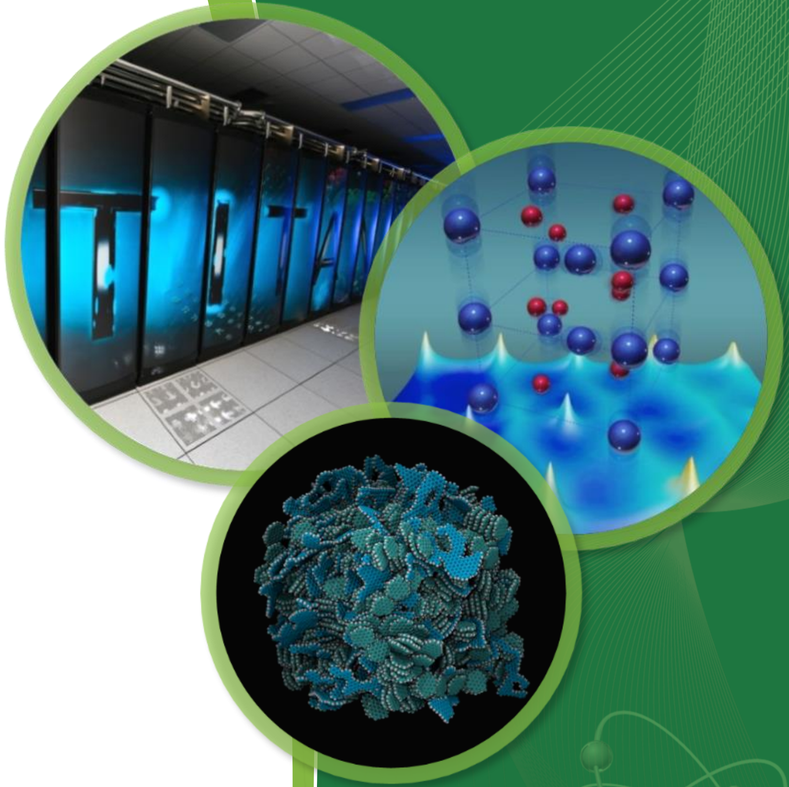
Materials Issues for (1) Advanced Supercritical CO_2 Cycles and (2) High Efficiency Gas Turbines



Bruce Pint

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Oak Ridge National Laboratory

November 1, 2017

Acknowledgments

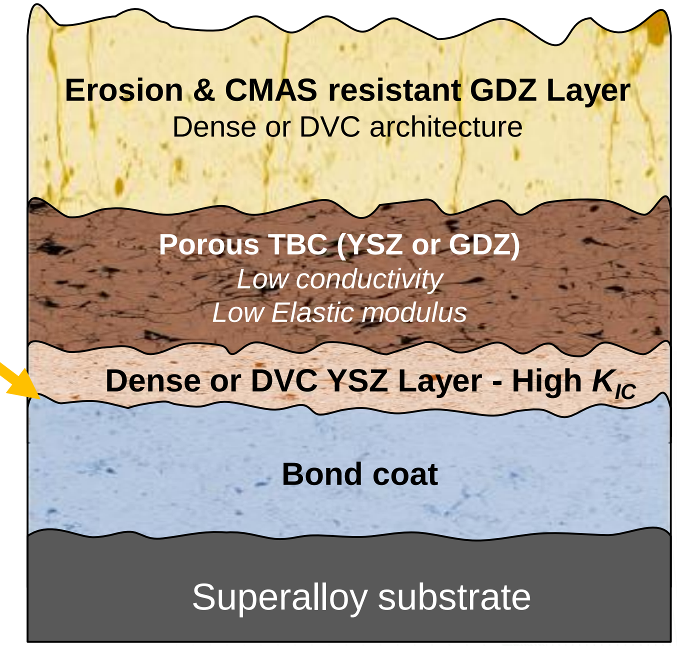
- TBC task leaders:
  - J. A. Haynes - coating procurement
    - G. Garner, M. Stephens - oxidation experiments
  - M. J. Lance - characterization (PSLS)
  - S. Sampath, Stonybrook U. – processing
- sCO_2 team:
  - Jim Keiser - autoclave design
  - Mike Howell - construction and operations
  - Characterization: R. Brese, T. Lowe, T. Jordan (metallography), M. Lance (GDOES)
  - TEM: K. A. Unocic, D. Leonard (FIB: D. Coffey)
- Alloys: Howmet, Siemens, Capstone Turbines, Haynes, Special Metals, Sandvik
- Research sponsored by: U. S. Department of Energy, Office of Fossil Energy
  - TBC project: Turbine Program (Rin Burke)
  - sCO_2 project: Crosscutting Technology Program (Vito Cedro)

OAK RIDGE National Laboratory

Looking for coating solutions

- More durable coatings will benefit
  - NGCC (natural gas combined cycle)
  - IGCC (i.e. coal syngas/H_2)
- Focus on alumina scale as “weak link”
- Partner with industry to advance testing
  - **pursue deployment of advanced TBC**

ORNL: New environments (higher H_2O, CO_2, SO_2)



CTSR: Multi-layer top coatings

Al_2O_3 scale

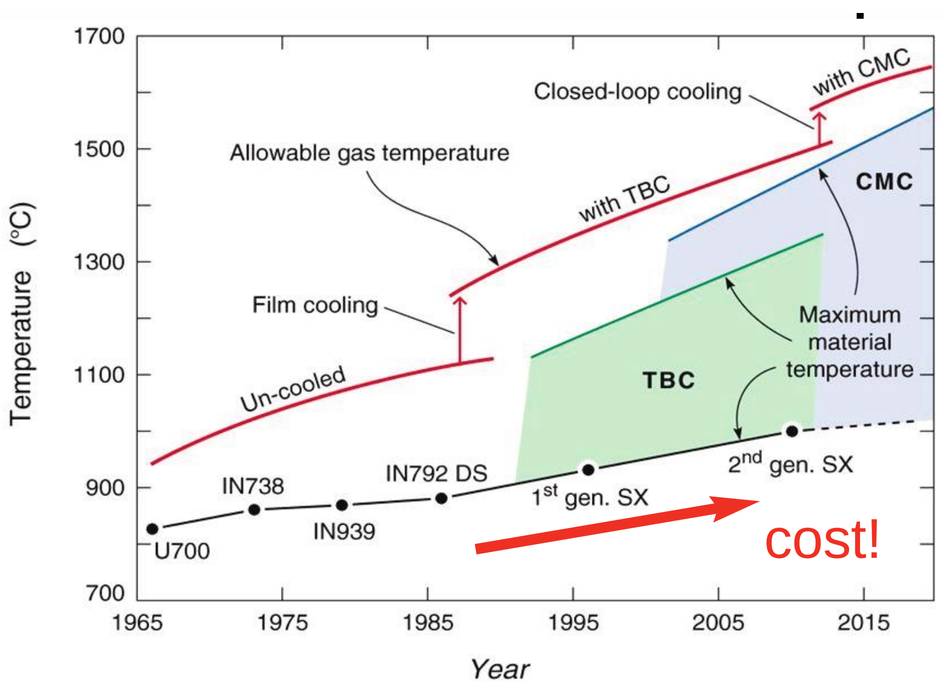
Optimal bond coating: PWA286 Y+Hf+Si

Explored different superalloy substrates

Thermal barrier coating =
oxidation-resistant, metallic bond coating +
durable, low conductivity, ceramic top coating

Coatings for Land-Based Turbines

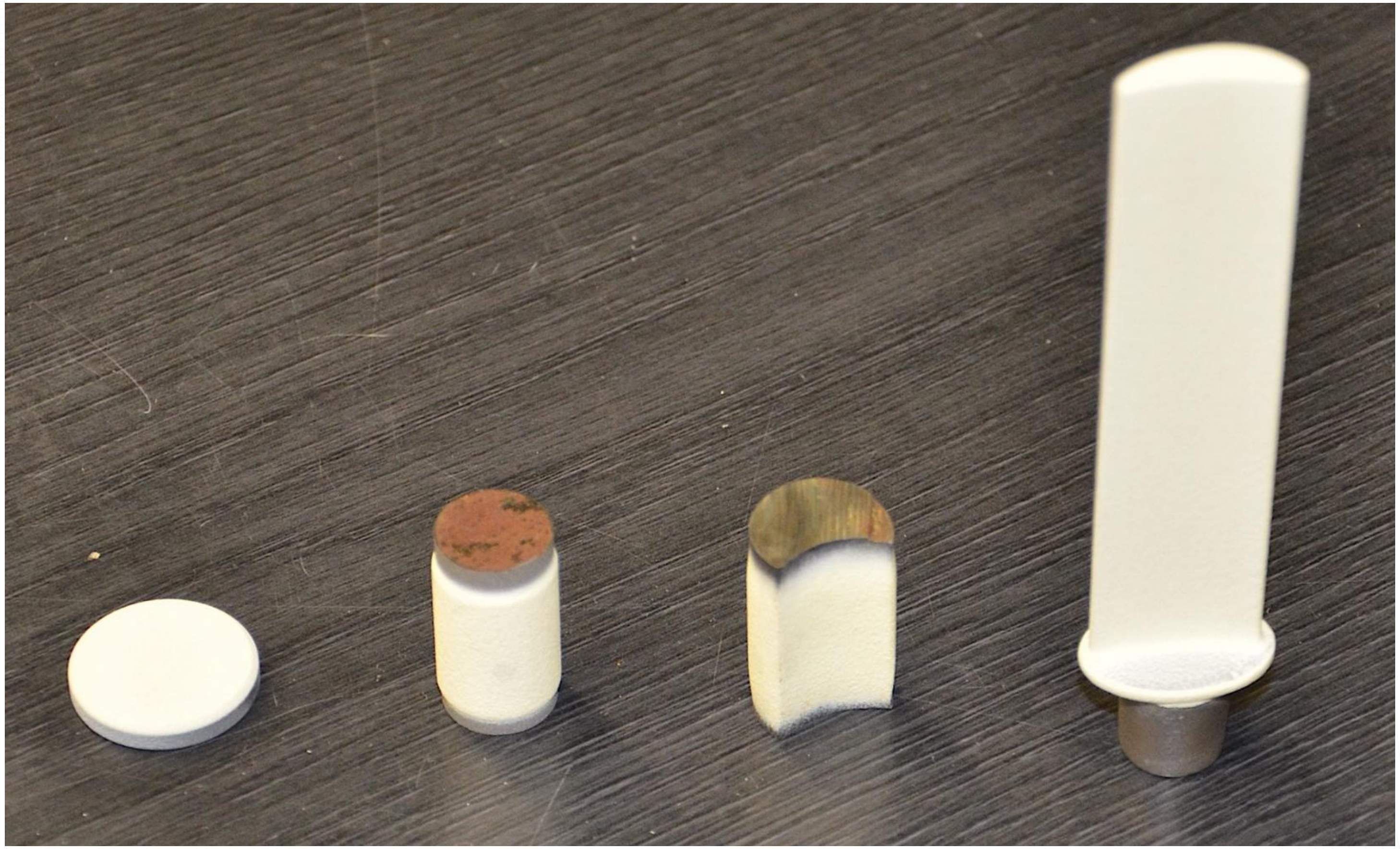
- Focus on thermally-sprayed coatings
  - HVOF: high-velocity oxy-fuel
  - APS: air plasma spray
- Current land-based turbine issues:
  - first cost drives sales
  - temperature/efficiency
    - not important today with cheap gas
  - hot corrosion in blade root
    - want higher Cr content alloys
- Future issues:
  - Higher efficiency via higher temperatures
  - Deploy ceramic components for 3000°F



MarM247 <- PWA1483 <- CMSX4

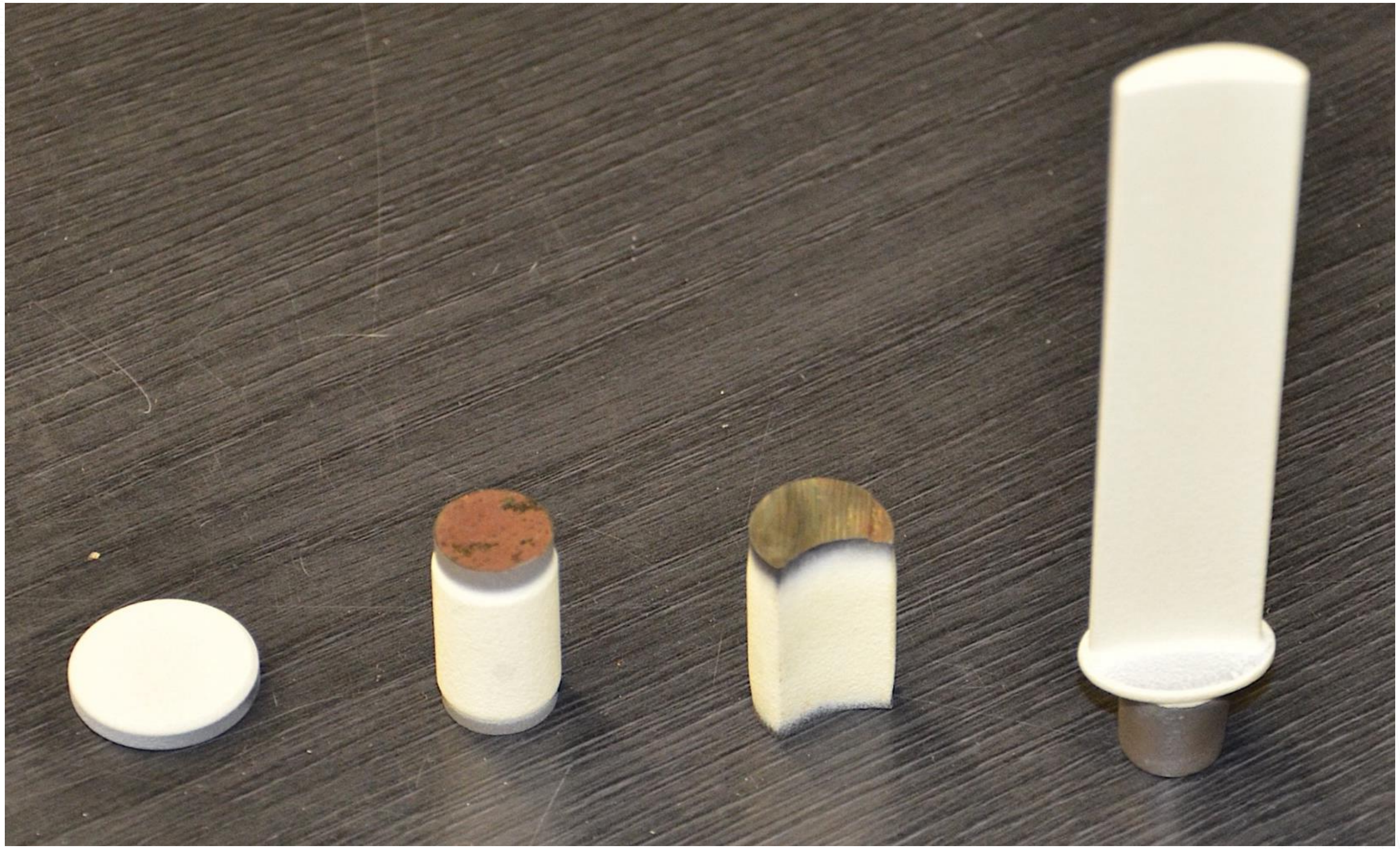
8Cr+1Hf 12Cr+4Ti 6Cr+3Re

Moving towards coating more realistic substrates



AM 718 “blade”

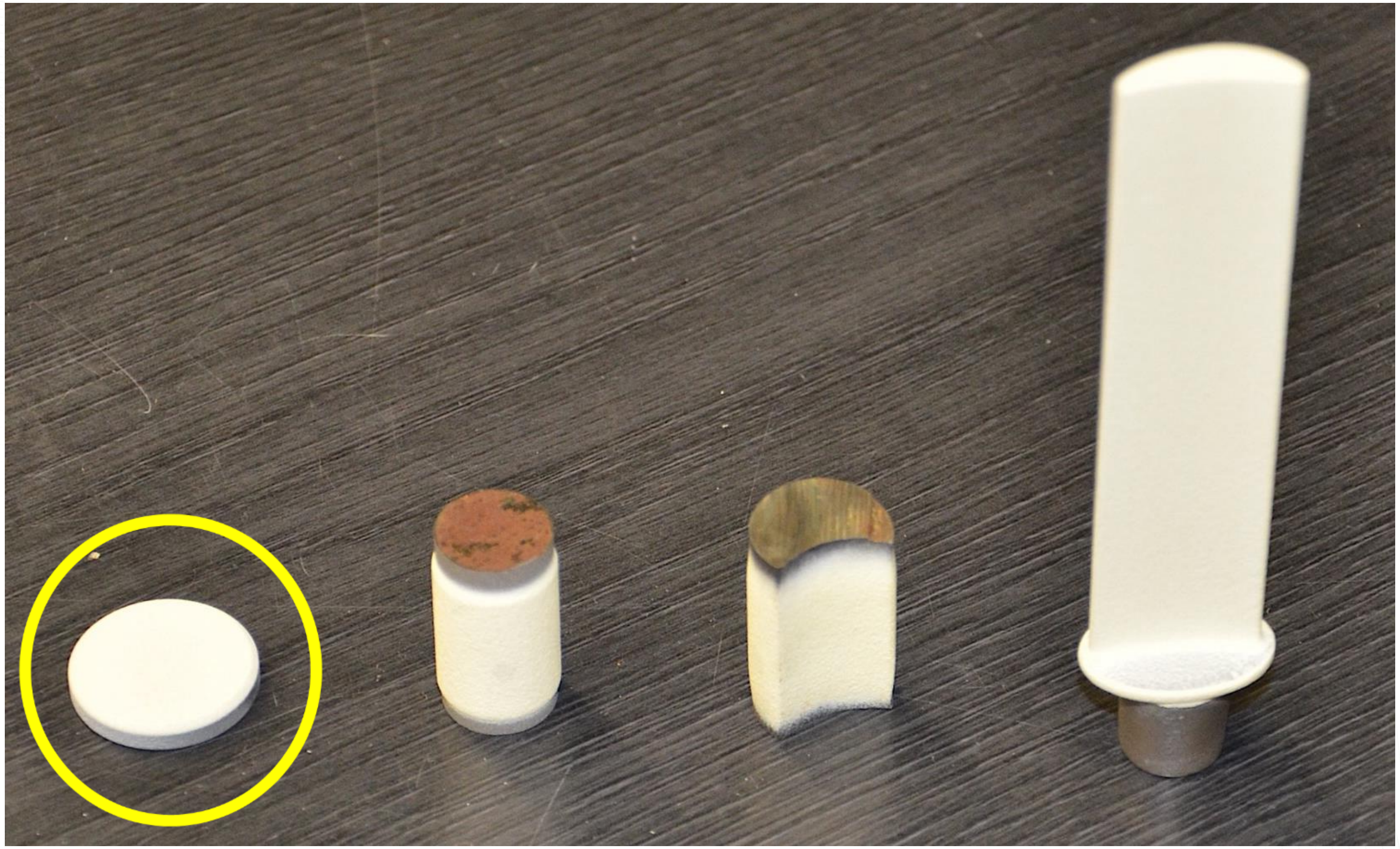
Easier to imagine than to coat…



AM 718 “blade”

Coating development not linear with time

Coating disks/coupons/buttons is a starting point



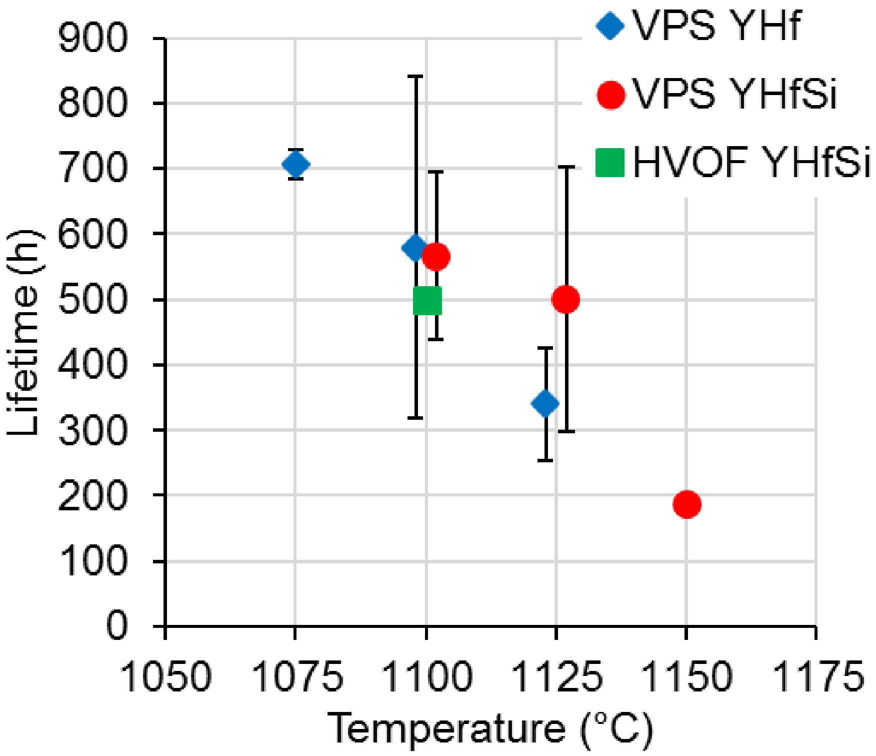
2010-2014: typical disk/coupon work summarized

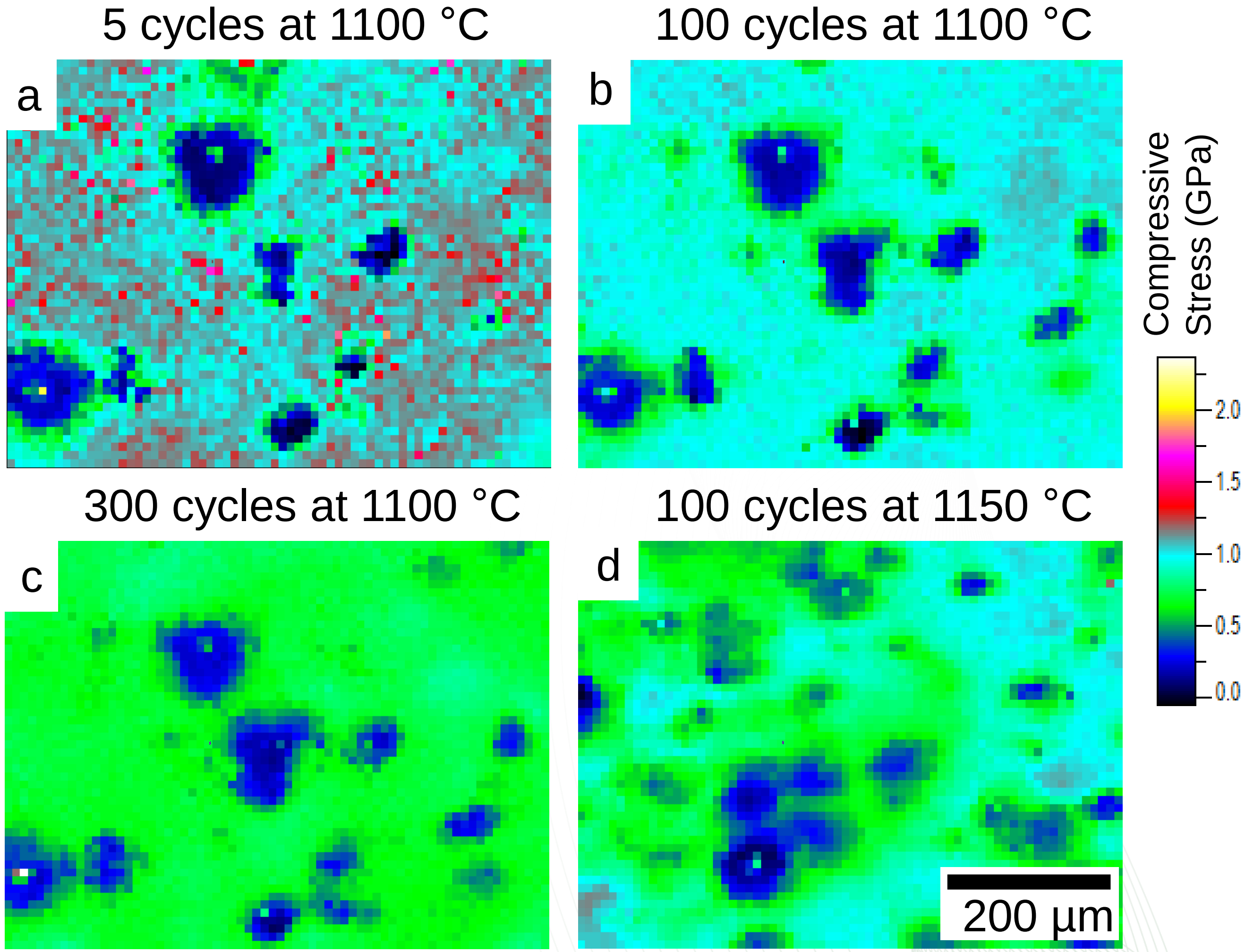
B. A. Pint, K. A. Unocic and J. A. Haynes, “The Effect of Environment on TBC Lifetime,” J. Eng. Gas Turb. & Power, 138 (8) (2016) 082102.

B. A. Pint, J. A. Haynes, M. J. Lance, H. L. Aldridge, Jr., V. Viswanathan, G. Dwivedi and S. Sampath, in M. Hardy, et al. eds., Superalloys 2016,

Work compared furnace cycle lifetimes and Characterized coating degradation (e.g. PLPS)

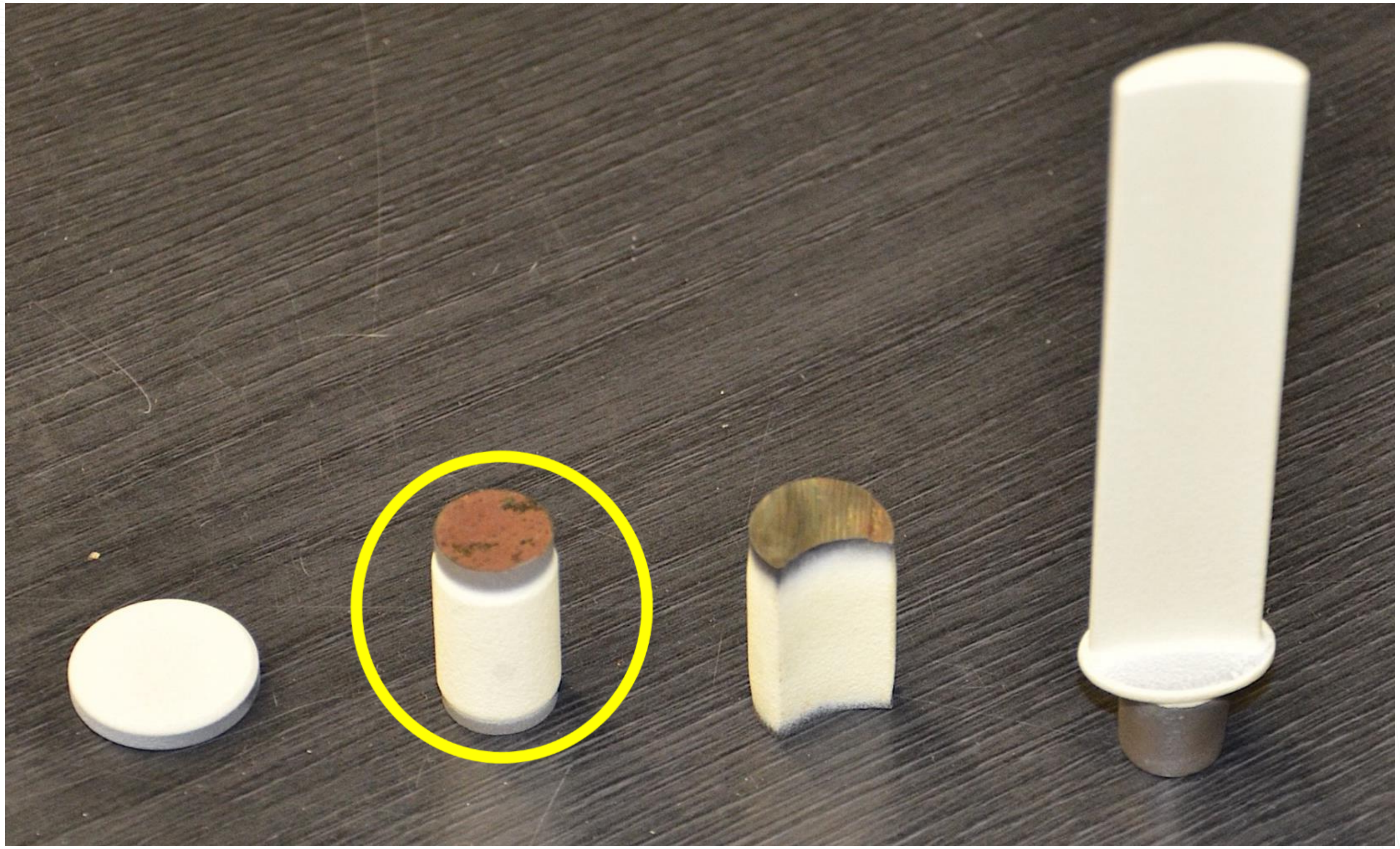
1-h cycles in "wet" air (10%H_2O)



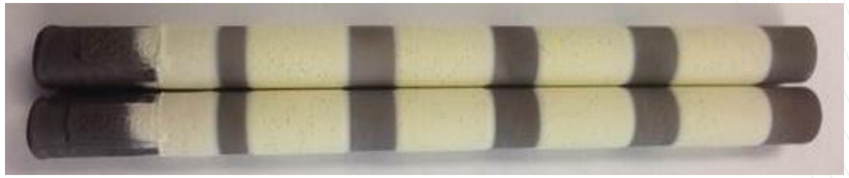


PLPS: photo-stimulated luminescence piezospectroscopy

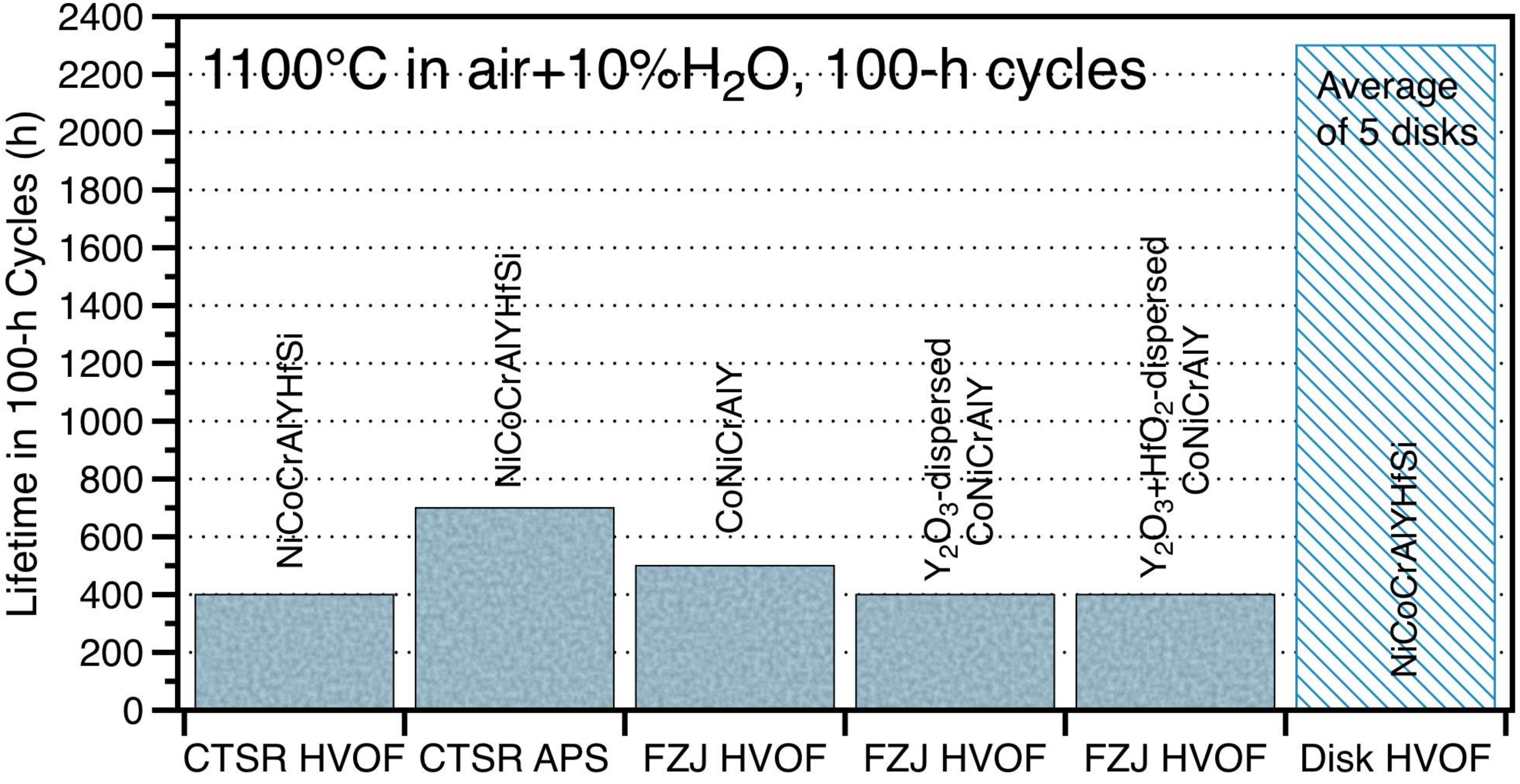
I thought it would be easy to change to rod specimens

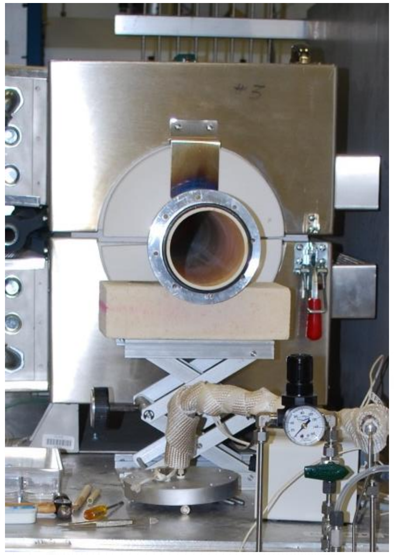


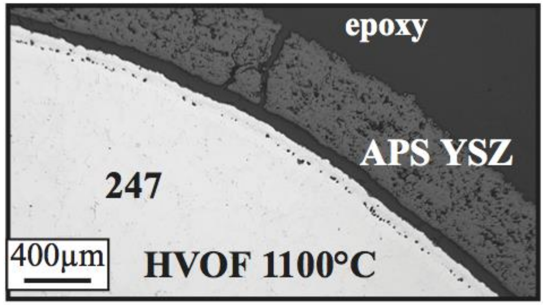
2015: began coating rods (DS alloy 247 "rodlets")



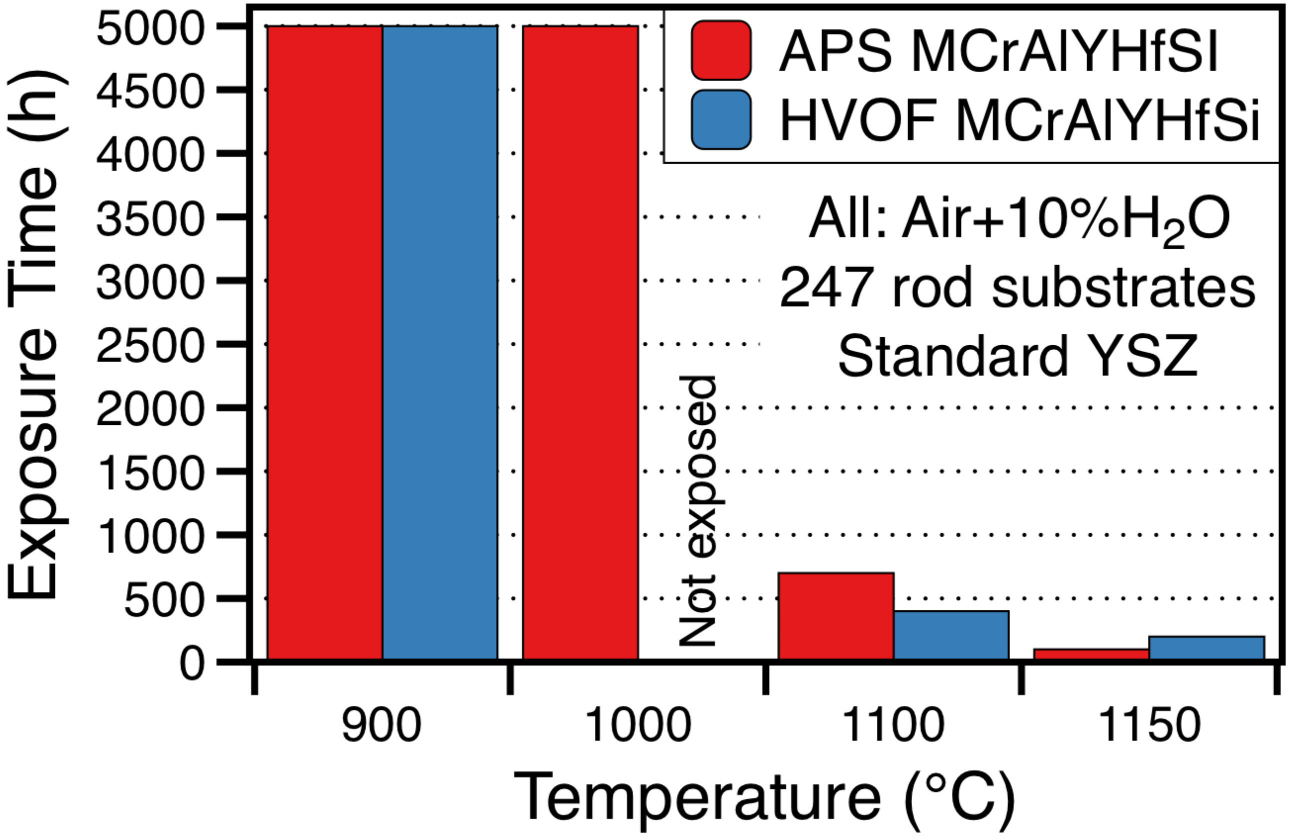
Rod lifetimes were much lower than previous results



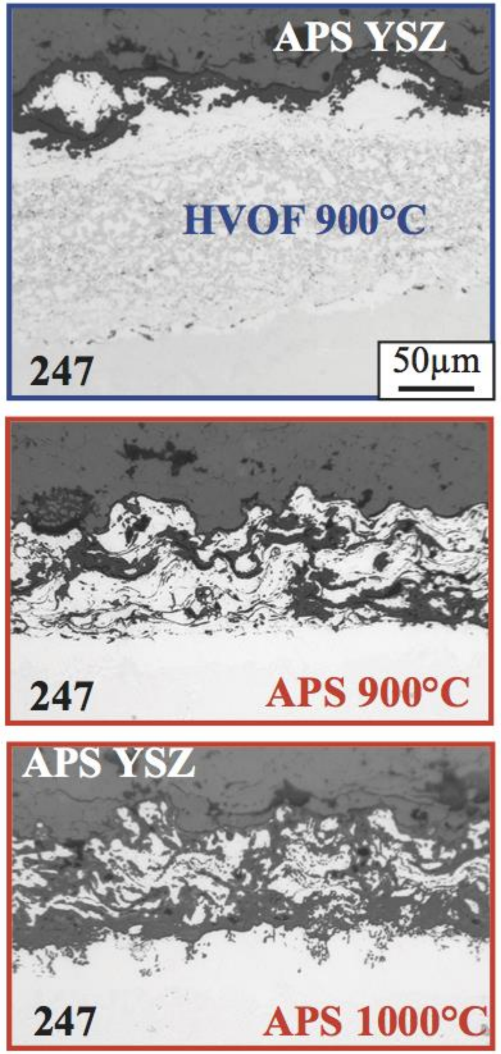




Long lifetimes observed at lower exposure temperatures



All: Air+10%H_2O
247 rod substrates
Standard YSZ



Retained
β-NiAl

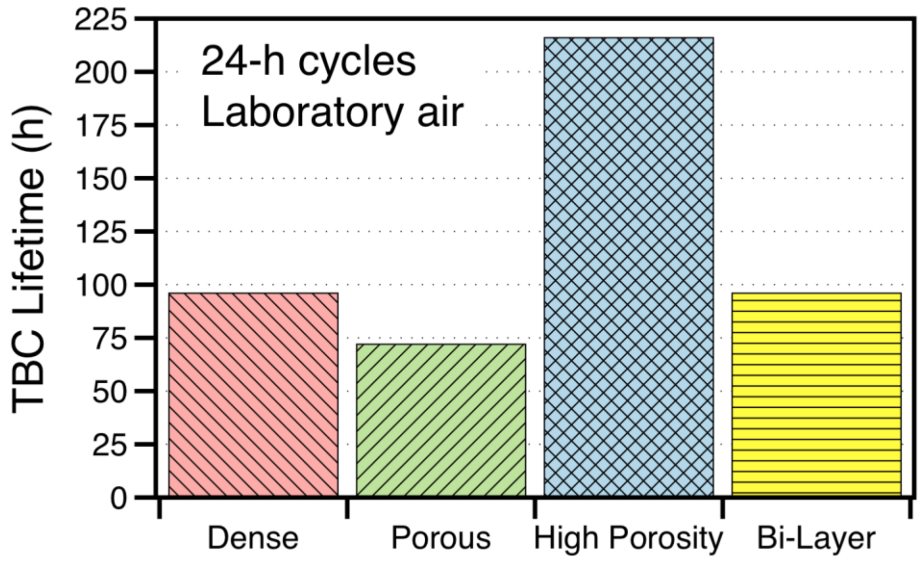
HVOF: similar to disk specimens

minimal degradation near operating temperature

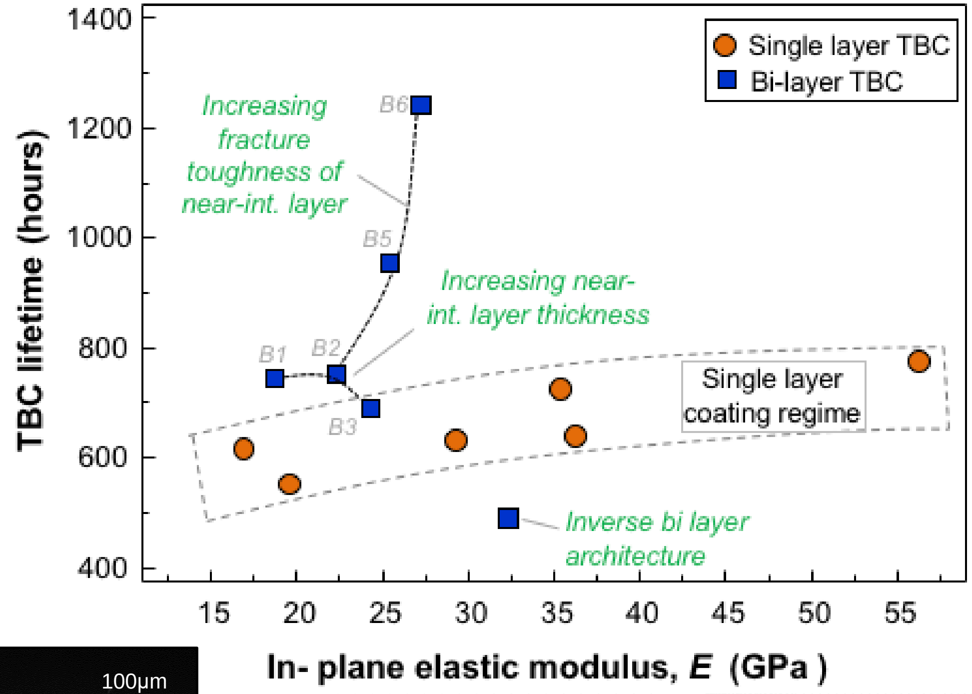
APS: bond coating too thin

CTSR performed additional parameter studies

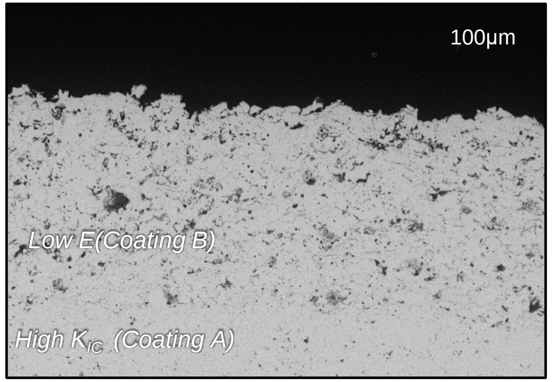
Additional rods tested at CTSR



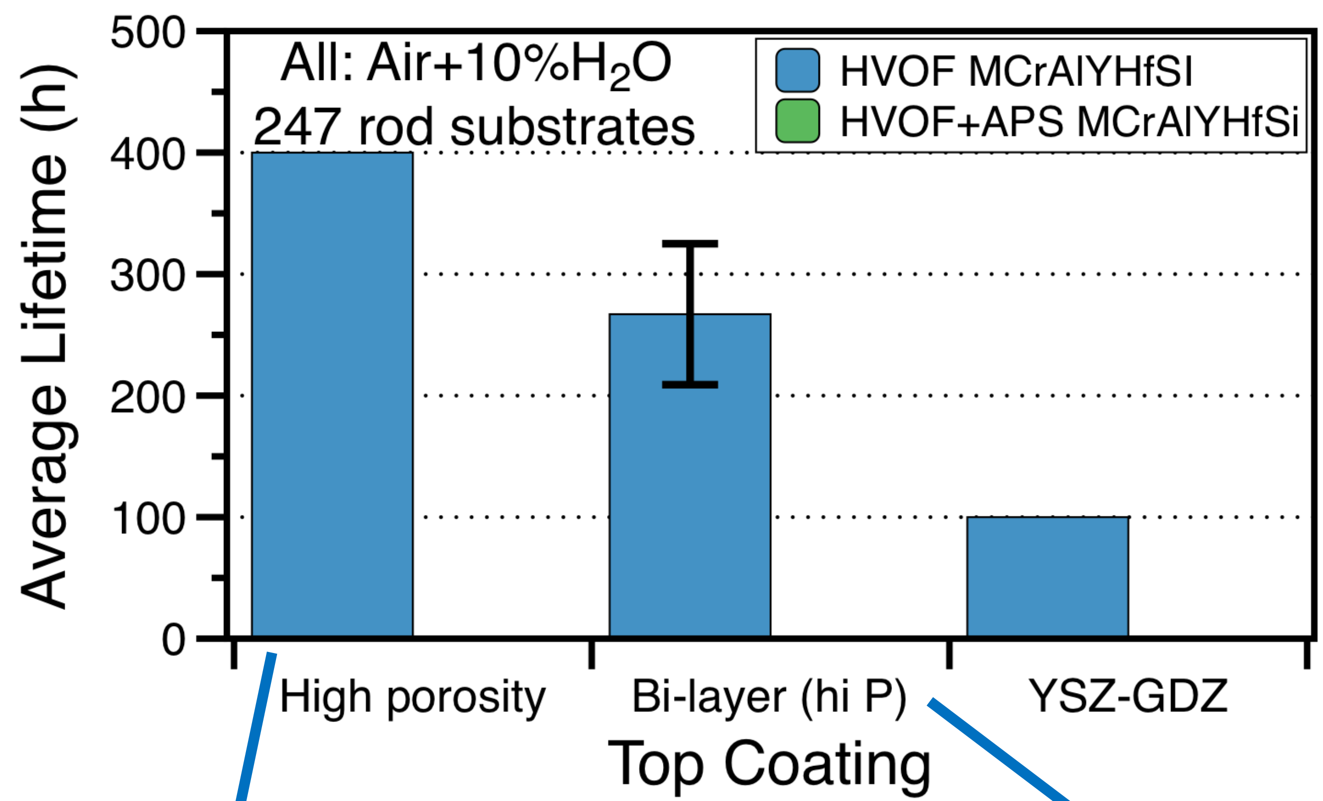
Opposite result from flat specimens



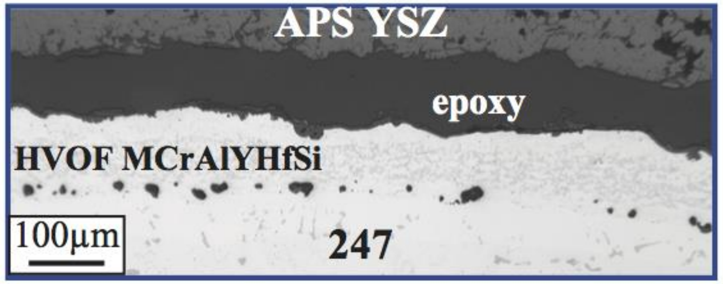
Bi-layer

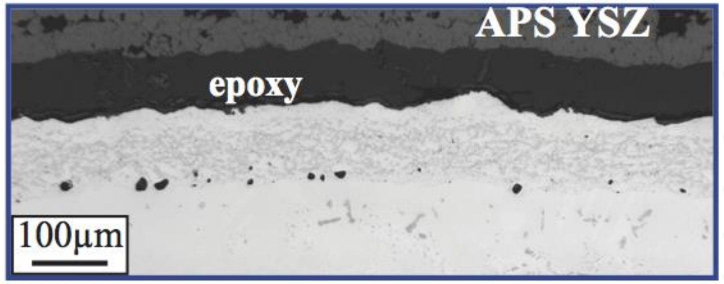


Phase 2 HVOF coatings did not perform better than Phase 1

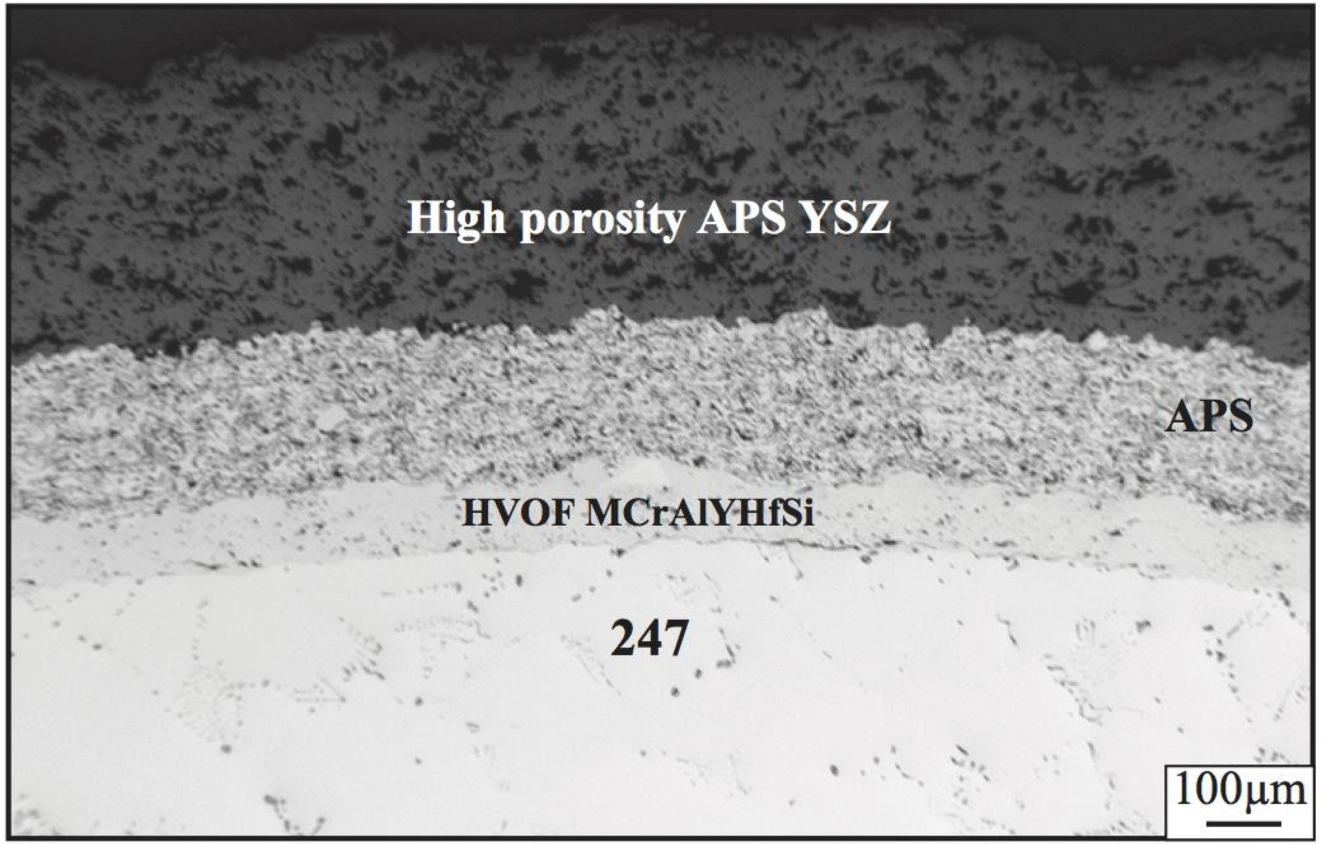


- Three top coat variations
  - 1 layer: high porosity YSZ
  - 2 layer: dense inner layer
  - 3 layer: outer $Gd_2Zr_2O_7$
- Concern about low bond coating roughness



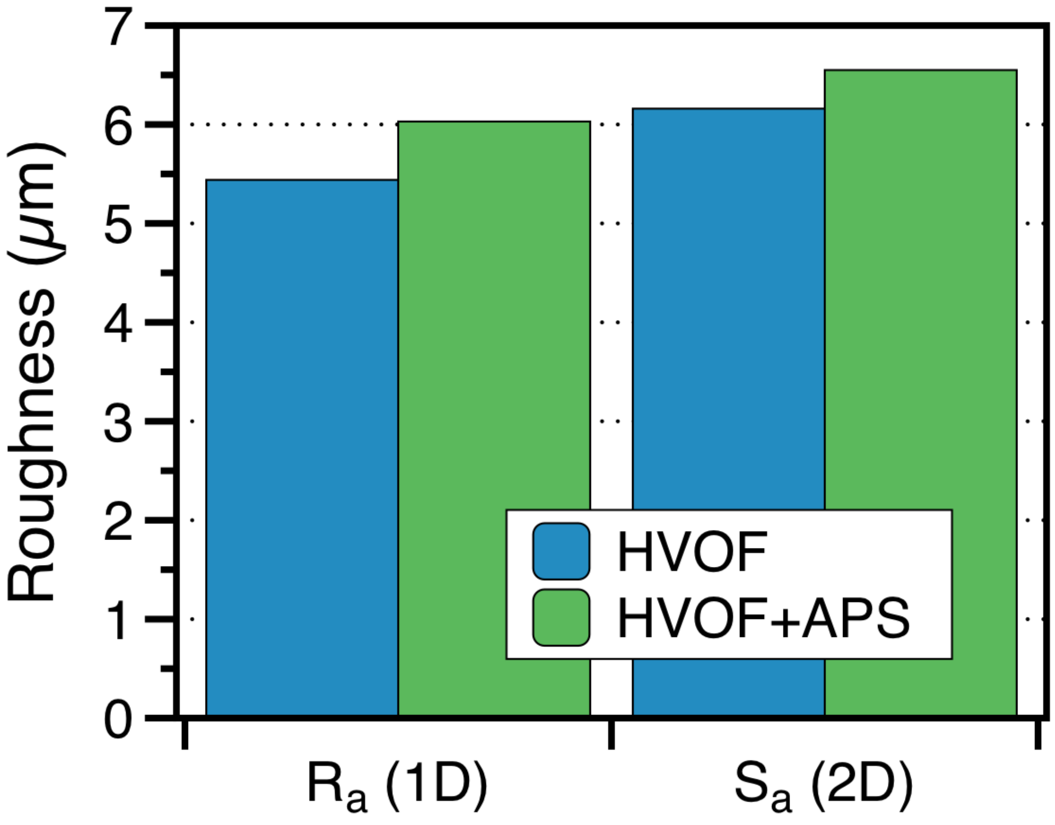


1st iteration was not really an APS “flash” coat on HVOF

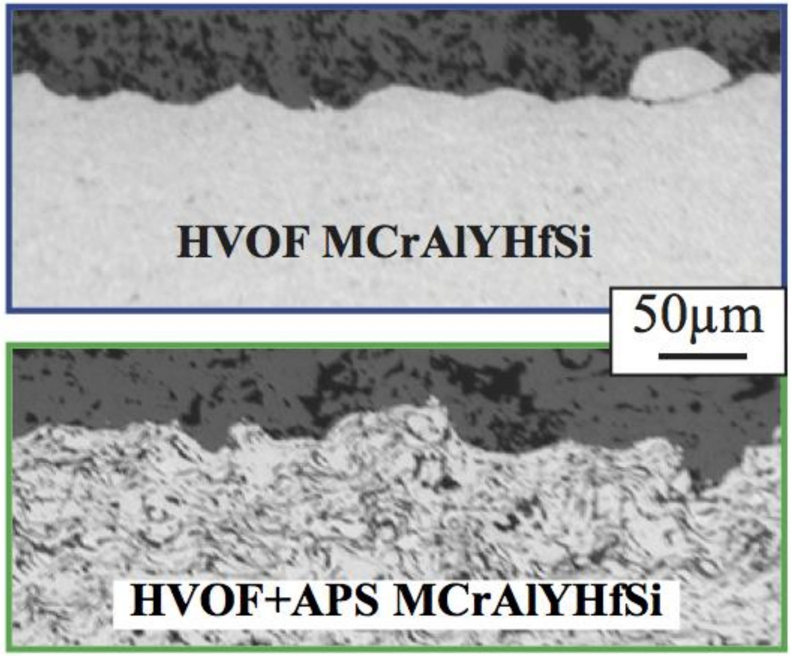


Average lifetime of 3 rods of each type
APS NiCoCrAlYHfSi ~200 µm layer (not 50 µm)
APS ~300+ µm top coating

HVOF+APS roughness only marginally higher than HVOF



- Disk: $R_a \sim 8$ µm
- Is R_a the correct parameter?
- Jülich used fractal analysis of "microroughness"



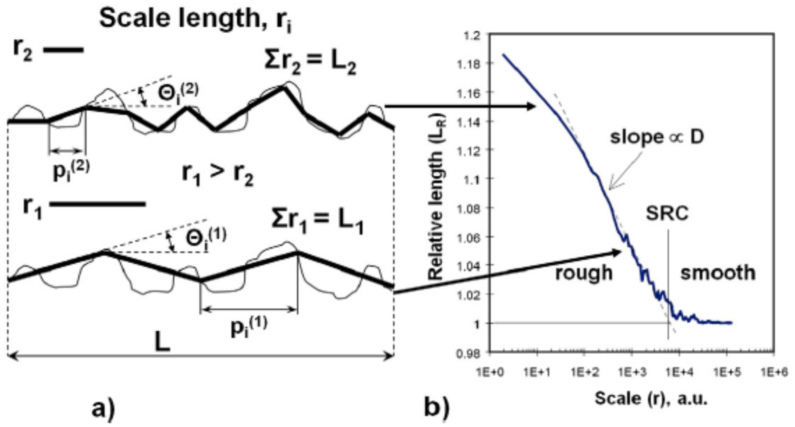
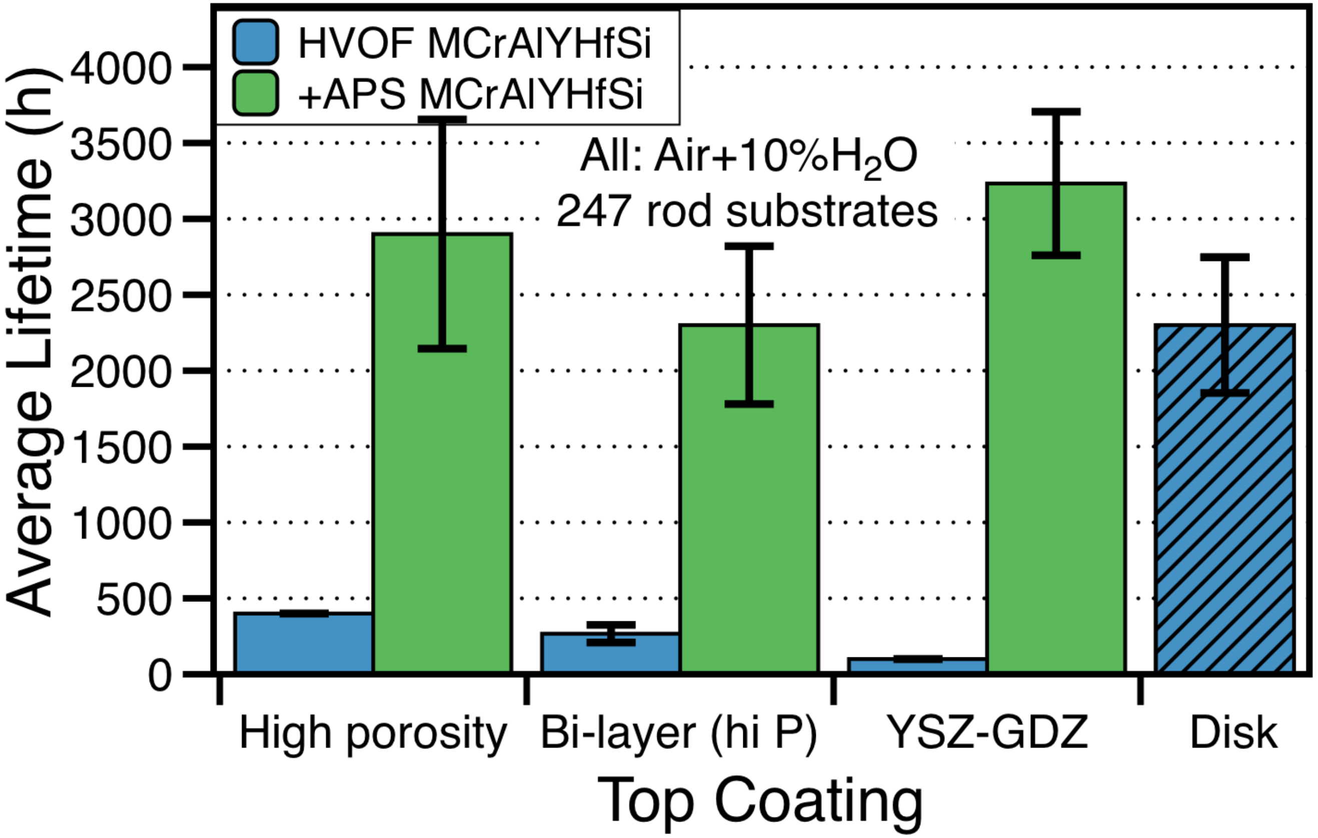


Fig. 2. Schematic showing: a) roughness profile description using different ruler length and b) typical plot obtained during fractal analysis of two dimensional surfaces (reproduced from Ref. [18]).

Nowak et al. Surf. Coat. Tech. 2014

Excellent results with APS layer on top of HVOF bond coating

- Standard testing at 1100°C
  - Air + 10%H_2O
  - 100-h cycles
- Rod specimens
  - Three different top coatings
    - 1 layer: extra porous
    - 2 layer: dense inner YSZ
    - 3 layer: add $Gd_2Zr_2O_7$ outer layer
  - Two bond coatings
    - Standard HVOF
    - HVOF+ ~200 μm APS “flash”



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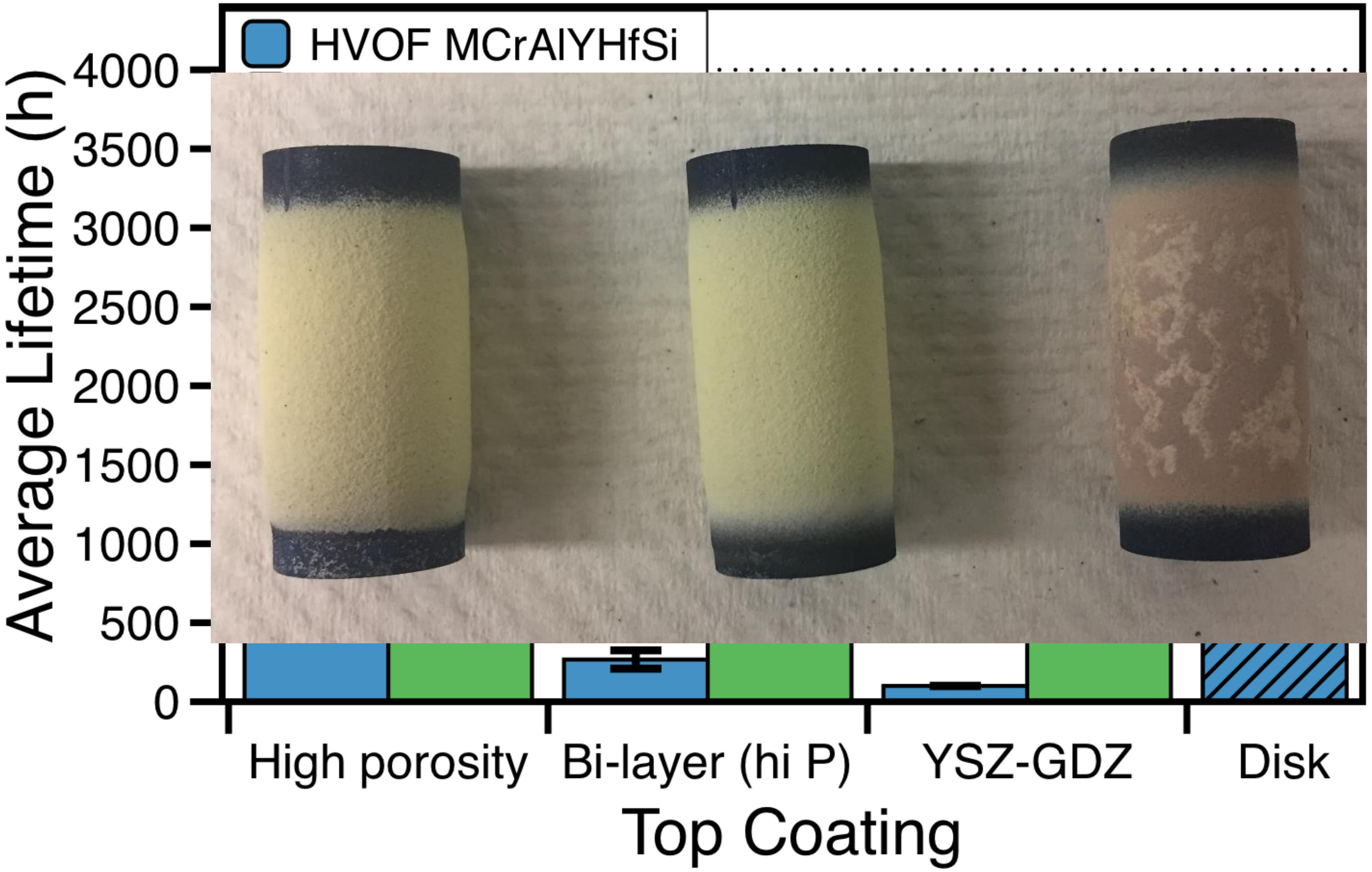
    - HVOF+APS "flash"



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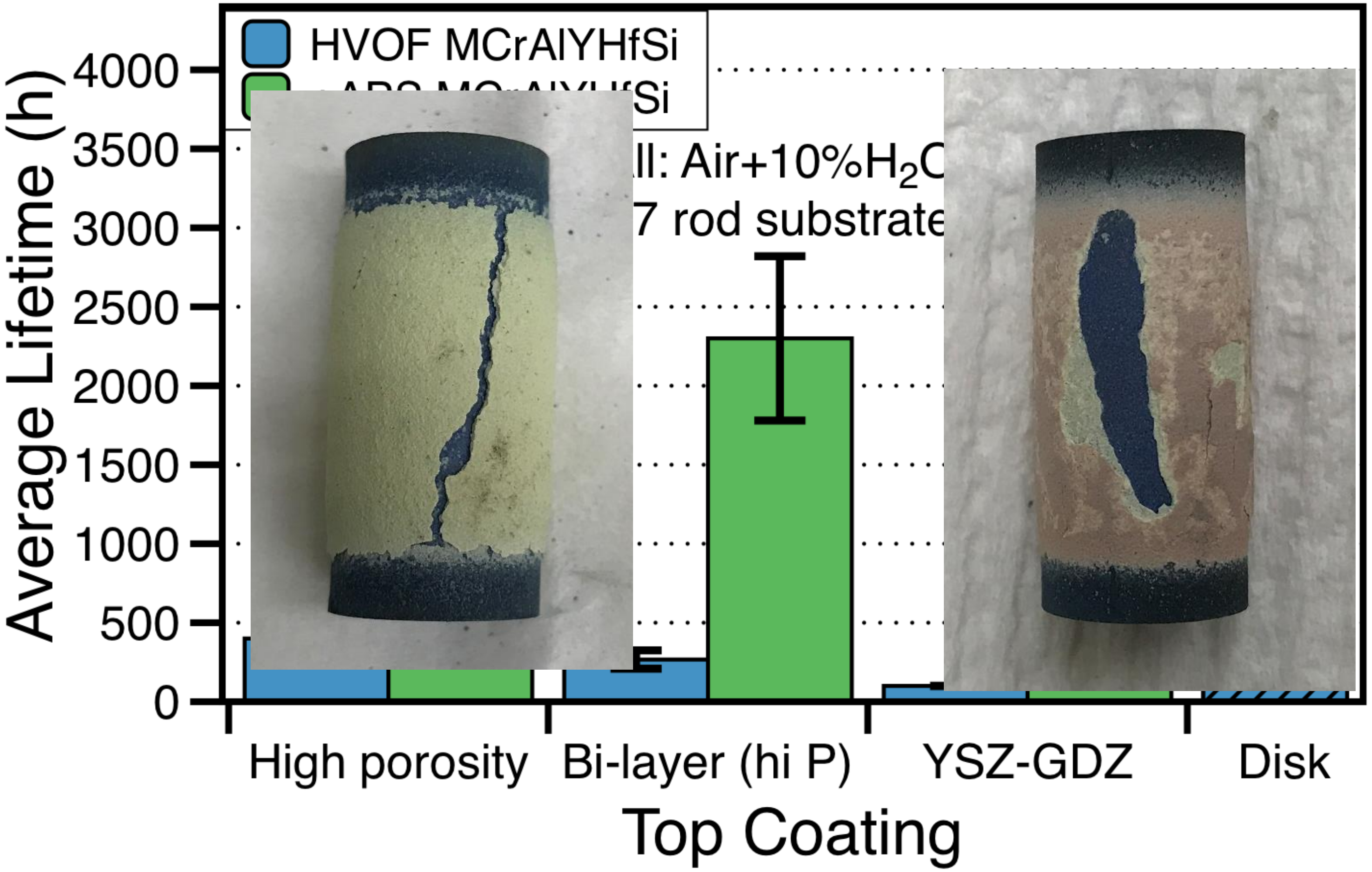
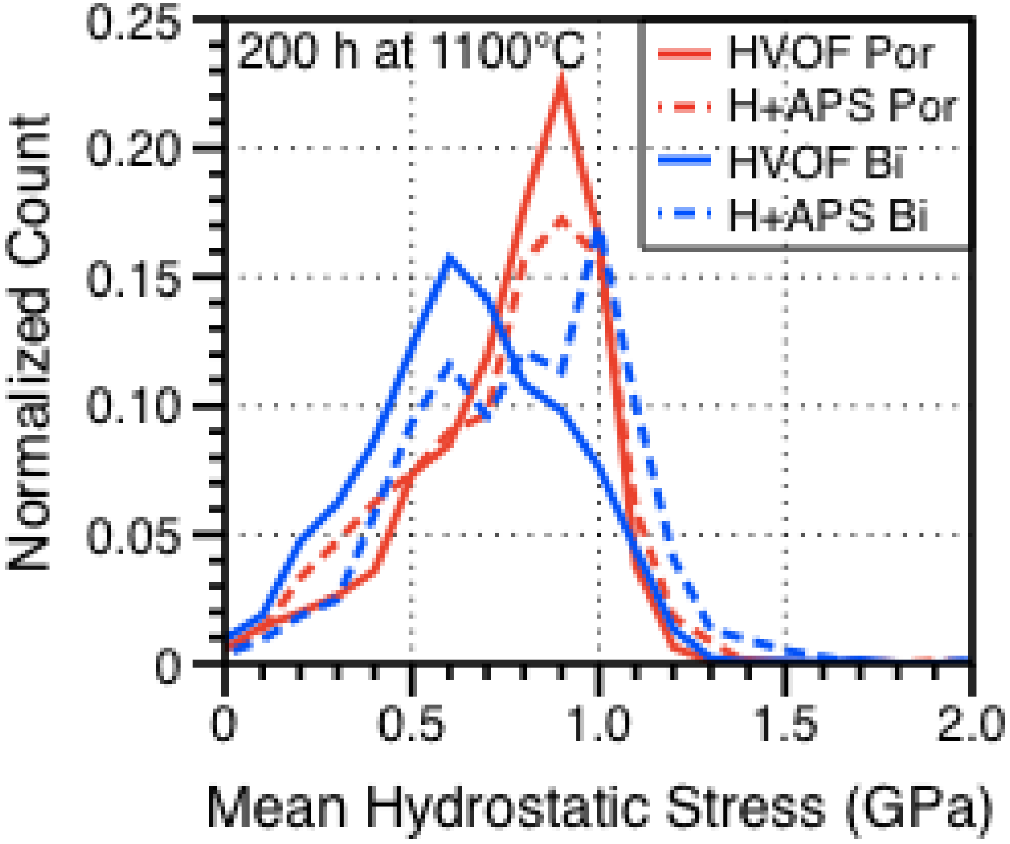
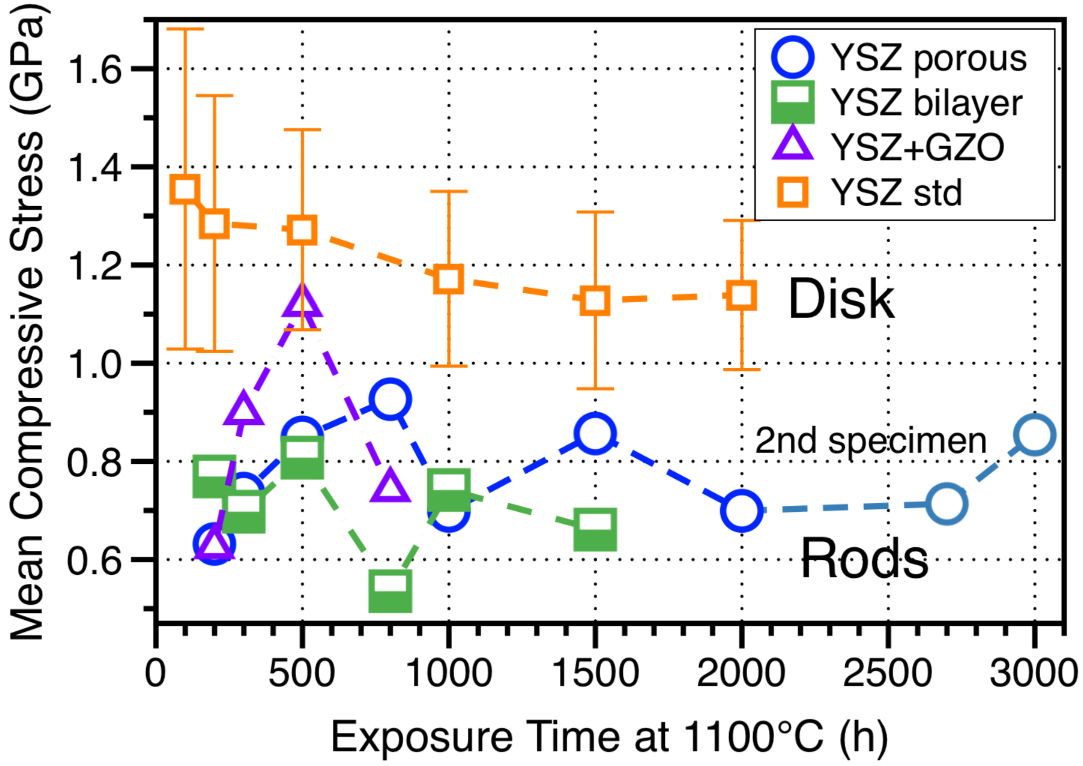


PLPS results: very weak signal through 300µm top coating

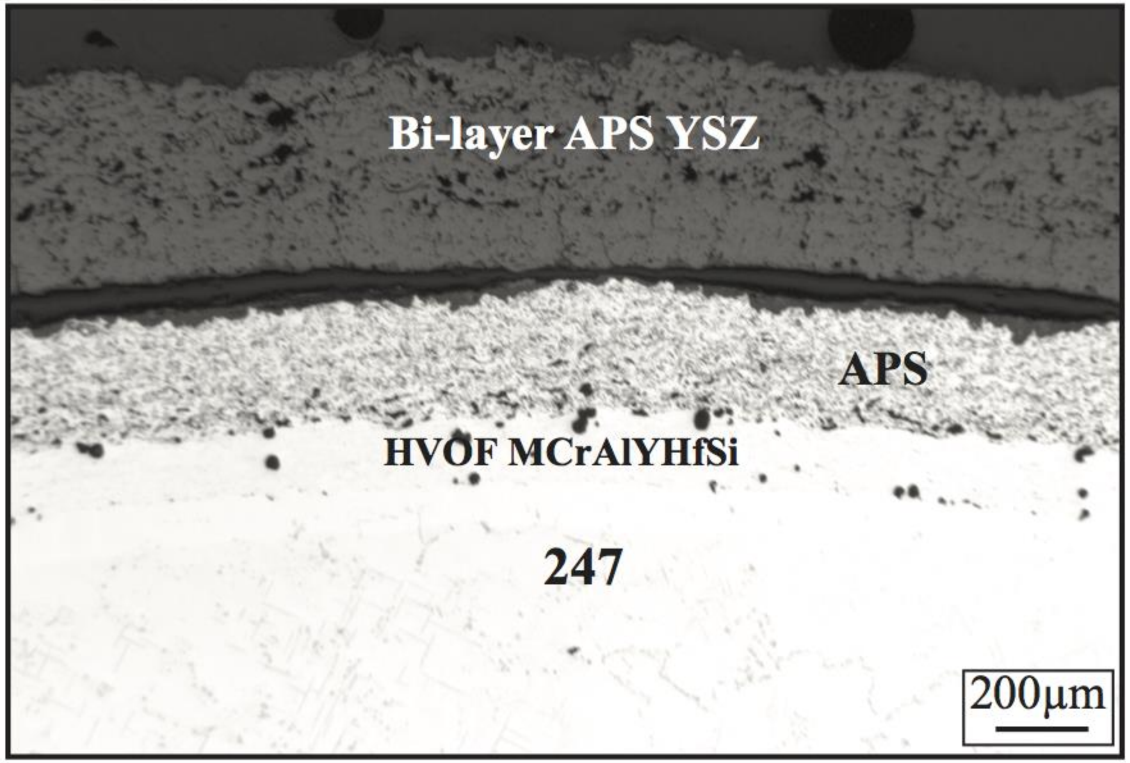
Similar residual stress in alumina scale on both bond coatings



Higher residual stress in flat disk specimen compared to rods



Characterization in progress: does failure fit proposed mechanistic model for flash coating?



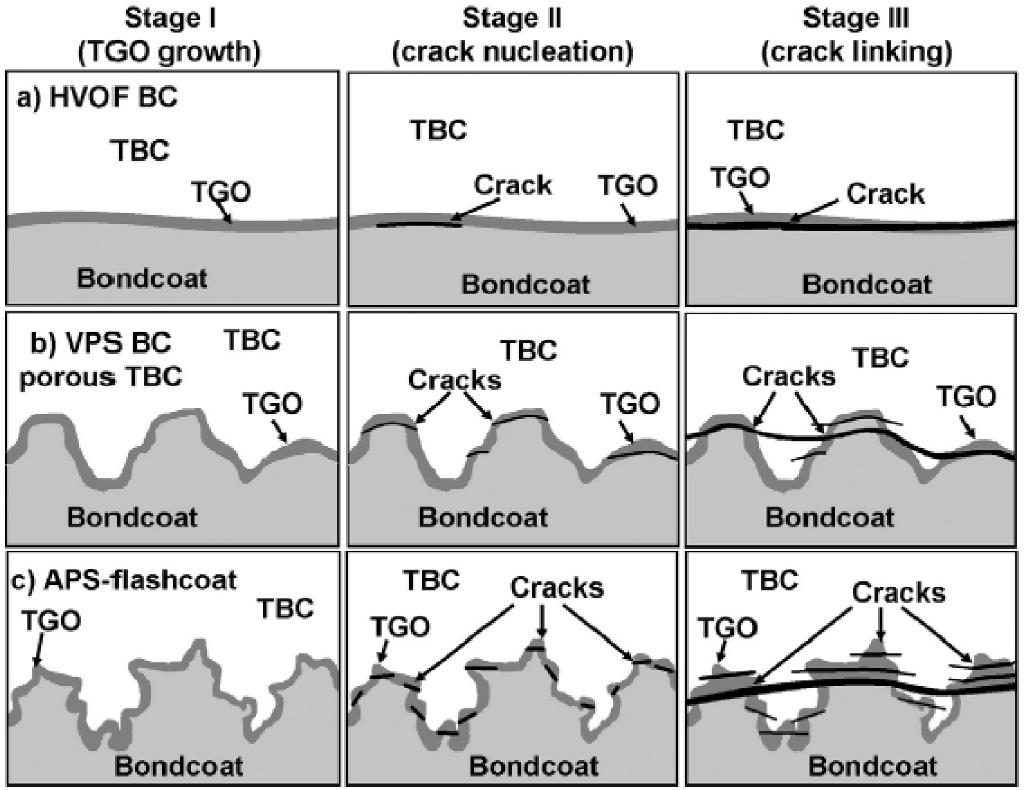
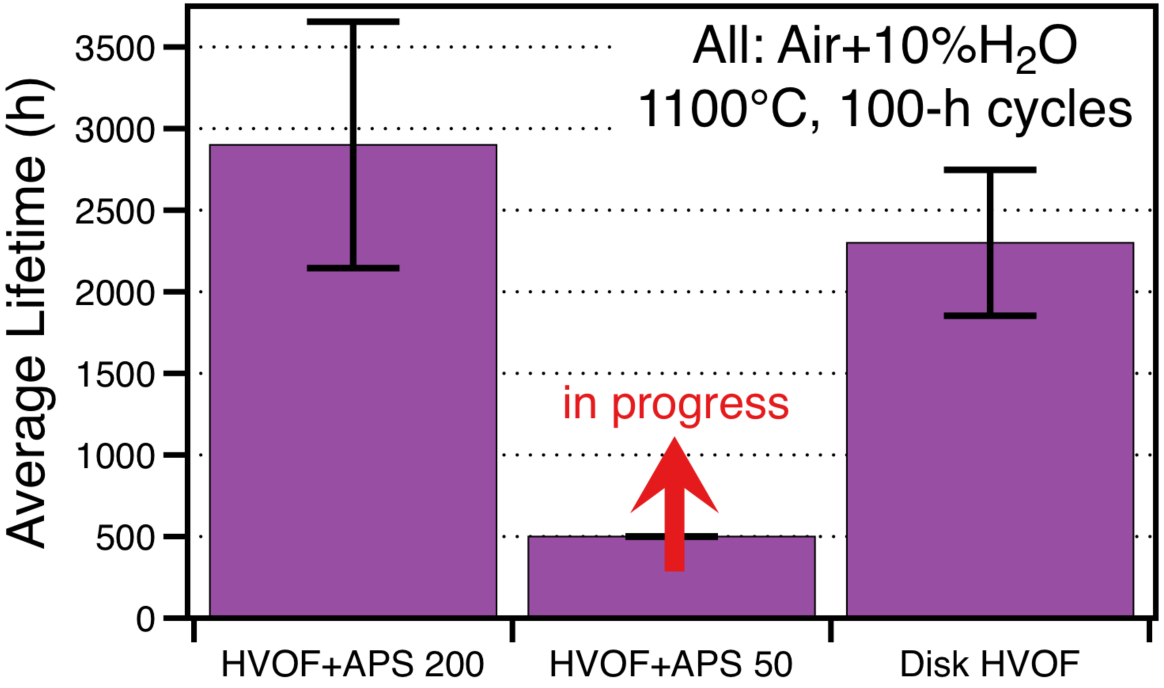


Fig. 11. Schematic showing proposed failure mechanisms for TBC systems with the studied bondcoats. Stage I: TGO growth, Stage II: Crack nucleation and growth, Stage III: Crack linking and macroscopic failure.

Nowak et al. Surf. Coat. Tech. 2014

Next round of experiments in progress

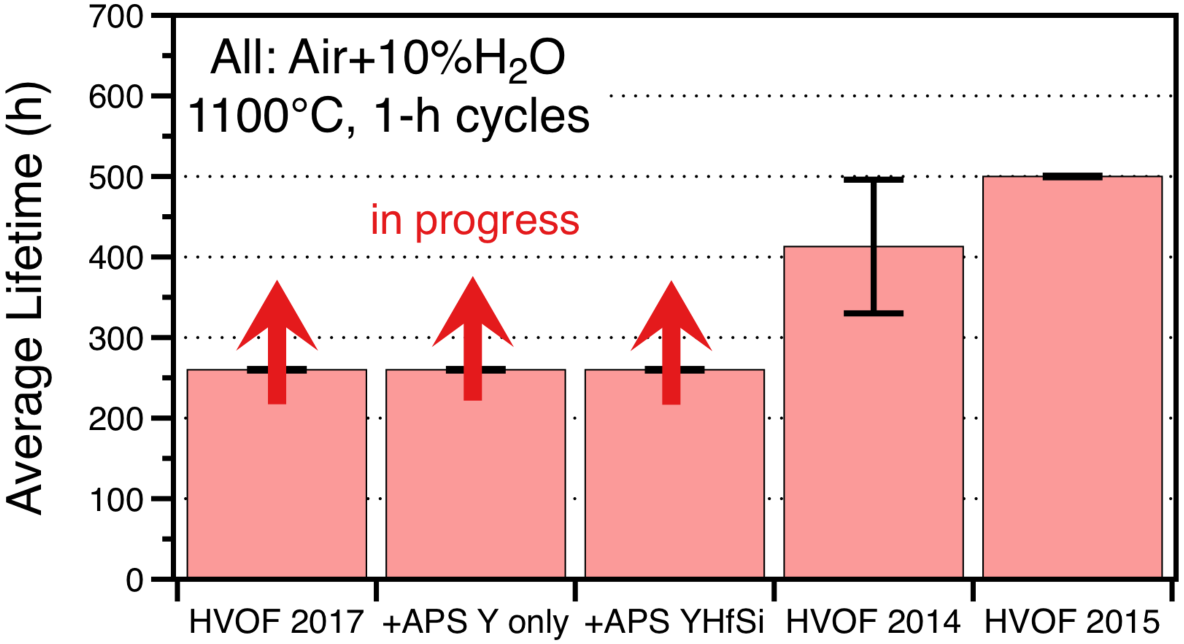
Next rod iteration: 50µm YHfSi APS 100-h cycles at 1100°C



Is longer life due to thicker bond coating?

Also launching experiments at lower temperatures

Return to disks in 1-h cycles: Is YHfSi needed for flash coating?

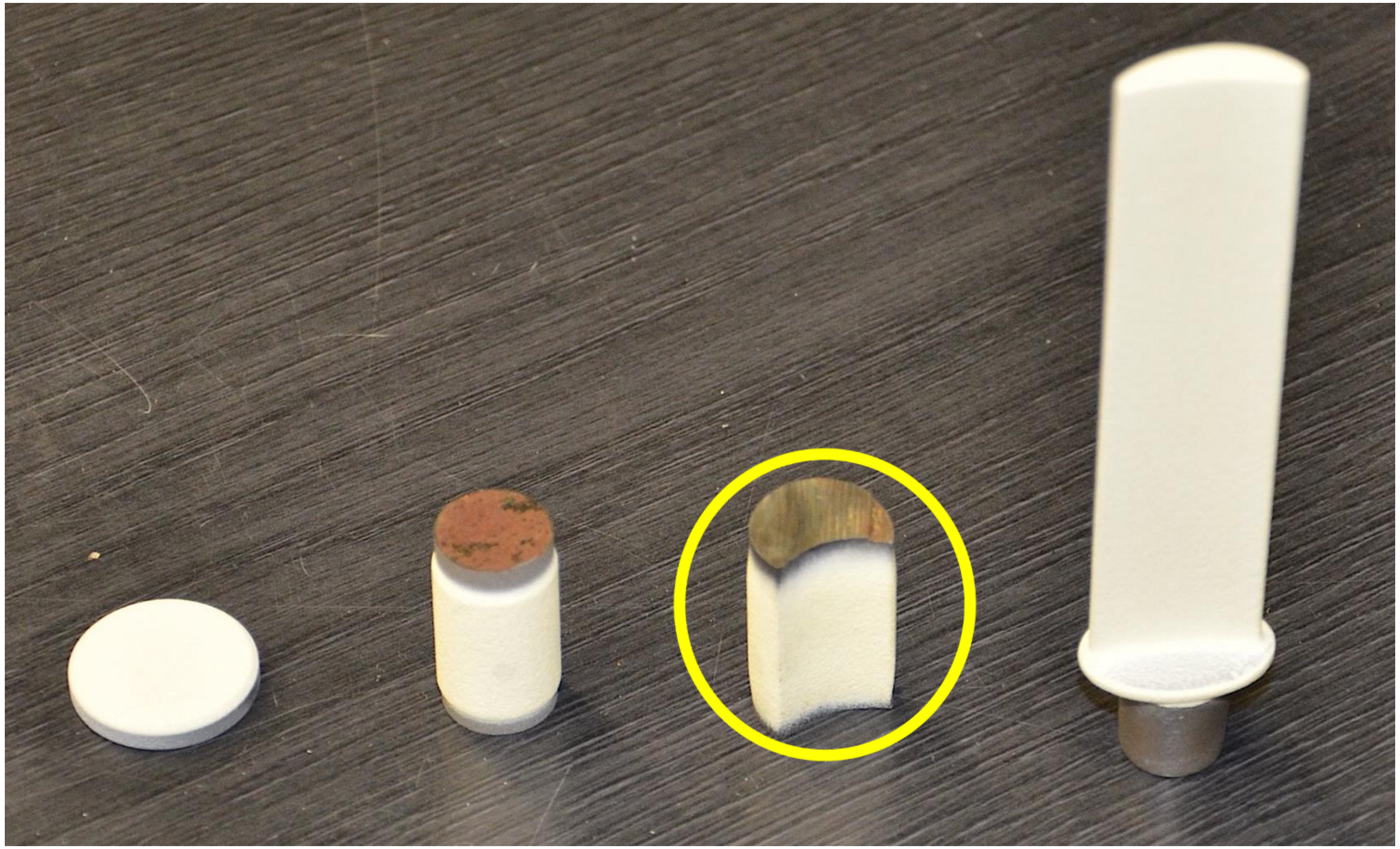


Standard HVOF as baseline

50 µm APS flash coating Y vs. YHfSi

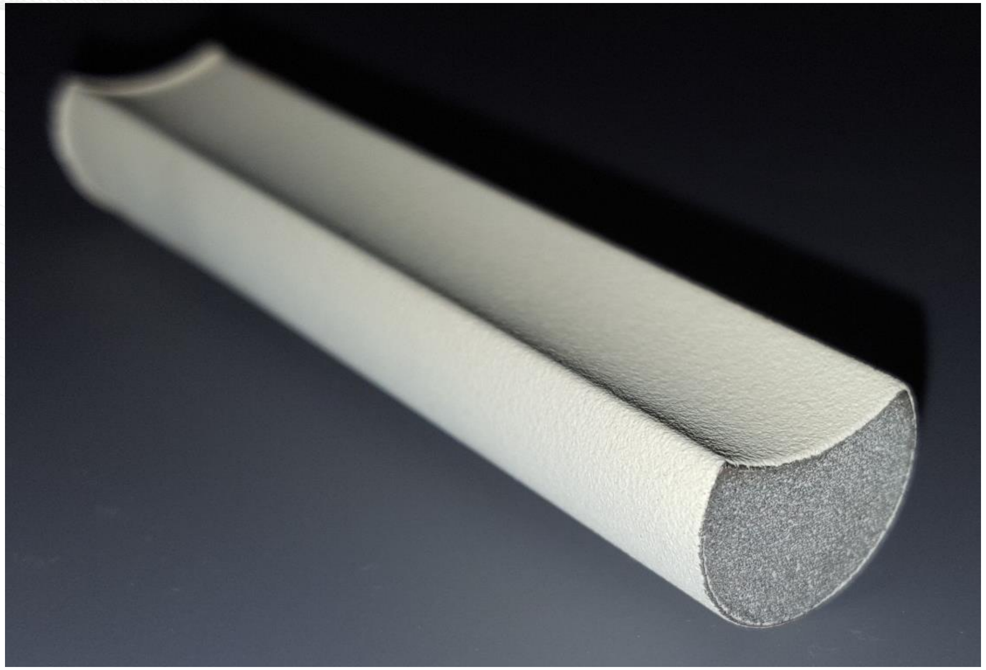
5 specimens of each coating

Convex surface provided a coating challenge



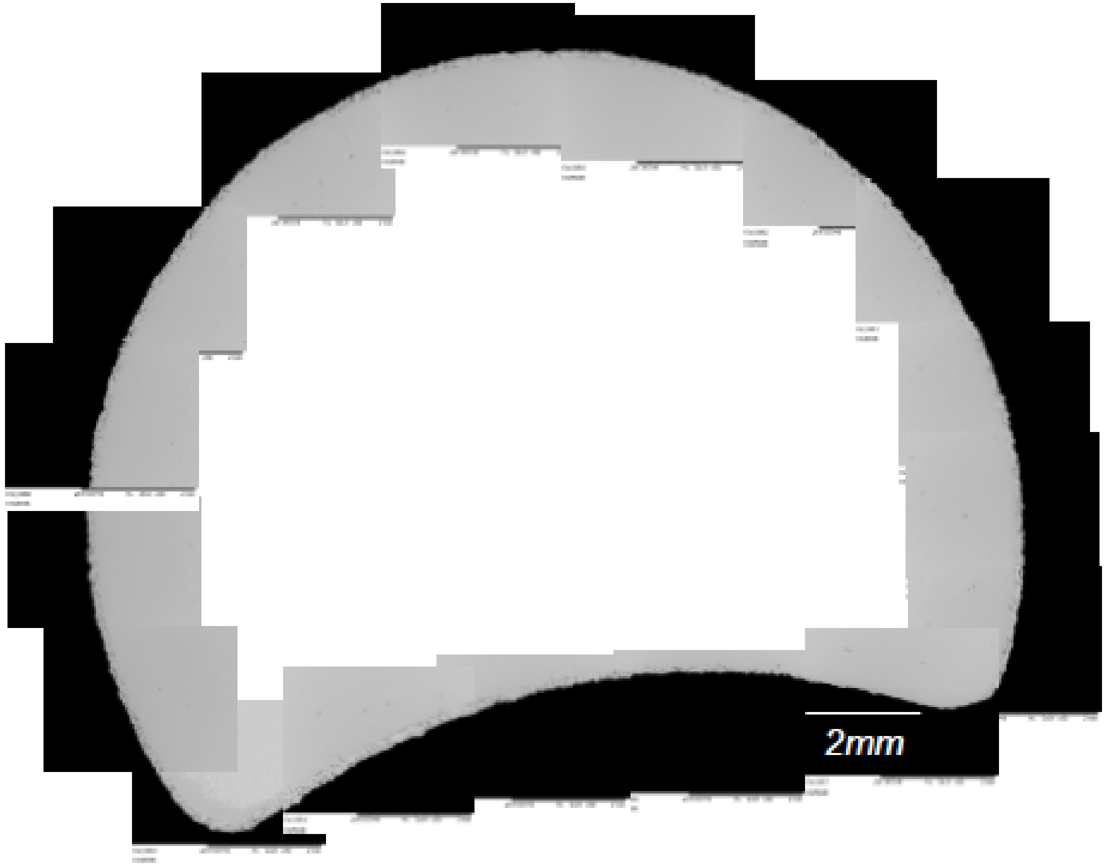
2017: industry feedback helped achieve uniform coating
(Feedback was “blade” was too difficult to coat)

Rod being divided and characterized



16mm diameter bar, ~8 cm long

Section of last trial specimen at CTSR



TBC project summary

- Furnace cycle testing of disks: perhaps a limit to their value
- Rods: learning curve near completion
  - Ready to make burner rig pins for industry
- Grooved rod: goal is study alumina growth and residual stress
  - Any difference between concave and convex side?
- Modeling: spray coatings are life limited by interdiffusion
  - Focus on interdiffusion at 900°-950°C
  - Task had been on hold while defining the best bond coating for rods
  - Resuming 900°-950°C experiments to feed model
- FY18 defining an EBC (environmental barrier coating) task
  - 1425°C (2600°F) without Si bond coating used at ≤1300°C
  - Possible topic: role of EBC porosity on SiC substrate reaction

Supercritical CO_2 Allam cycle: first clean fossil energy?

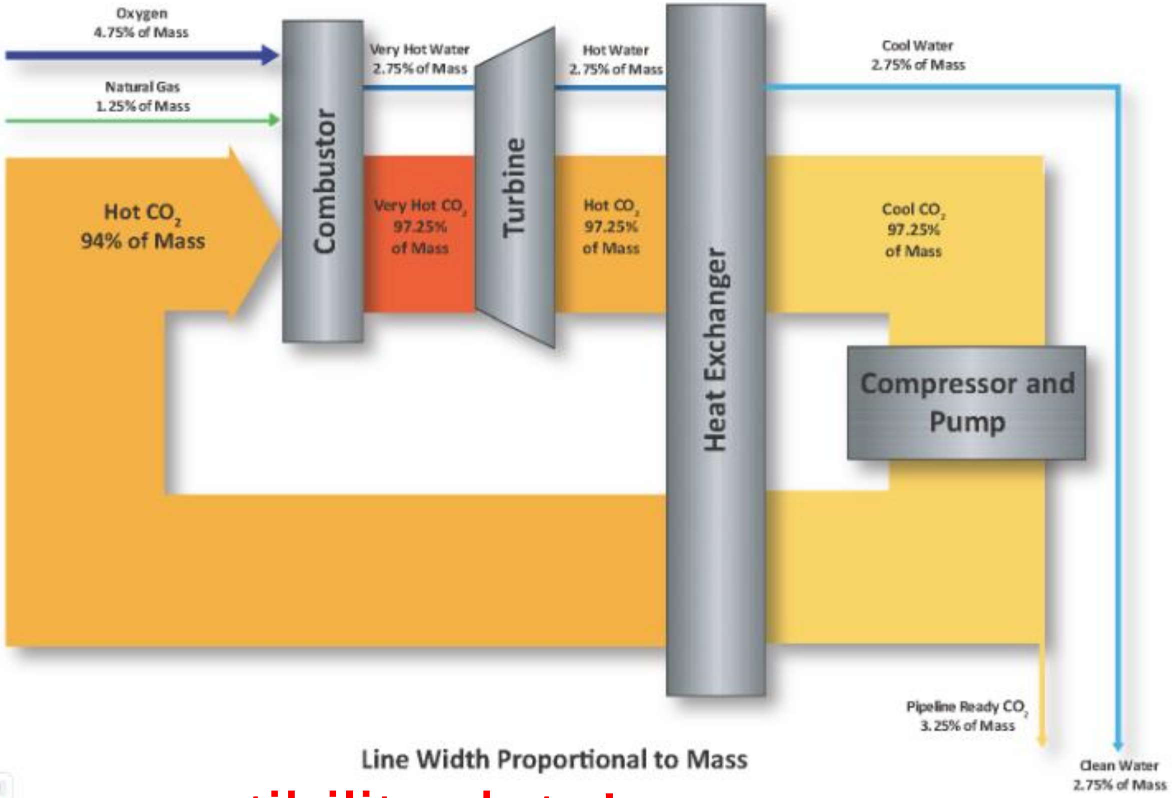
NetPower 25MWe demo plant (Texas)

Exelon, Toshiba, CB&I, 8Rivers Capital: $140m

The prototype NET Power plant near Houston, Texas, is testing an emission-free technology designed to compete with conventional fossil power. CHICAGO BRIDGE & IRON

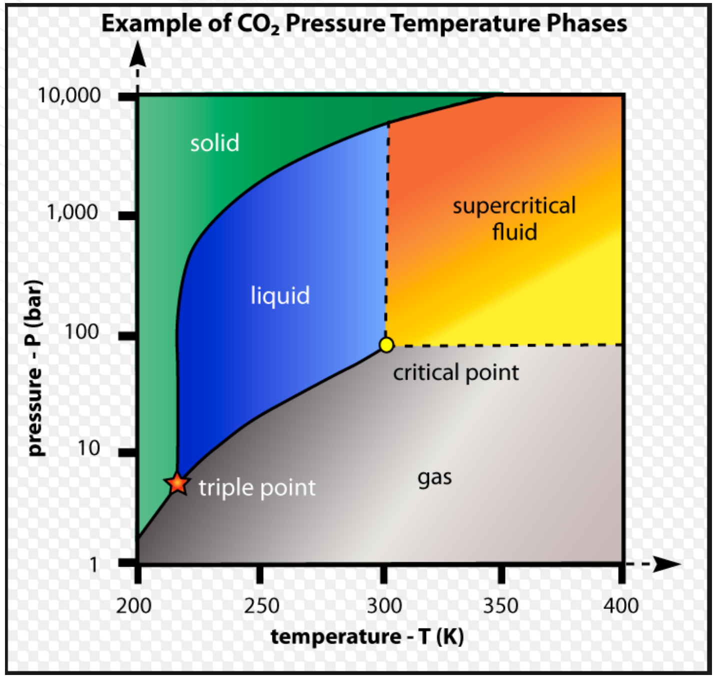
Reported 95% complete

Material challenges:
Combustor: 1150°C (!?!)
Turbine exit: 750°C/300 bar



Moving forward with limited compatibility data!
As audacious as Eddystone in 1960

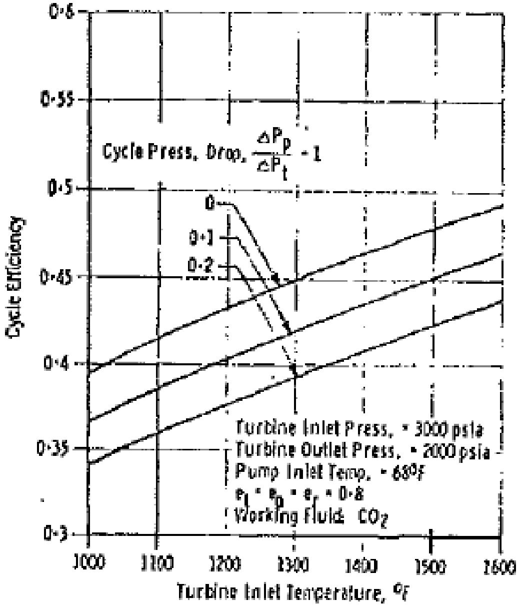
Supercritical CO_2 (sCO_2) has high efficiency potential for several power generation applications



- High density
  - Like a liquid
- Flexible
  - small turbomachinery

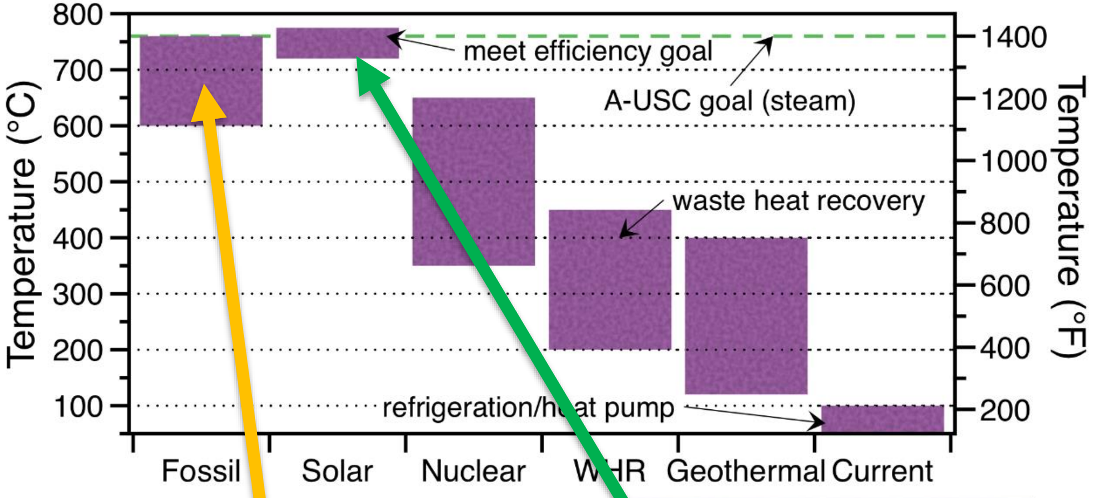
Critical Point: 31°C, 74 bar

50% eff @ >720°C



Feher, 1965

Temperature range estimates for various applications



Fossil bottoming cycle

Courtesy: Business Wire

Word of warning: New technology vs. new mechanism

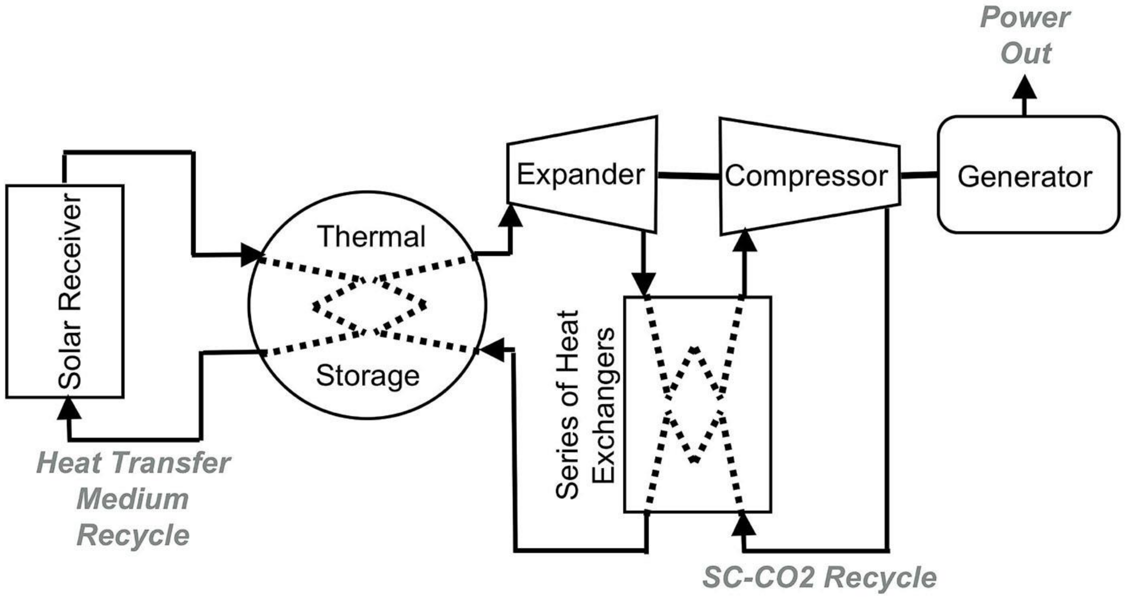
Fantastic new failure mechanisms can derail new technologies

The prototype NET Power plant near Houston, Texas, is testing an emission-free technology designed to compete with conventional fossil power.

CHICAGO BRIDGE & IRON

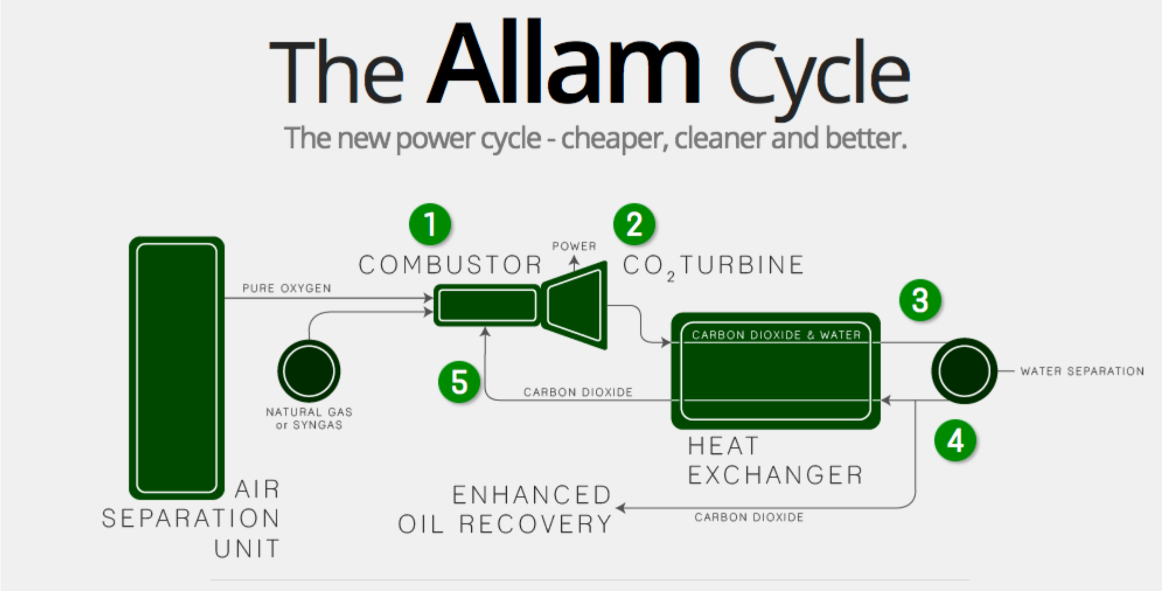
Indirect- vs. direct-fired sCO_2 systems (i.e. closed vs. open)

Closed cycle: "pure" CO_2 100-300 bar



DOE SunShot funding

Open cycle: sCO_2 + impurities (O_2,H_2O…)



DOE Fossil Energy funding

Two sCO$_2$ projects at ORNL

DOE Fossil Energy

- 750°C/300 bar: 500-h cycles
- Focus on impurity effects for direct-fire
  - Baseline research grade CO$_2$
  - New autoclave with controlled O$_2$+H$_2$O
- Alloys
  - 310HCbN (HR3C, Fe-base SS)
  - 617
  - 230
  - MarM247 (Al$_2$O$_3$-forming superalloy)
  - 282 (Heat #1)
  - 740

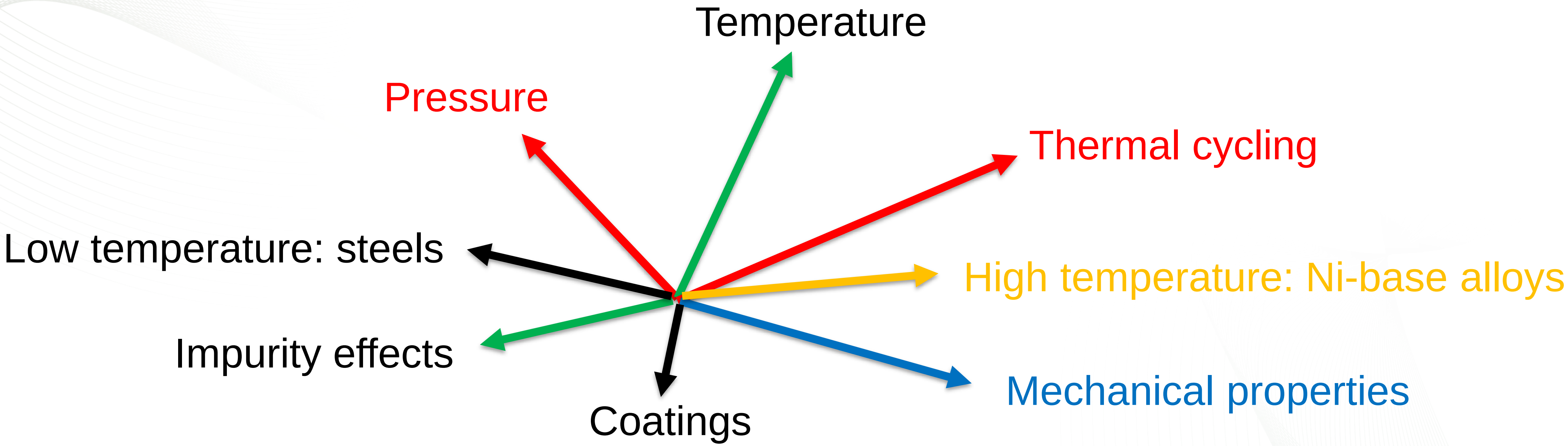
DOE SunShot (CSP)

- 750°C/300 bar: 500-h cycles
  - Including 750°C/1 bar, 10-h cycles
- Focus on industrial grade CO$_2$
  - Indirect fired (closed loop)
- Alloys
  - Sanicro 25 (Fe-base SS)
  - 625
  - 740H
  - 282 (Heat #2)

Cooperative test matrix:

	Air	RG CO$_2$	IG CO$_2$	FE: CO$_2$+O$_2$/H$_2$O
1 bar	5,000 h	3,000 h	3,000 h	——
300 bar	——	2,000 h	5,000 h	Nov. start

Lifetime modeling: which way to go?



Temperature

Pressure

Thermal cycling

Low temperature: steels

High temperature: Ni-base alloys

Impurity effects

Mechanical properties

Coatings

- Read and listen
- Thermodynamic calculations
- Cross your fingers and go!

Oxford CO_2 lifetime model for UK gas-cooled reactors

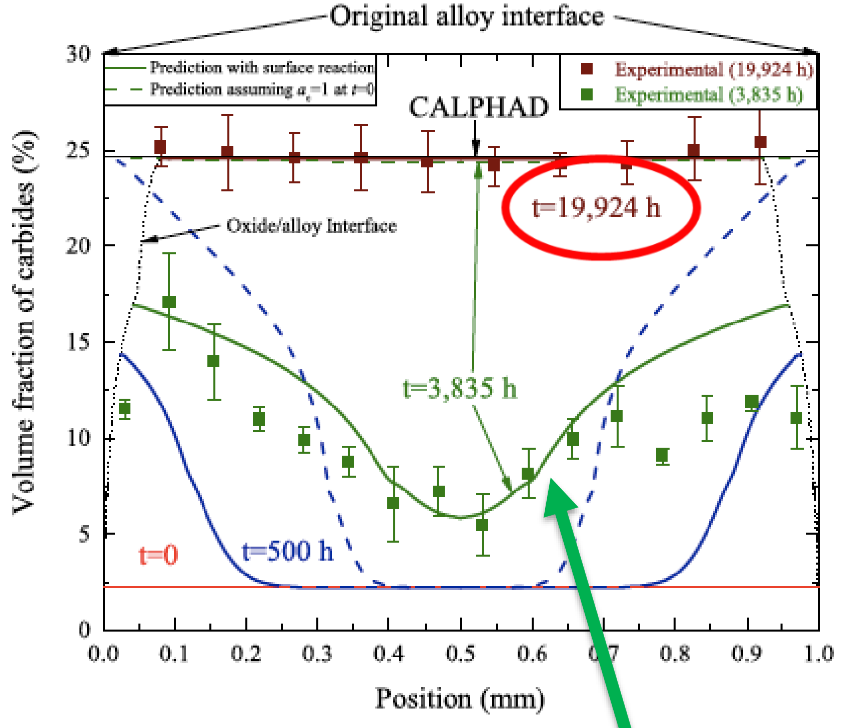


Fig. 8. Predicted profiles of volume fraction of carbides for a mm fin exposed to experimental gas conditions at 600 °C at 0, 500 h, 3835 h and 19 24 h, in comparison with measurements corresponding to black box marked in Fig. 1(b); simulations were conducted by 1D-DiCTra as described in § 3.2 treating migration of oxide/alloy interface and non-steady state carburisation with $\alpha_{\mu,C} = 1.2 \times 10^{-12}$ mol m s^{-1} J^{-1} (solid lines) or fixed $a_C = 1$ at the oxide/alloy interface (dashed lines).

Gong,Young...Reed, Acta Mater. 2017

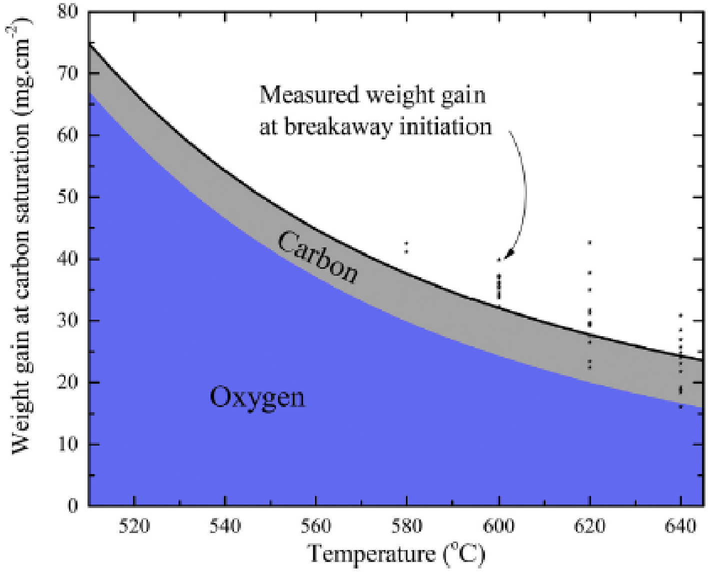


Fig. 13. Predicted weight gain contributed by oxidation and carburisation at the time of carbon saturation, in comparison with measured weight gain at breakaway (WGB) data. Note only carbon in the substrate and oxygen in the oxide scales are considered in the predictions.

Breakaway in years!

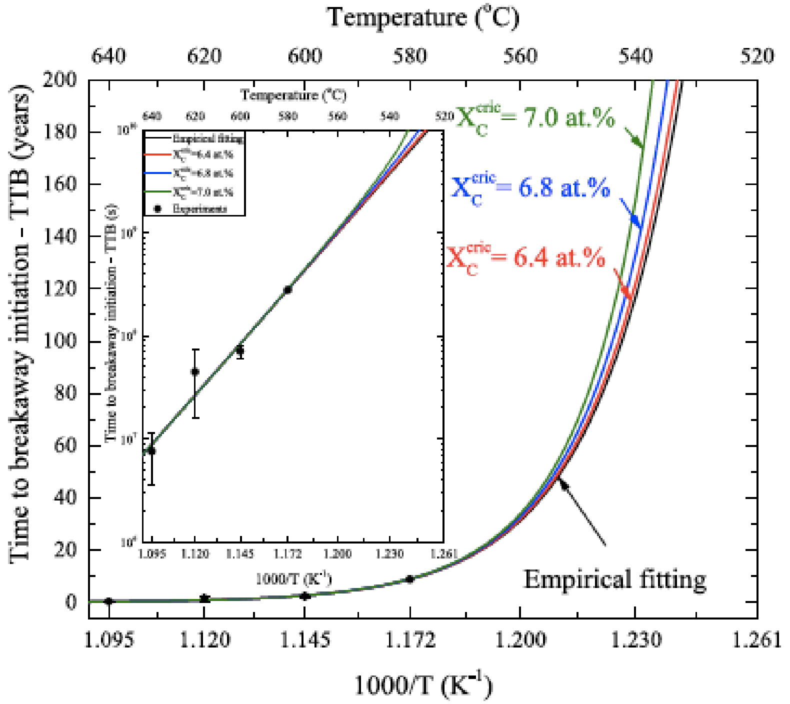
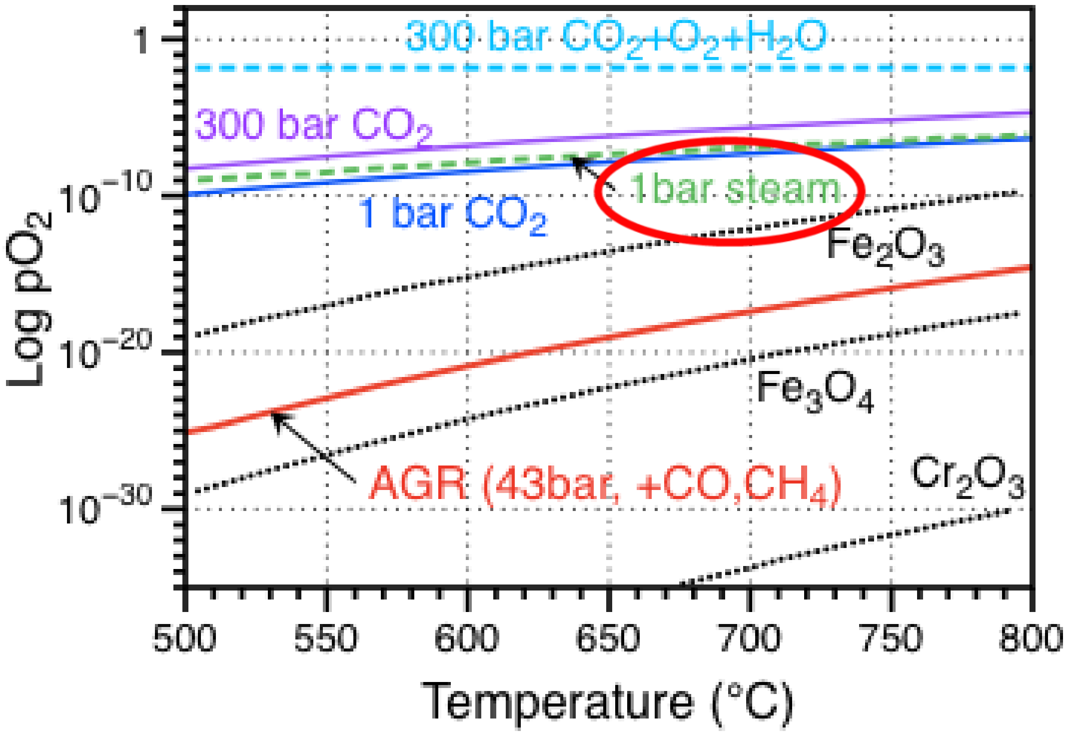


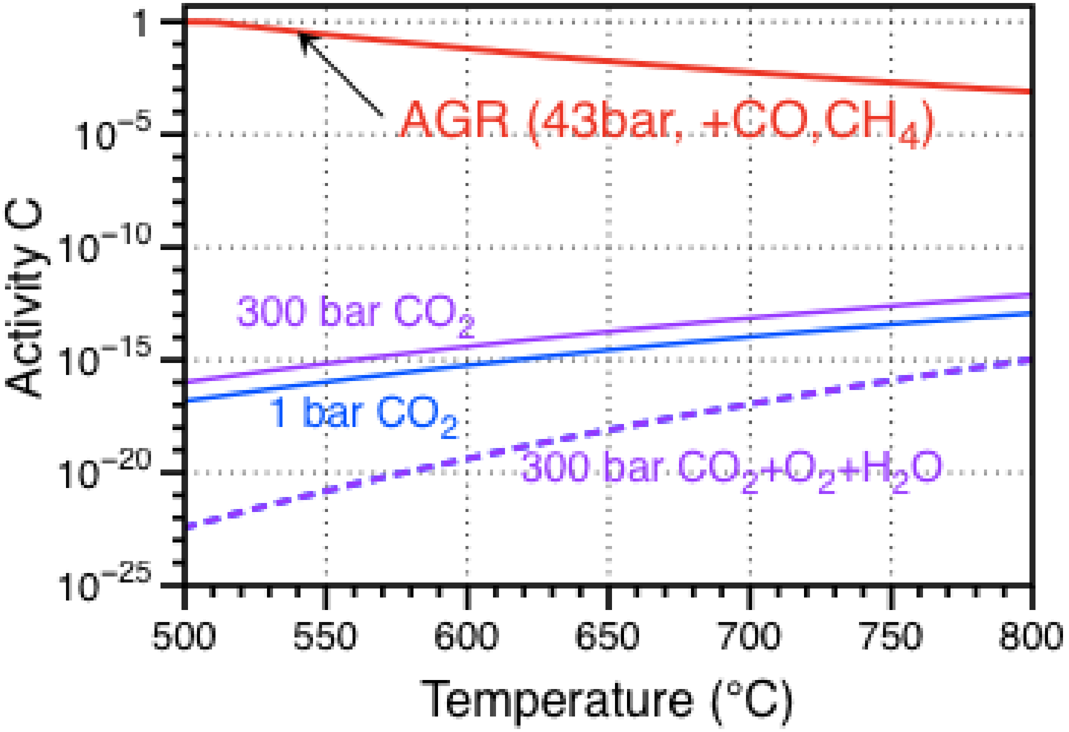
Fig. 14. Predicted time to breakaway initiation from an empirical ln(TTB)-1/T linear fitting and carbon saturation model with different carbon saturation criteria.

Experimental data (80-200 kh) from EDF: like a treasure map

AGR gas composition is highly carburizing, unlike sCO_2

43 bar, CO_2 +1%CO-0.03%H_2O-0.03%CH_4-0.01%H_2



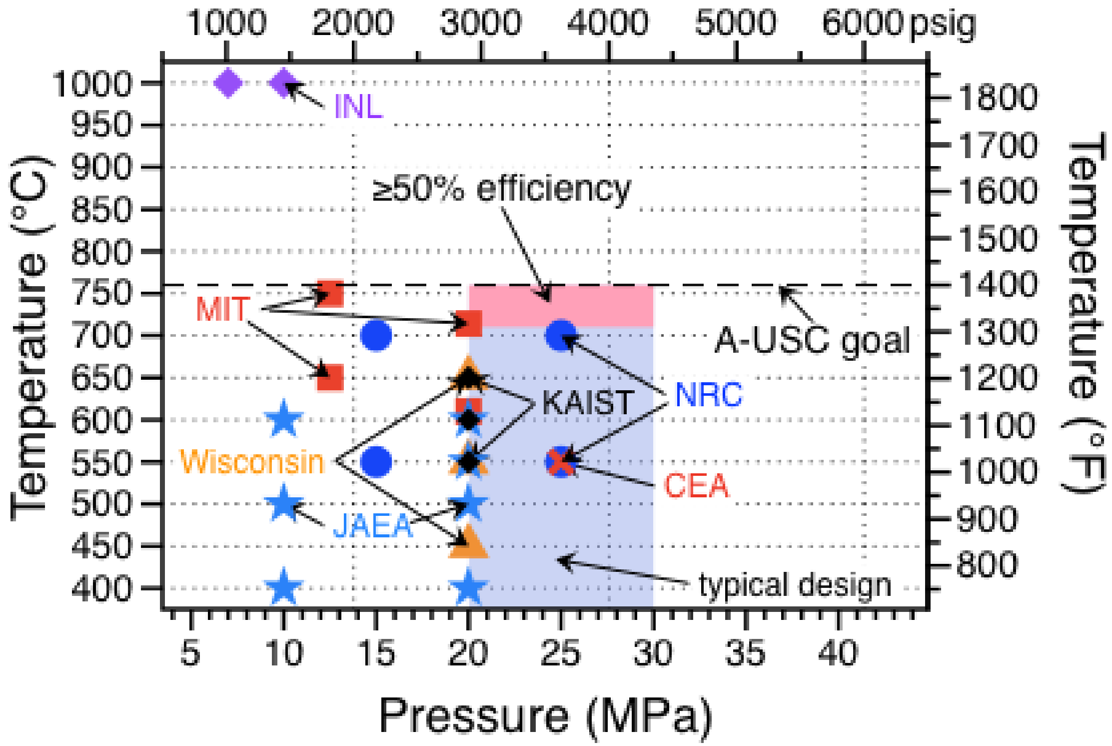


Similar pO_2 in steam and CO_2

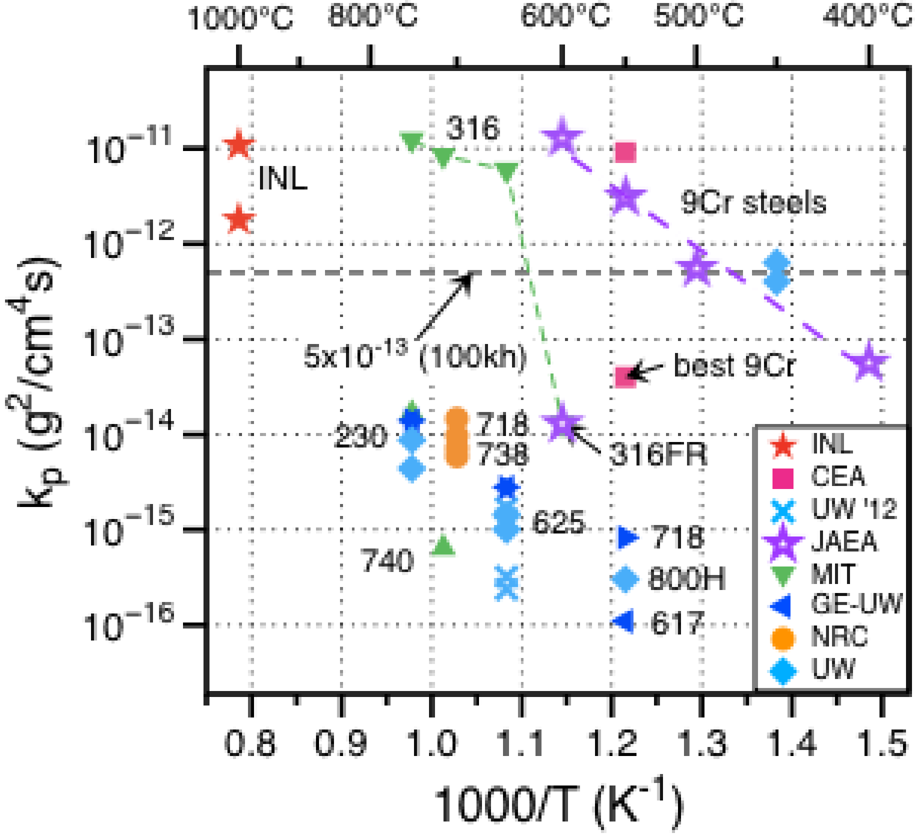
Direct-fired gas: CO_2-1%O_2-0.25%H_2O

Literature review found limited data >700°C and >200 bar where sCO_2 efficiencies are >50%

Conditions investigated



Reported rates



From Pint and Brese, Chapter 4 High Temperature Materials in *Fundamentals and Applications of Supercritical Carbon Dioxide (2017)*

Literature review found limited data >700°C and >200 bar where sCO_2 efficiencies are >50%

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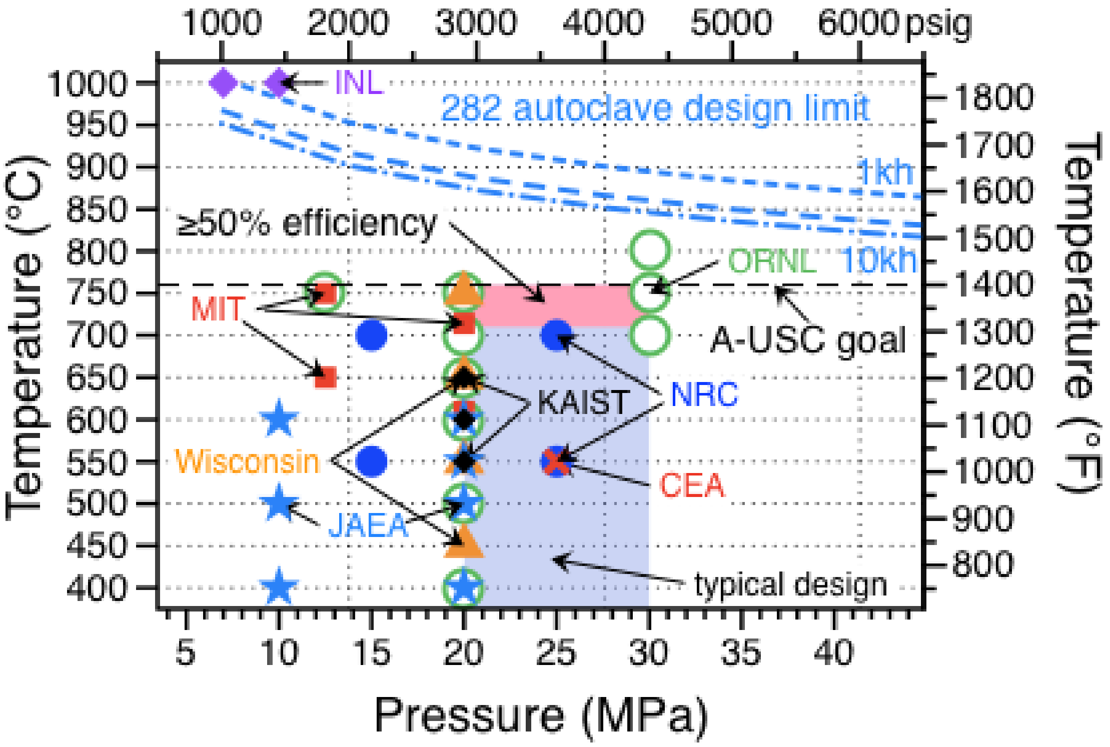
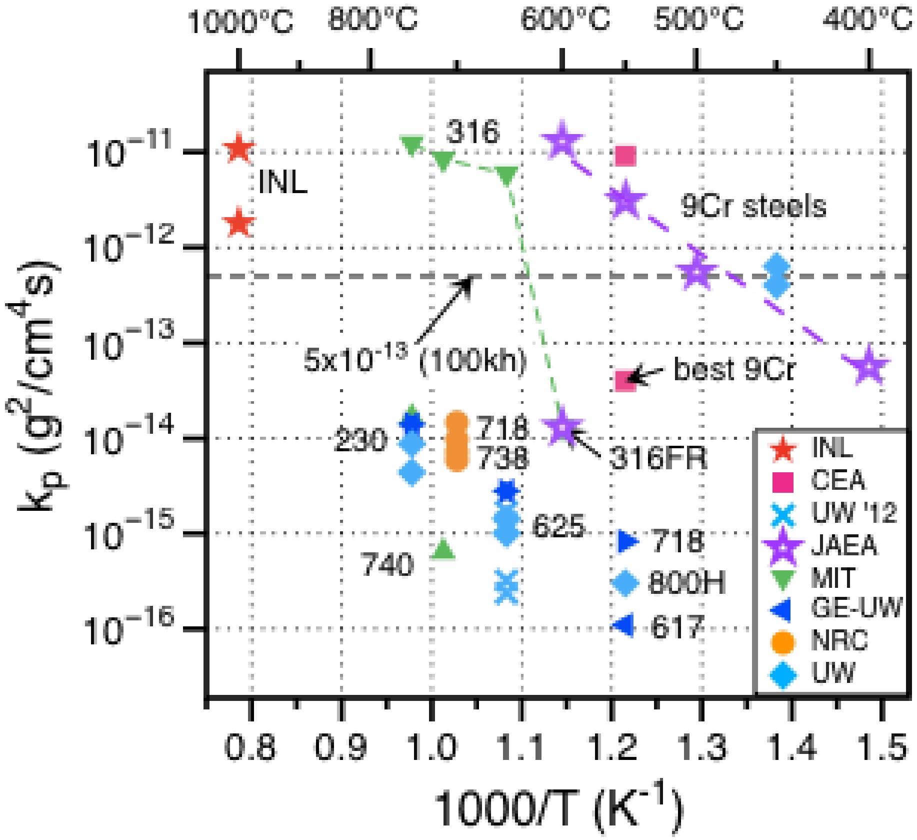


Reported rates



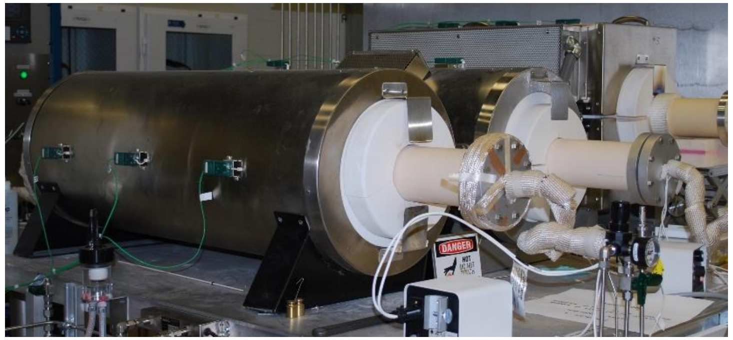
From Pint and Brese, Chapter 4 High Temperature Materials in *Fundamentals and Applications of Supercritical Carbon Dioxide (2017)*

CO_2 compatibility evaluated three ways at 700°-800°C

Autoclave: 300 bar sCO_2
500-h cycles

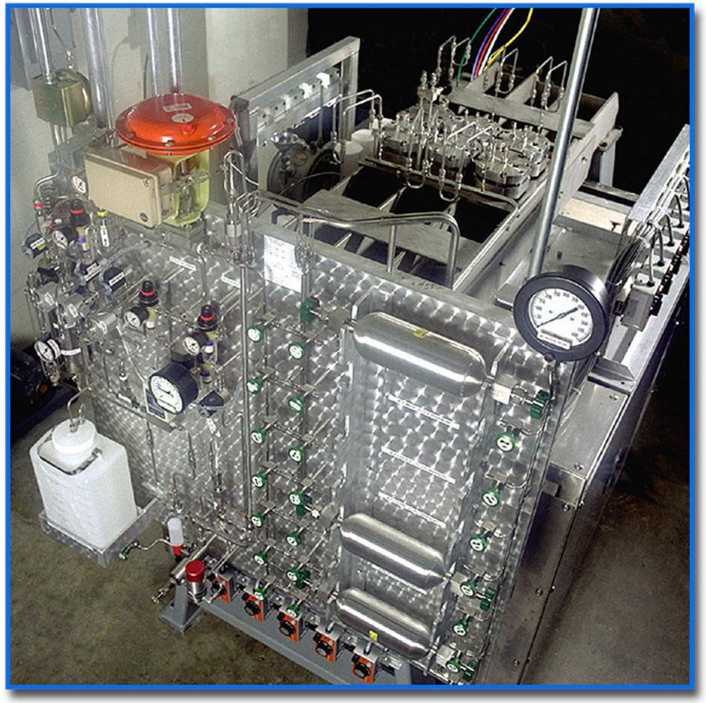
Correct temperature and pressure

Tube furnace: 1 bar CO_2
500-h cycles



Same cycle frequency as autoclave

"Keiser" rig:
500-h cycles, 1-43 bar CO_2

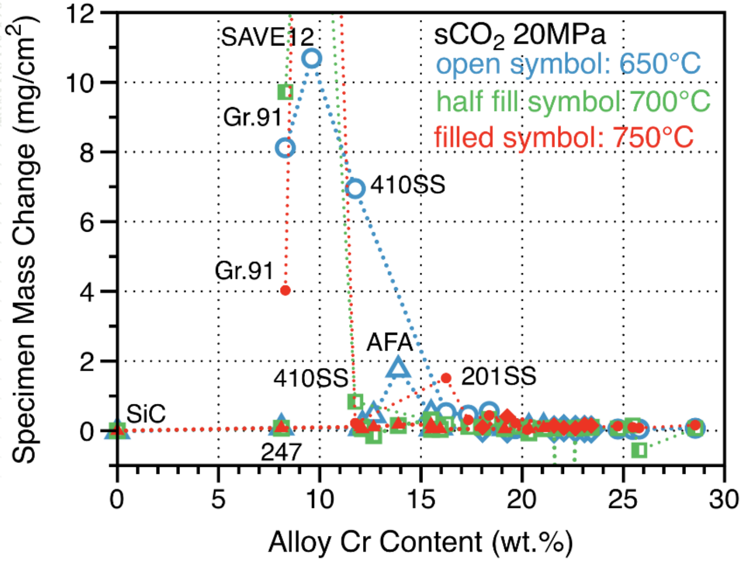


Study impurities at 1-43 bar

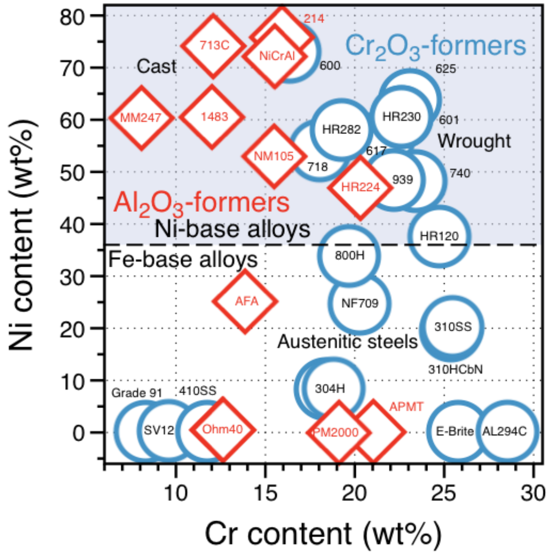
Typically using research grade (RG) CO_2: ≤ 5 ppm H_2O and ≤ 5 ppm O_2

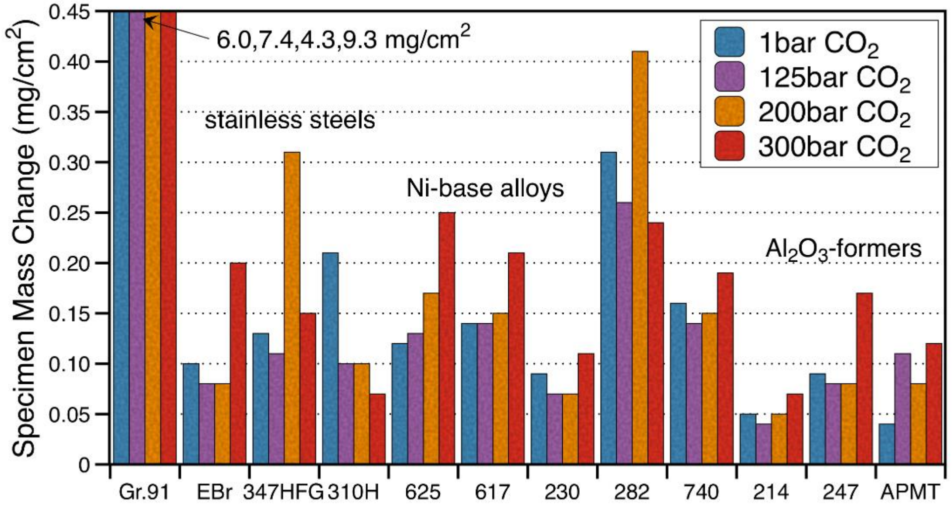
OAK RIDGE
National Laboratory

Initial work has focused on commercial alloys



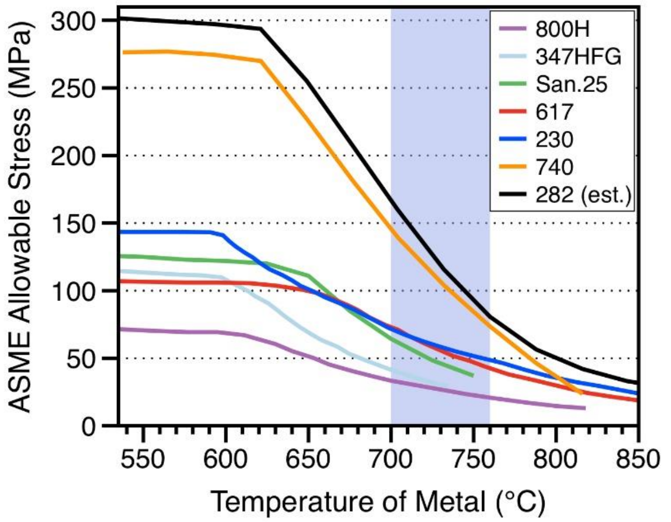
2014: screening 30+ alloys





2015: 12 alloys still too much

740H/282 are precipitation-strengthened (γ´) Ni-base alloys investigated under A-USC



2017: 6 Fossil/4 Solar

310HCbN
617B
230
MarM247
740H
282

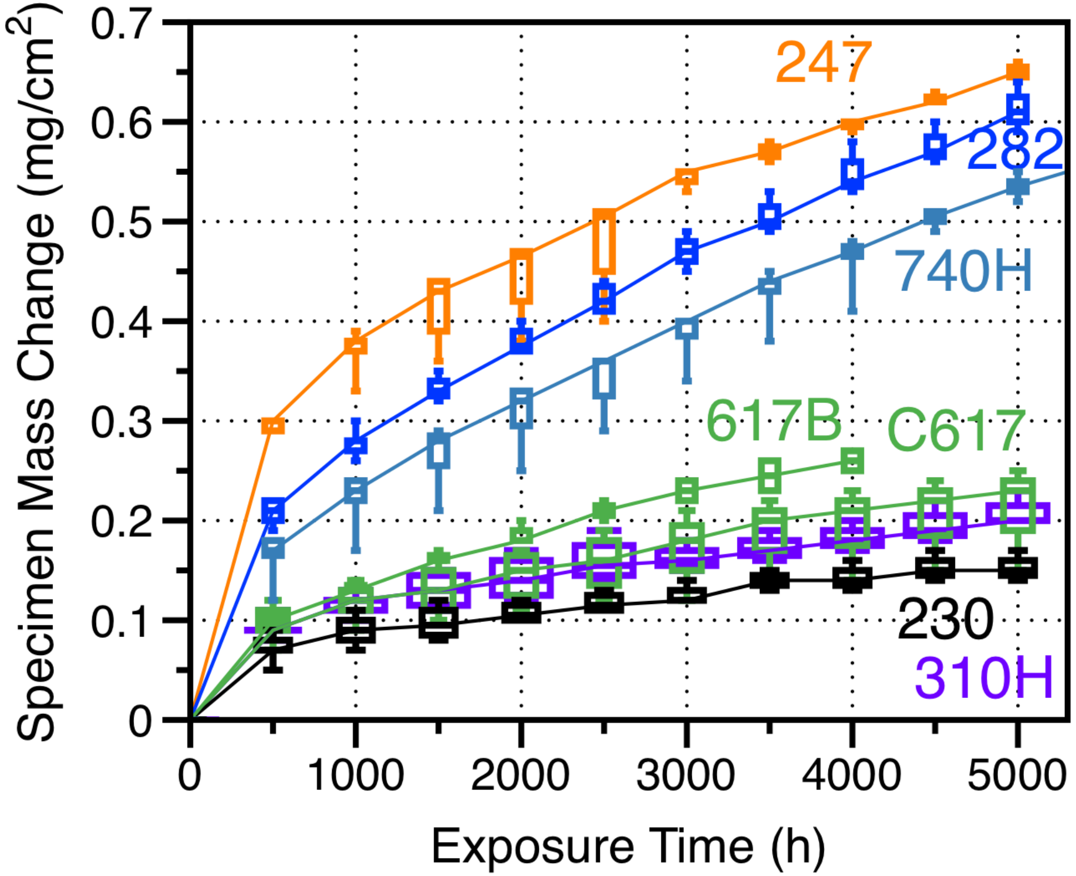
25 (SS)
625
740H
282

Project goal is to study O_2+H_2O effects on sCO_2 compatibility

- BUT, we can't easily pump impurities into flowing 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 reported previously, more effect of H_2O addition
2) Constructing rig for 300 bar/750°C testing with 1%O_2+0.25%H_2O
   - First experiment to begin this month
3) Compare 1 & 300 bar: industrial vs. research grade CO_2 vs. lab air
   - Test matrix in progress, creating a baseline for understanding #2
4) Study 1 & 25 bar CO_2 vs. CO_2+10%H_2O vs. CO_2+10%H_2O+0.1%SO_2
   - 500 h exposures complete at 700° and 800°C

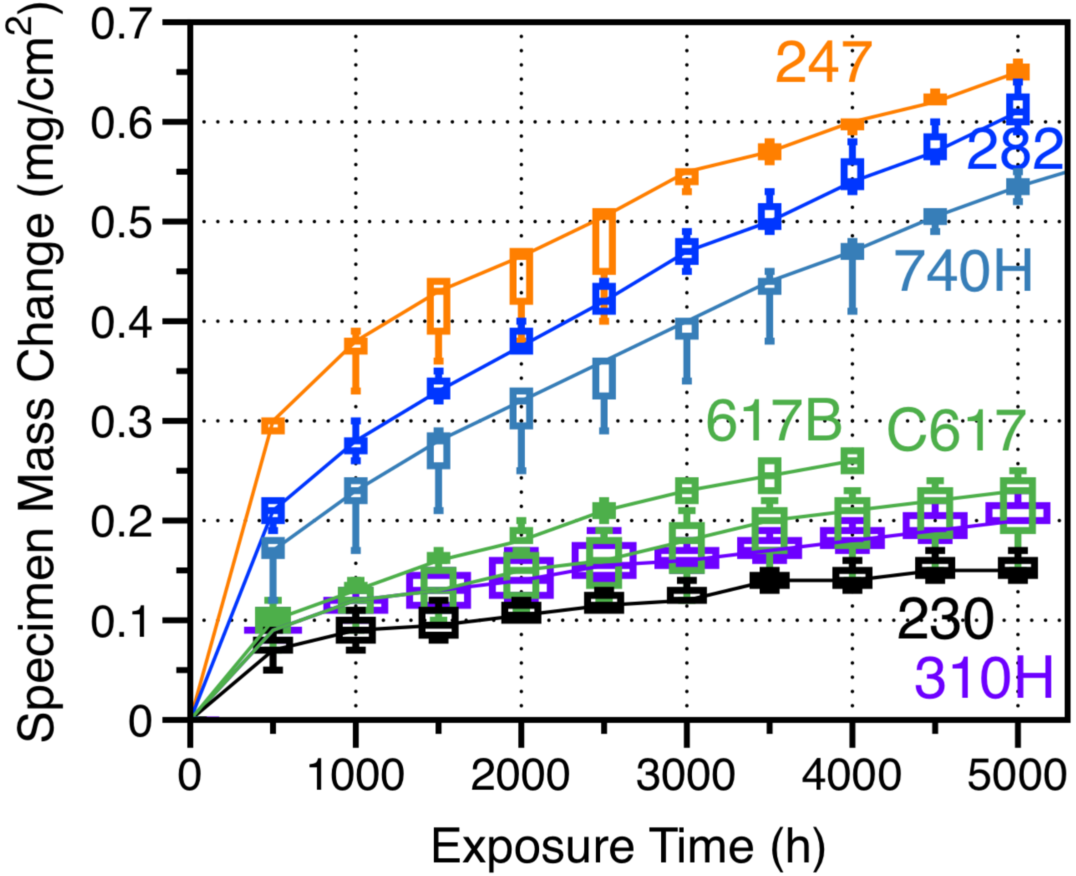
300 bar IG sCO_2 completed in conjunction with SunShot



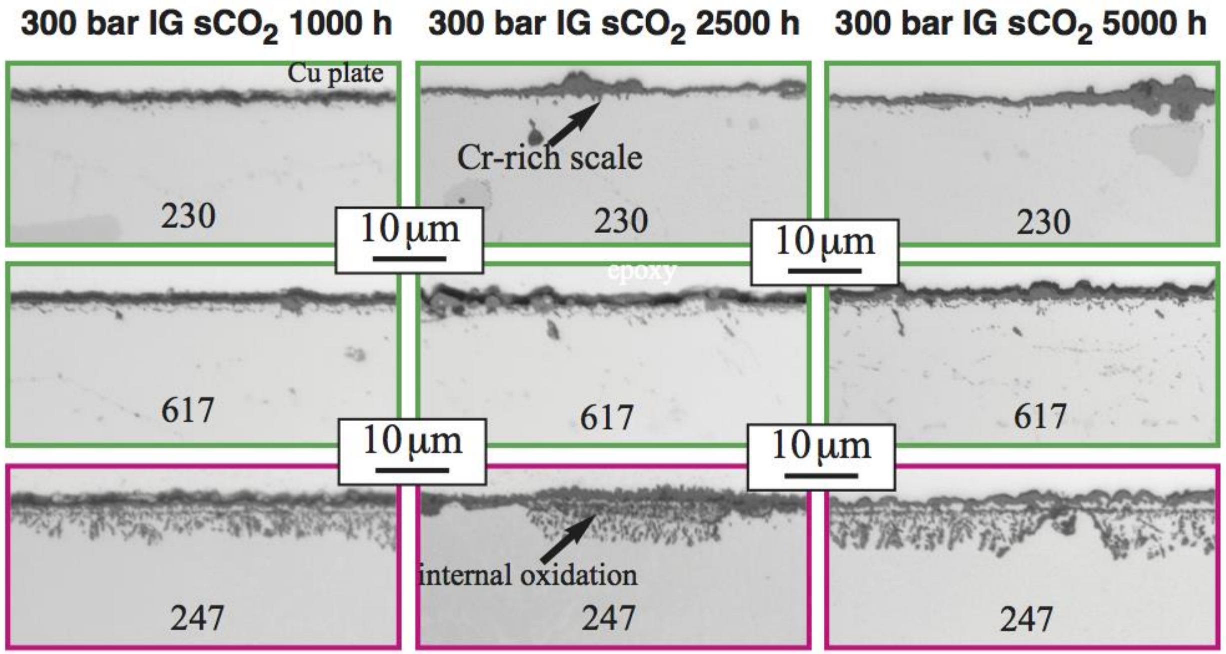
- Both CCA617 and 617B in test
- Highest mass gain with Al
  - – 247 (5%Al)
  - – 282 (1.6%Al)
  - – 740 (1.4%Al)

Industrial grade (IG) CO_2: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

300 bar IG sCO_2 completed in conjunction with SunShot



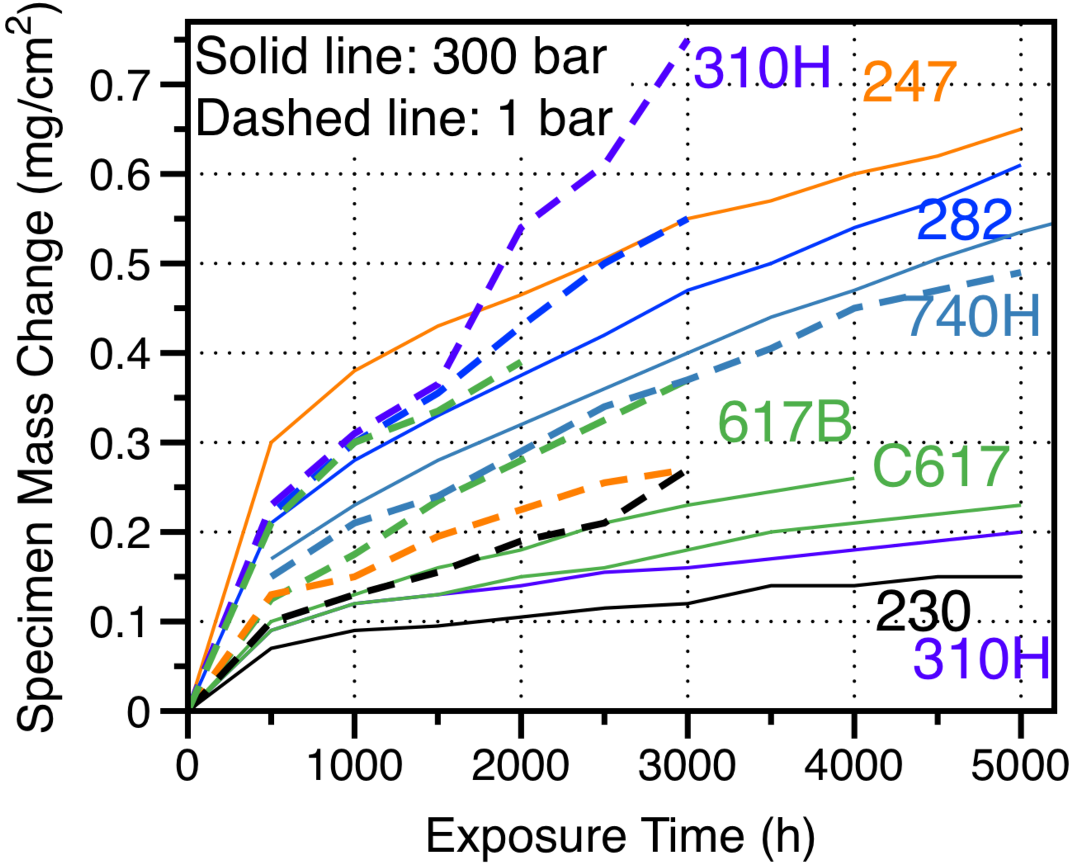
Developing a time series of observations

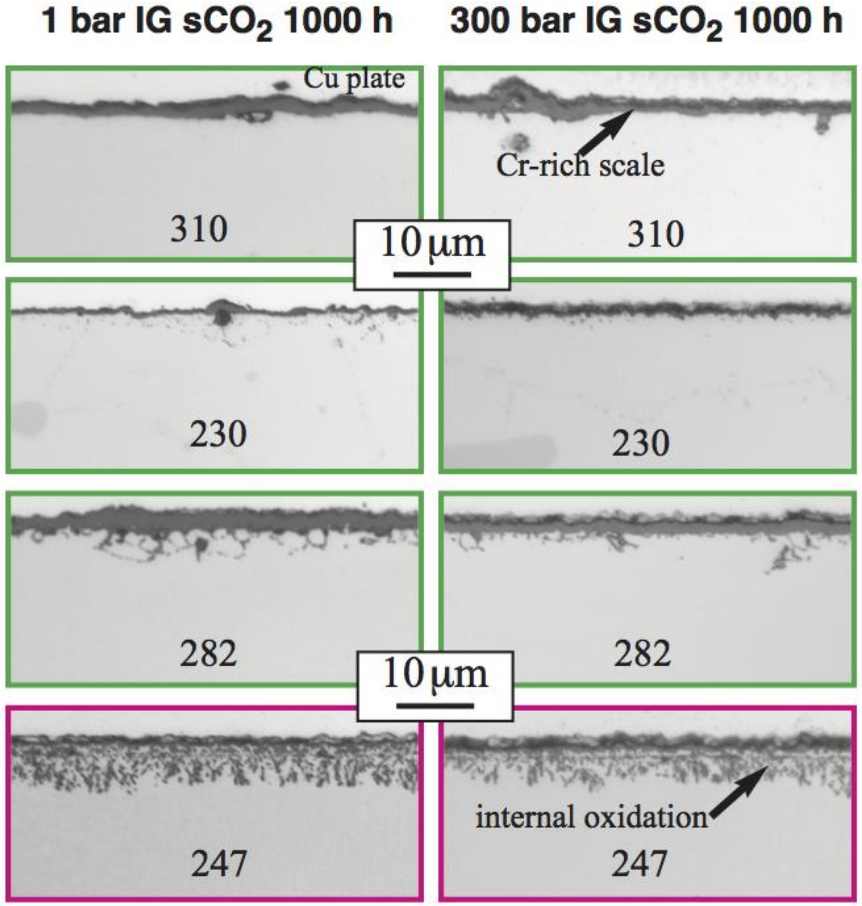


Industrial grade (IG) CO_2: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

OAK RIDGE National Laboratory

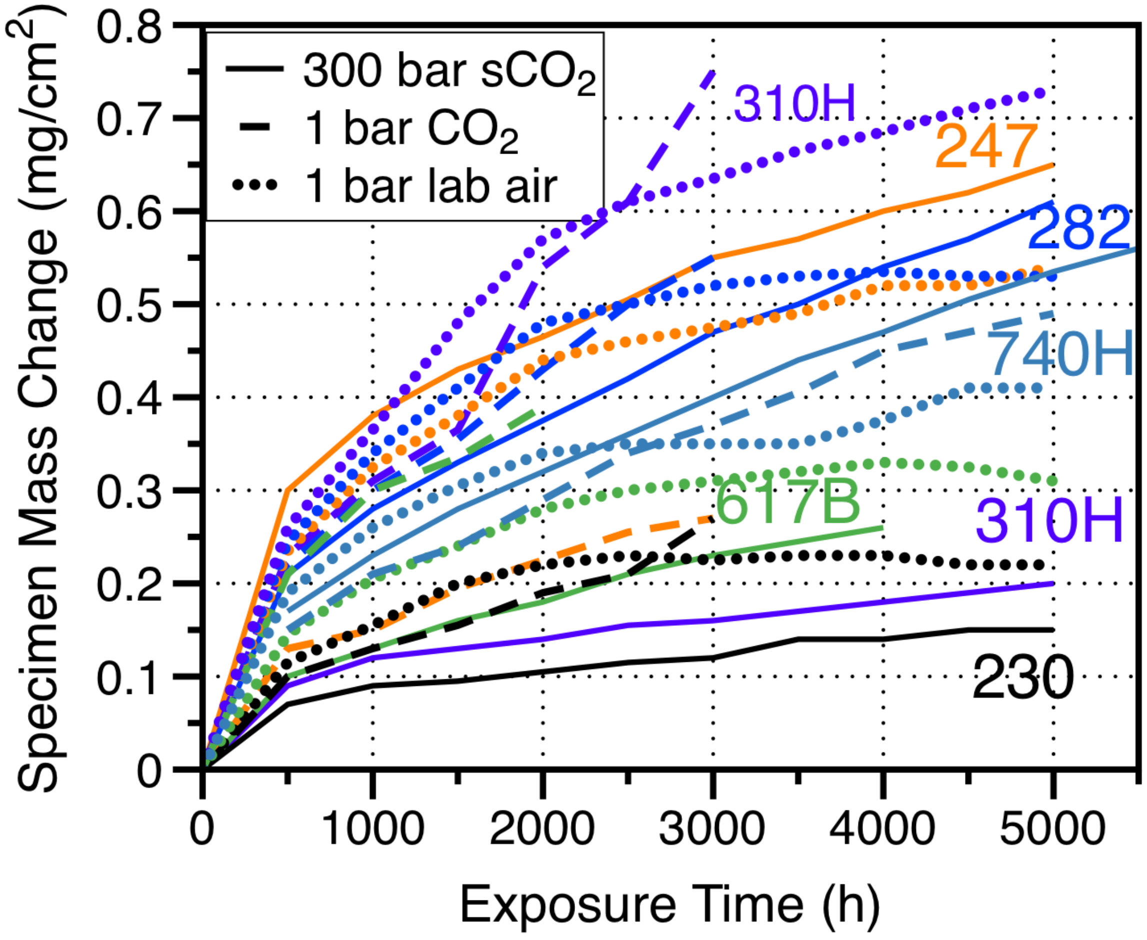
Similar rates of attack in 1 bar IG CO_2

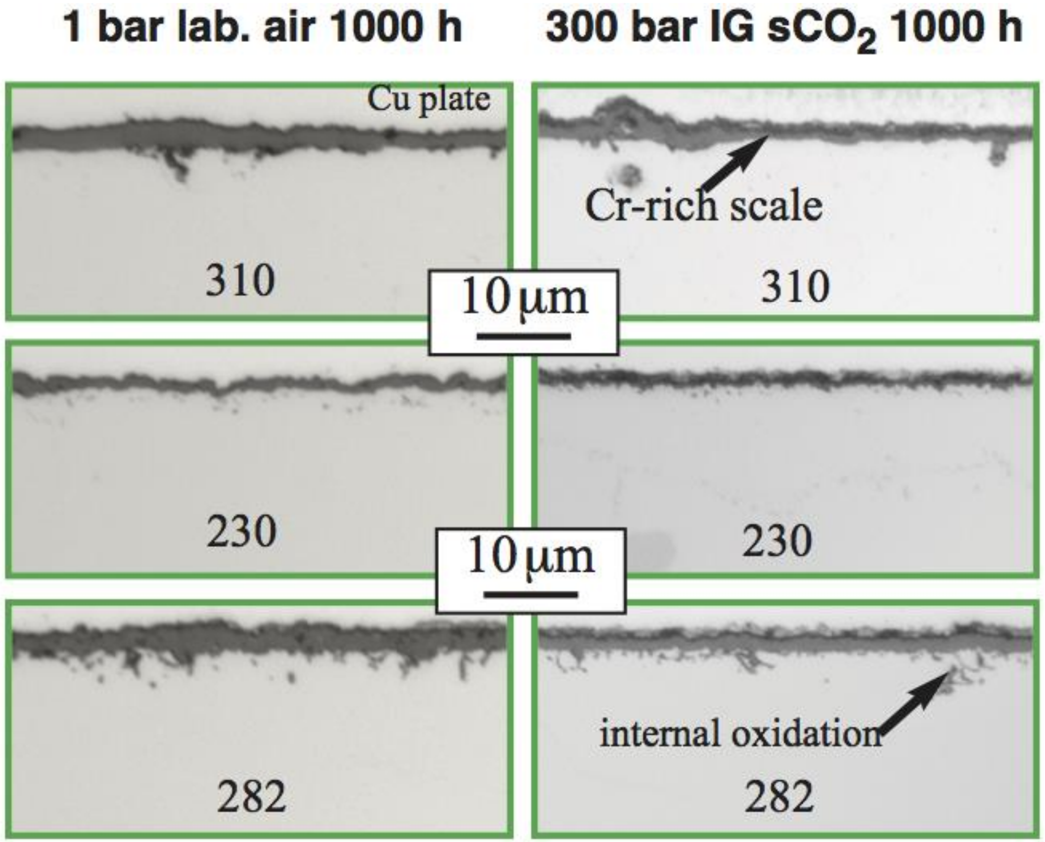




Industrial grade (IG) CO_2: ≤ 50 ppm H_2O and ≤ 32 ppm O_2

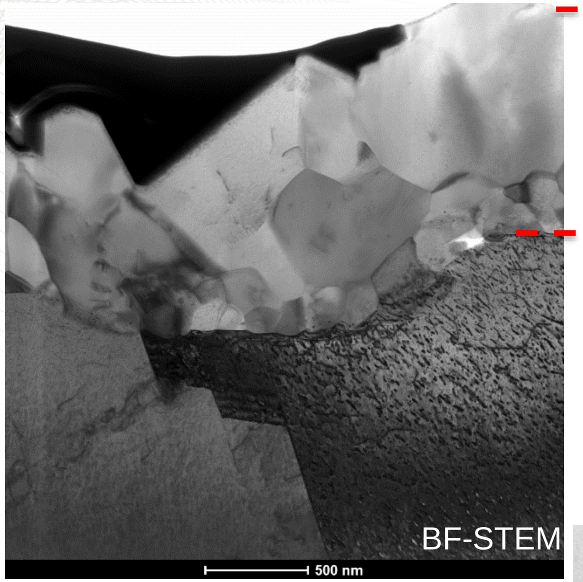
Similar mass change in laboratory air



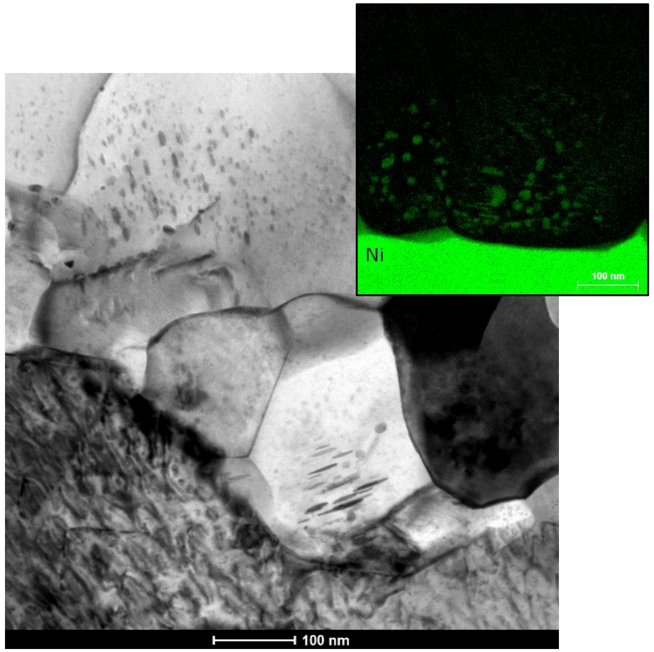


FE project studying model Ni-22Cr alloy specimens

750°C, Air, 1000h

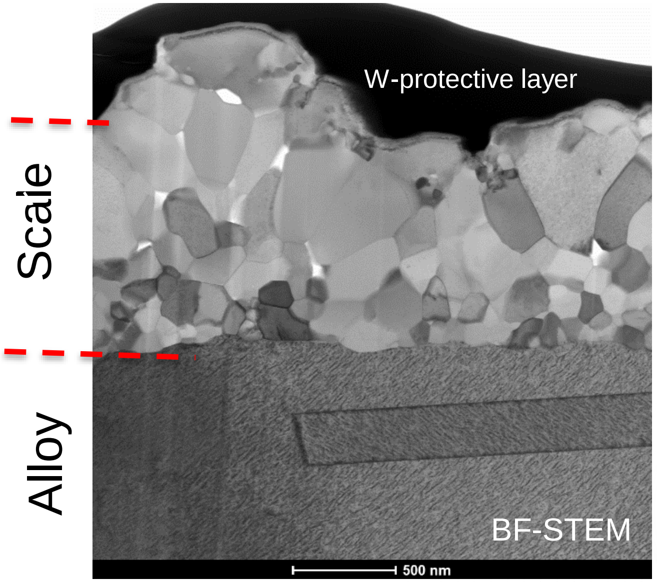


Scale

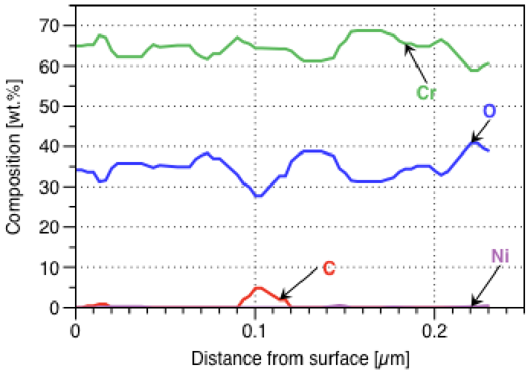


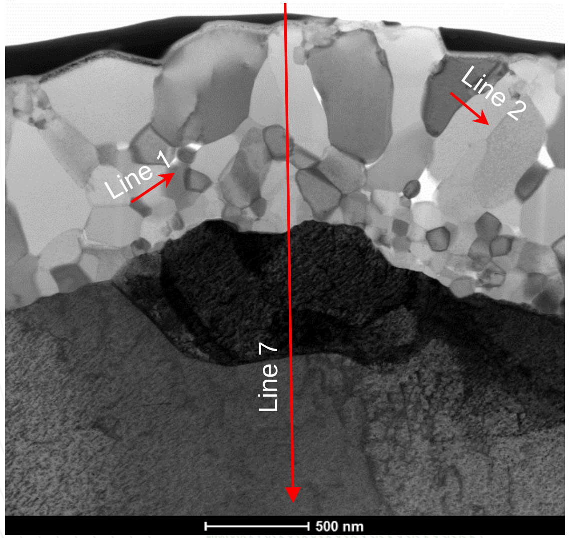
Air only: Metallic Ni particles in scale near substrate interface

750°C, 300 bar sCO_2, 1000h

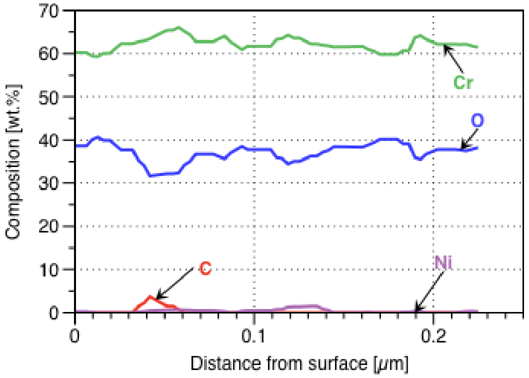


EDS Line 2





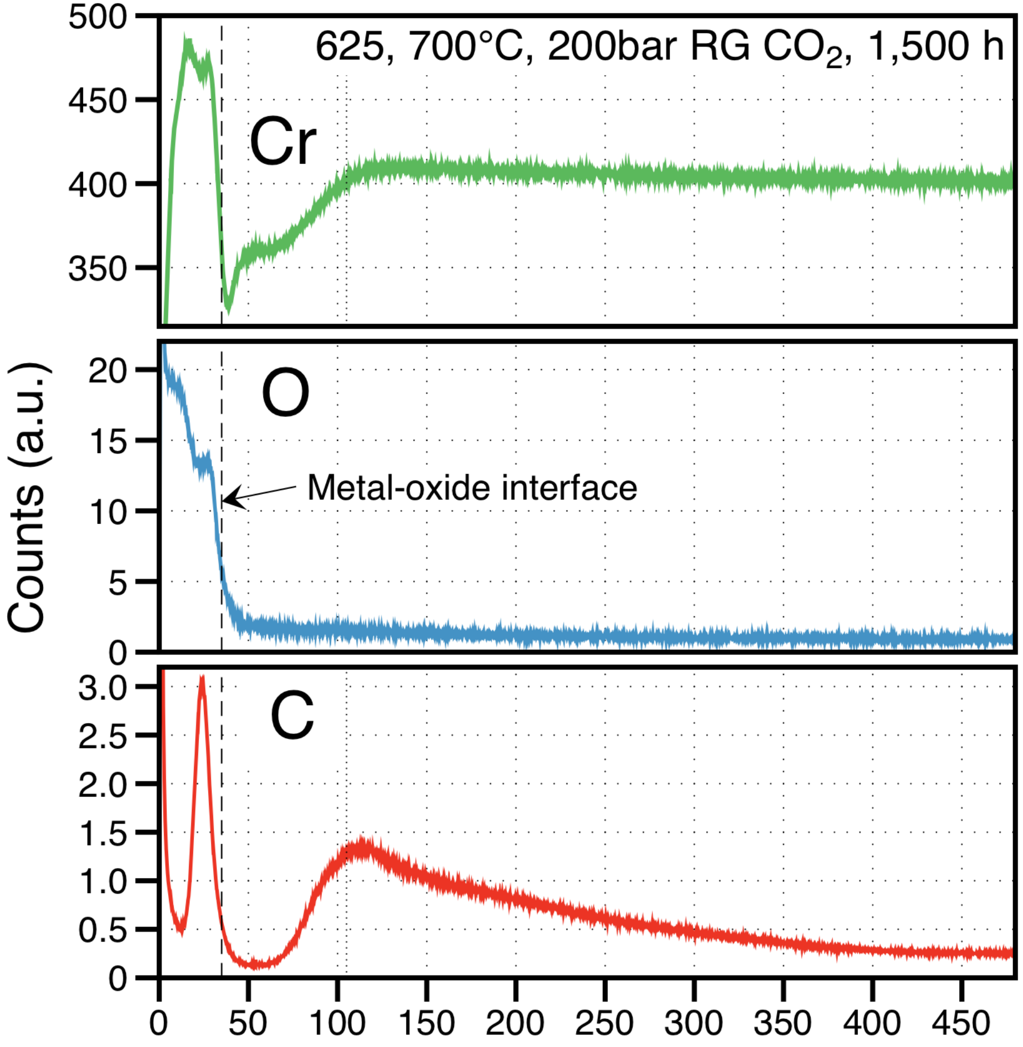
EDS Line 1



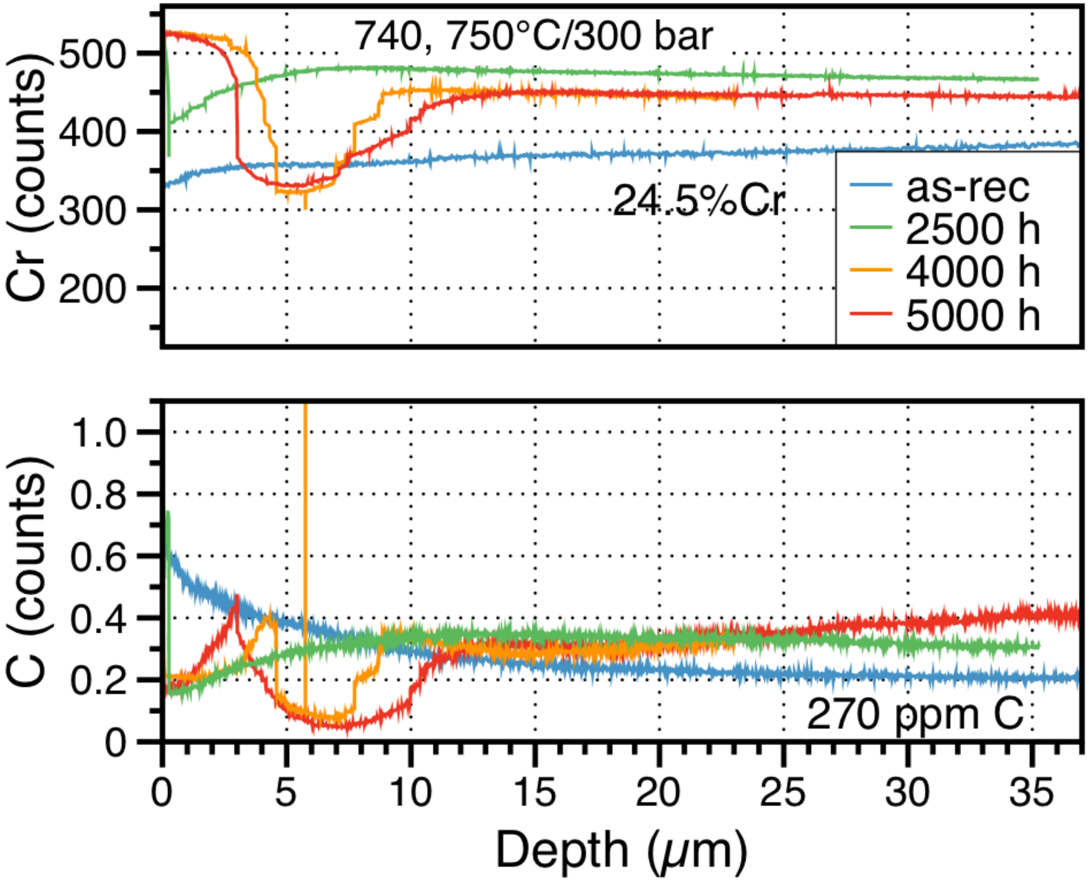
C on oxide grain boundaries

GDOES can detect C ingress (when it occurs)

GDOES: glow discharge, optical emission spectroscopy



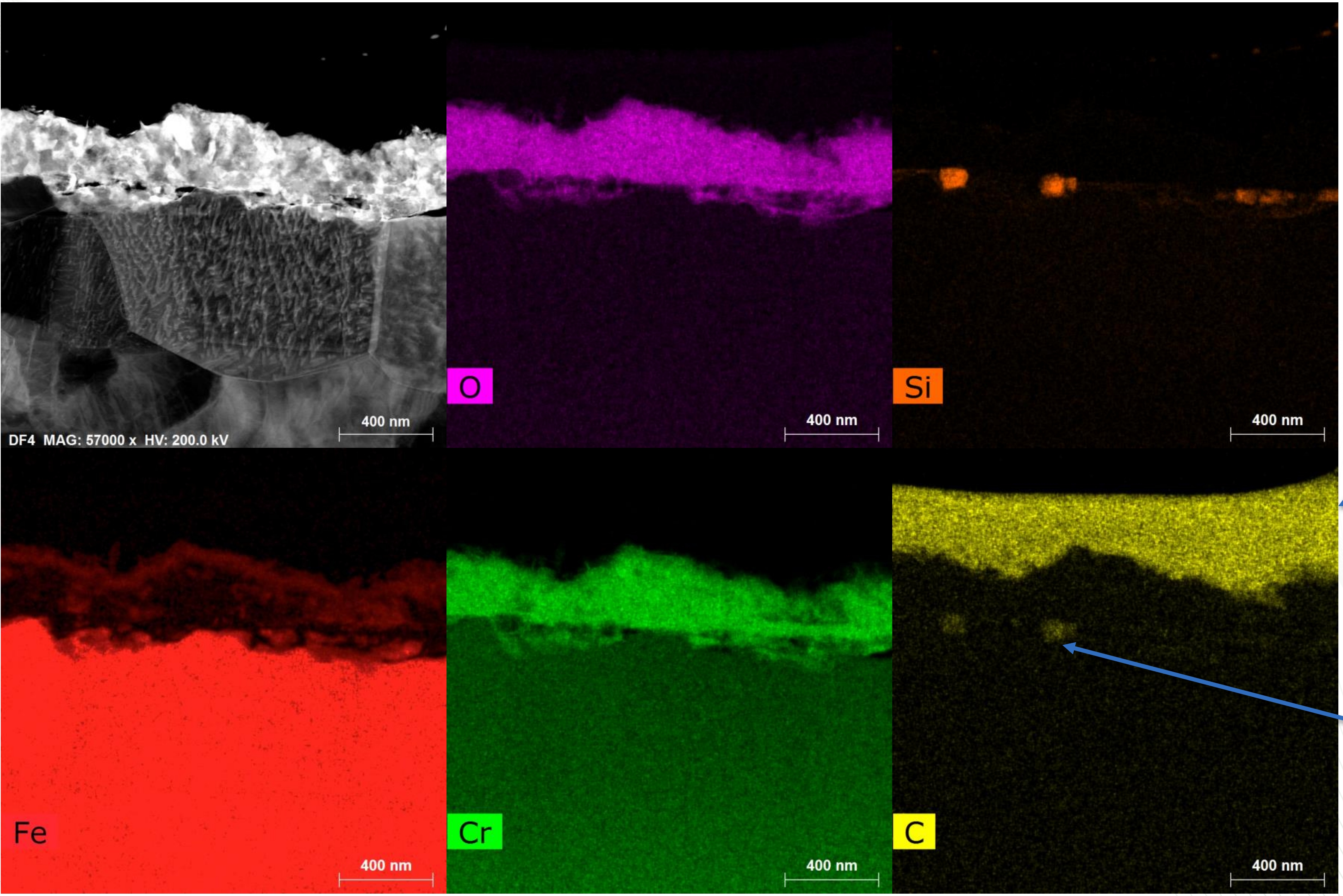
No C detected in 740H at 750°C/300 bar



E-Brite exposed 600°C 200 bar sCO_2 500 h: Si-C at interface

Fe-26Cr-1Mo

Cr_2O_3 scale



C film for prep

C with Si, not from prep

Project goal is to study O_2+H_2O effects on sCO_2 compatibility

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- 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 reported previously, more effect of H_2O addition
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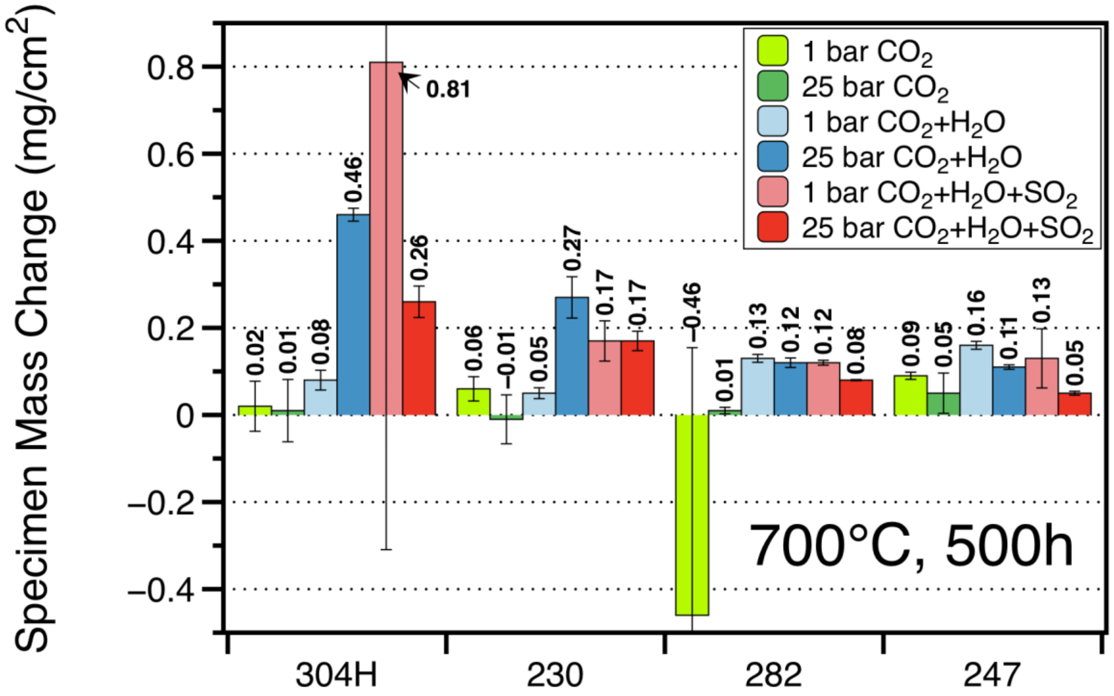
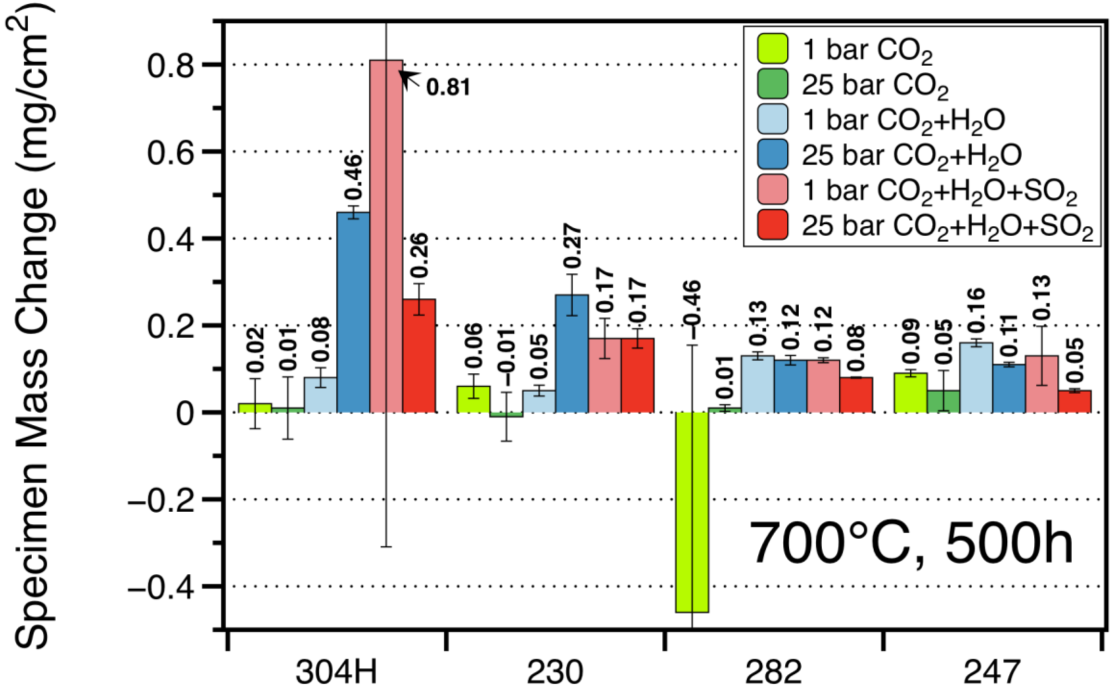
4) Study 1 & 25 bar CO_2 vs. CO_2+10%H_2O vs. CO_2+10%H_2O+0.1%SO_2
    - 500 h exposures complete at 700° and 800°C

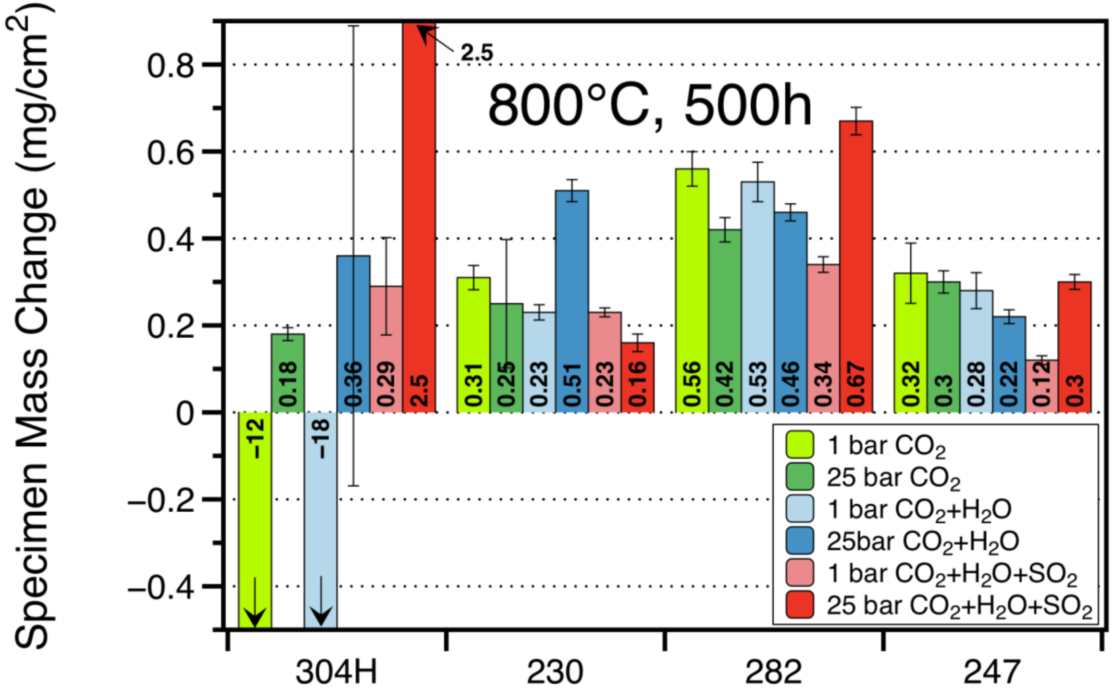
700°C: small effects of pressure and H_2O/SO_2 observed



3 specimens of each alloy
exposed in each condition:
Bar = average
Whisker = standard deviation

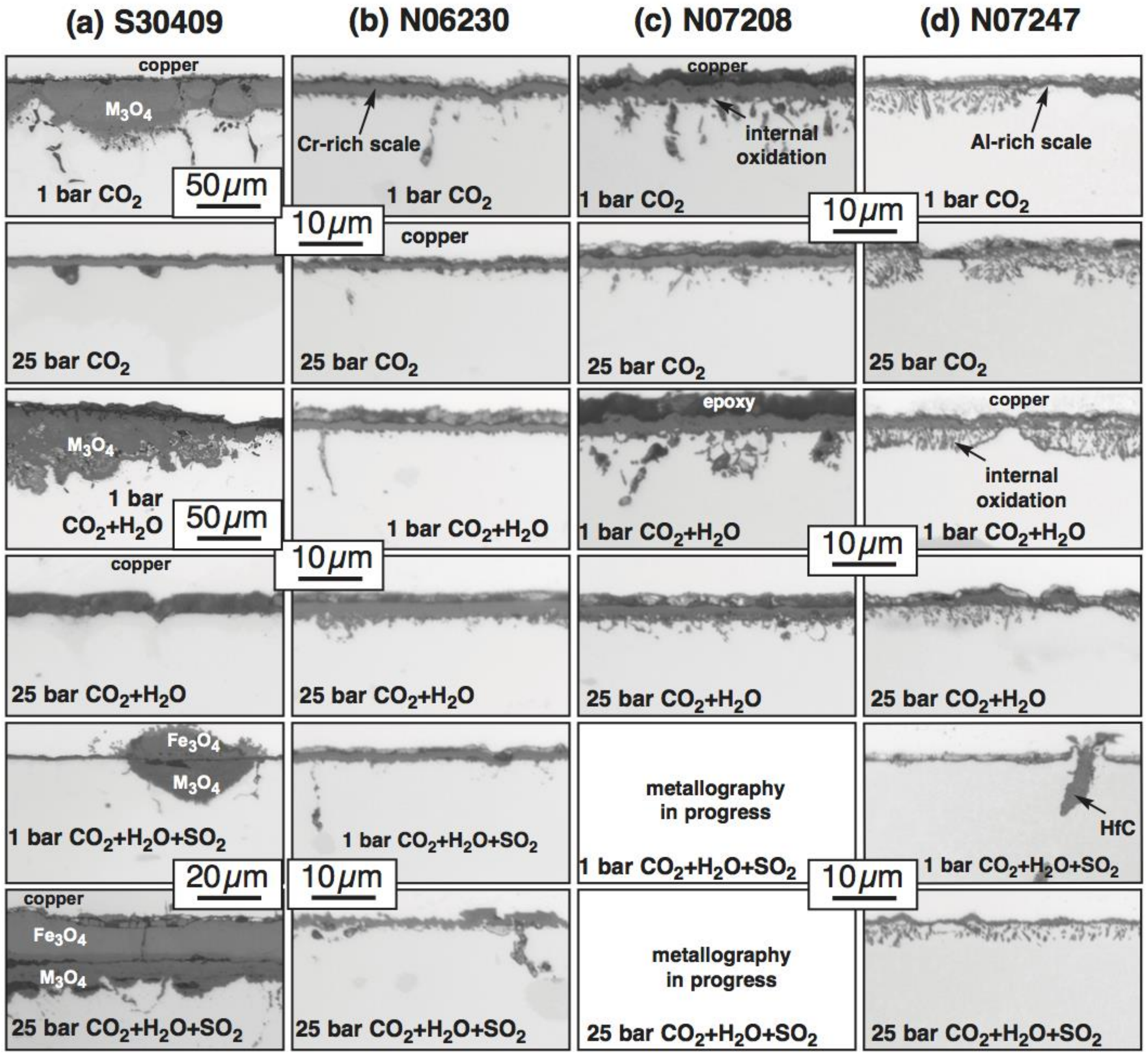
800°C: 304H strongly affected





3 specimens of each alloy
exposed in each condition:
Bar = average
Whisker = standard deviation

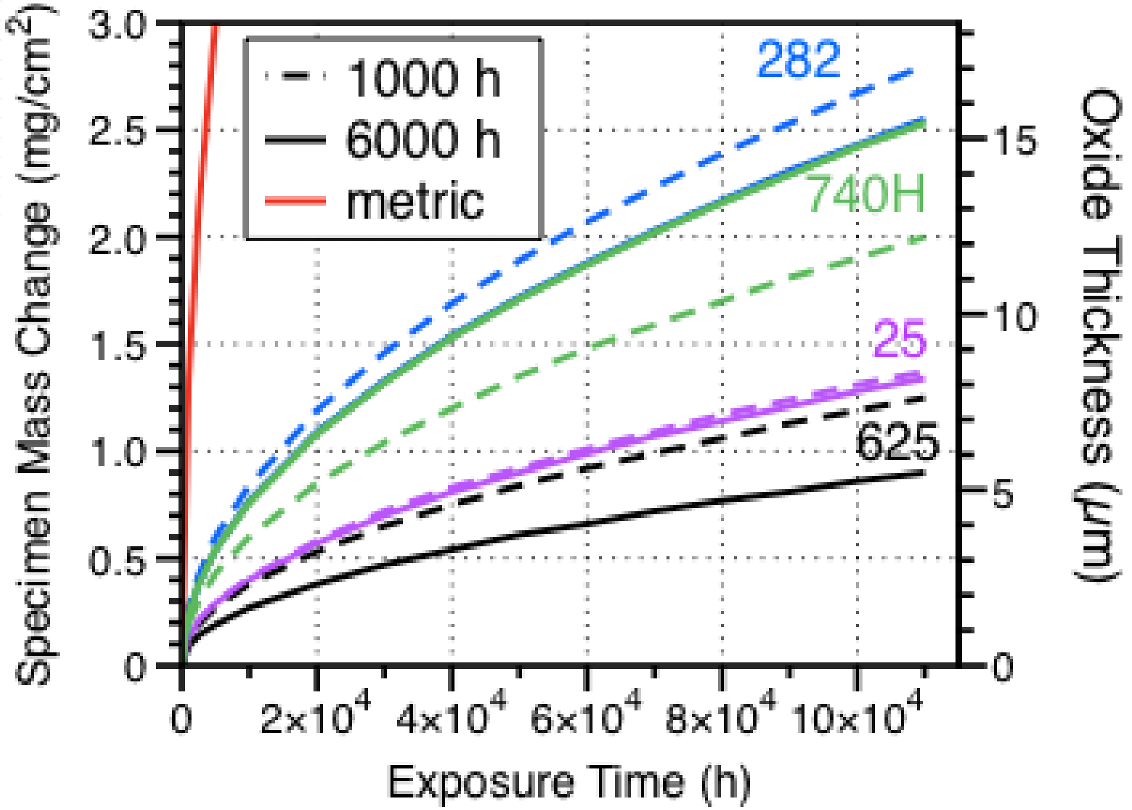
800°C: thicker oxides easier to discern P and H_2O/SO_2 effects



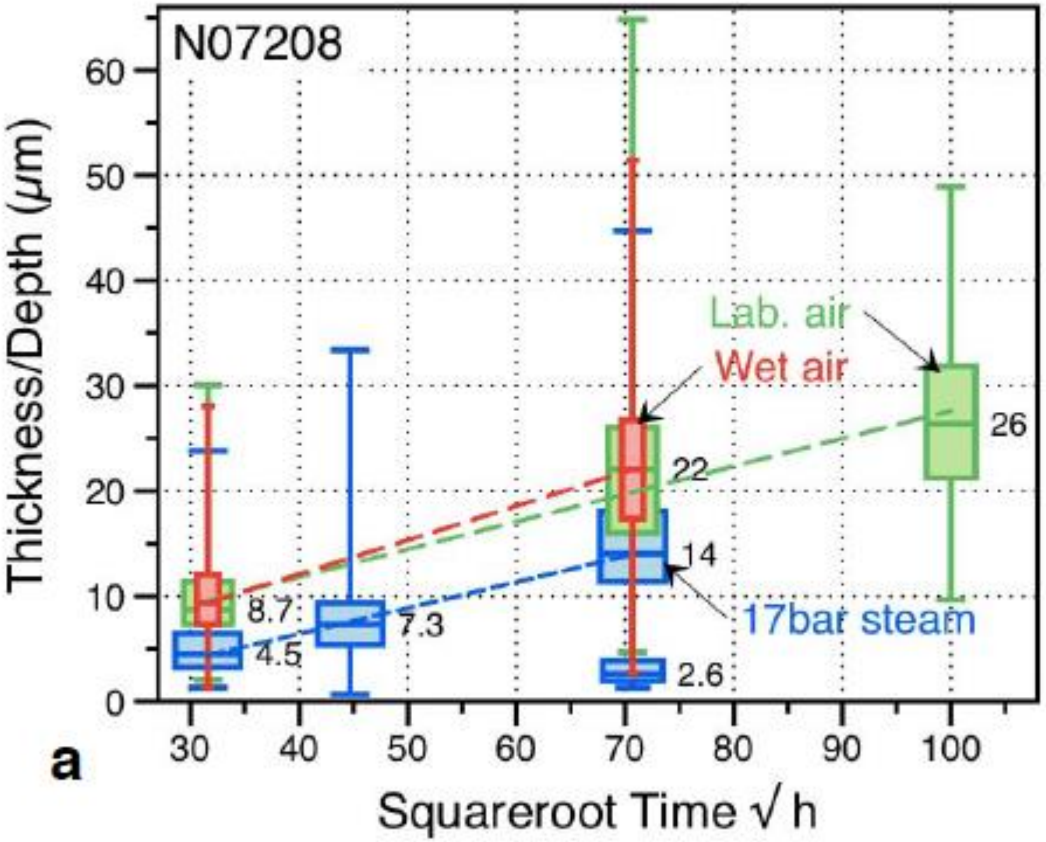
0.1%SO_2 suppressed internal attack

If C ingress minimal, what is there to model? Mass gain? Internal oxidation?

Extrapolation of CSP rate constants



282 internal oxidation already studied (Pint and Thiesing, 2015 NACE)

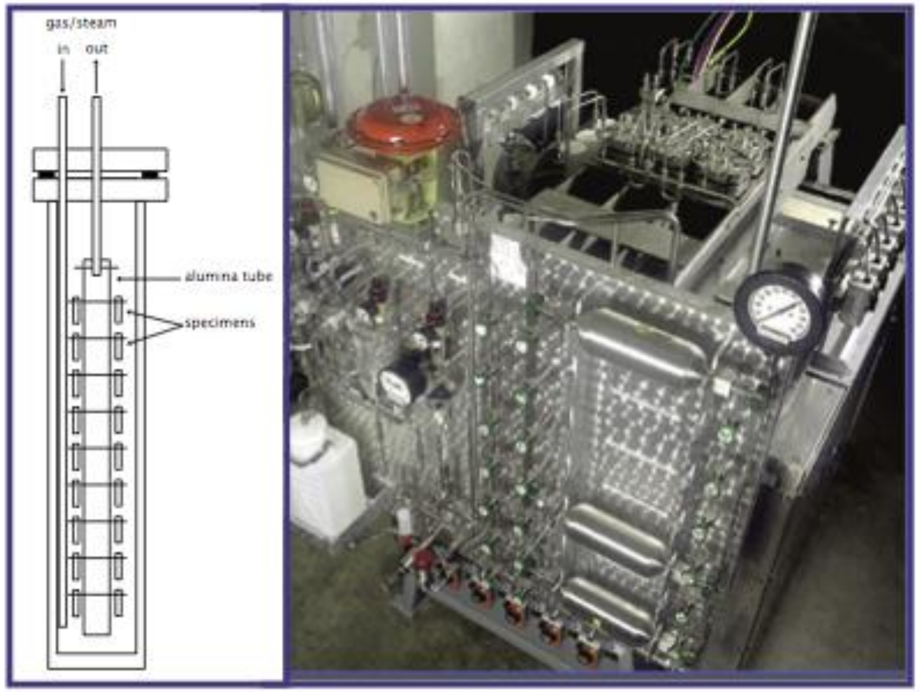


sCO_2 project summary

- Several experiments planned to study H_2O and O_2 effects in supercritical CO_2, need a system:
  - to study conditions relevant to direct-fired cycles
  - that can pump controlled impurity levels at 300 bar
  - (ideally) that can detect levels entering and leaving autoclave
- Additional experiments:
  - Comparing industrial and research grade CO_2
    - 1 and 300 bar
    - Collaboration with SunShot-funded project
  - comparing 1 & 25 bar CO_2 & CO_2+10%H_2O & CO_2+10%H_2O+0.1%SO_2
- More characterization in progress
  - TEM, GDOES & Quantification of oxide thickness and internal oxidation
- FY18: recreate AGR test conditions (43 bar) with IG CO_2

backups

“Keiser” rig



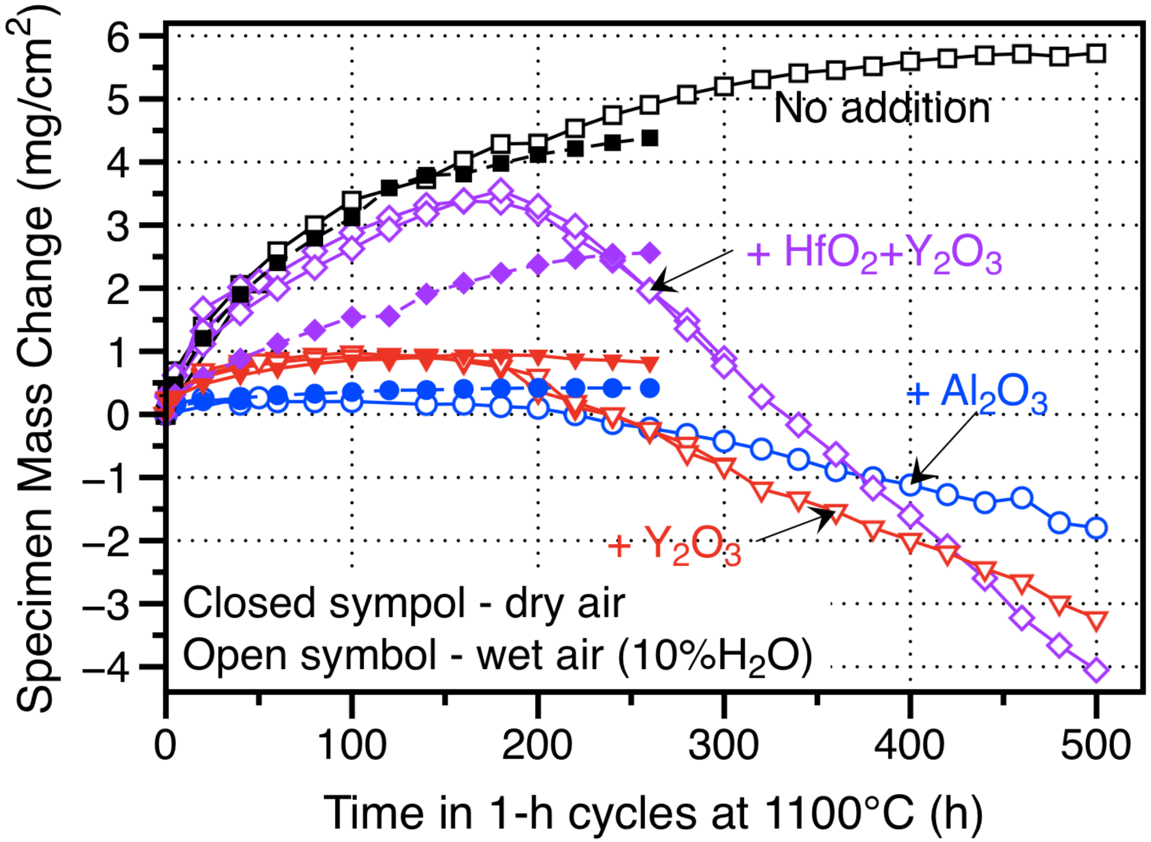
1 + 25 bar

500°-1300°C

500 h cycles

Collaboration with Jülich

- PhD student Jan Bergholz
  - Advisor: R. Vassen
- Investigating CoNiCrAlY with ODS dispersion
  - No oxide
  - Al_2O_3
  - Y_2O_3
  - $Y_2O_3+HfO_2$
- Bond coat only specimens
  - Isothermal: 1100°C, air + 10%H_2O
  - Cyclic: 1100°C, air ± 10%H_2O
- Rod specimens

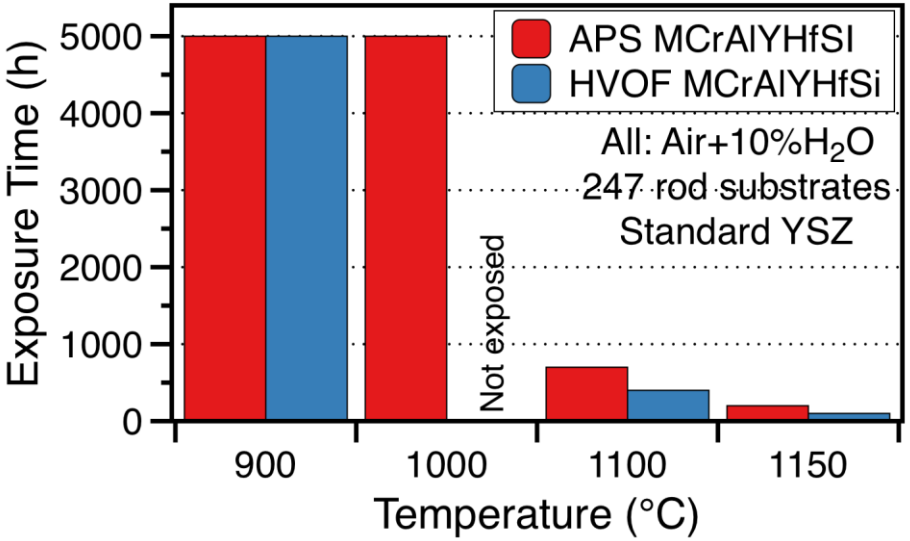


FY2016 FEAA122 Peer Review

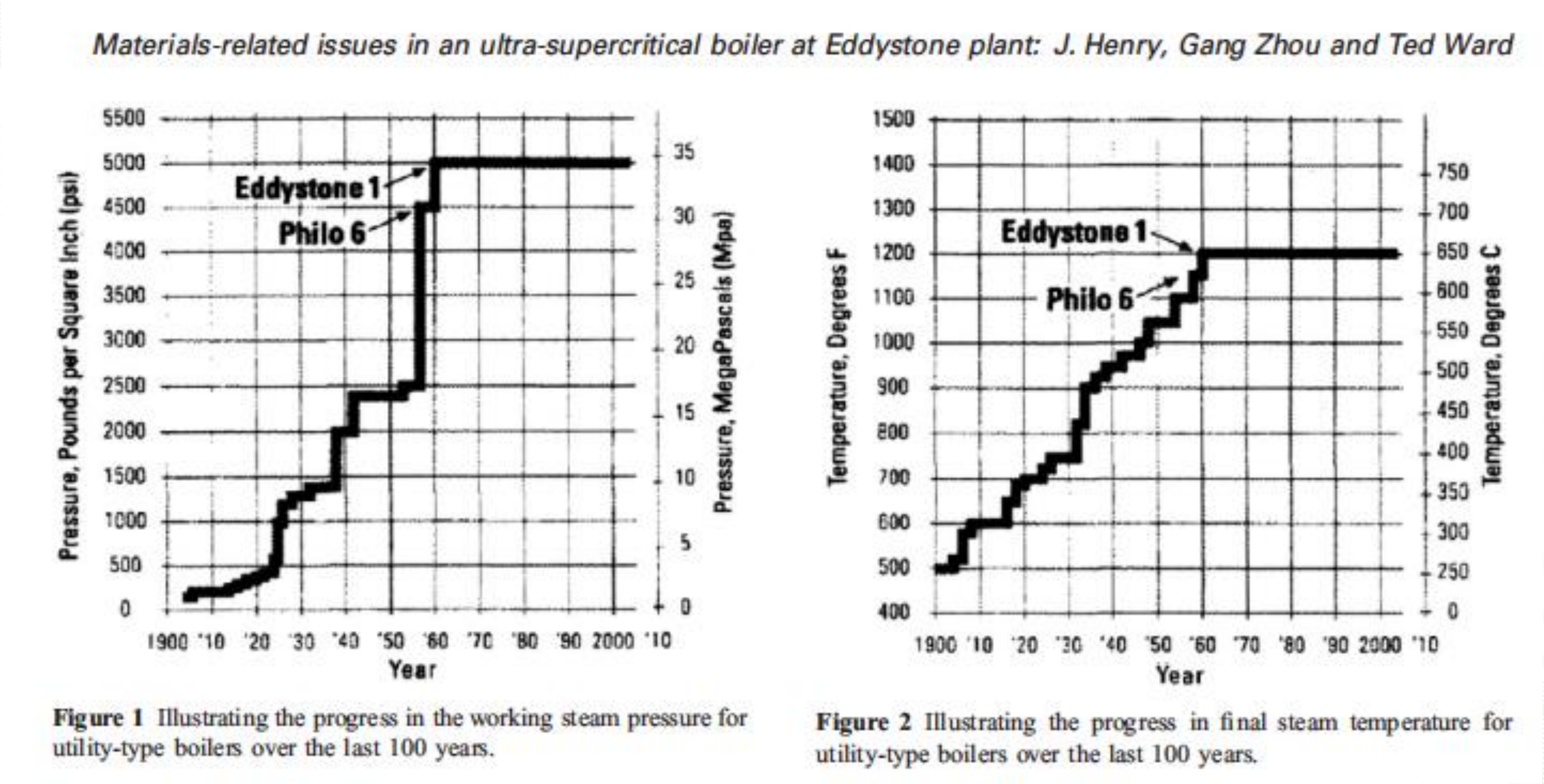
- April 2016 presentation
  - Limited results on rods at that point
- July 2016 feedback incorporated
  - Measure and control coating thickness and roughness
  - Incorporate literature data in modeling
  - Investigate simpler geometries
  - Define value of project
- Feedback not incorporated
  - Effect of thickness on thermal resistance (scope/cost)
  - Effect of thermal gradient (scope)
  - Increase number of specimens (cost)
  - Effect of contaminants (scope)

FY15 milestones: fabricate + test rods

- Fabricate different multilayer variants of coated specimens on rod specimens for laboratory evaluations (**Met9/2015**)
- Optimize coating architecture , and processing protocols for rod specimens (**Met, 7/2015**)
- Complete quantification of 900°C interdiffusion experiments (**Met, 8/2015**)
  - Results in Superalloys 2016 manuscript
- Summarize comparison of TBC performance across all coating and environmental parameters investigated (**Met. 8/2015**)
  - 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.
- Initiate laboratory testing of rod specimens and complete 2000h of exposure at two temperatures (**Met 3/2016**)



Eddystone: 1960 when coal-fired boiler progress stopped



Materials-related issues in an ultra-supercritical boiler at Eddystone plant: J. Henry, Gang Zhou and Ted Ward

Figure 1 Illustrating the progress in the working steam pressure for utility-type boilers over the last 100 years.

Figure 2 Illustrating the progress in final steam temperature for utility-type boilers over the last 100 years.

J. Henry (2007) Materials at High Temperature

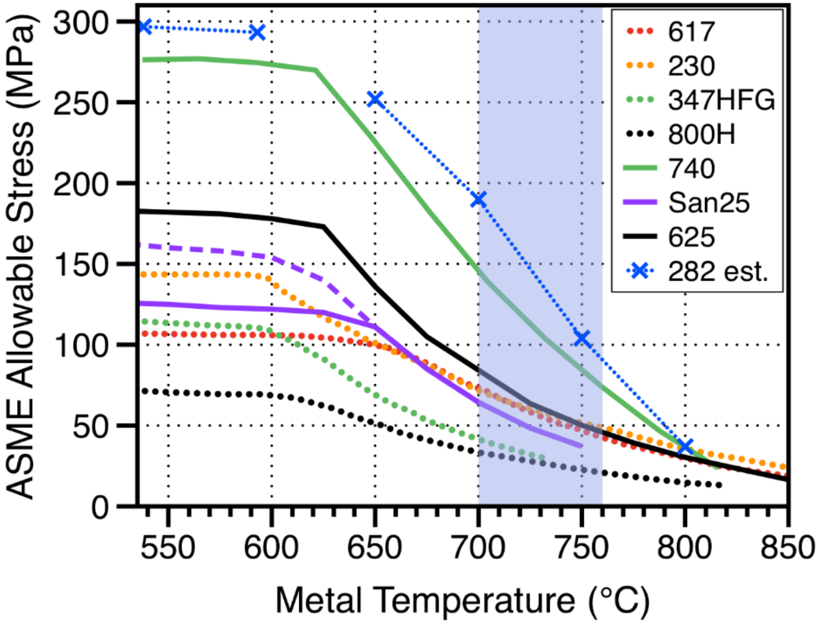
Four alloys selected for SunShot study

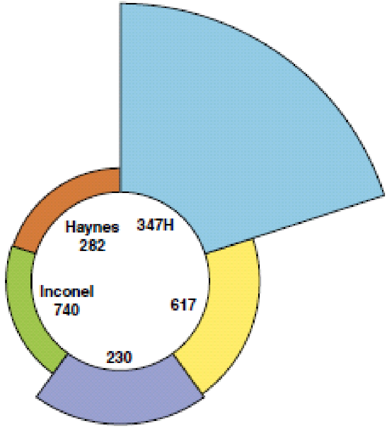
- Composition analyzed by ICP-OES and combustion analyses

Alloy	Fe	Ni	Cr	Al	Co	Mo	Nb	Ti	Mn	Si	Other
Sanicro 25 (Sandvik)	42.6	25.4	22.3	0.03	1.5	0.2	0.5	0.02	0.5	0.2	3.5W, 3.0Cu, 0.2N 0.068 C
Haynes 282 (Haynes International)	0.2	57.1	19.6	1.6	10.6	8.6	<	2.2	0.02	0.04	0.059 C (< is less than 0.02)
Inconel 740H (Special Metals)	0.1	49.7	24.5	1.4	20.6	0.3	1.5	1.4	0.3	0.2	0.027 C
625 (industry selection)	4.0	61.0	21.7	0.12	0.1	8.8	3.5	0.2	0.2	0.2	0.06W,0.09Cu,0.016C

ASME Boiler & Pressure Vessel Code allowables:

Precipitation-strengthened (γ´) Ni-base alloys





Shingledecker ~2011