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

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Turbine Program (P. Burke, project manager)

Acknowledgments

TBC Task leaders: J. A. Haynes - coating procurement
M. J. Lance - characterization (PSLS)
S. Sampath, Stonybrook U. - processing

G. Garner, M. Stephens - oxidation experiments

sCO_2: Jim Keiser - autoclave design
Mike Howell - construction and operations
Robert Brese - UTenn PhD student

T. Lowe - characterization; T. Jordan - metallography
D. W. Coffey - TEM specimen preparation, FIB
D. Leonard - EPMA

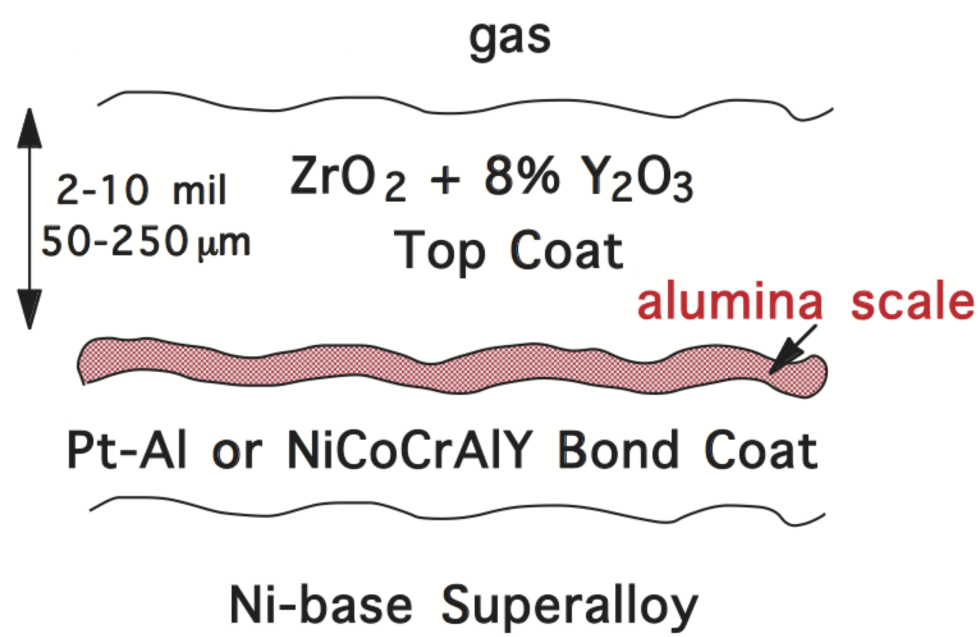
Superalloys: Howmet, Siemens, Capstone Turbines
Alloys: Haynes, Special Metals, ATI, Sumitomo, Sandvik...

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

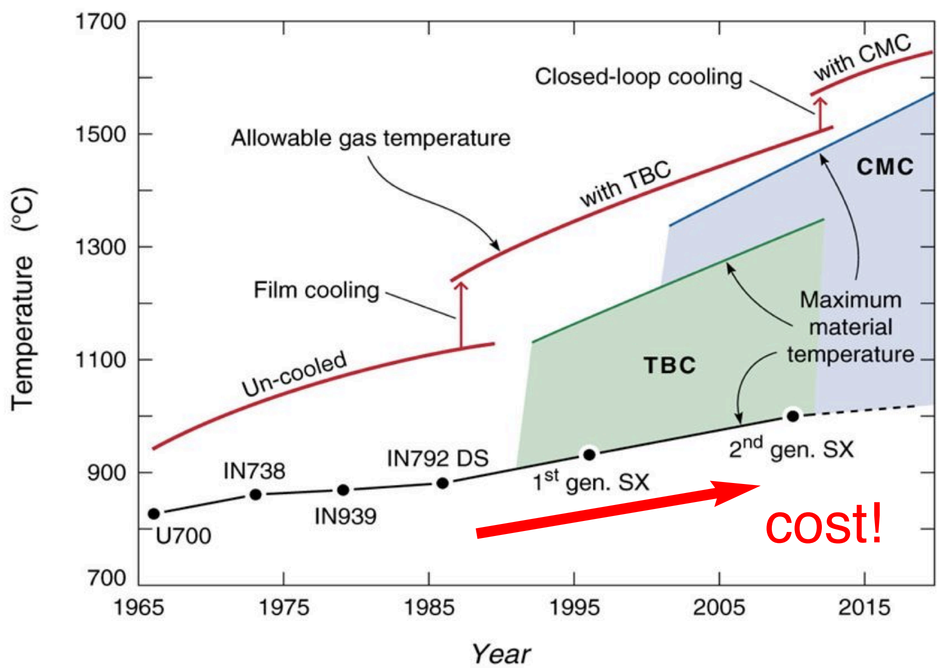
#2 Focus on alumina scale as "weak link"

Coatings for Syngas-H_2 Turbines

Focus on thermally sprayed coatings

Land-based turbine drivers:

- first cost drives sales
- temperature/efficiency (not with cheap gas)
- hot corrosion in blade root (want higher Cr)

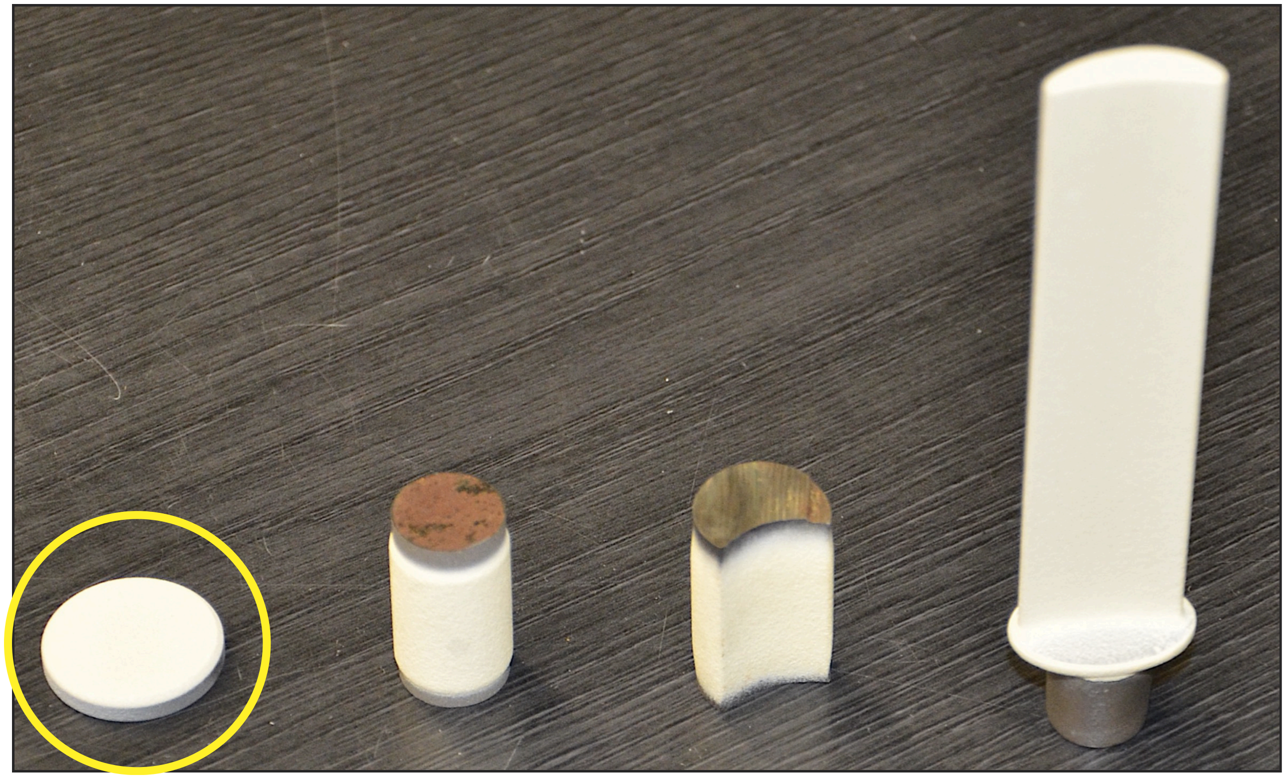


MarM247 <- PWA1483 <- CMSX4

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

"de-evolution"

Moving towards coating more realistic substrates



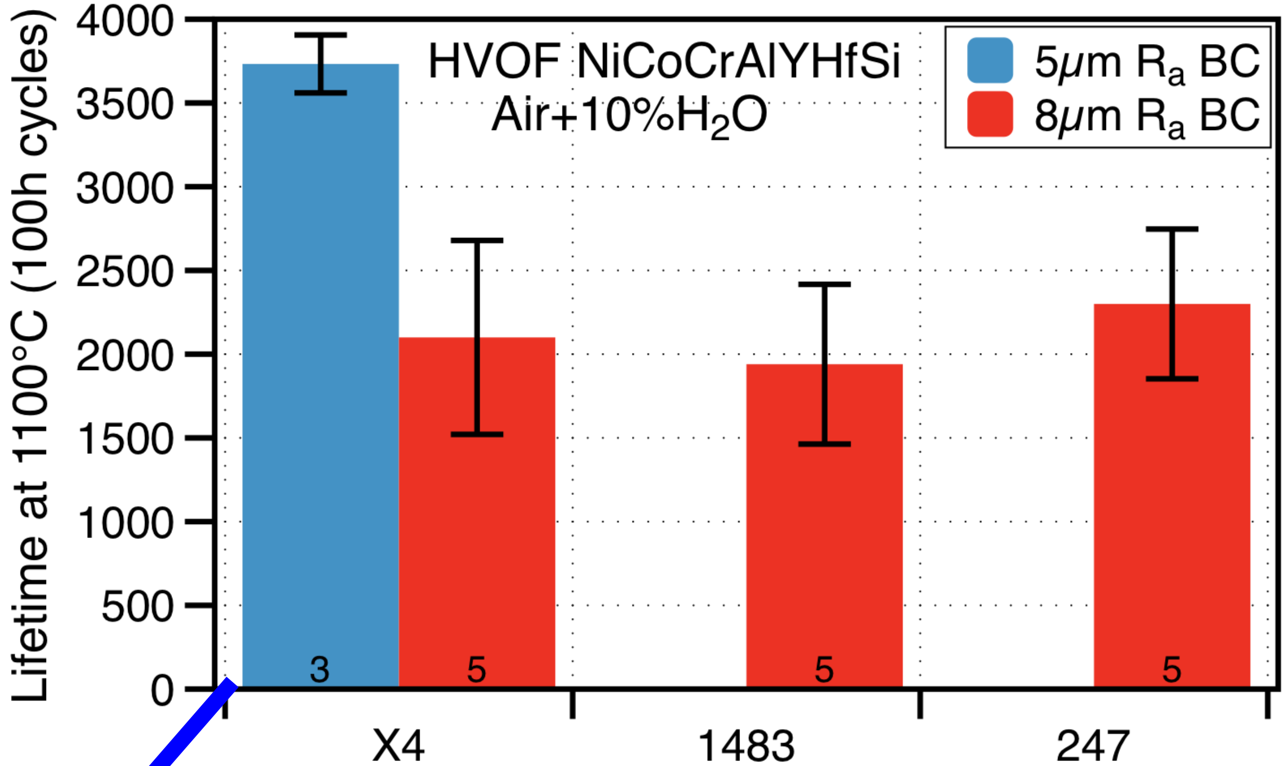
FY10-FY14: typical disks/coupons

B. A. Pint, K. A. Unocic and J. A. Haynes, “The Effect of Environment on TBC Lifetime,” J. Eng. Gas Turb. & Power, 138 (8) (2016) 082102.

Turbo Expo 2015 Best Paper award
Manufacturing Materials & Metallurgy Committee

Some things we did not plan to study

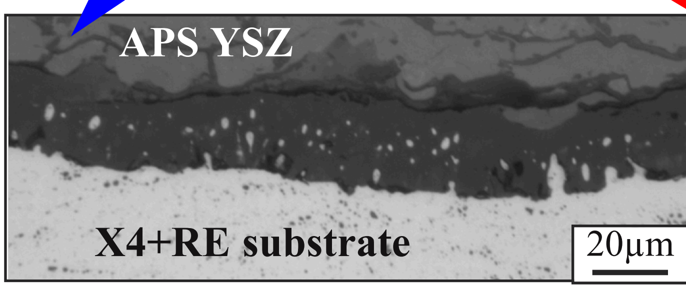
Like the need for "good" roughness

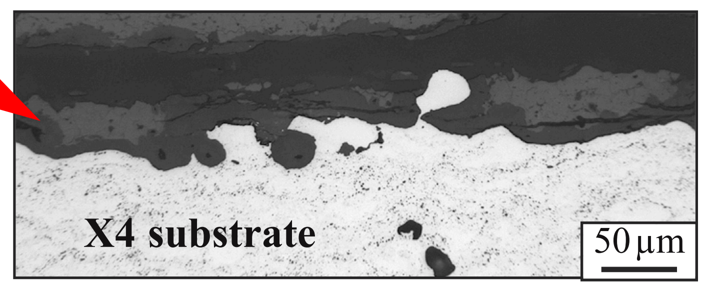


1100°C
2012°F

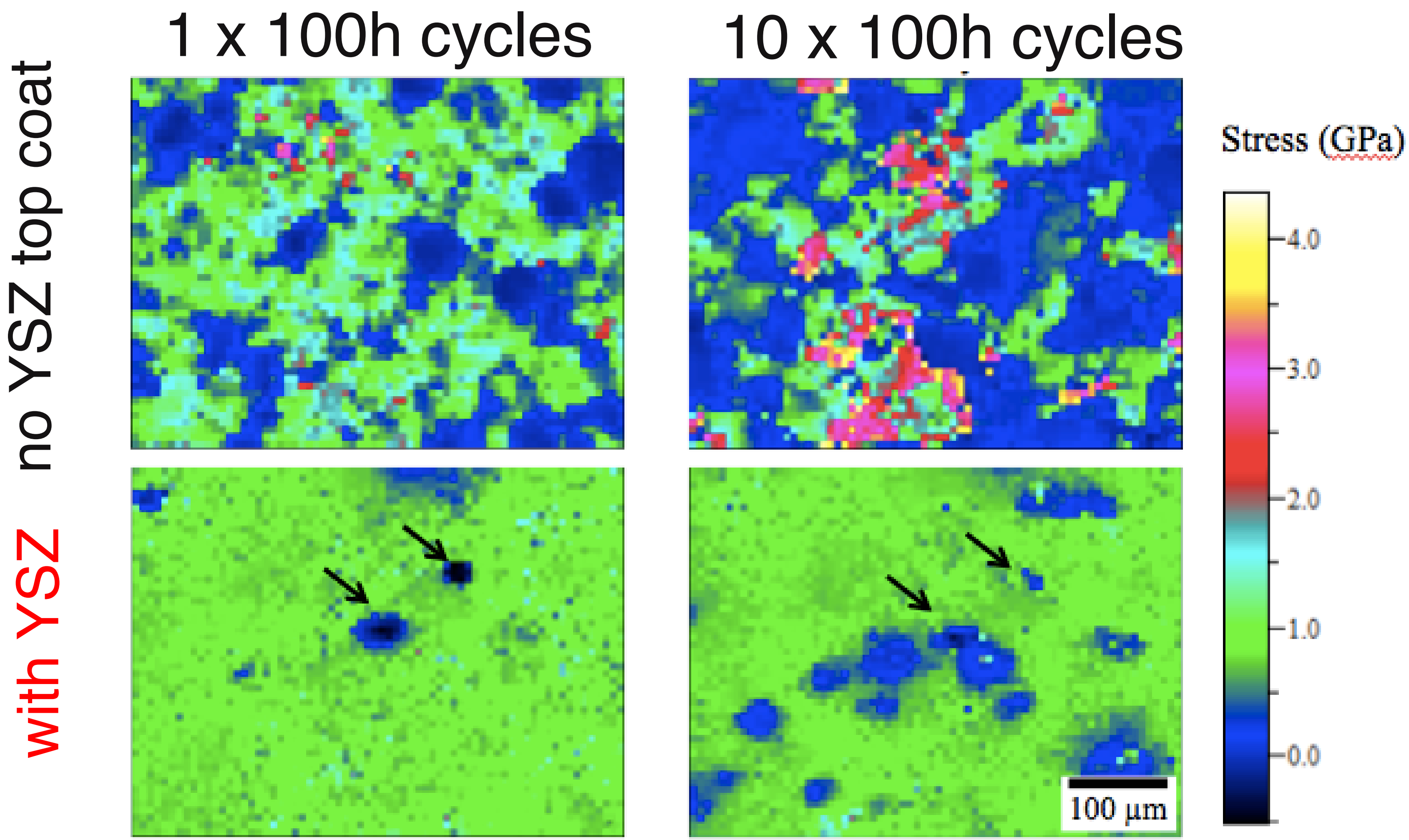
10% H_2O simulated exhaust

5.8wt.%Al 3.4%Al 5.5%Al



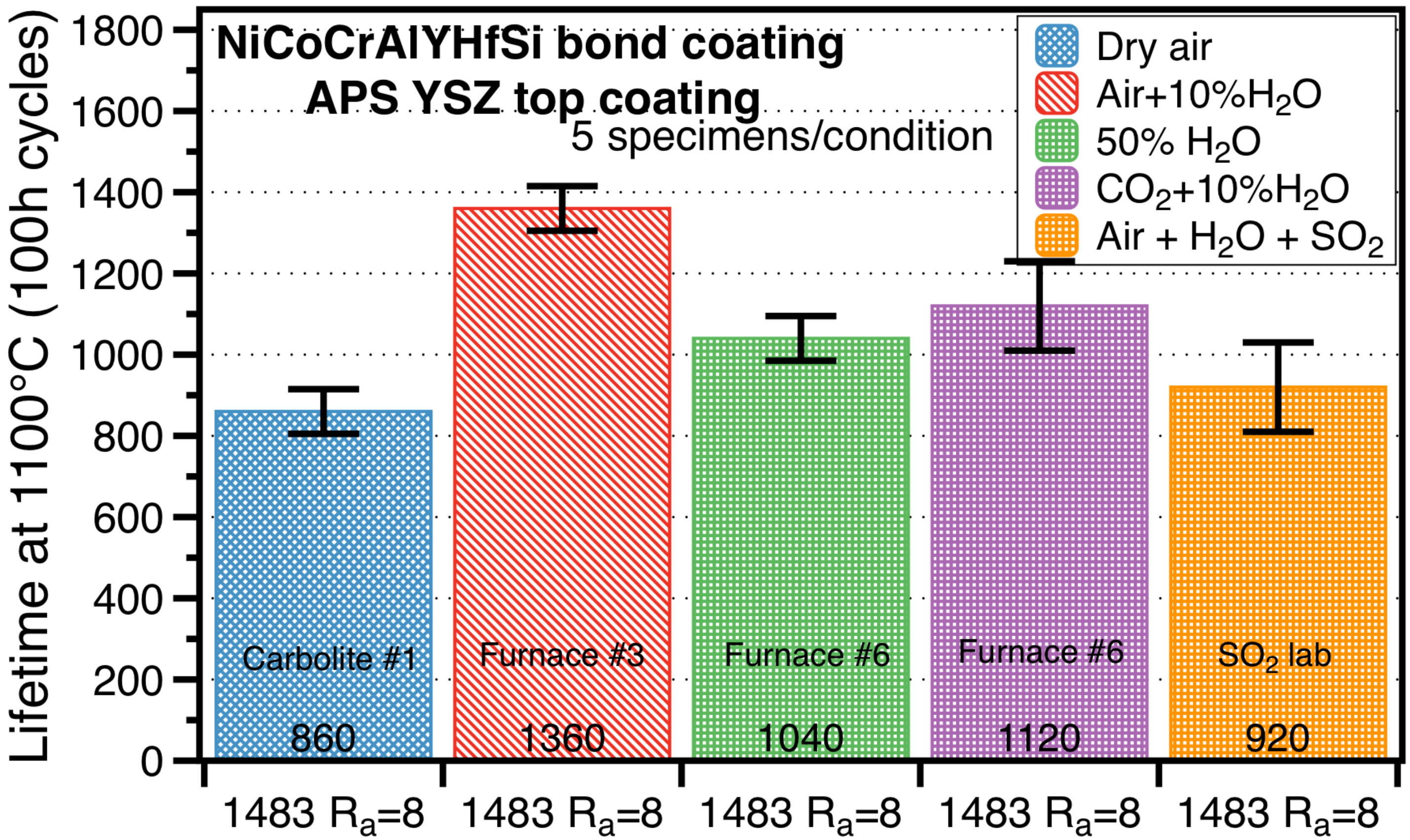


PSLS: Alumina residual stress without a top coating is less meaningful



HVOF MCrAlYHfSi/APS YSZ on 1483 in 50%H_2O

Environment did not affect lifetime with 100-h cycles and thin bond coating



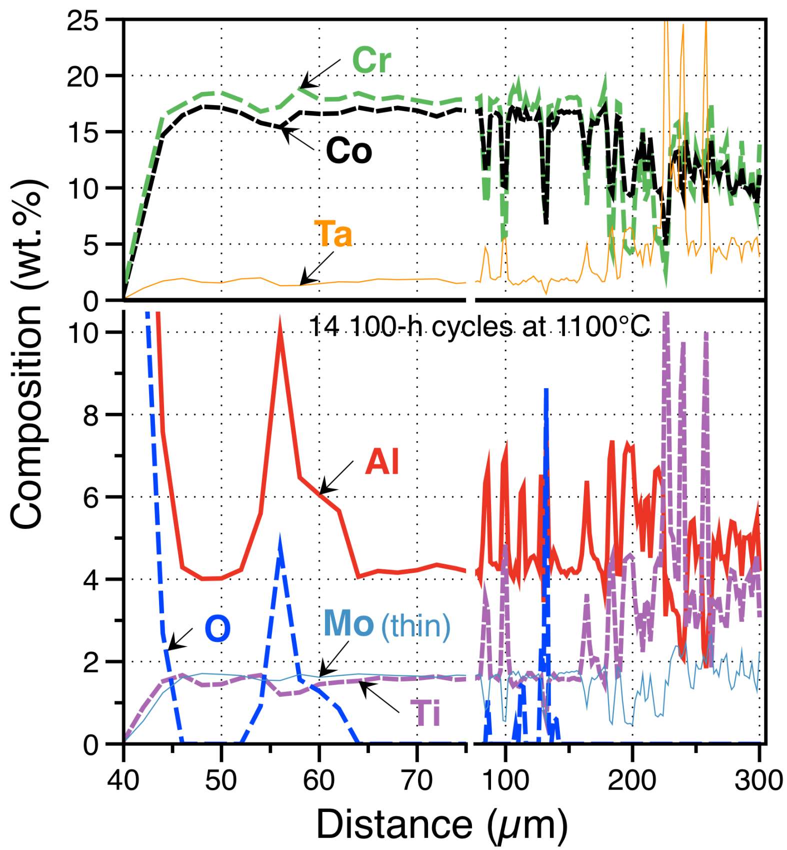
Five samples per group with 1483 substrate

1100°C, 100-h cycles

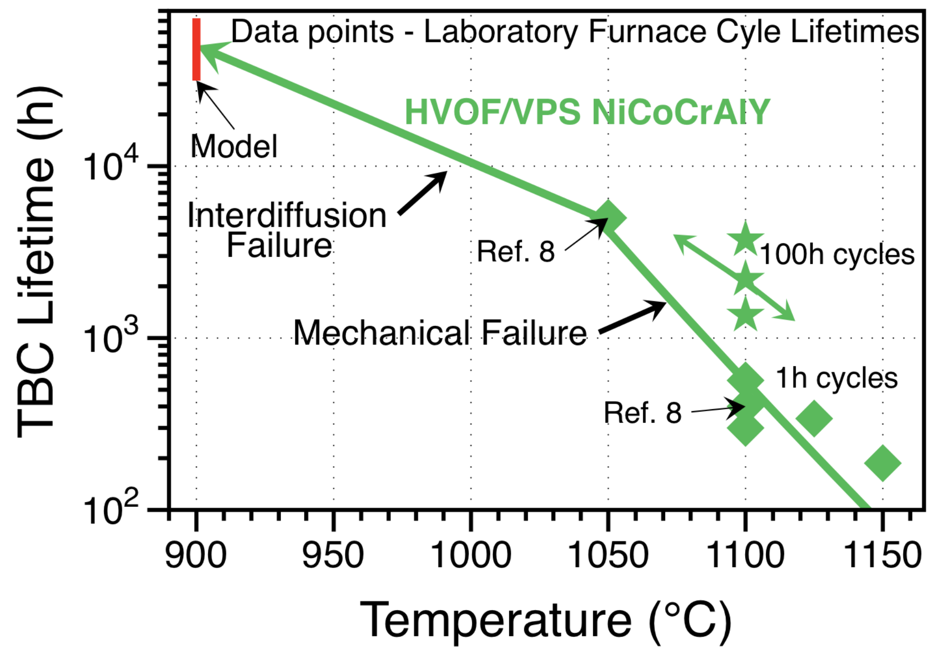
Air with 10%H_2O showed longest lifetime!

Al diffusion limits 100 h cycle life

Especially interdiffusion with 3%Al 1483



1483 substrate: 1400h 1100°C

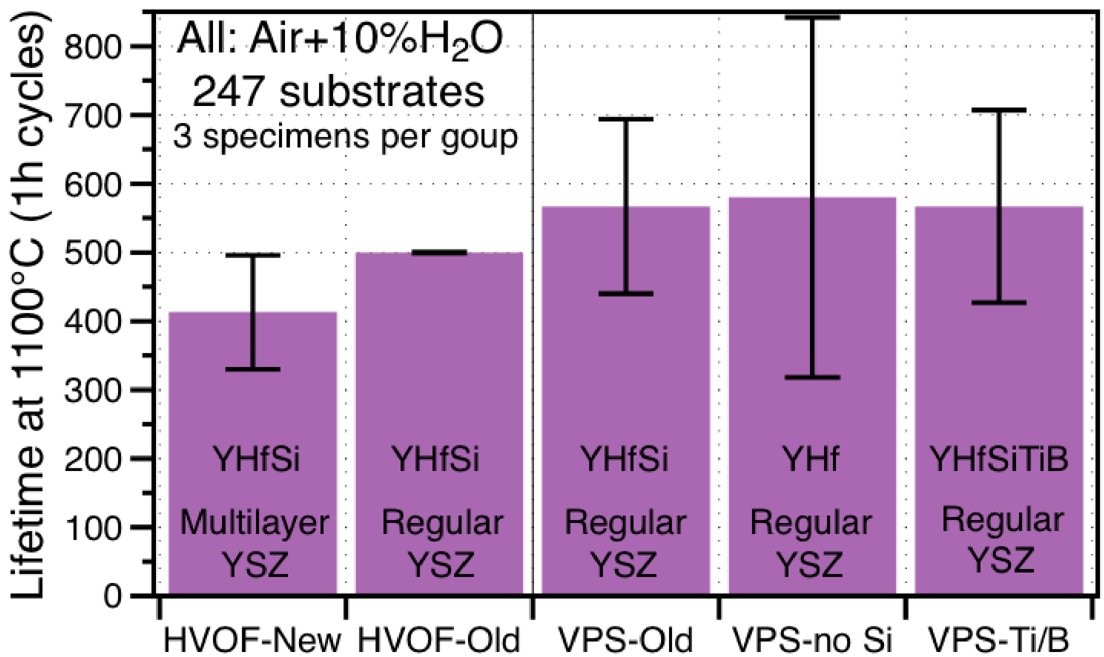


Eschler, Renusch, Schütze 2004+2008

If interdiffusion limits life, does environment matter?

Could other bond coatings do better?

Last group questioned whether coupons were a good method

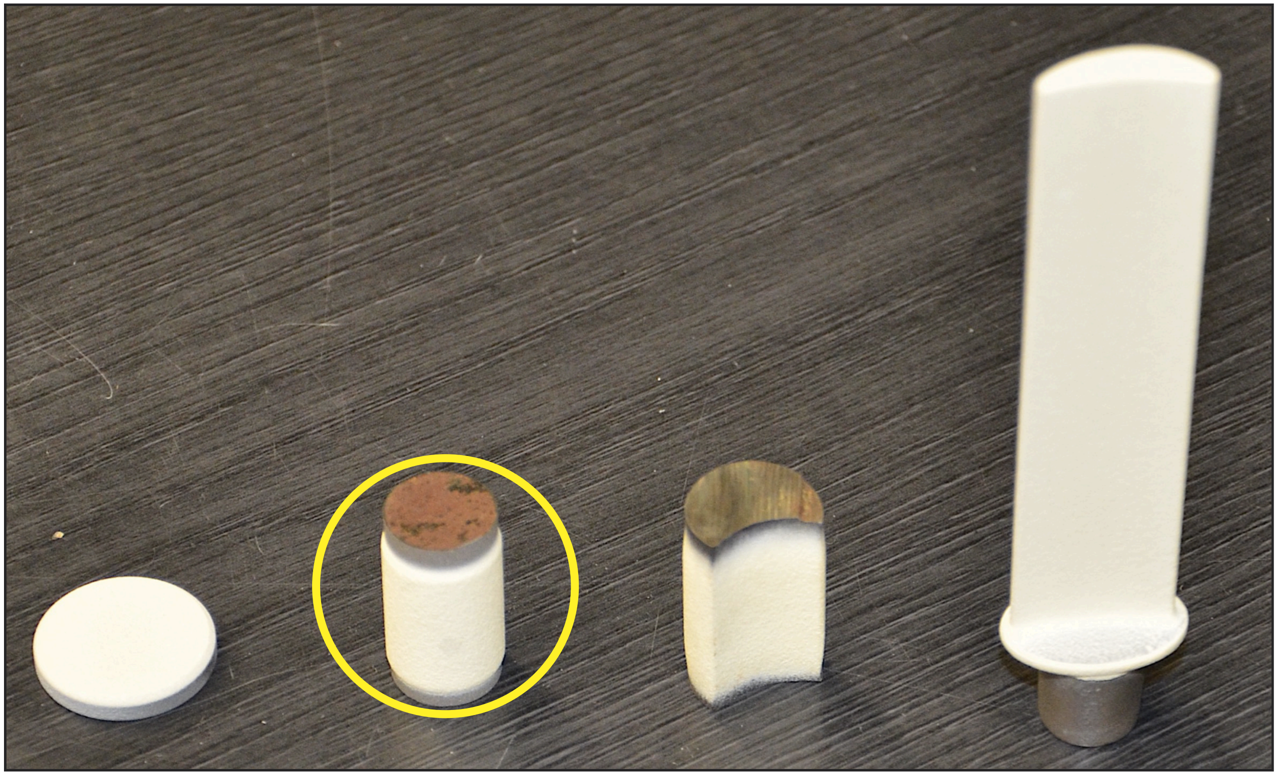


1100°C, 2012°F
1-h cycles
air + 10%H_2O
247 substrates
3 specimen average

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 effect of four parameters studied

I thought it would be easy to change to rod specimens

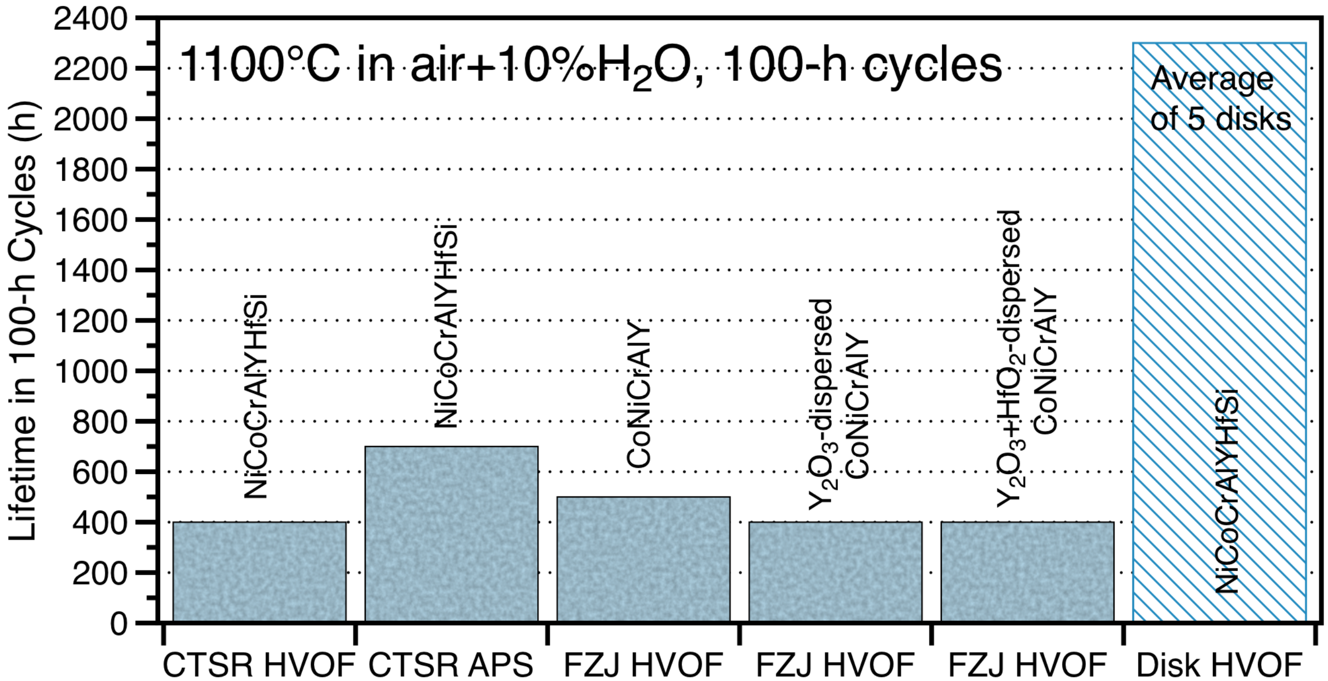


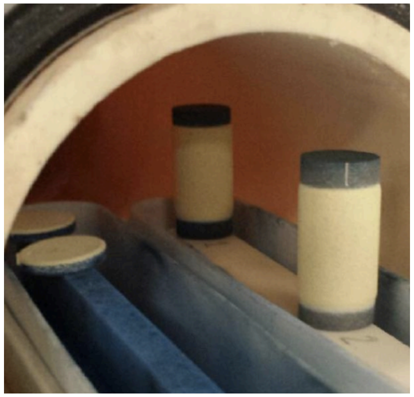
FY15: coat and test rod specimens

First step in moving towards commercialization

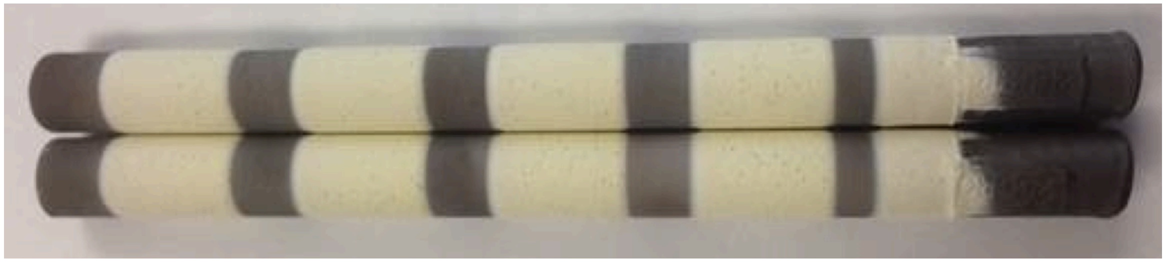
e.g. industrial partner, burner rig testing

Rod lifetimes were much lower than previous results

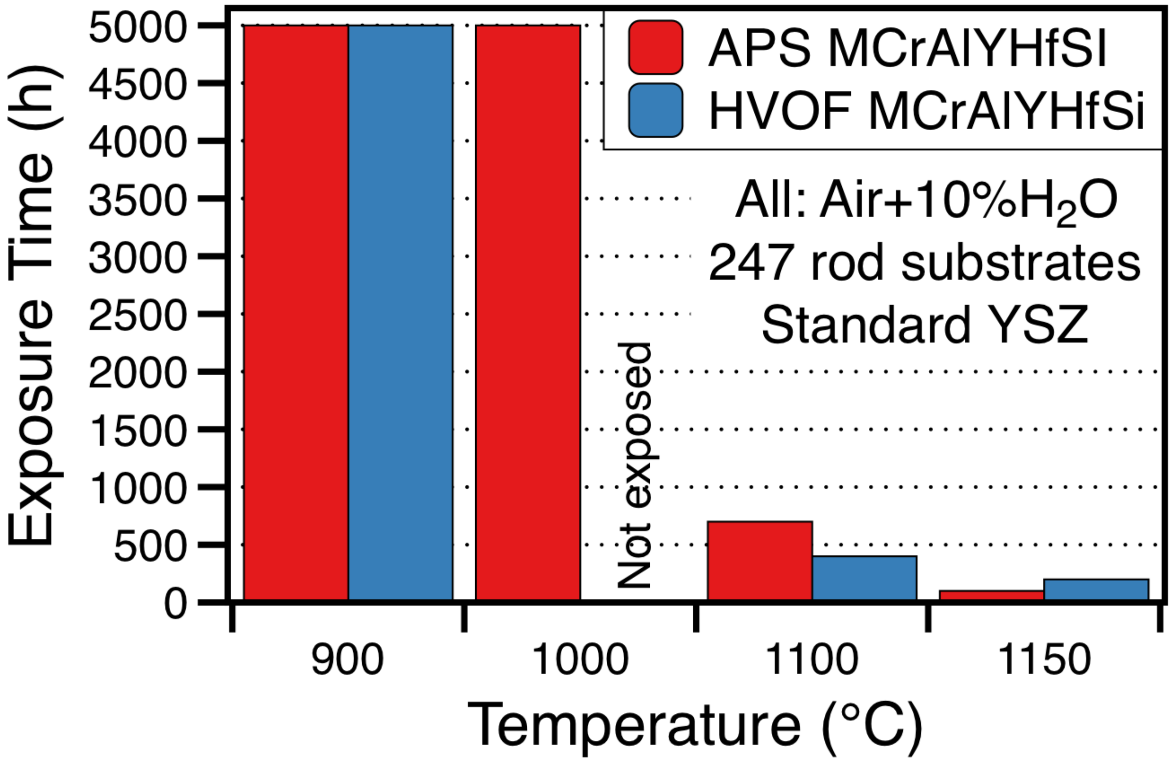


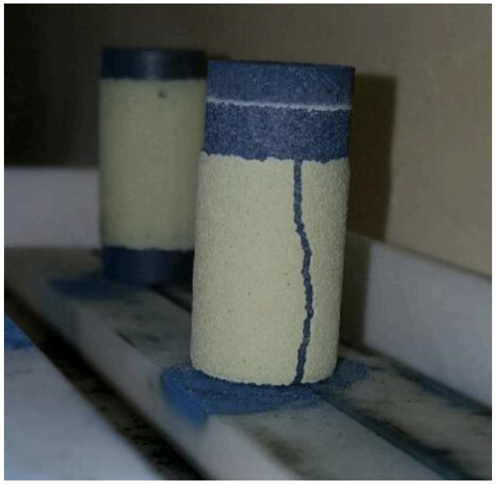


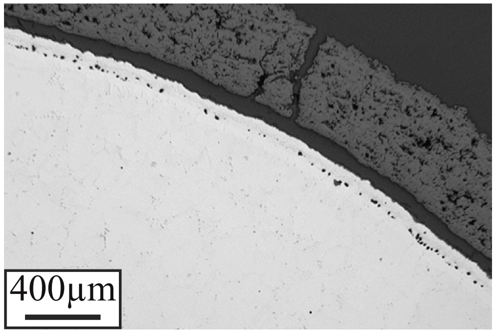
Rods: only single specimens (average for 5 disks)



Lower exposure temperatures were used to get long lifetimes



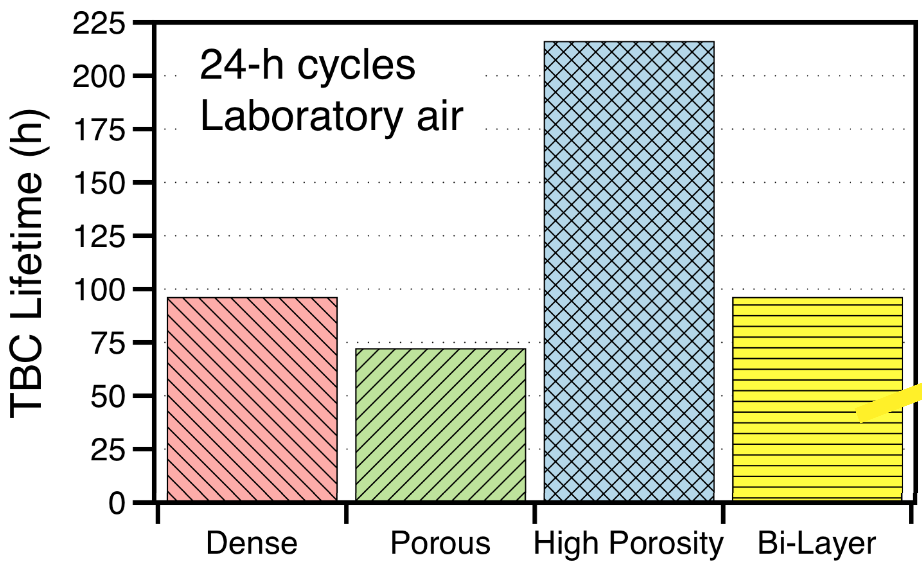


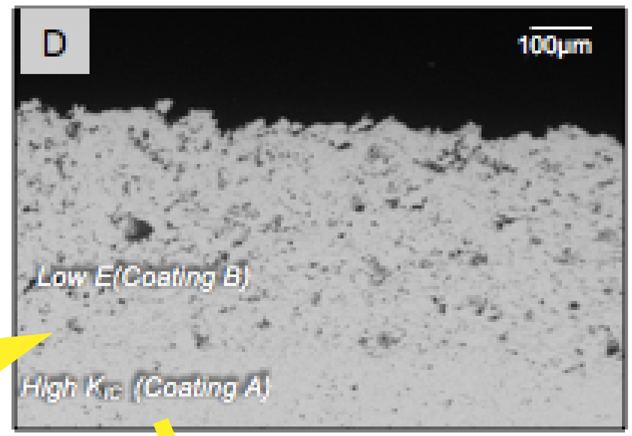


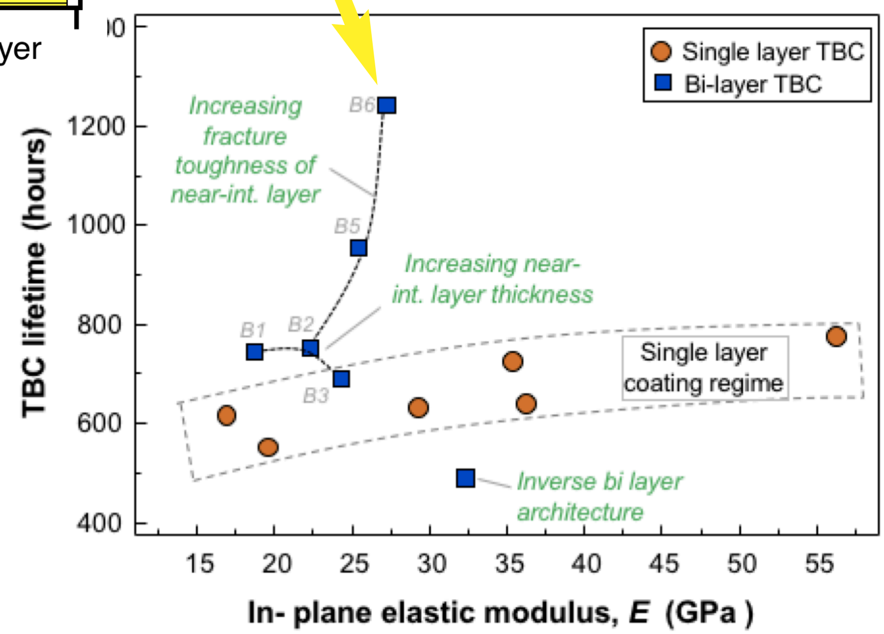
900° and 1000°C to support modeling effort

1150°C: mistakenly thought lifetime would be high

Stonybrook has worked to optimize coatings on rods

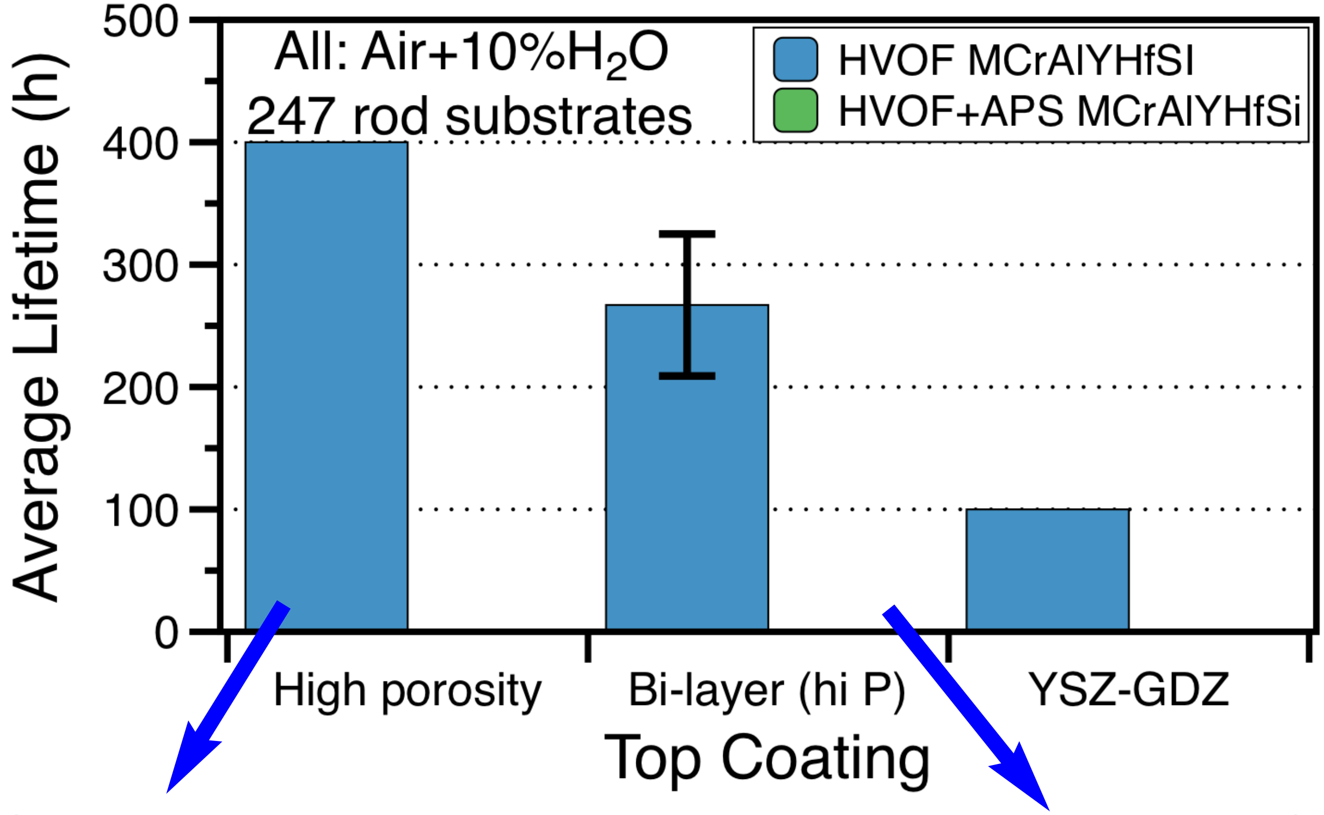




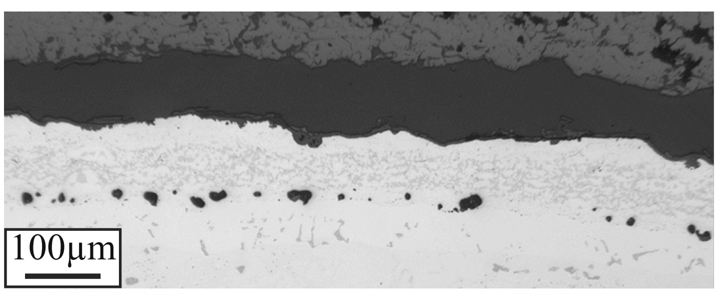


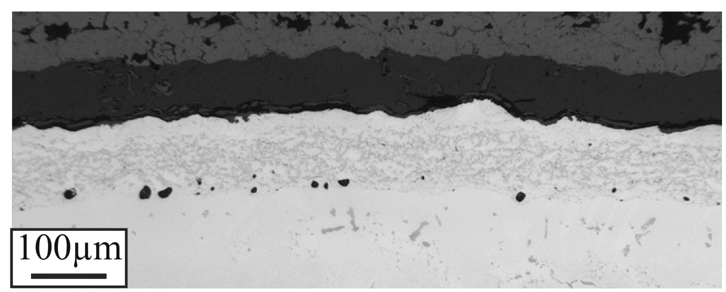
Results are opposite those for disks

Unfortunately, Phase 2 coatings did not perform better than Phase 1

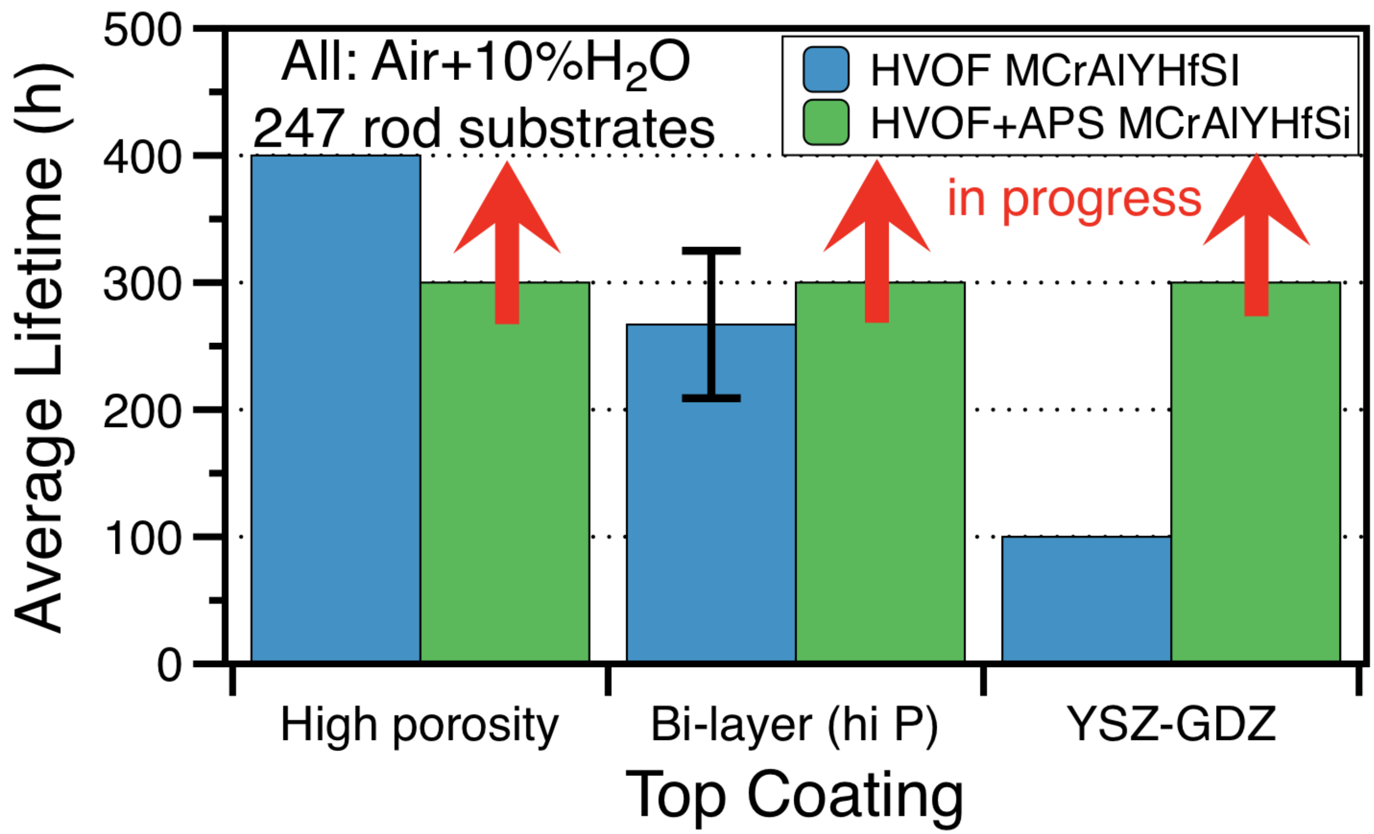


Concern about low surface roughness of NiCoCrAlYHfSi



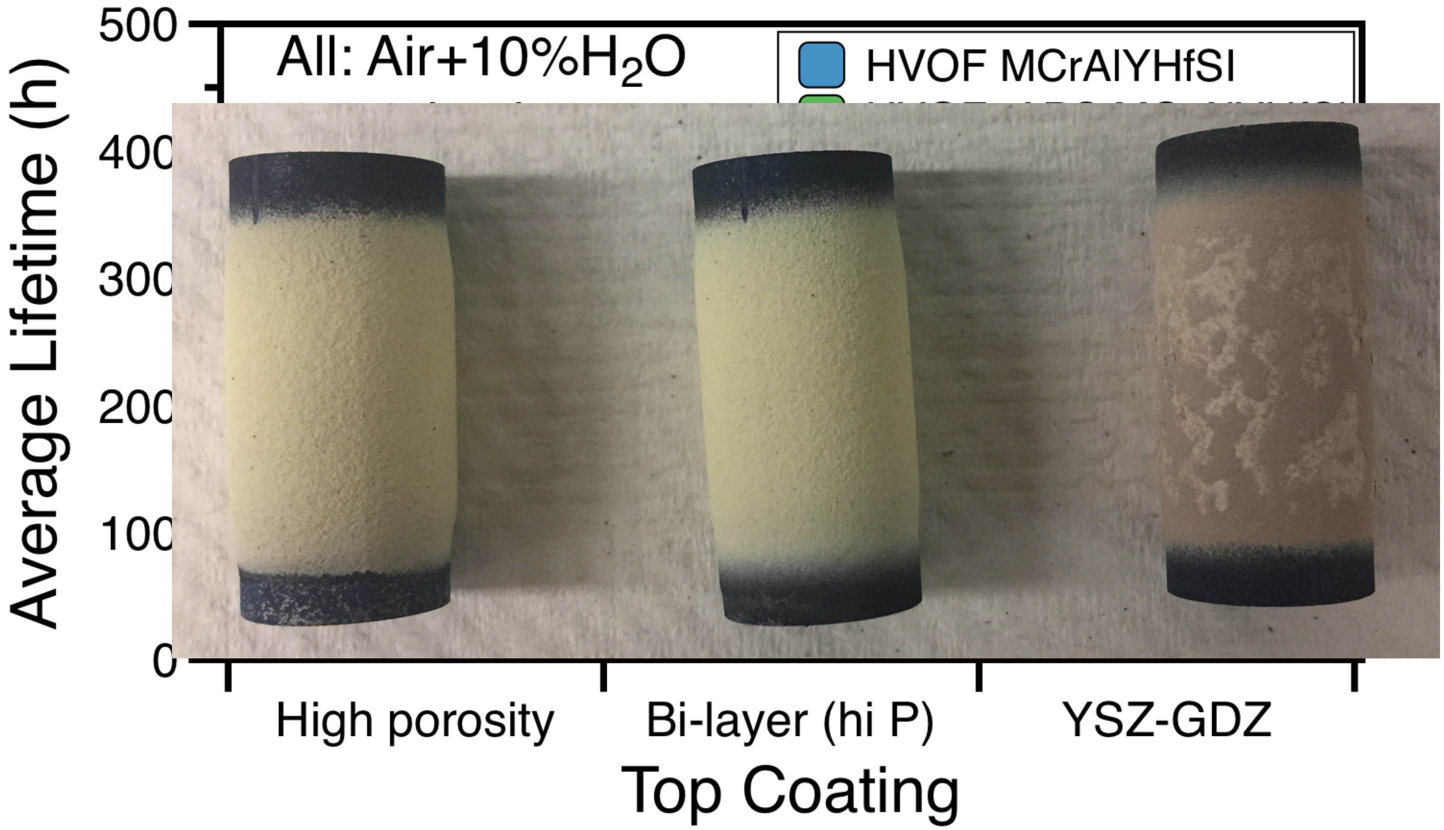


More promising results with APS flash coating on top of HVOF bond coating



APS NiCoCrAlYHfSi ~170 μm layer
Comparison of bond coating roughness is in progress

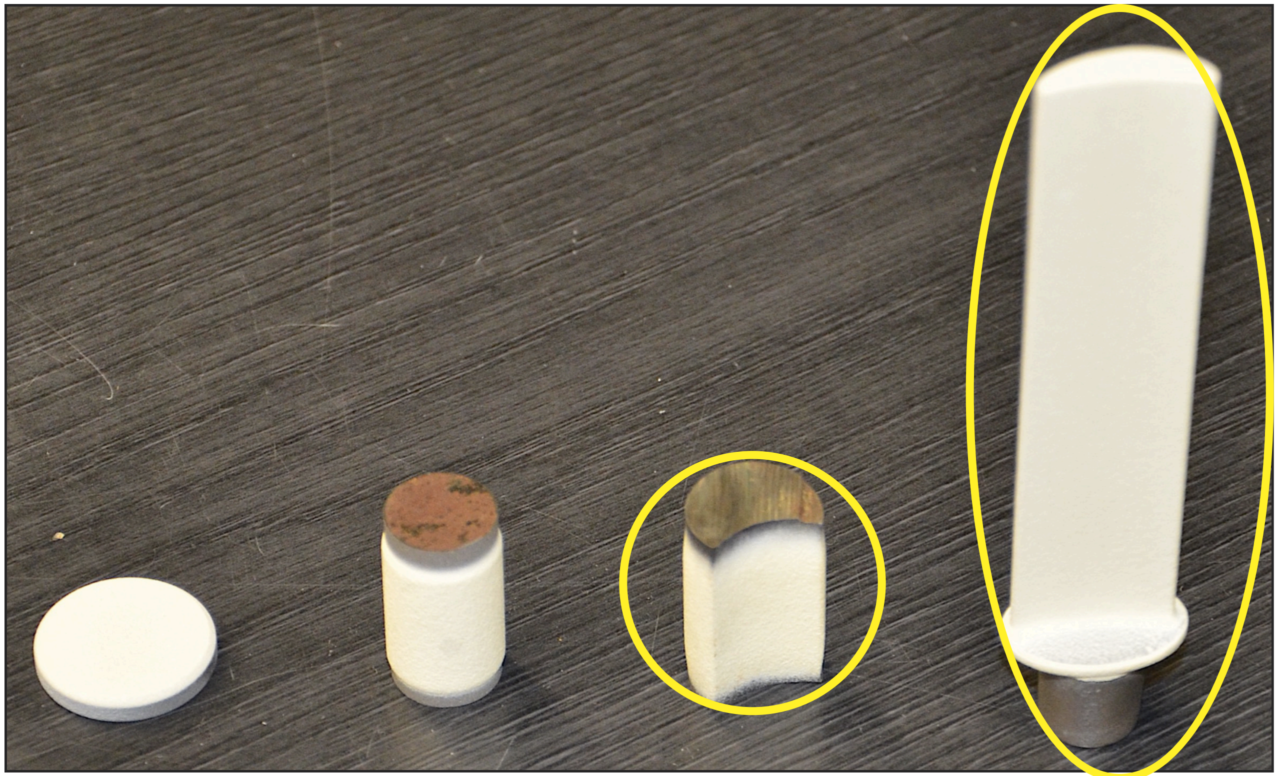
$Gd_2Zr_2O_7$ layer appears to be spalling



APS NiCoCrAlYHfSi ~170 μm layer

Comparison of bond coating roughness is in progress

FY16 goal is to study effect of curvature on oxide growth



Basic: 247 rod with concave side

Complex: 718 "blade" by laser additive collaboration with Meyer Tool

Part 1: TBC Summary

Moving away from flat coupon specimens

2015 goals

- coating 12.5mm diameter rod specimens (247)
- low coating lifetime in 100-h cycles at 1100°C
    - 5,000h exposure at 1000°C without failure
- Switch to lower porosity YSZ top coatings
    - No significant change in lifetime
- Promising results adding flash APS bond coating
    - Perhaps HVOF roughness not optimized

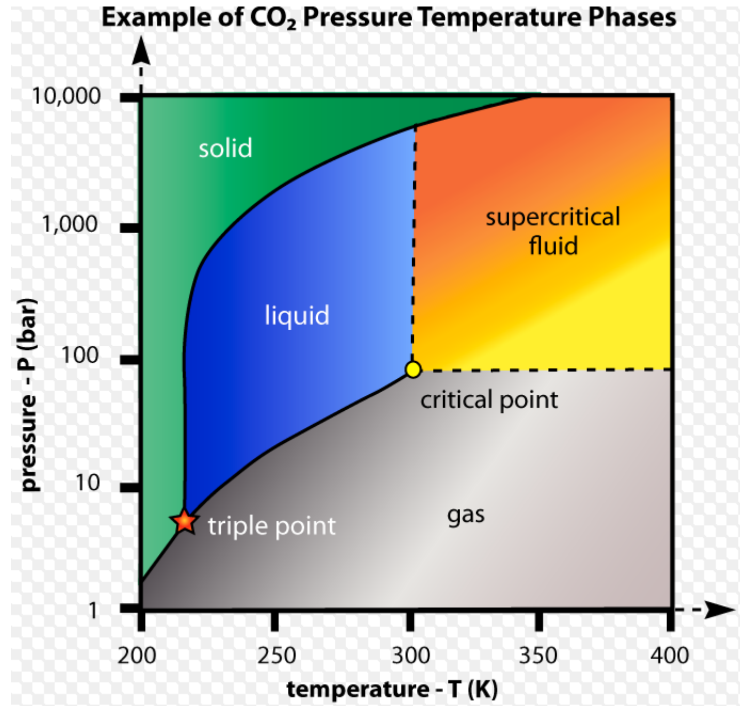
2016 goals

- coating specimen with concave & convex sides
- coating optimization ongoing at Stonybrook
- substrates (simple and "blade") ready to coat

Part 2: Why use supercritical CO_2?

Potential supercritical CO_2 (sCO_2) advantages:

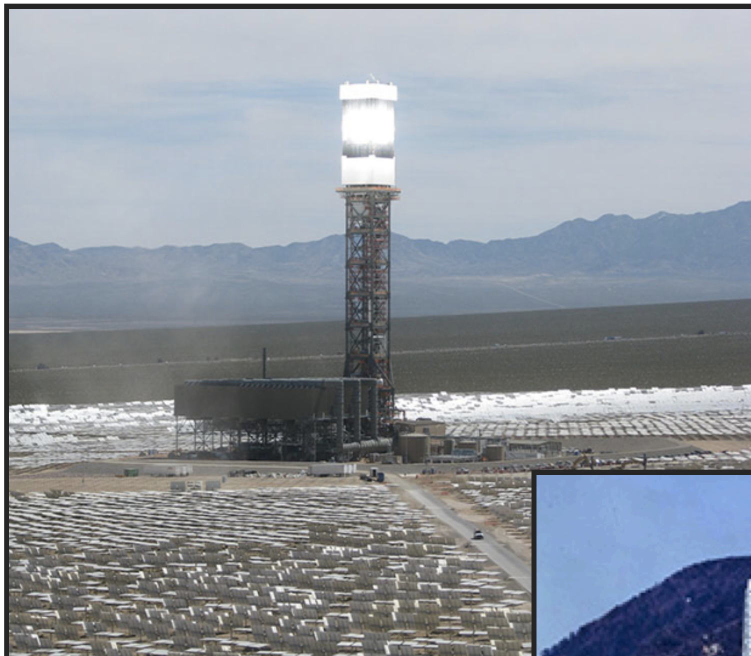
- no phase changes
- high efficiency
- more compact turbine
- short heat up
- less complex
- lower cost (?)



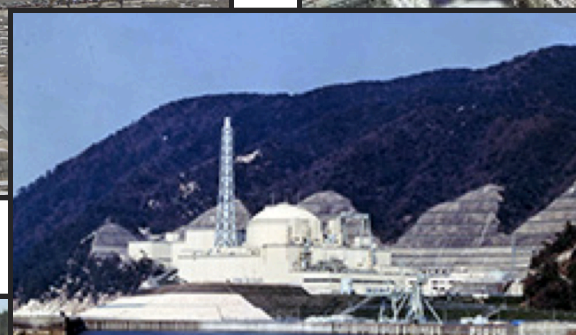
Direct- and indirect-fired sCO_2 Brayton cycles for:

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

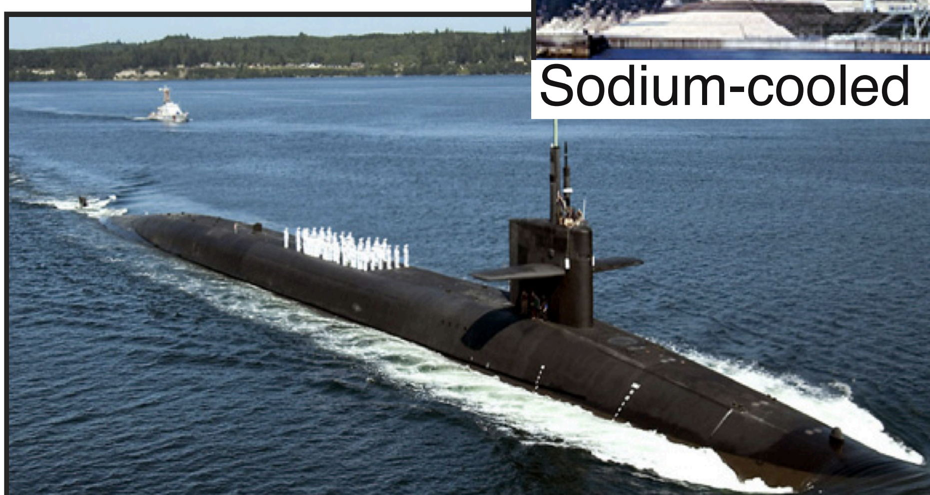
Many possible applications



Smaller fossil systems



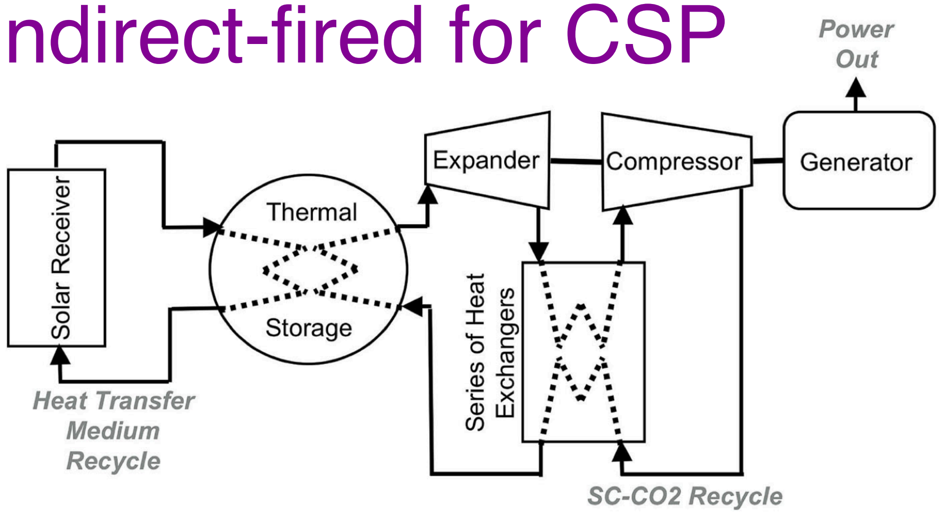
Sodium-cooled reactor



7MW Echogen, waste heat

Direct-fired system of special interest

Indirect-fired for CSP



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

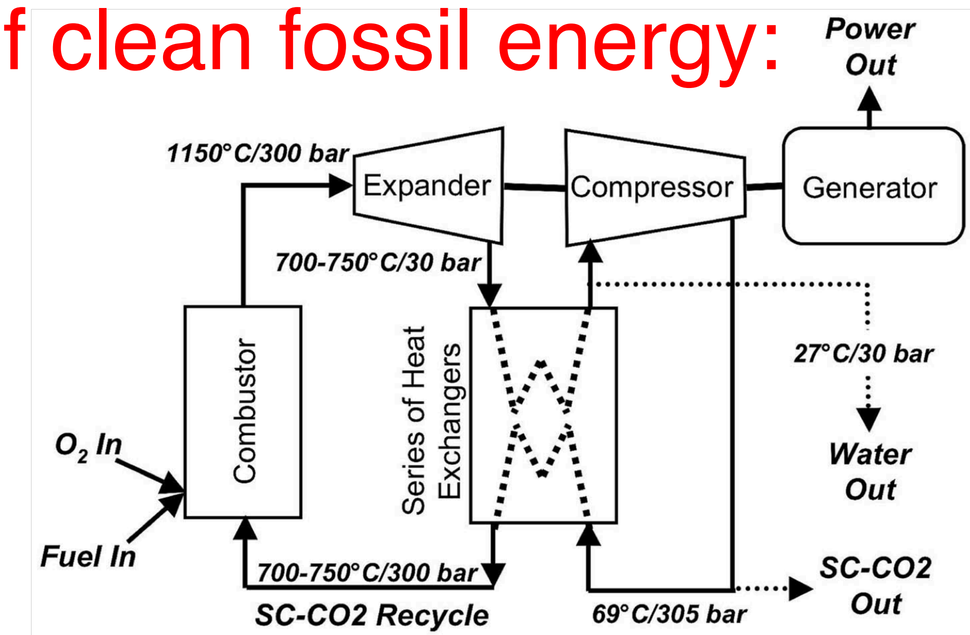
Also, waste heat recovery, bottoming cycle for Fossil

Direct-fired (e.g. Allam cycle by Netpower) offers the promise of clean fossil energy:

In: natural gas + O_2

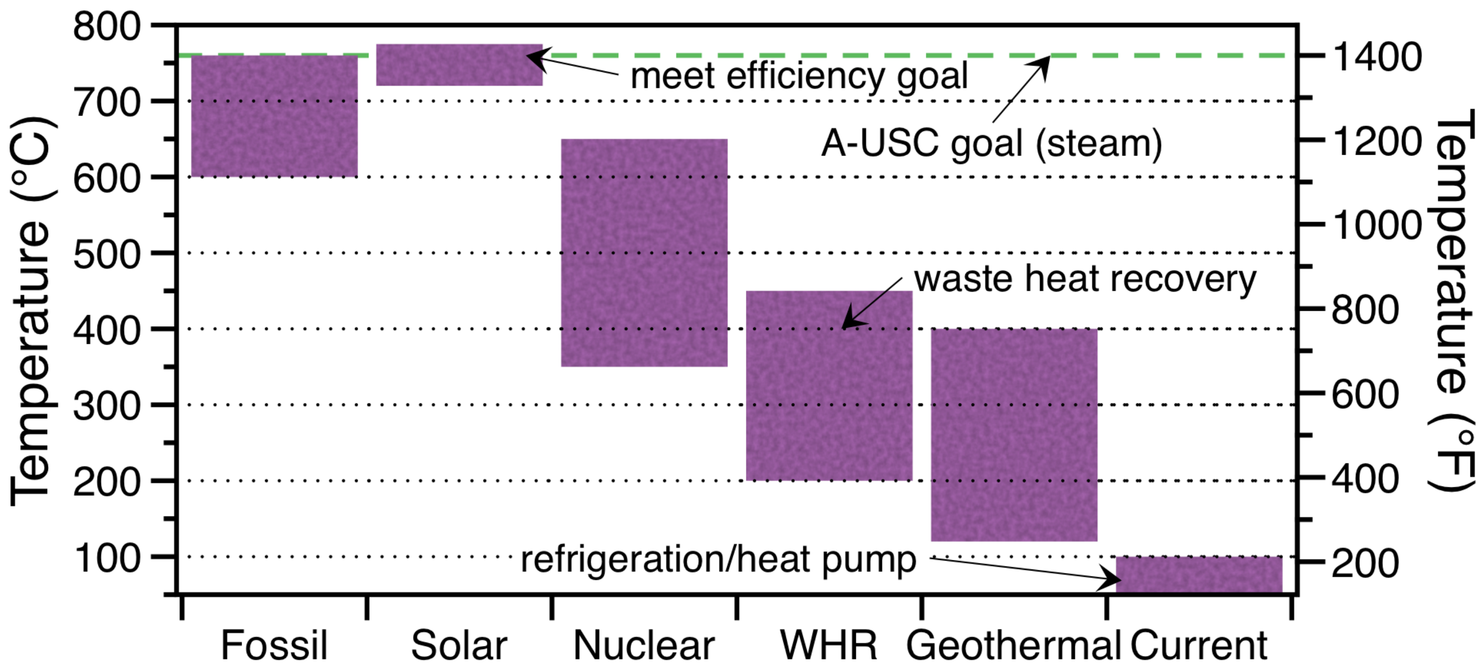
Impurities: ~10%H_2O ~1%O_2, CH_4?, SO_2?

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
- Direct-fired system may have very high T's:
  1150°C combustor
  750°C/300 bar turbine exit
- Indirect-fired: Primary HX operating at higher T

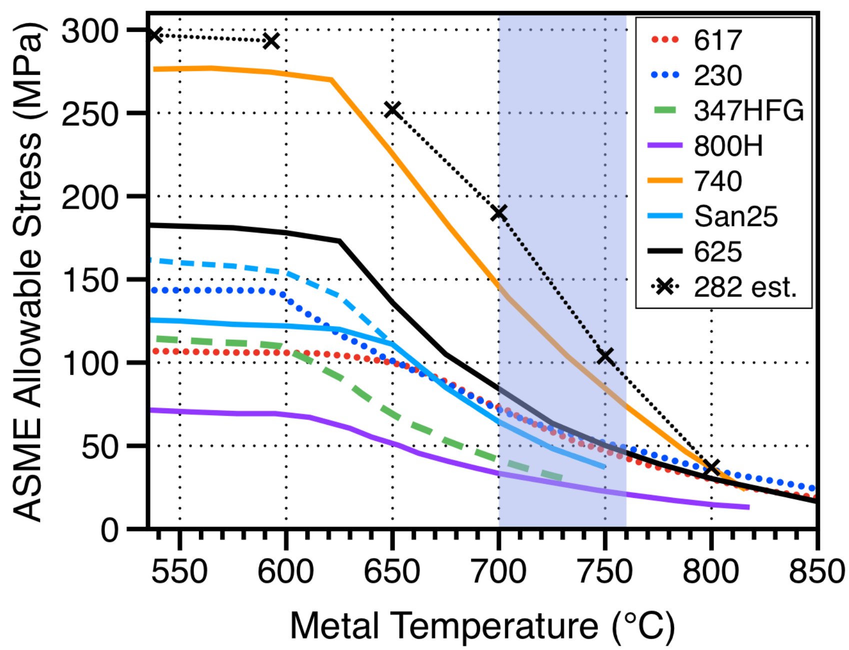


Materials for sCO_2 ~ A-USC steam

Temperatures (600°-750+°C) and pressures:
- challenge for strength
- limited number of materials available
- ! Adv. Ultra-supercritical (steam) same T range

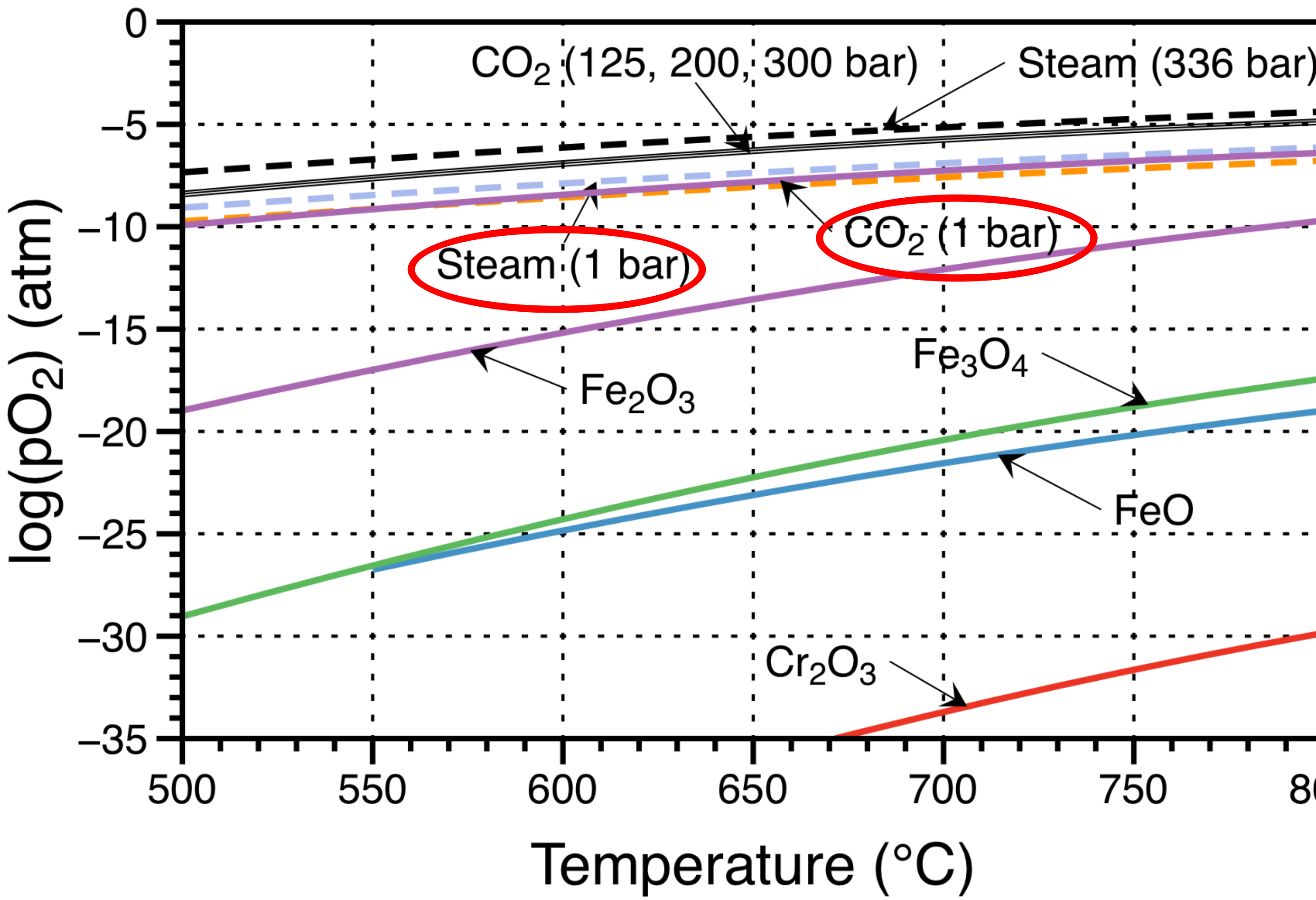
Limited materials choices:
- capability
- ASME Boiler & Pressure Vessel Code:

Materials are key to:
- reliability
- availability
- maintainability



Oxygen levels similar in steam/CO_2

Factsage calculations: CO_2 <-> $1/2O_2$ + CO

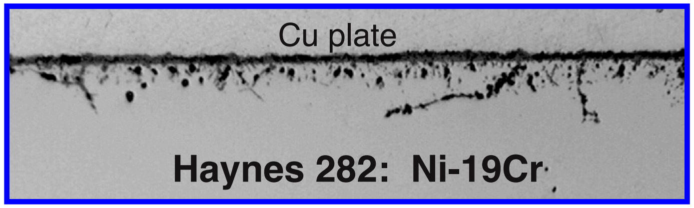


Similar pO_2 levels in steam & CO_2, higher at 200bar

All oxides of interest are stable

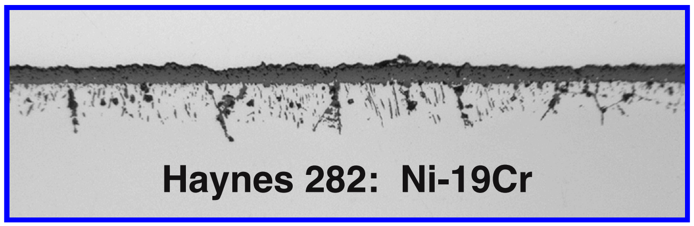
Why worry about 740/282?

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



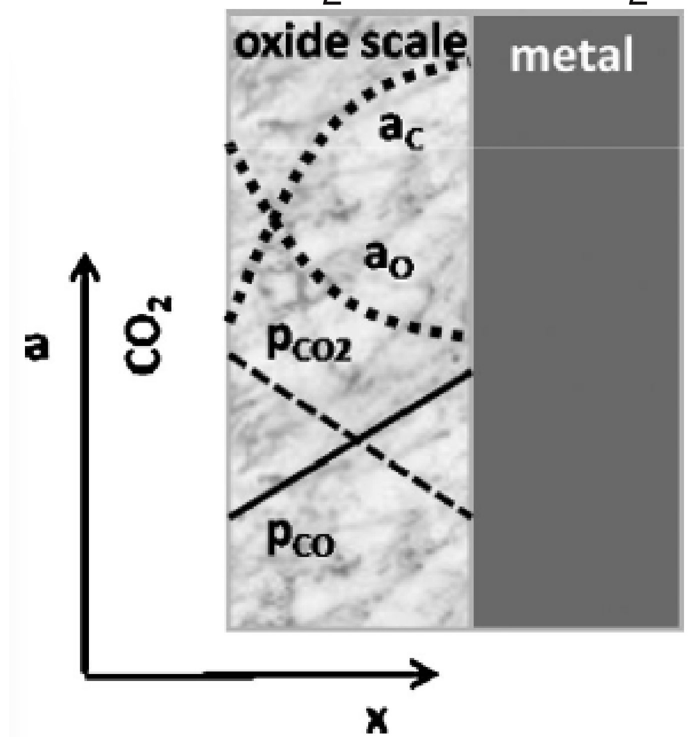
800°C, 5,000h in air+10%H_2O

10 μm



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

Gas only: C activity (a_c) relatively low, favors oxidation

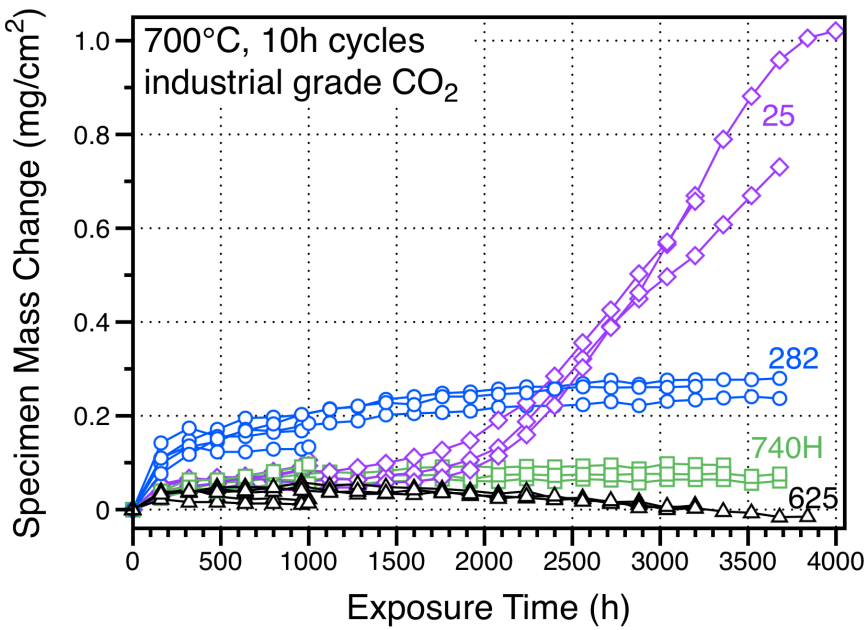
McCoy 1965: Inconel 600 and 18Cr-8Ni steel internally carburized in 1bar CO_2

High a_c predicted - what about NiCr in sCO_2 + 1%H_2O?

Maybe we should be worried

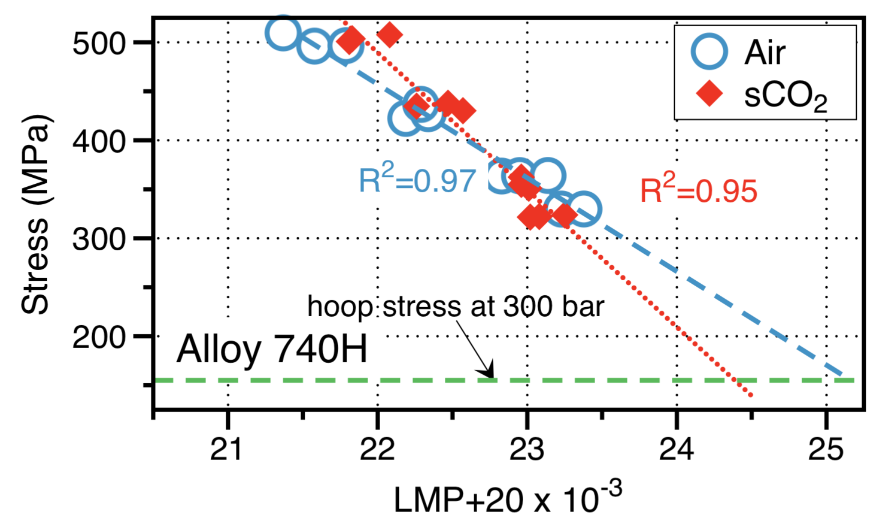
Year 1 results from concentrated solar power study

Laboratory simulation of CSP duty cycle (700°C, 1 bar)



Fe-base Sanicro 25 showed accelerated mass gain (Fe_2O_3) after ~1500 h in 10-h cycles in industrial grade CO_2

Tube creep rupture testing in supercritical CO_2

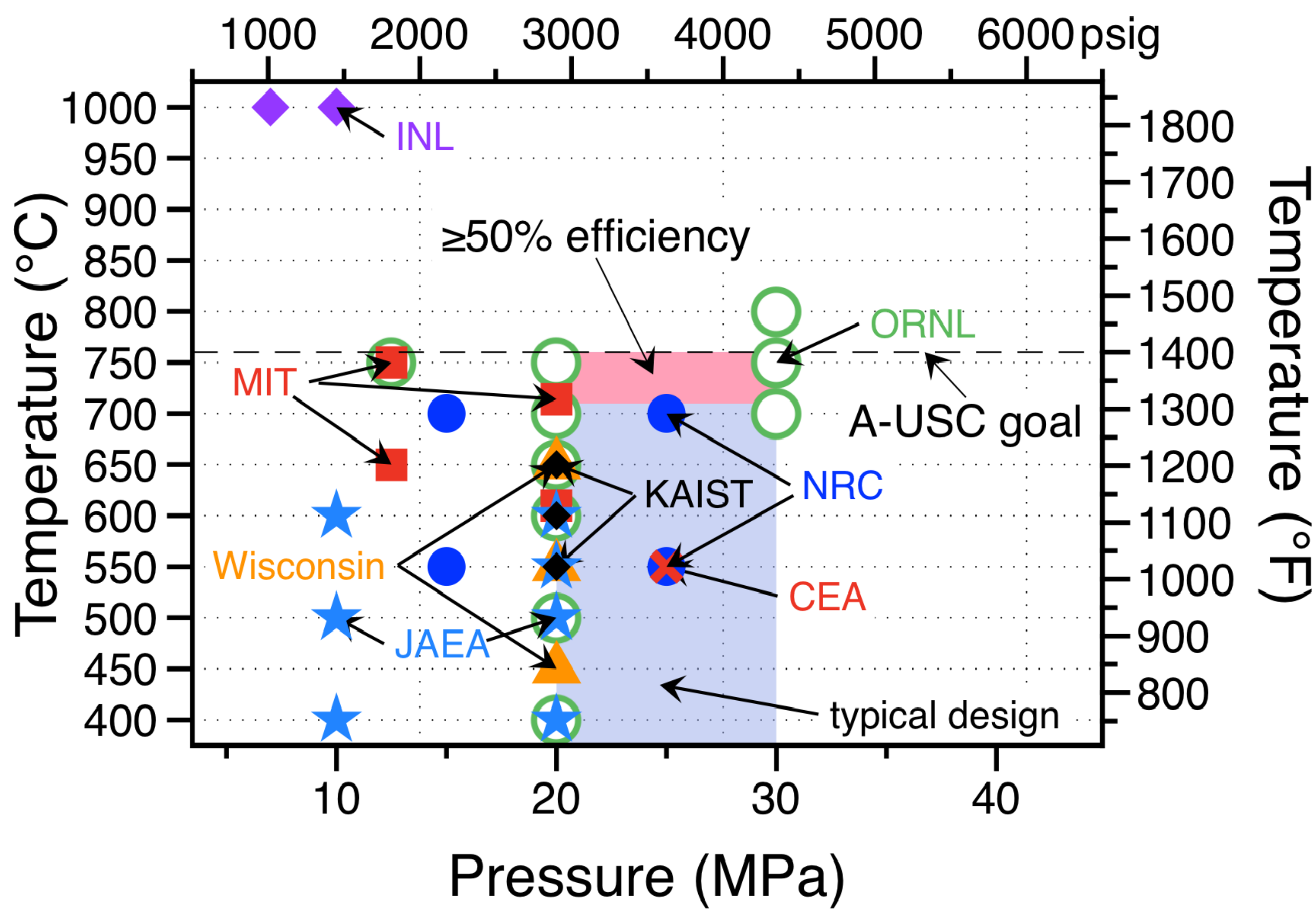


LMP = T(in K) (20 + log(time in h))

Ni-base 740H showed decreased creep rupture lifetime at 750°C at longest exposure time in sCO_2 compared to high pressure air

Relatively little prior sCO_2 work

Especially at >650°C and >200 bar



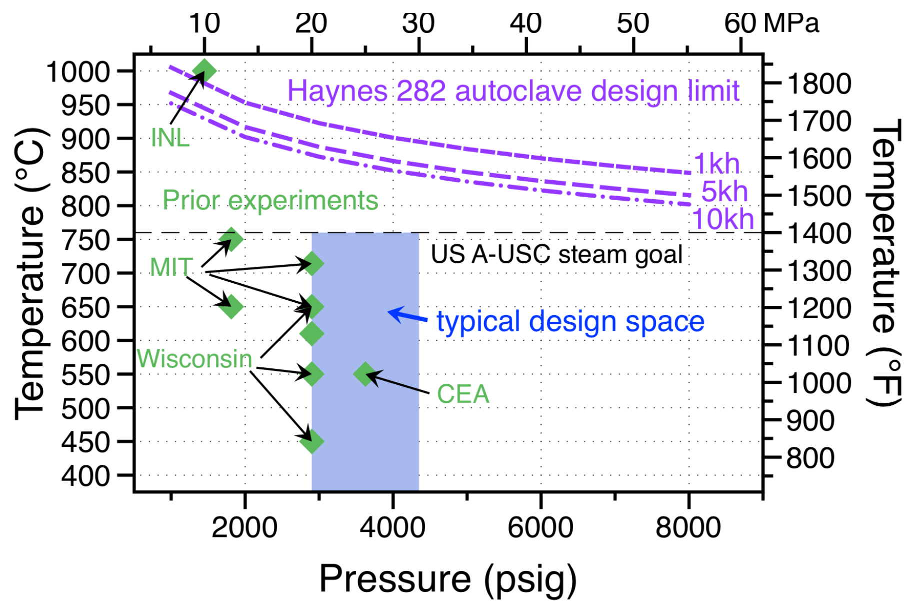
Several groups active in the past 10 years

U. Wisconsin group has published the most results

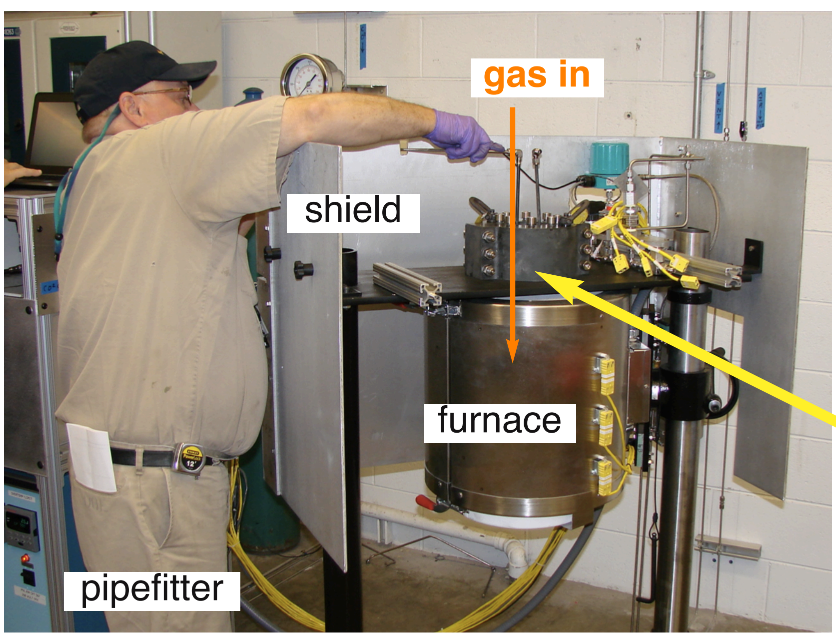
Temperature/pressure limited by autoclave design

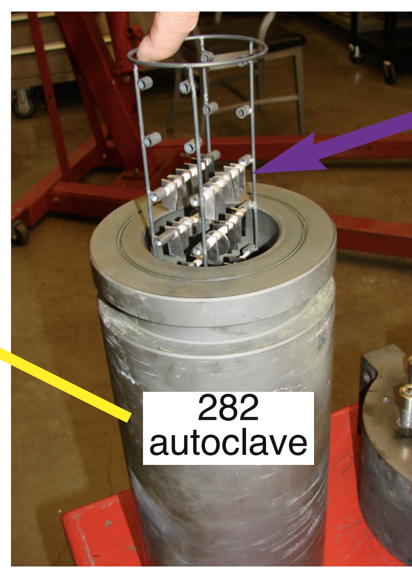
ORNL sCO_2 rig finished in 2014

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

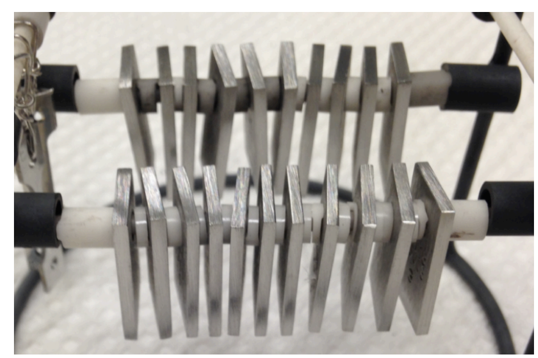


ORNL sCO_2 rig:



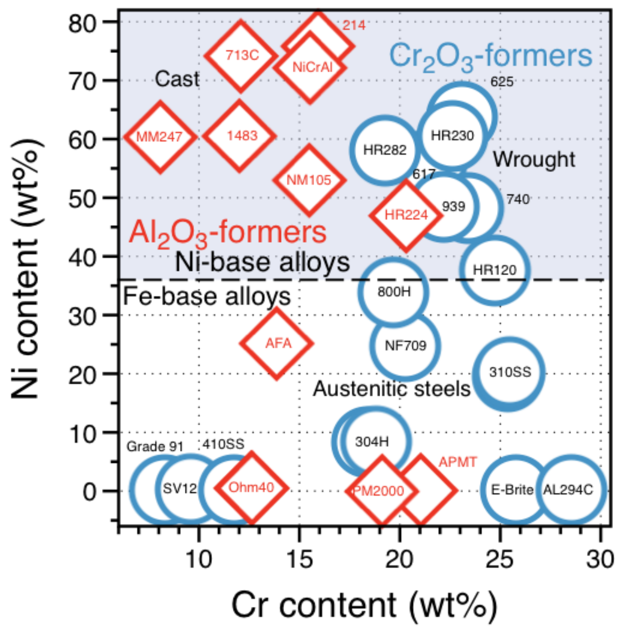


specimen
holder



Range of alloys exposed

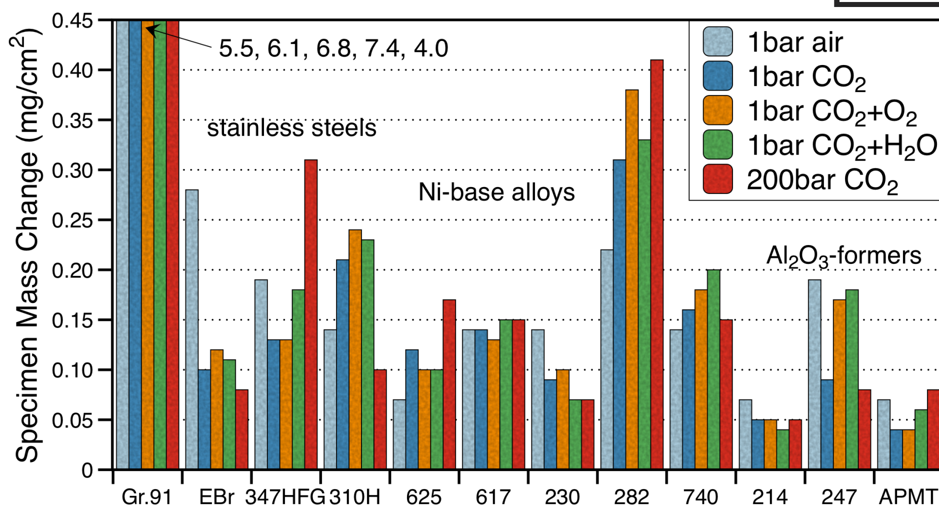
Narrowing scope as project progresses



2014: 30 alloys screened

2015: 12 alloys studied

2016-17:
6 alloys:
310HCbN
617
230
740H
282
247

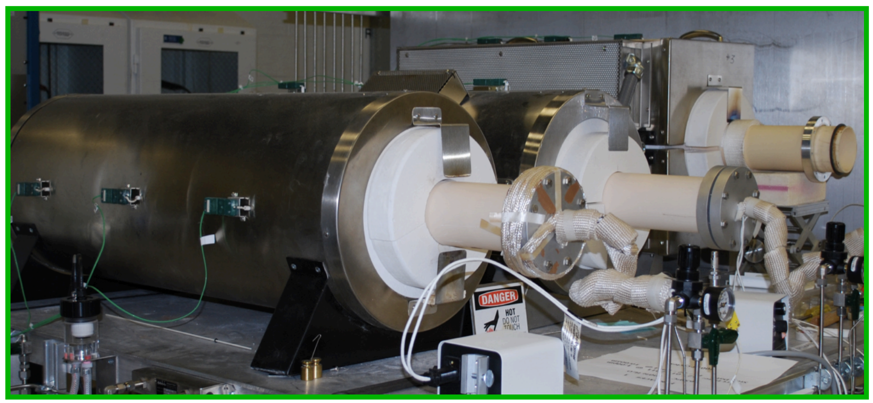


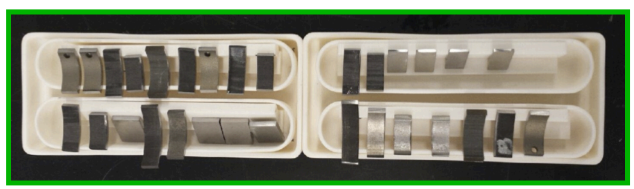
Several testing options

High temperature exposure in controlled gas environment

automated
cyclic rigs

3-zone tube furnace





282 autoclave

1 bar	1 bar	300 bar
500°-1200°C	500°-1200°C	200°-800°C
0.1-24 h cycles	100-500 h cycles	500 h cycles

Want to study sCO_2 impurity effects

Goal: study effect of H_2O & O_2 on sCO_2 corrosion

BUT, we can't pump impurities into sCO_2 gas

AND can't monitor H_2O or O_2 level at pressure

(1) 1 bar dry air, CO_2(99.995%), CO_2+0.15%O_2, CO_2+10%H_2O

2014-2015 results

(2) Constructing rig for 300 bar/750°C testing

Pumping system and detector being built

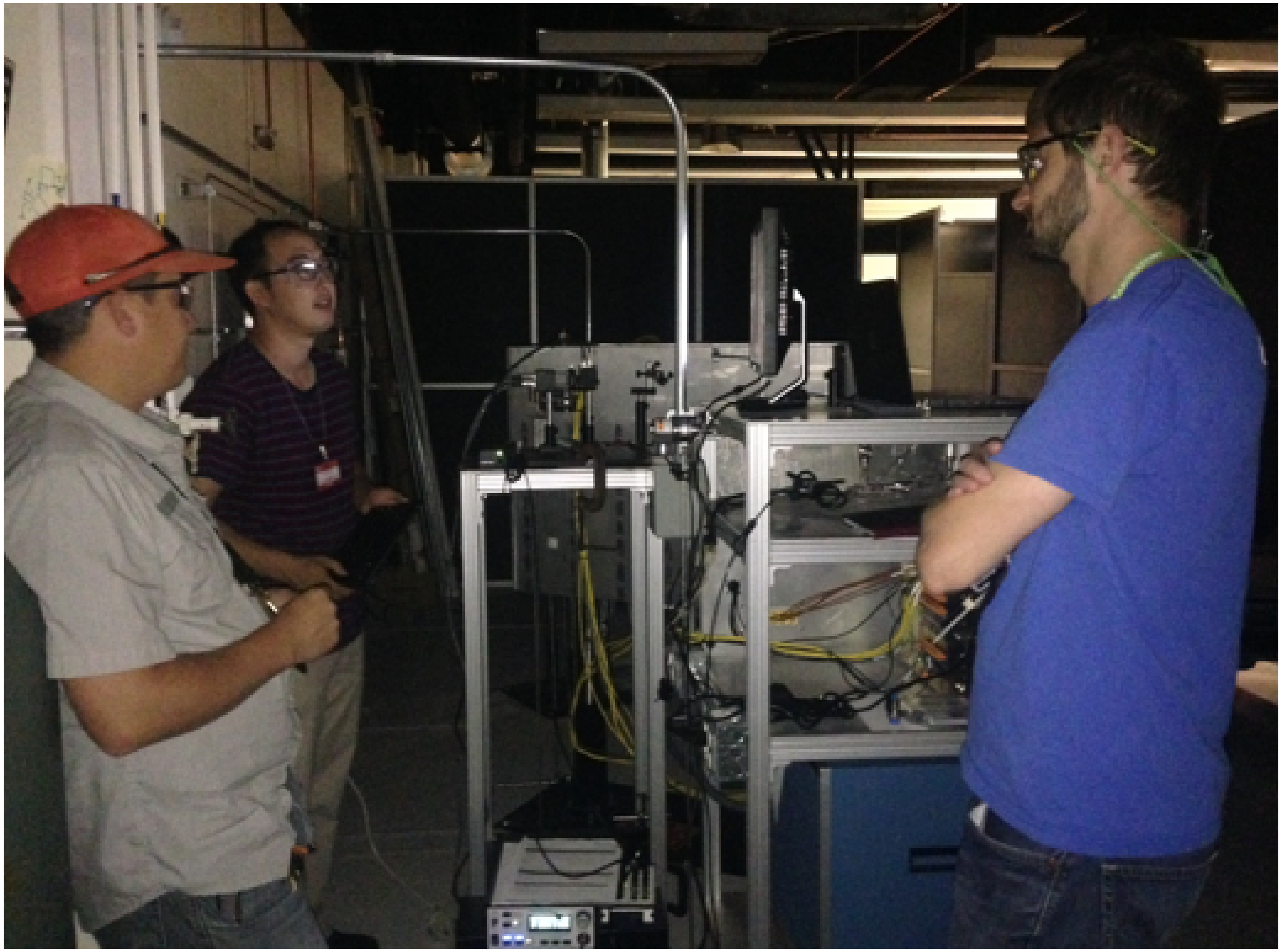
(3) 1 & 300 bar: industrial vs. research grade CO_2

Just starting experiments

(4) 1 & 25 bar CO_2 vs. CO_2+H_2O vs. +SO_2?

Test matrix in progress

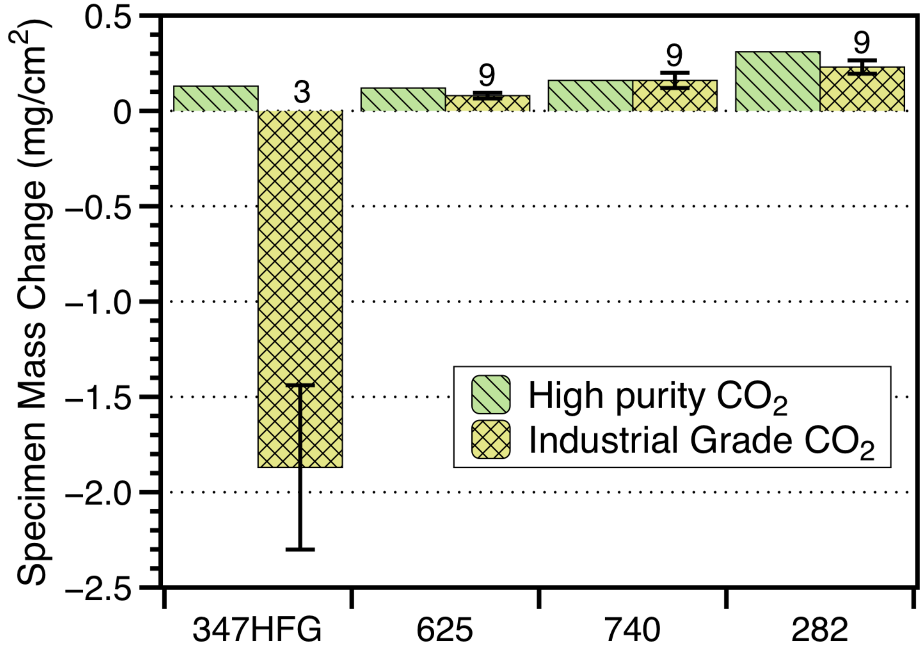
New system under construction



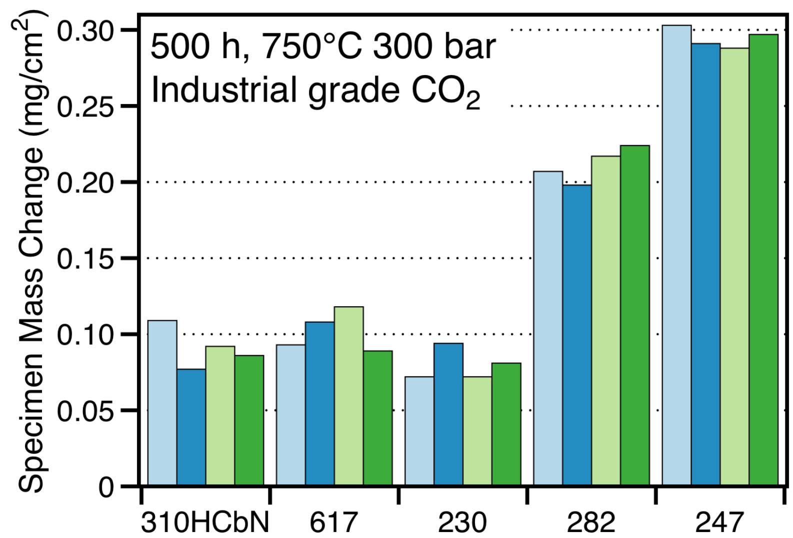
Laser-based system to detect O_2 and H_2O in CO_2 at pressure (200-300 bar)

RG vs. IG CO_2: minor differences

Focus on 750°C: 500 h results



1 bar



300 bar

1 sample of each in first RG test

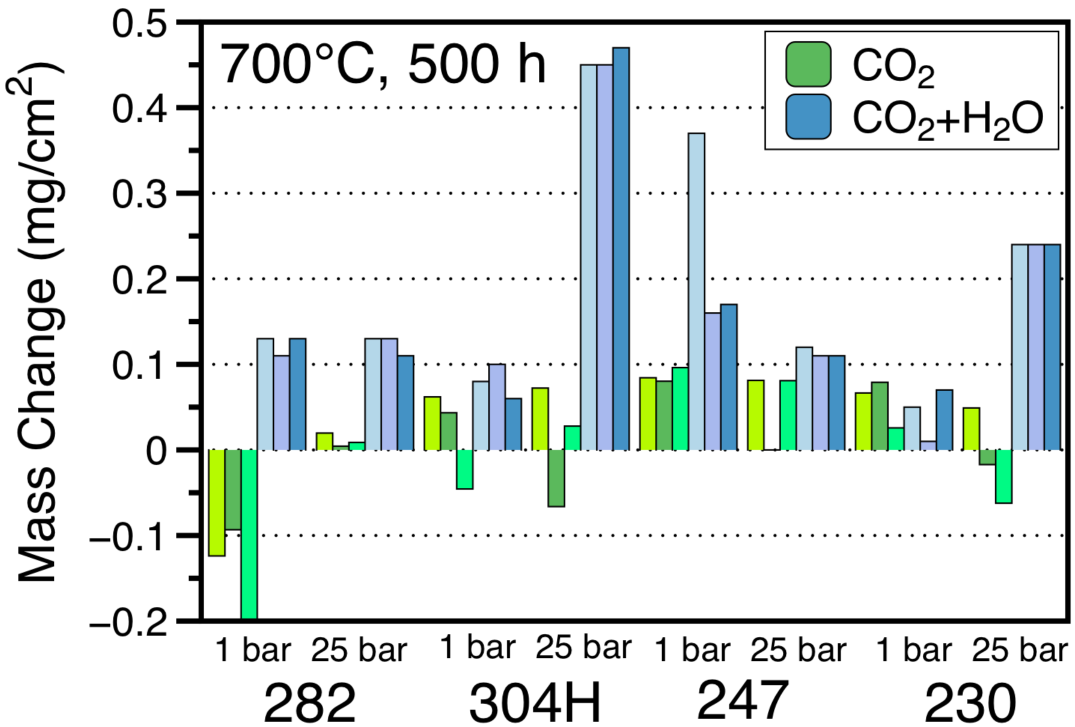
Multiple samples in IG test for better statistics

Industrial grade: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

Research grade: < 5 ppm H_2O and < 5 ppm hydrocarbons

Initial results in 1 & 25 bar

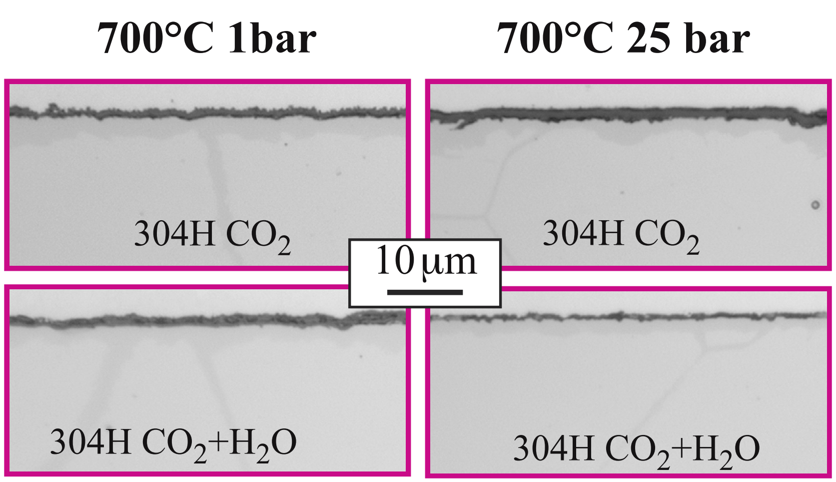
Three specimens of each alloy per condition

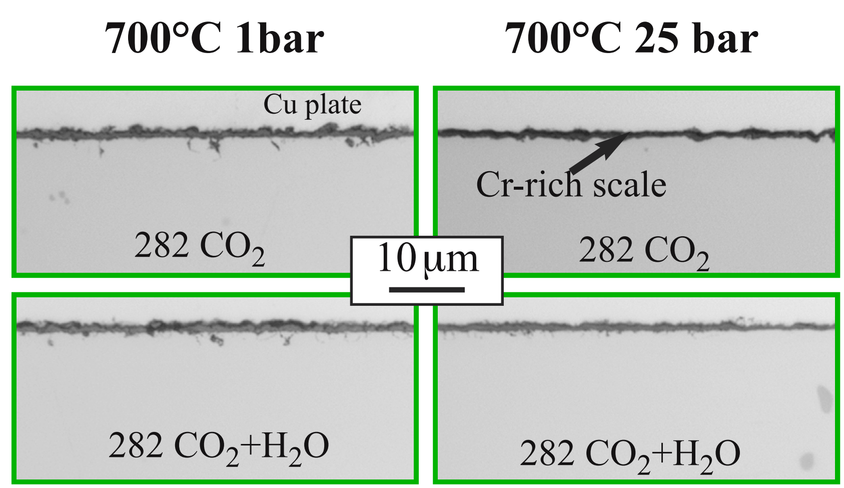


700°C, 1292°F

RG CO_2±10%H_2O

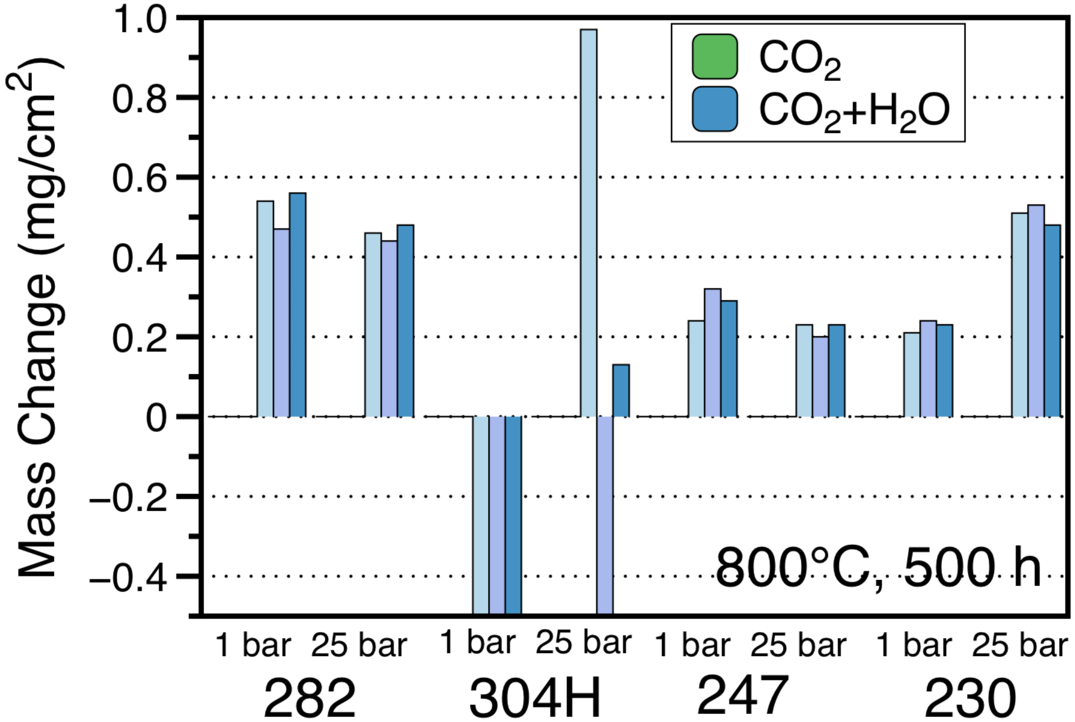
500 h exposure





Recent results in 1 & 25 bar

Three specimens of each alloy per condition



800°C, 1472°F

RG CO_2±10%H_2O

500 h exposure

Second 800°C experiment finished Monday

Summary: sCO_2 project

Several experiments planned to study H_2O and O_2 effects in supercritical CO_2, need a system that:
- can pump controlled impurity levels
- detect levels entering and leaving autoclave

to study conditions relevant to direct-fired cycles

Additional experiments:

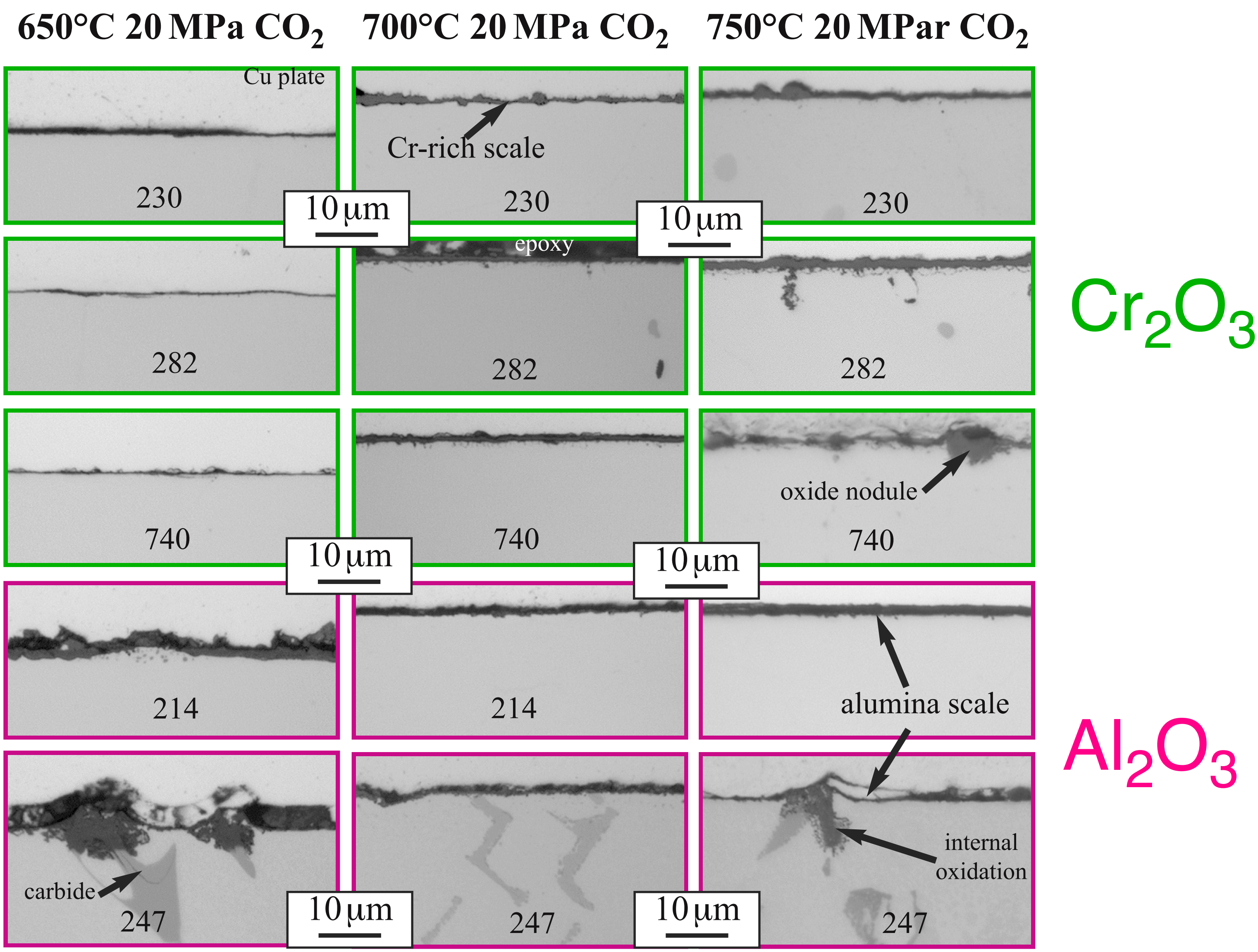
(1) comparing industrial and research grade CO_2
- 1 and 300 bar
- collaboration with SunShot project

(2) comparing 1 & 25 bar CO_2 & CO_2+10%H_2O
- thin oxides formed on higher-alloyed materials
- no clear effect of impurities from this data

backup slides

Ni-base alloys: thin scales

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



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

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

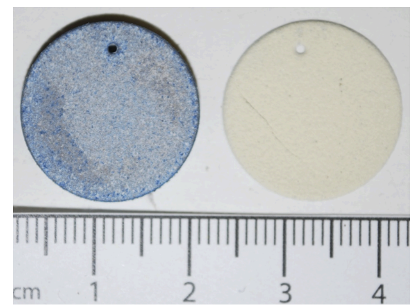
SEM/EDS/EBSD

EPMA (WDS)

PSLS, 3D LM

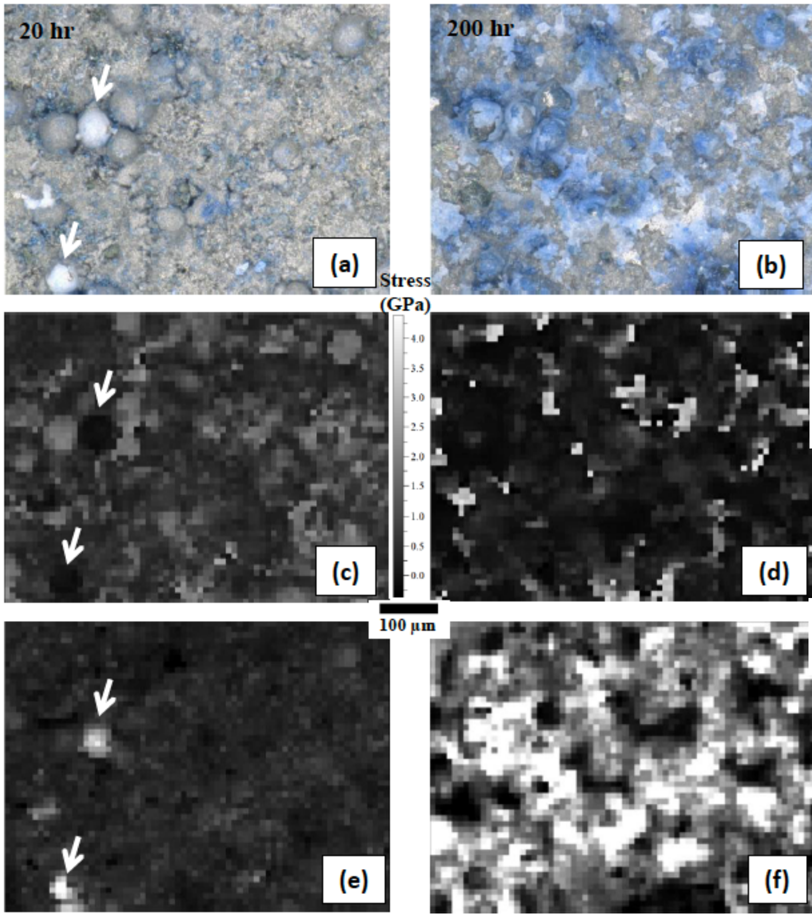
FIB/TEM

16mm diameter coupon



3D image + PSLS: maps & histograms

1483: 1100°C, dry air, 1h cycles



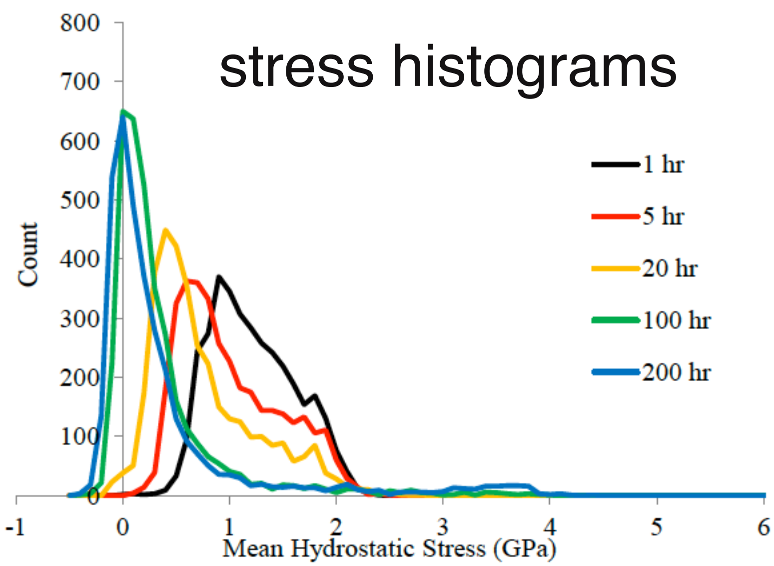
3D Light microscopy (Keyence)

Photo-Stimulated Luminescence Spectroscopy: mean stress

PSLS: total R-line area

20 cycles

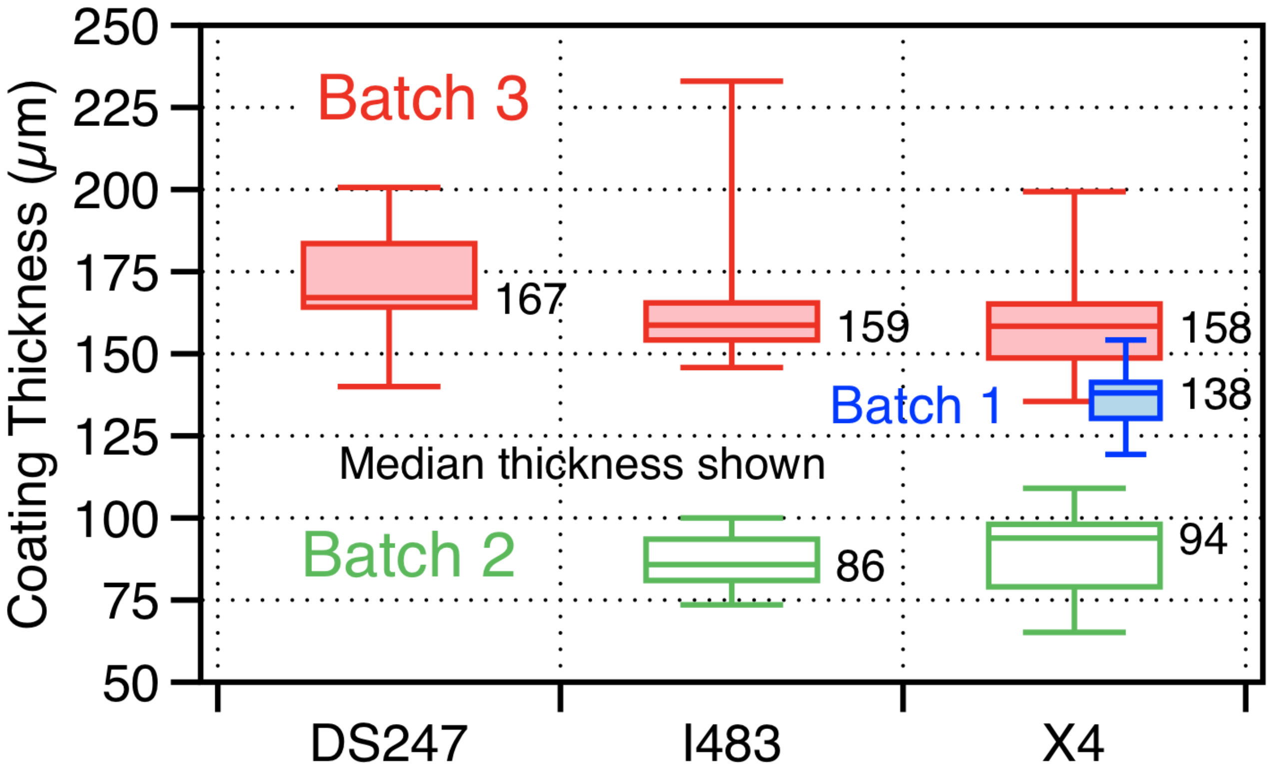
200 cycles

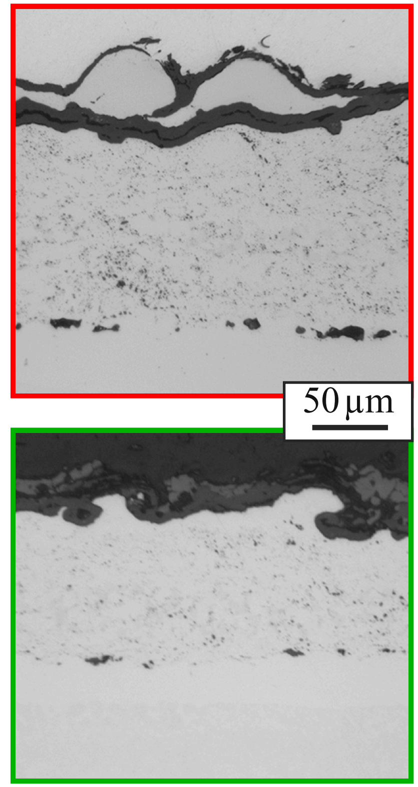


No YSZ top coat:
nothing to constrain spallation

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

2015 focus areas

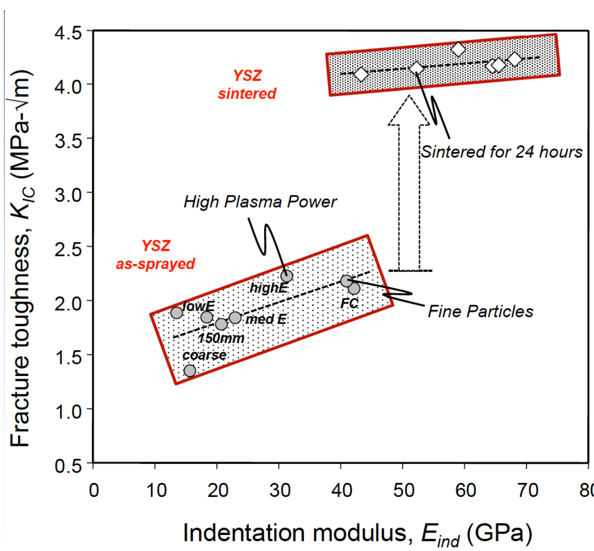
1. Use CTSR/ORNL experience for best TBC
2. Get away from testing flat coupons

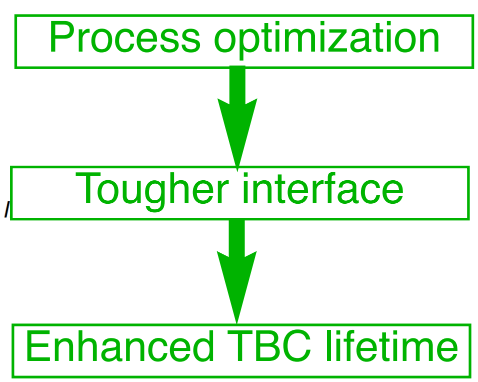
Cranfield/Jülich coat more complex shapes

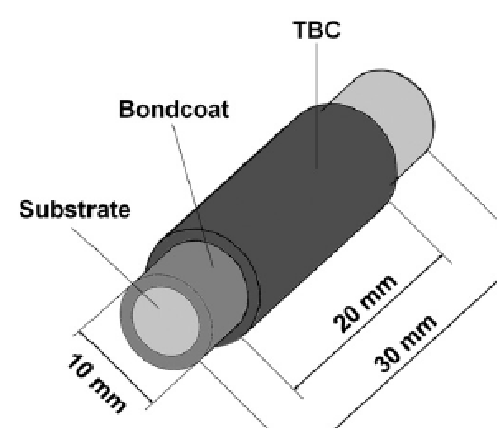
~4 specimens from each rod/tube: 100h cycles

- measure lifetime, alumina stress...

Optimize coating process for rod (CTSR)



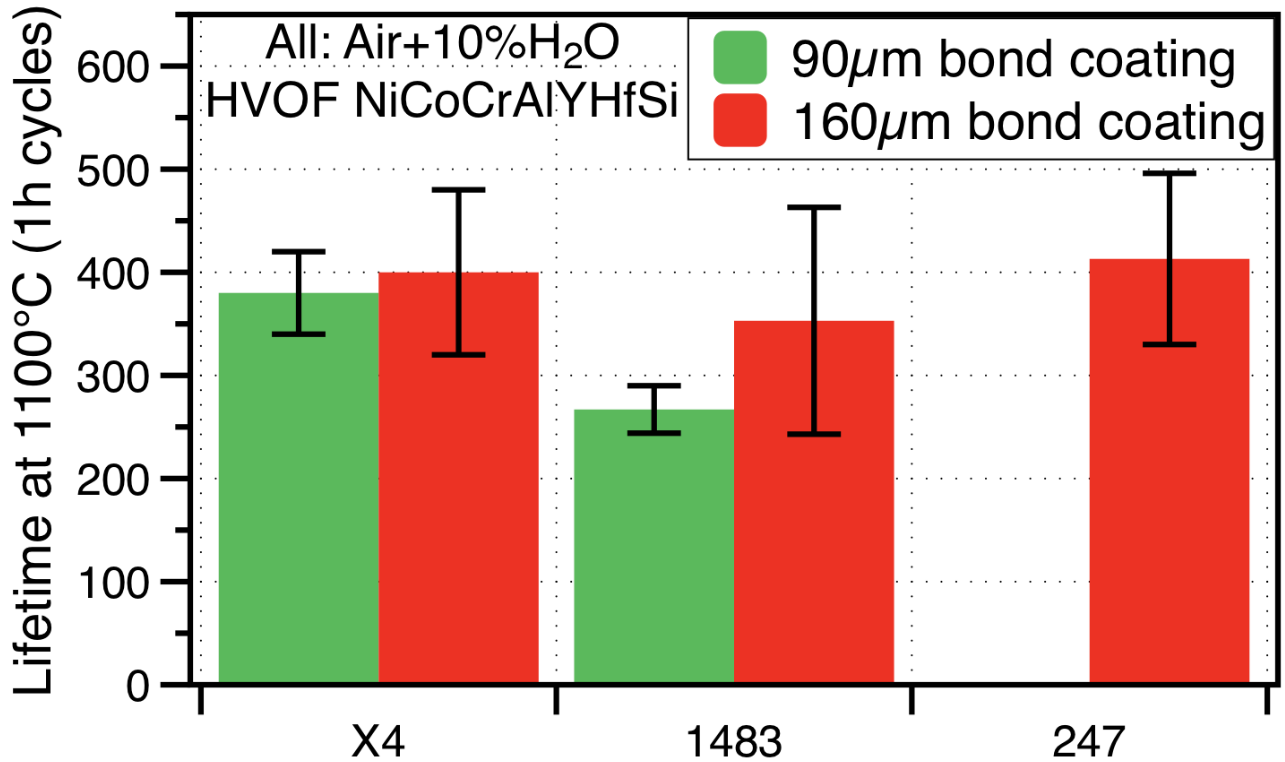




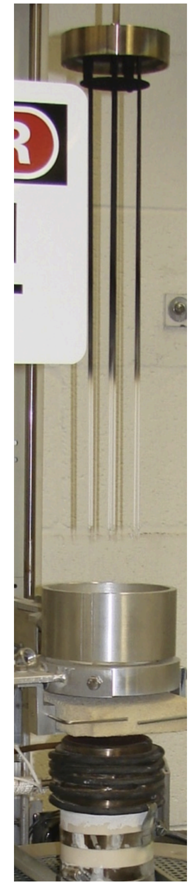
Jülich specimen design

Some things we did not plan to study

Like thick bond coating covered substrate effect



5.8wt.%Al 3.4%Al 5.5%Al

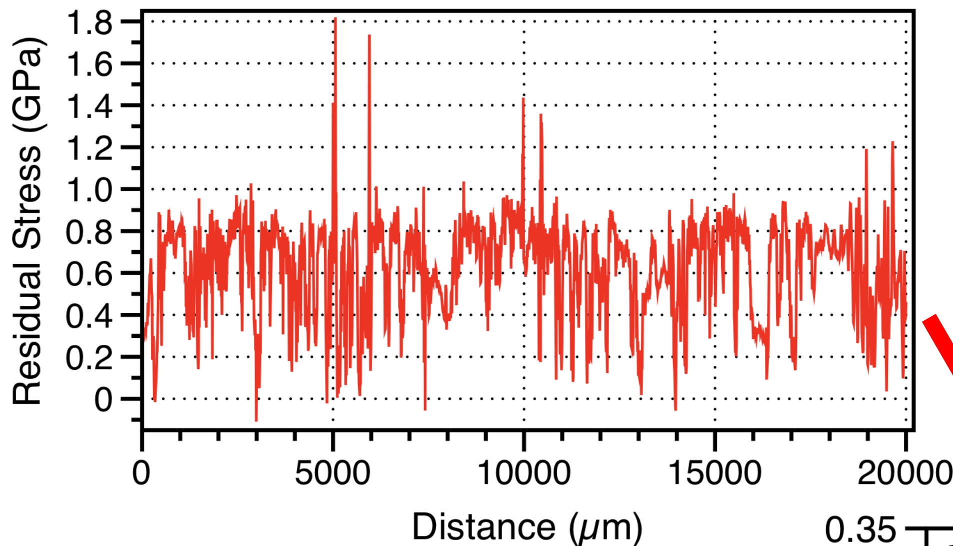


1100°C average lifetime of 3 similarly coated specimens

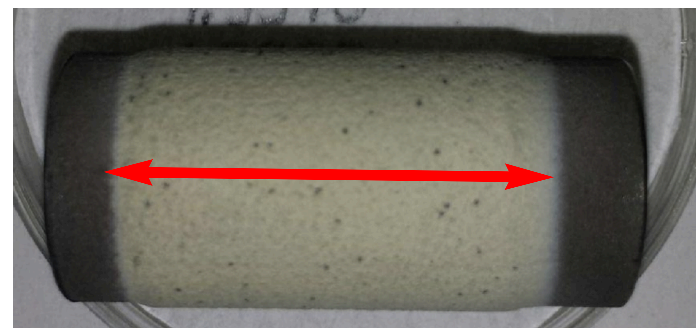
1483 had shorter lifetime only with thin coating

Initial stress measurements

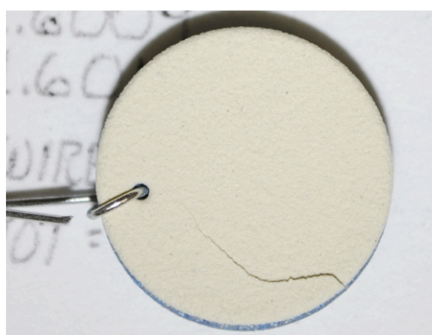
One 100-h cycle at 1100°C in air+10%H_2O

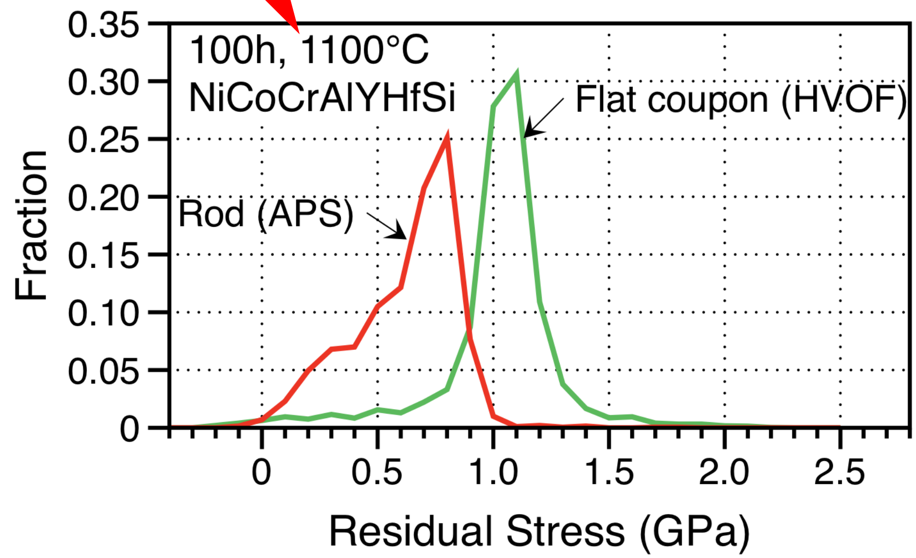


PSLS measurement along length of rod



Next measurement at 500 h

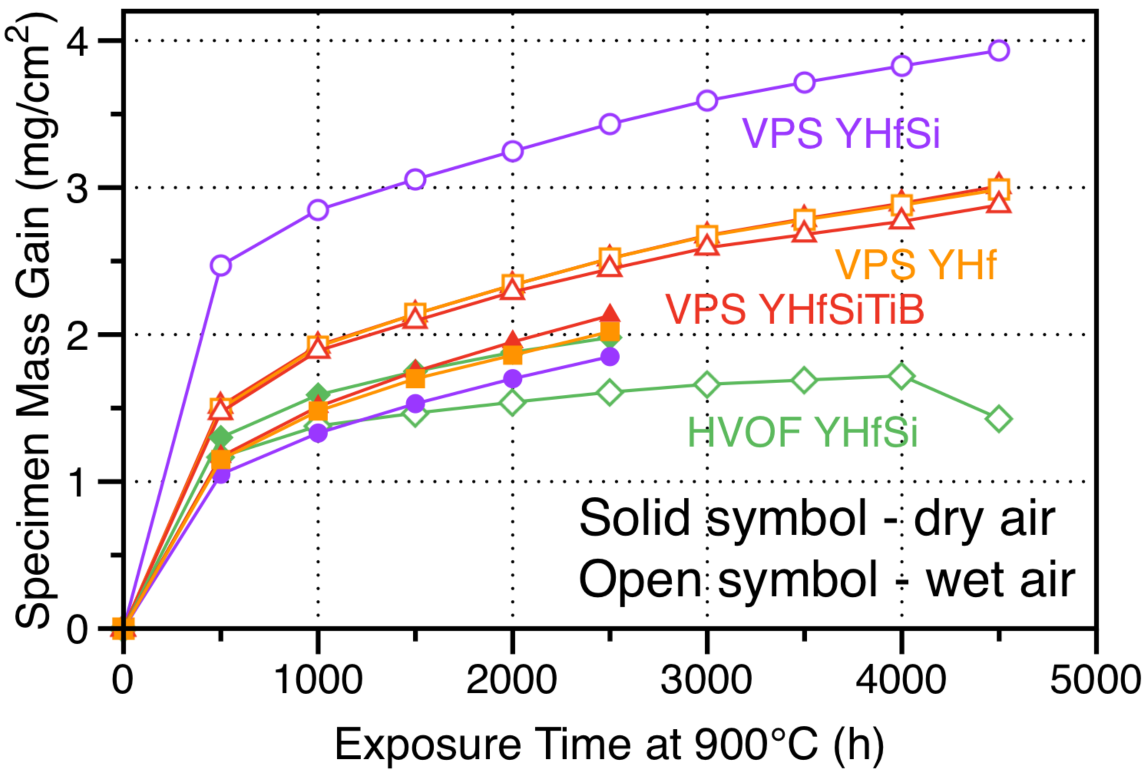




Lower mode stress in APS rod specimen after 1 cycle

What is effect of H_2O at 900°C?

500-h cycles in wet air and laboratory air



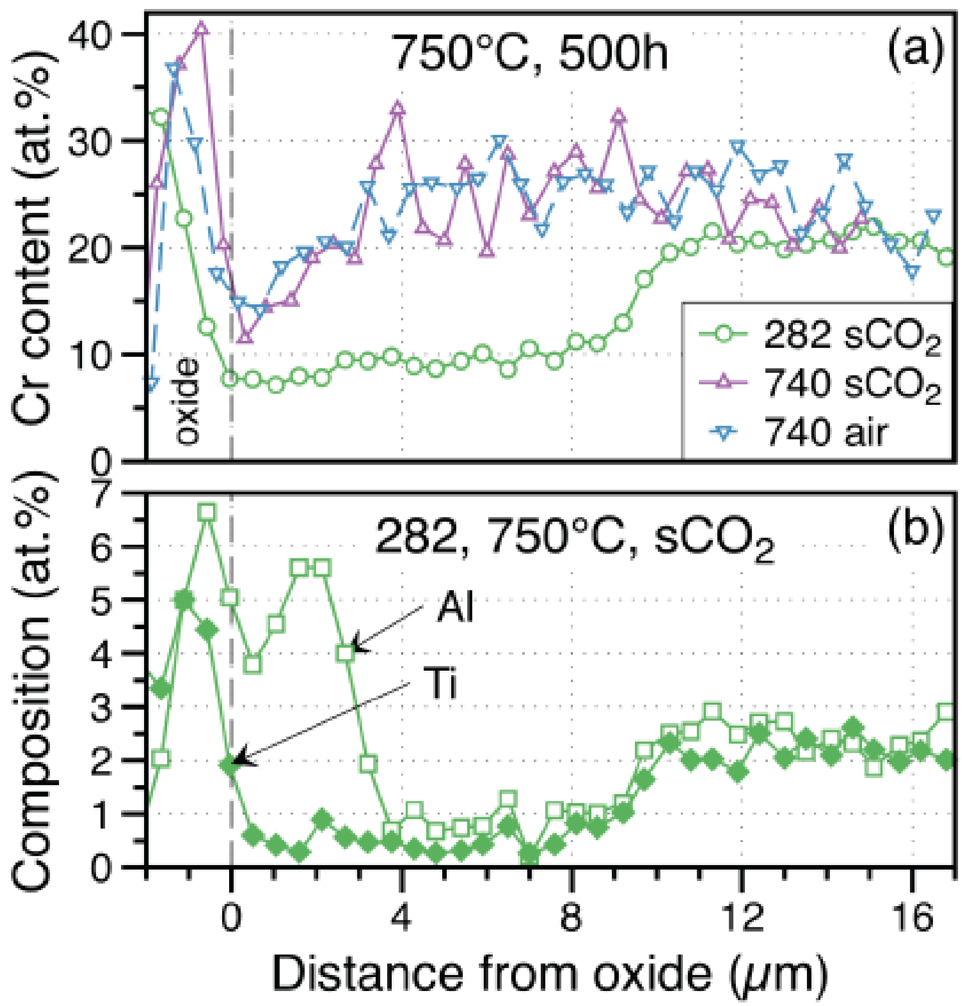
Slight change in rate constants with H_2O

Stop specimens at 5,000h for metallography

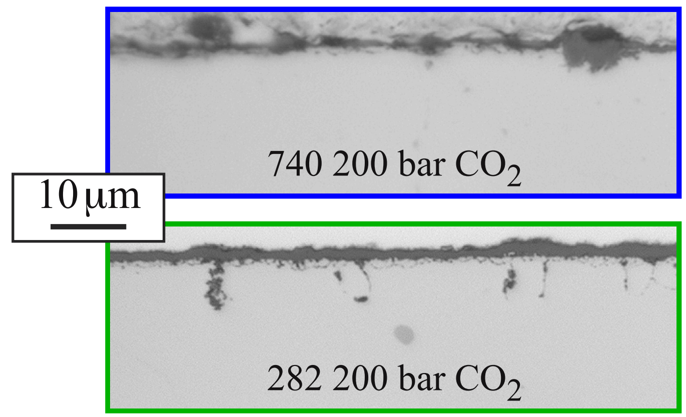
- compare change in oxide thickness

282 deeper Cr depletion than 740

EPMA depth profiles beneath scale at 750°C



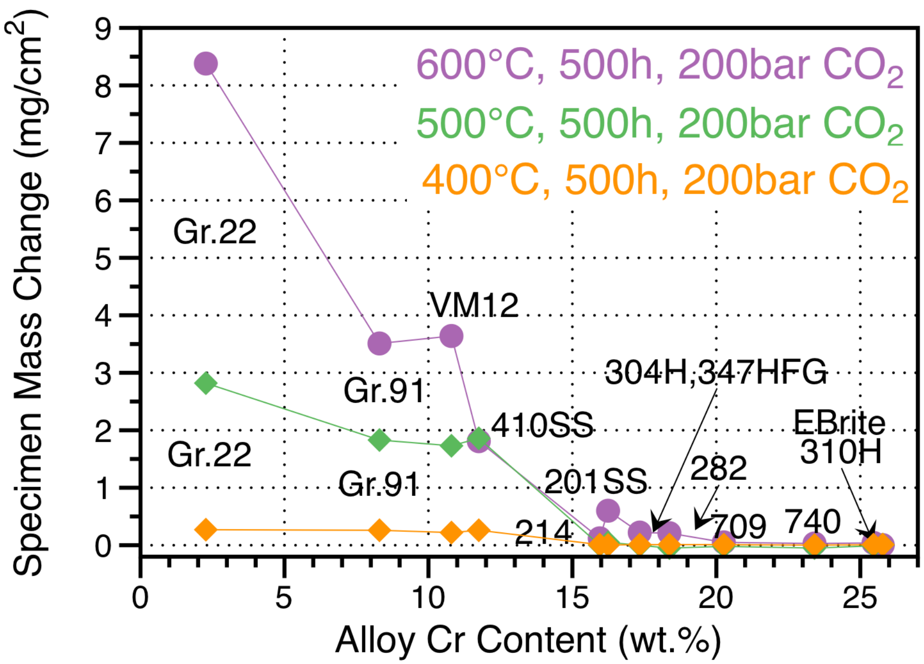
1 bar air vs. 200bar CO_2

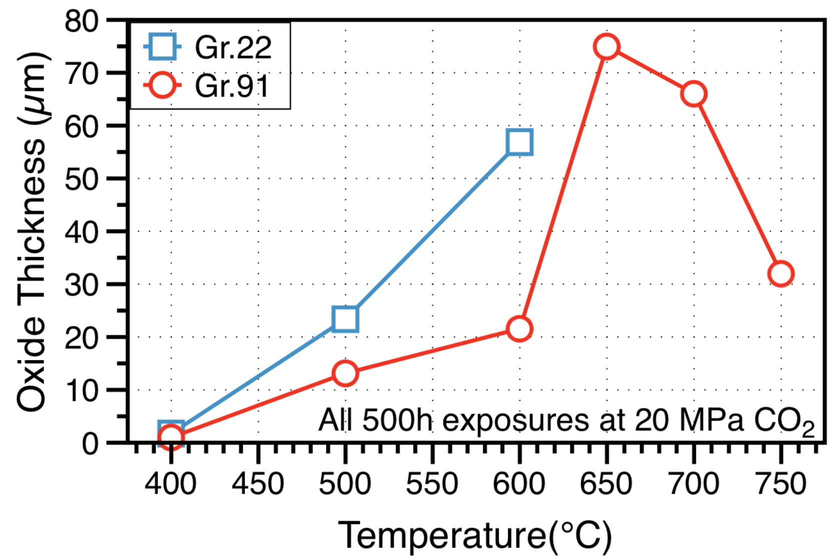


282: 58Ni-19Cr-10Co-8Mo-1.5Al-2.2Ti

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

Steels exposed at 400°-600°C
500h exposures in 20 MPa CO_2



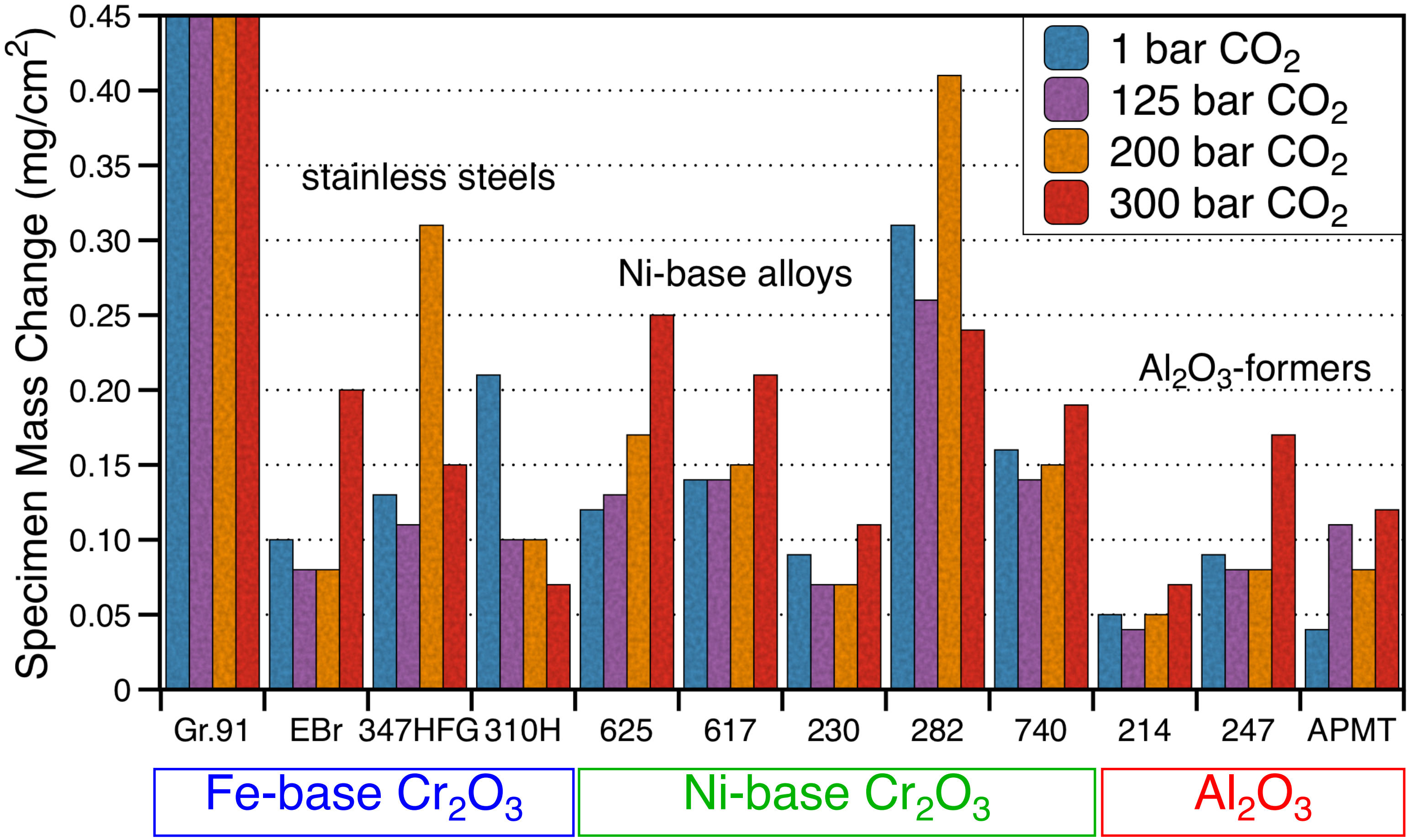


Industry interested in where
low-cost alloys can be used

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)

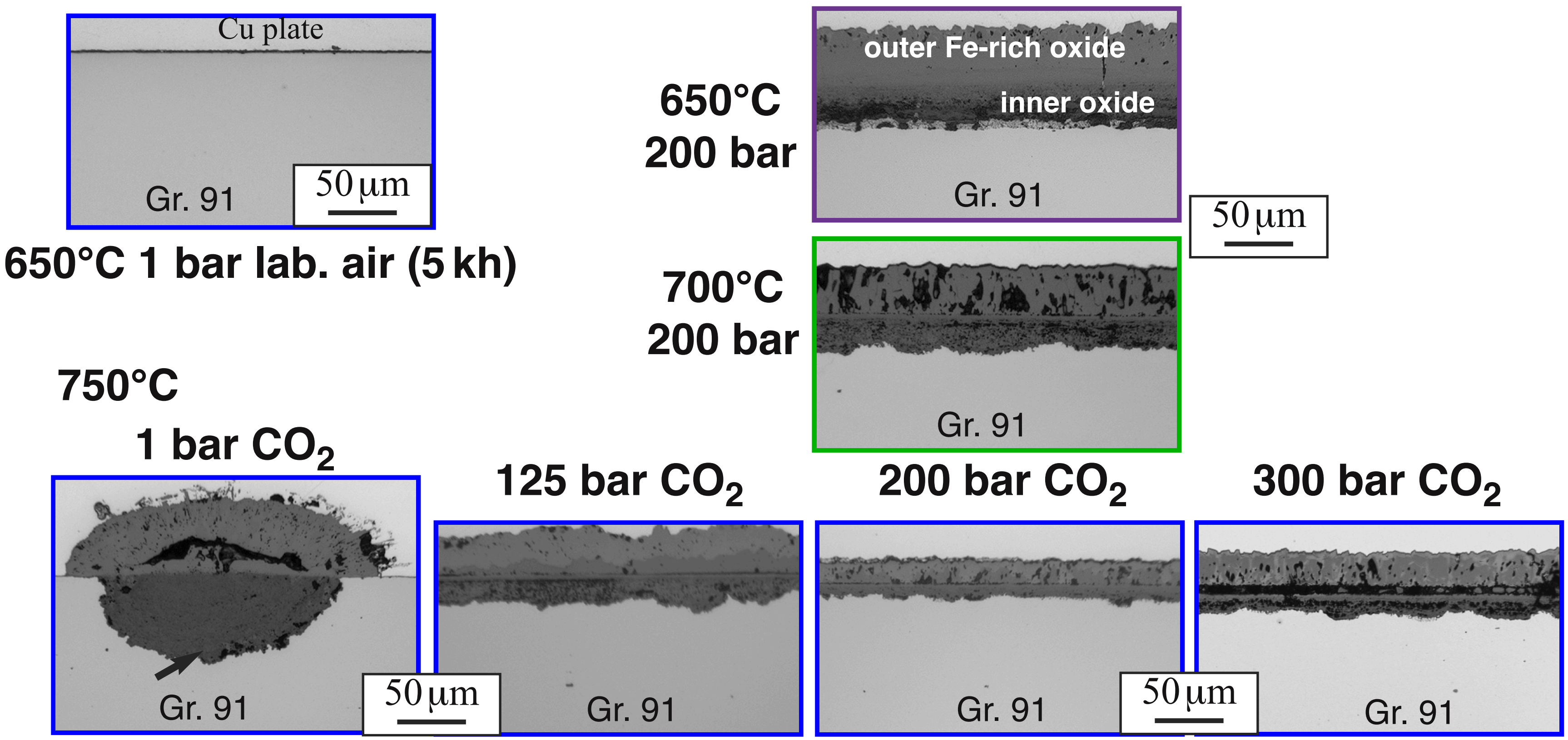
Typical Fe-rich oxide on Gr.91

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

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