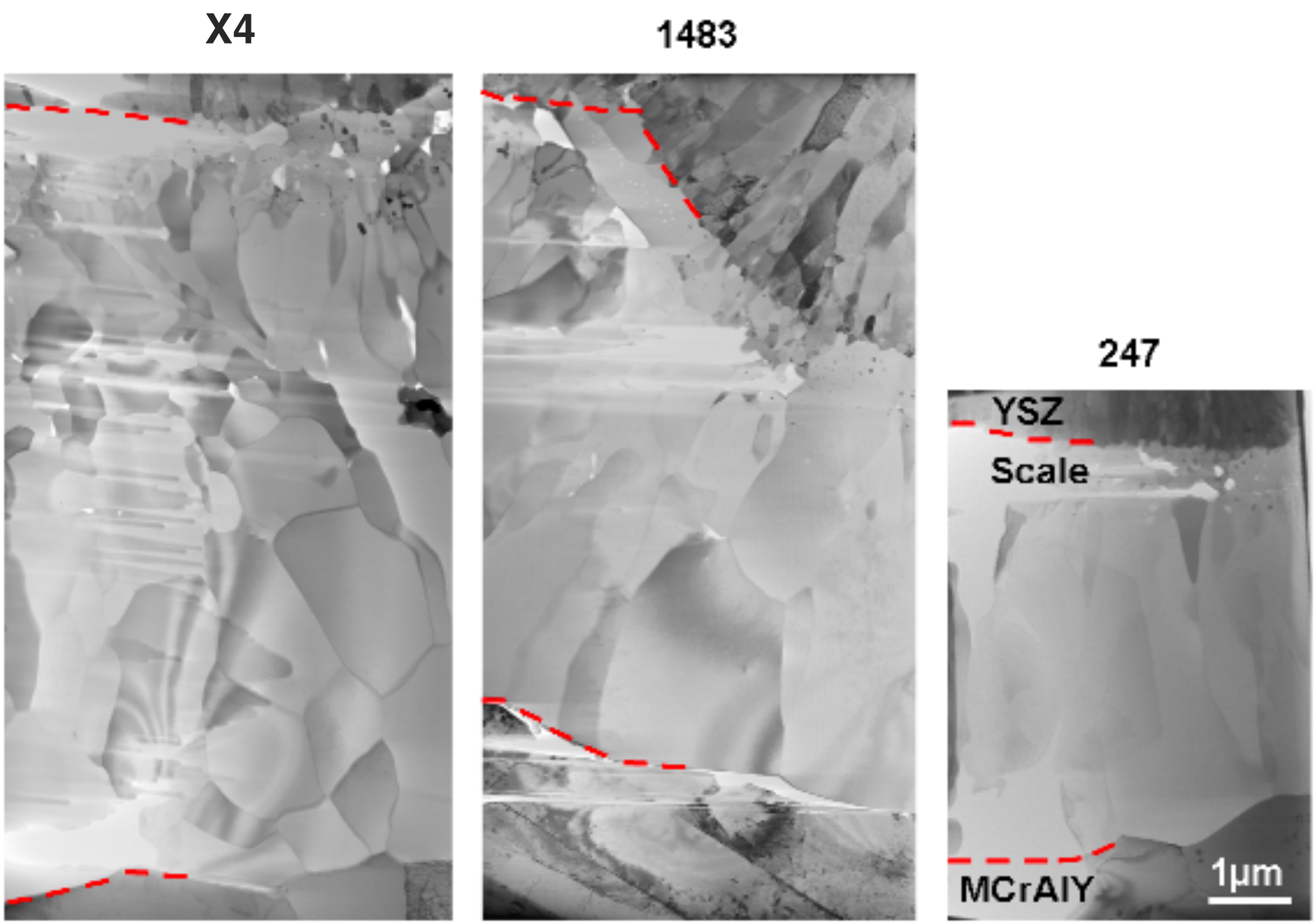


Thoughts

More characterization needed of current results
- Better understand some unusual results

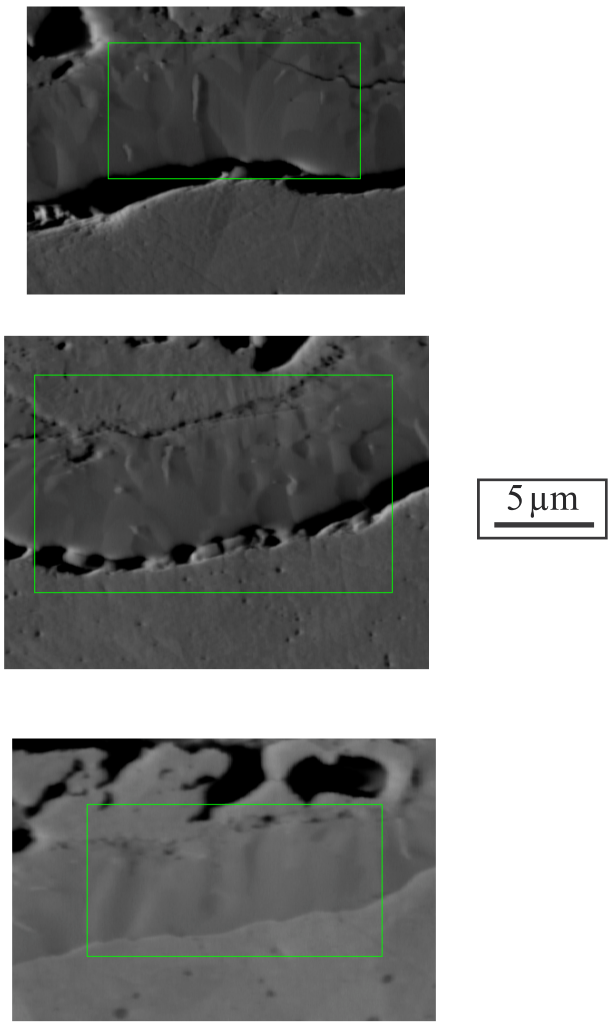
Concern:
- Degradation by C penetration through Cr_2O_3
  - H. McCoy 1965 at 1bar
  - D. J. Young et al. (2011-2014) at 1bar
- Need to evaluate longer times + ex-situ ductility
- Al_2O_3 thought to be better barrier to C ingress
  - Pre-oxidation may assist in Al_2O_3 formation
  - Al-containing alloys can be difficult to fabricate

Possible to make FIB/TEM specimens but not as “pretty” as model systems

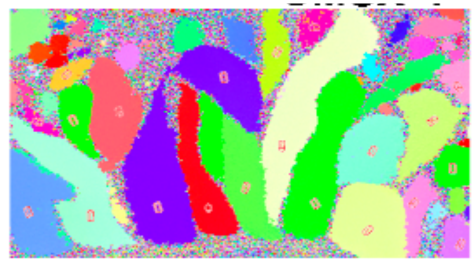


Each specimen failed after 480 1-h cycles at 1100°C

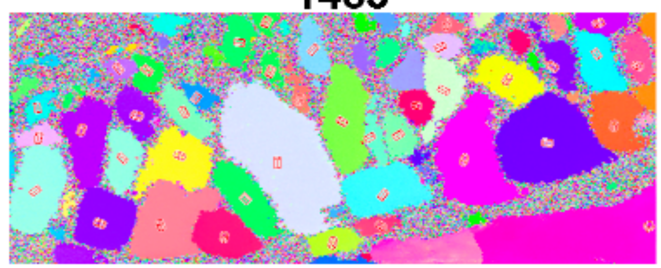
EBSD showed more fine grains for scale formed on 1483 with highest Ti content



X4

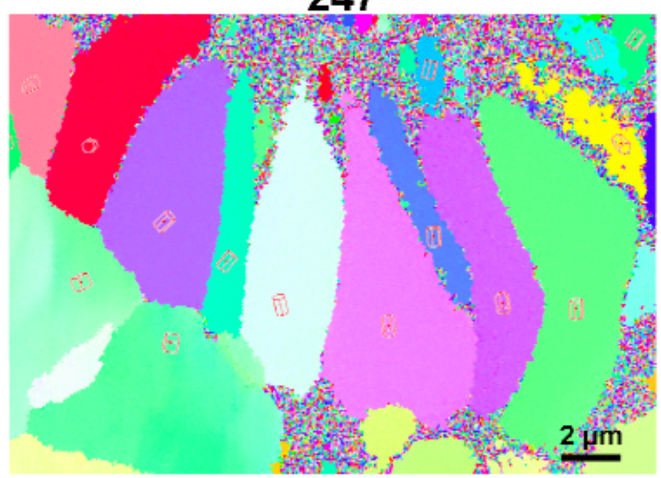


1483



Smallest grains

247



Each specimen failed after 480 1-h cycles at 1100°C