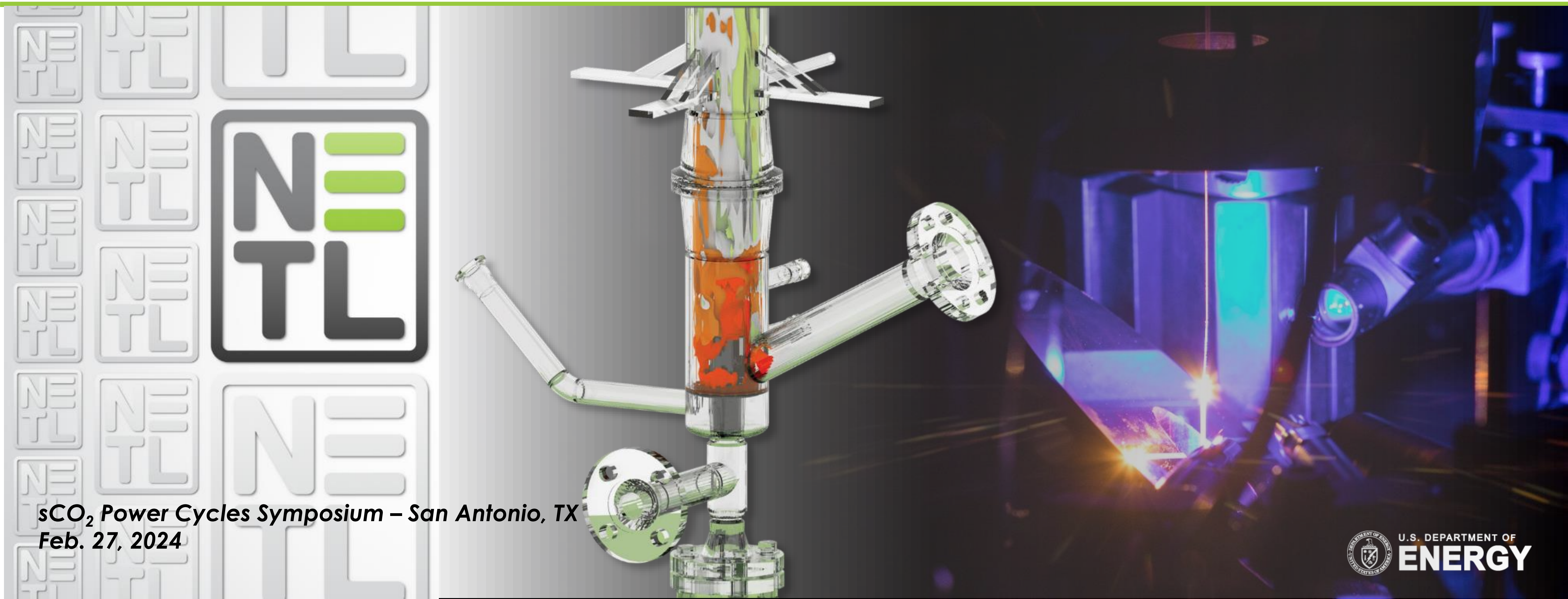
High-Temperature Oxidation Behavior of Wrought and Additive Manufactured Ni-Based Alloys in Direct-Fired Supercritical CO_2 Power Cycle Environments

Casey S. Carney
NETL Support Contractor



sCO_2 Power Cycles Symposium – San Antonio, TX
Feb. 27, 2024

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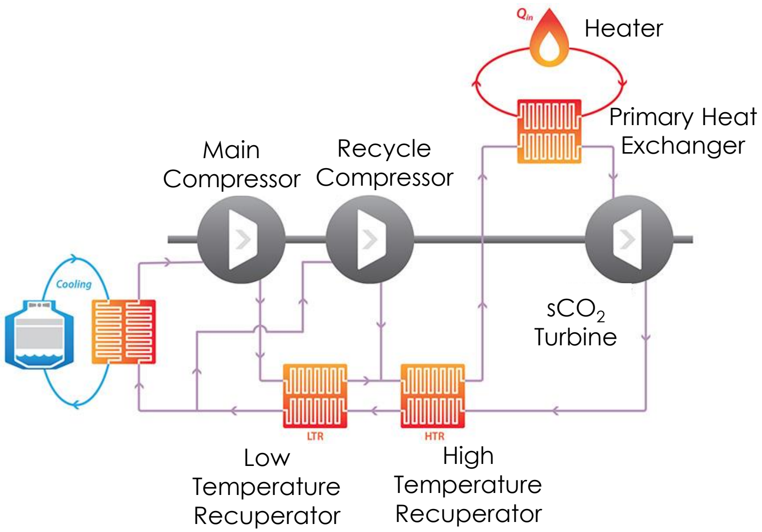
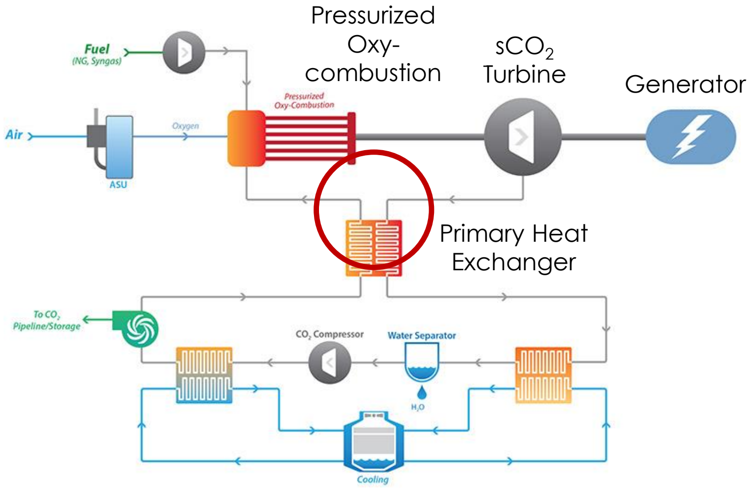
Materials Considerations

Indirect-fired sCO_2 cycle



Direct-fired sCO_2 cycle



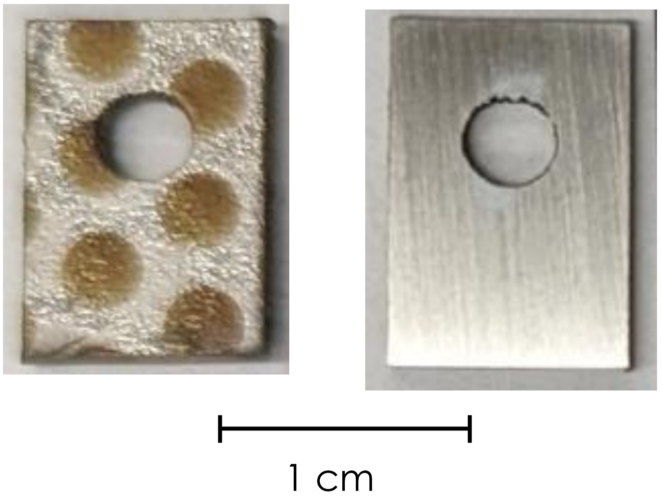
Cycle Type	Component	Inlet		Outlet		Fluid Components
		T (°C)	P (MPa)	T (°C)	P (MPa)	
Indirect	Heater	450-535	1-10	650-750	1-10	High purity CO_2
	Turbine	650-750	20-30	550-650	8-10	
	HX	550-650	8-10	100-200	8-10	
Direct	Combustor	750	20-30	1150	20-30	CO_2 containing H_2O, O_2, and other impurities based on fuel (e.g., SO_2)
	Turbine	1150	20-30	800	3-8	
	HX	800	3-8	100	3-8	

Additive Manufacturing Sample Prep (CMU)

- Test coupons additively manufactured (AM) from H282 powder with varying laser powder bed fusion processes
- Three varieties chosen for oxidation study
  - High densities with different scan speeds (laser velocity/power)
    - S1 (959 mm/s – 250 W) ρ > 99.99%
    - S2 (1366 mm/s – 350 W) ρ > 99.9%
    - S3 (1772 mm/s – 370 W) ρ > 99.9%
- Three step heat treatment (under Ar)
  - 1250 °C for 2 h (solution annealing)
  - 899 °C for 4 h (aging)
  - 788 °C for 8 h (aging)
- Samples exposed "As Printed" and after a Surface Finishing step (600 grit polish)
- Test coupons also prepared from wrought H282 and other Ni-based alloys
  - Also exposed at ambient pressure direct-fired conditions

AP
As Printed

SF
Surface
Finished



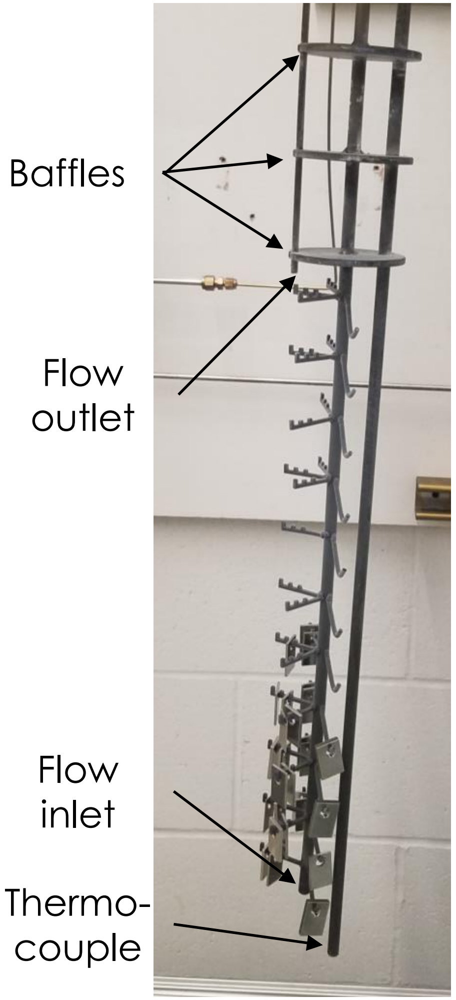
The test coupons were exposed to direct-fired conditions at:
750 °C 200 bar

Alloy	Ni	Cr	Fe	Co	Mo	W	Al	Si	Ti	Mn	Nb	C (ppm)
230	60.4	21.3	0.4	0.3	1.2	14.8	0.4	0.45	0.01	0.4	0.04	903
263	51.1	19.9	0.01	20	5.6	-	0.4	0.28	2.1	0.5	0.1	560
282	58.4	19.2	1.5*	10.2	8.4	-	1.3	0.04*	2.1	0.1	0.02	600
617	55.1	21.8	0.4	11.4	9.6	-	1	0.02	0.5	0.04	0.03	843
625	61	21.4	4.4	0.1	8.4	-	0.2	0.35	0.3	0.1	3.3	181
740H	50.6	24.5	-	20.1	0.3	-	1.2	0.12	1.4	0.2	1.5	238

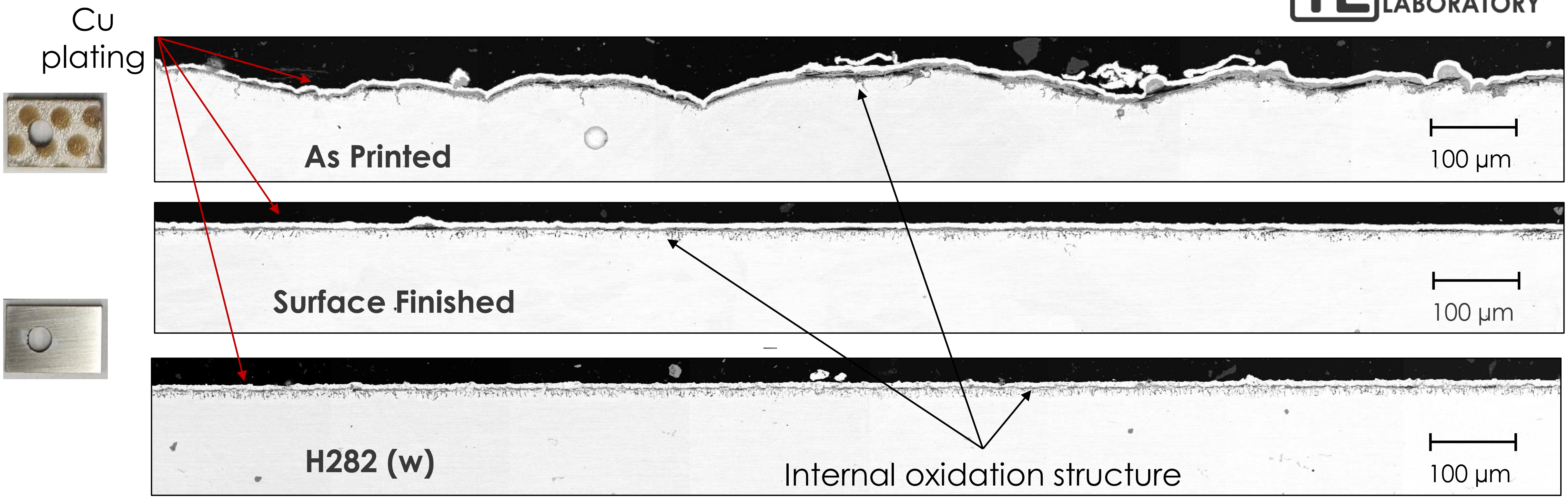
Oxidation Exposures at 200 bar

Direct-fired fluid flow environment:

- **750 °C, 200 bar, $95CO_2 – 4H_2O – 1O_2$**
  - – CO_2 (99.999% purity)
  - – H_2O (DI, aerated)
  - – 20 % O_2 in Ar (99.999% purity)
- Flow controlled with two high-pressure liquid pumps (CO_2, H_2O) and a pneumatic booster pump (O_2/Ar)
- Pressure controlled with an adjustable back pressure regulator
- Test duration: ~1,500 h (300-500 h increment)
- Replicates of each alloy (2-3)
- 10 Ar purge cycles before heating



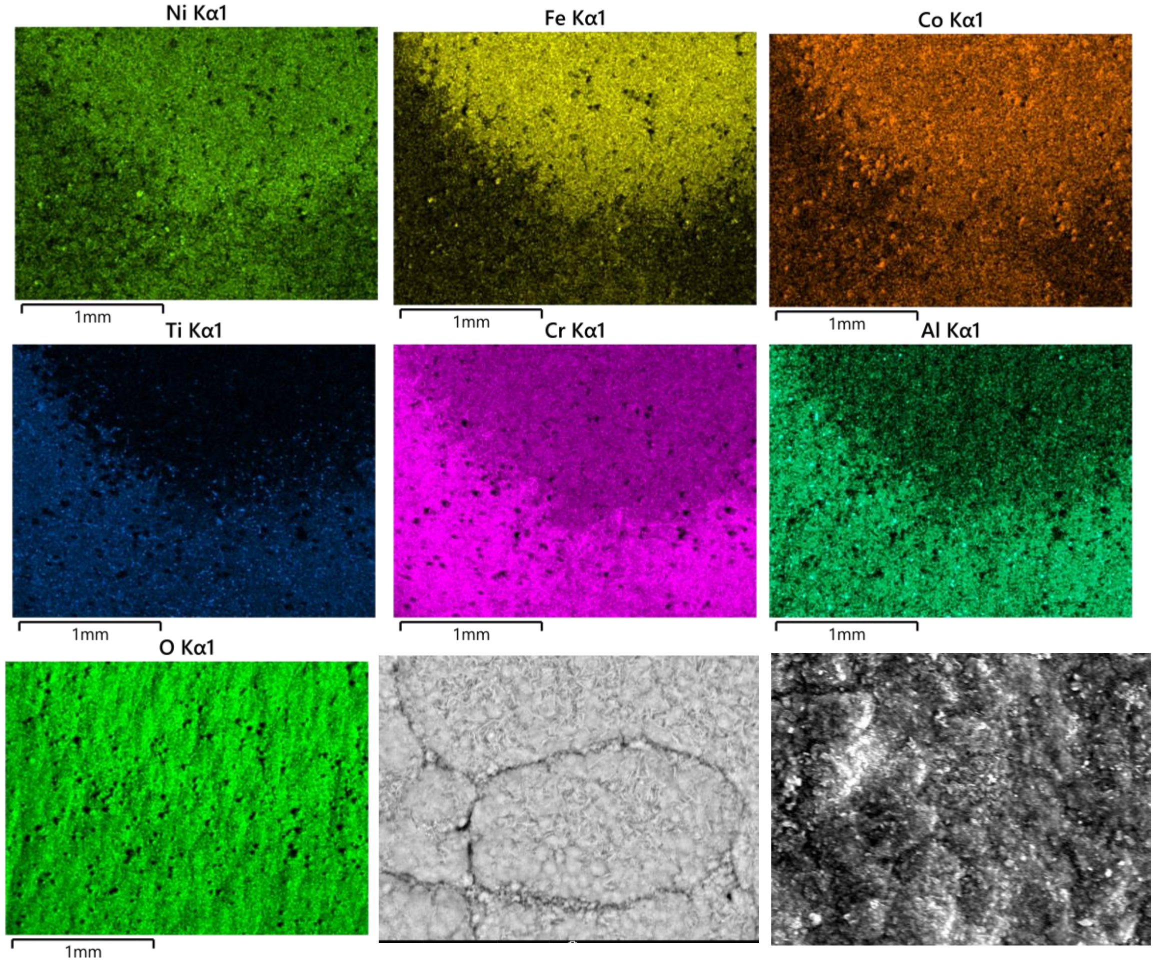
Effect of Surface Finish on Bulk Oxidation



- Surface Finished sample more uniform oxide layer (thinner) than As Printed
  - More consistent internal oxidation regions
- As Printed sample has binary oxide thickness regions
  - Artifact of initial heat treatment step?
- Surface Finished sample similar to H282 wrought (also surface finished)

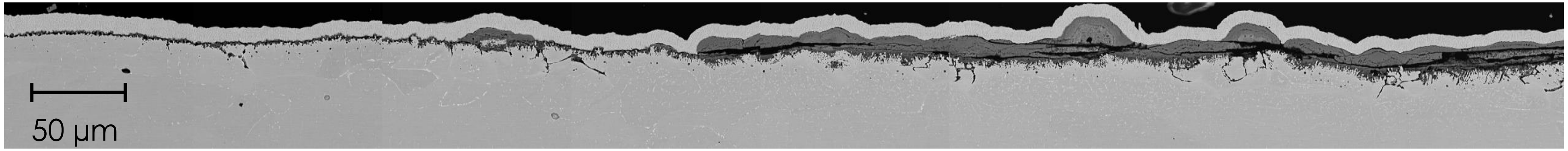
750 °C 200 bar, 95 CO_2 – 4 H_2O – 1 O_2

Heat Treatment Artifact

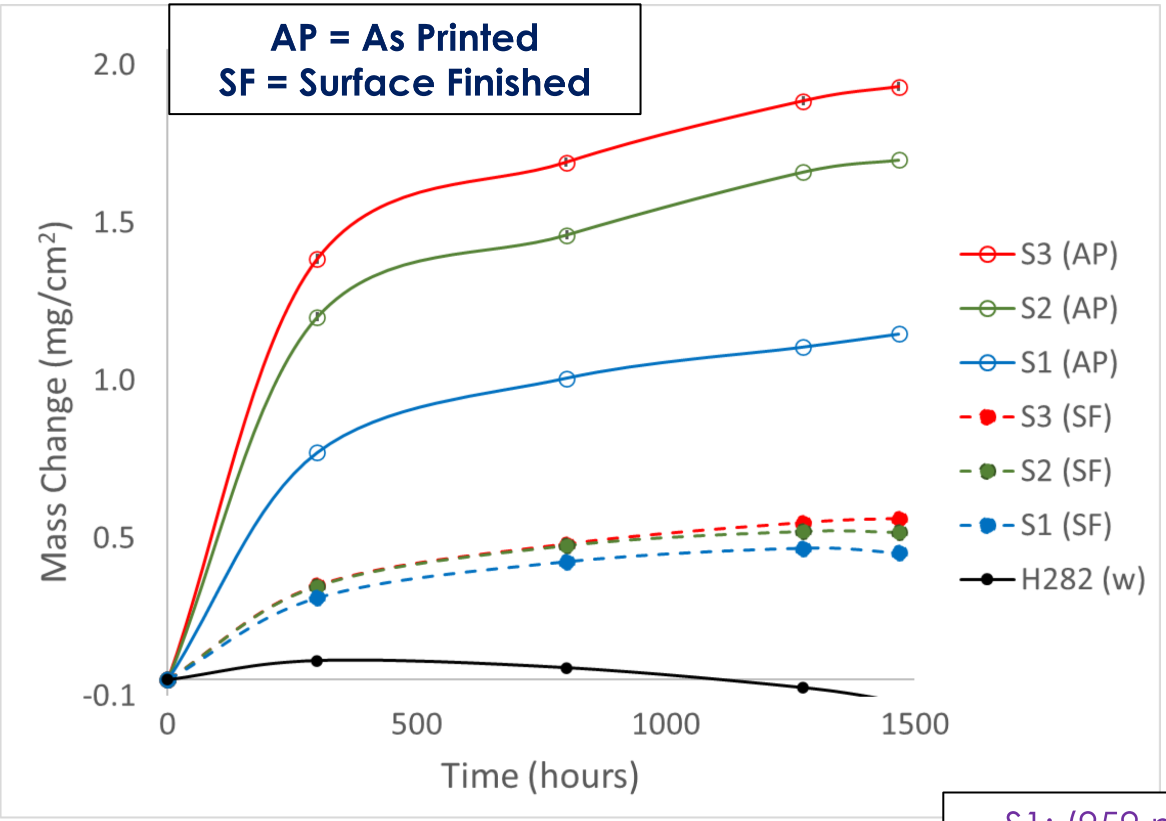


Localized Compositions	Al	Ti	Cr	Fe	Co	Ni	Mo
Spot	0.5	1.1	20.6	19.1	8.1	15.0	0.0
Non-Spot	2.1	7.1	36.7	3.4	3.2	8.7	0.6

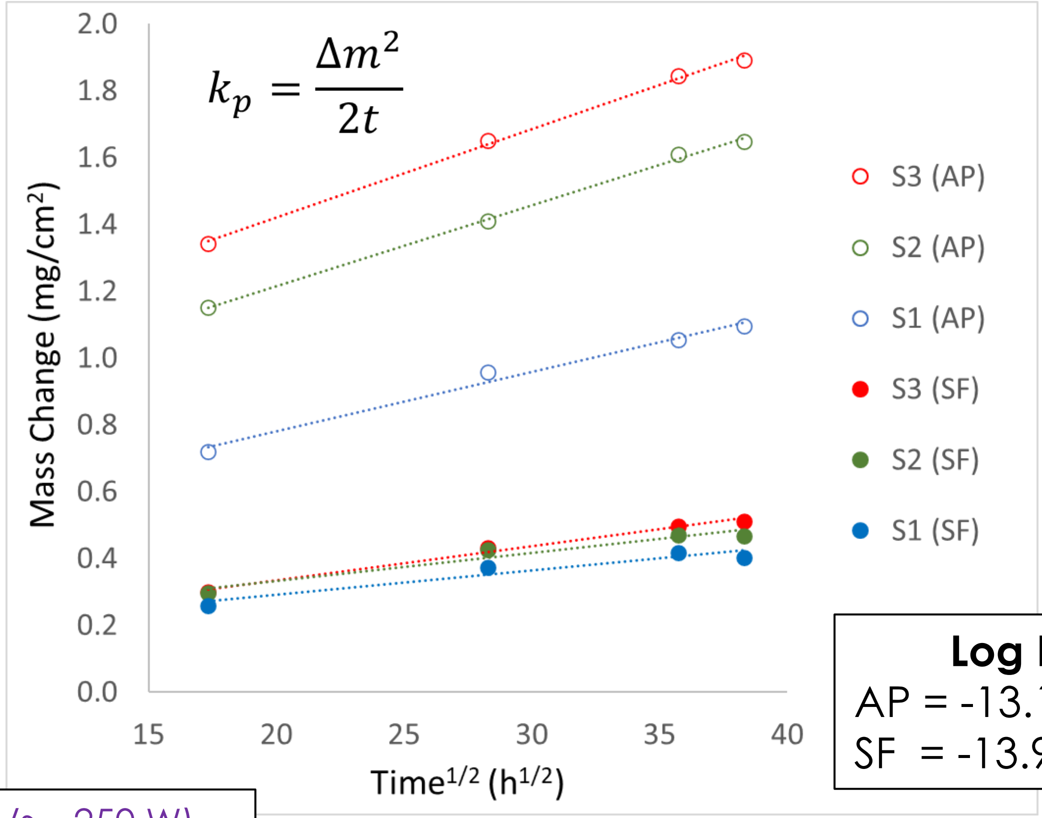
- Differing outer surface oxide regions resulting from placement on a mesh grid during heat treatment
  - Potentially leads to binary oxide regions
  - Some duplex oxides scales→ less protective
- Needs more investigation
  - Examine sample post heat treatment but before oxidation exposure



Oxidation Behavior of AM H282



AP = As Printed
SF = Surface Finished



$$k_p = \frac{\Delta m^2}{2t}$$

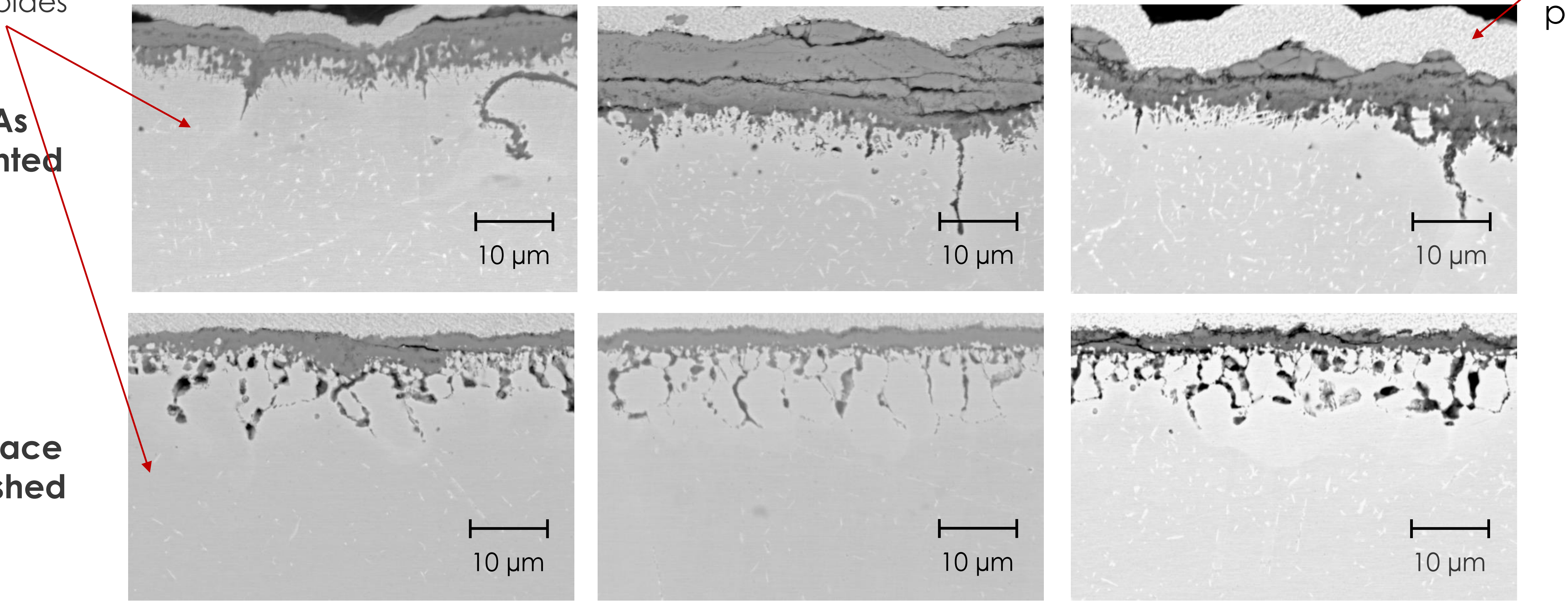
Log Kp
AP = -13.1 ± 0.2
SF = -13.9 ± 0.1

S1: (959 mm/s – 250 W)
S2: (1366 mm/s – 350 W)
S3: (1772 mm/s – 370 W)

- Surface Finishing step greatly reduced main gain
- Mass gains significantly lower for wrought H282
  - Chromia scale volatilization at high pressure with H_2O
- Laser scan speed varies directly with overall mass gains

- All AM samples do obey parabolic kinetics
  - Diffusion limited through the surface oxide
  - More negative log k_p = slower reaction
- Slower oxidation rate for Surface Finished

Surface Finish Effect on Oxidation


S1 (lo)

S2 (med)

S3 (hi)

As Printed

Surface Finished

Mo-rich carbides

Cu plating

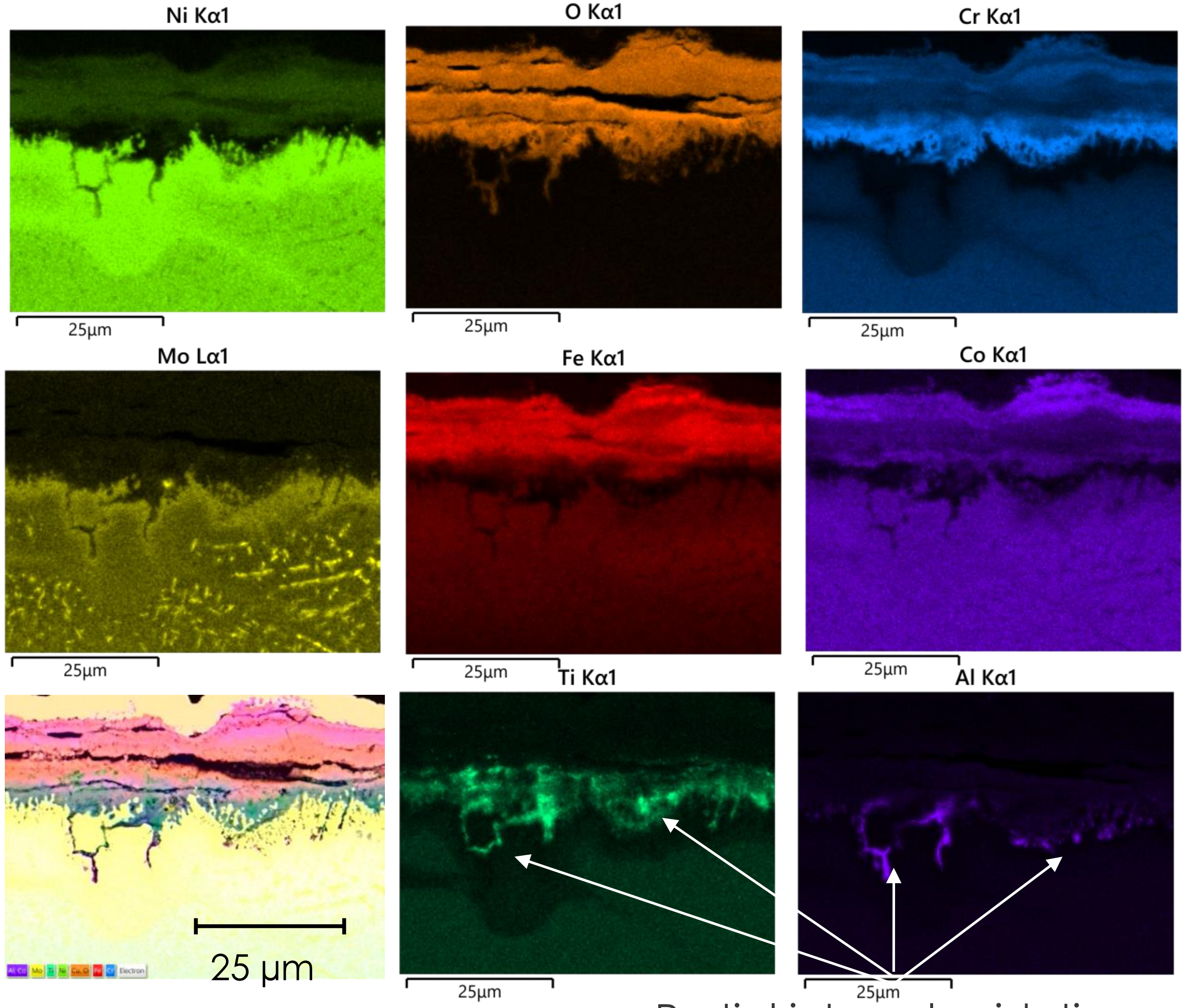
S1: (959 mm/s – 250 W)
S2: (1366 mm/s – 350 W)
S3: (1772 mm/s – 370 W)

Less carburization for SF?

750 °C 200 bar, 95 CO_2 – 4 H_2O – 1 O_2

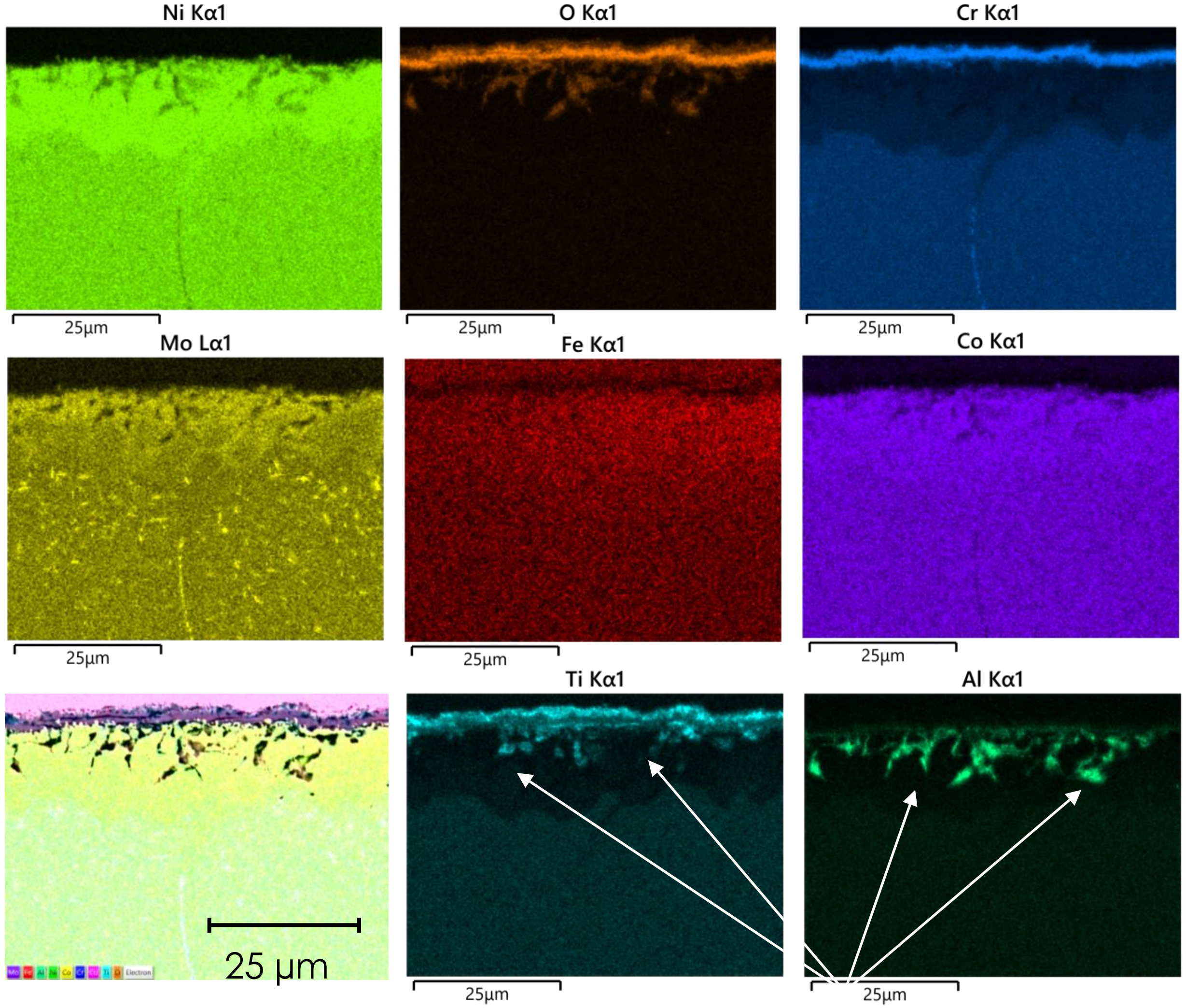
Elemental Mapping (AM)

As Printed



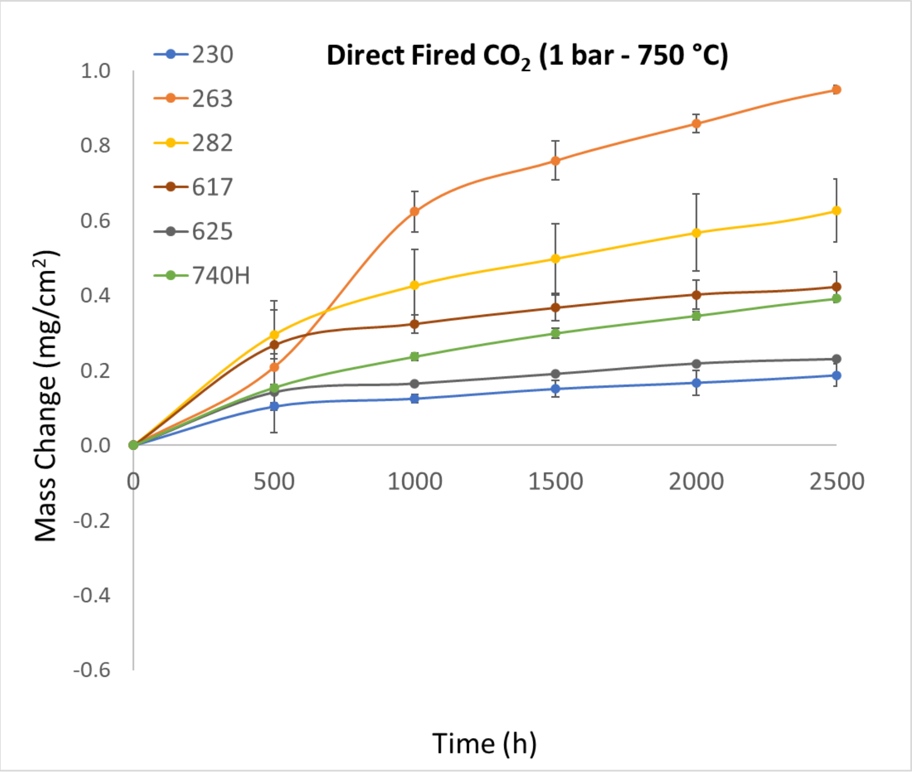
Partial internal oxidation

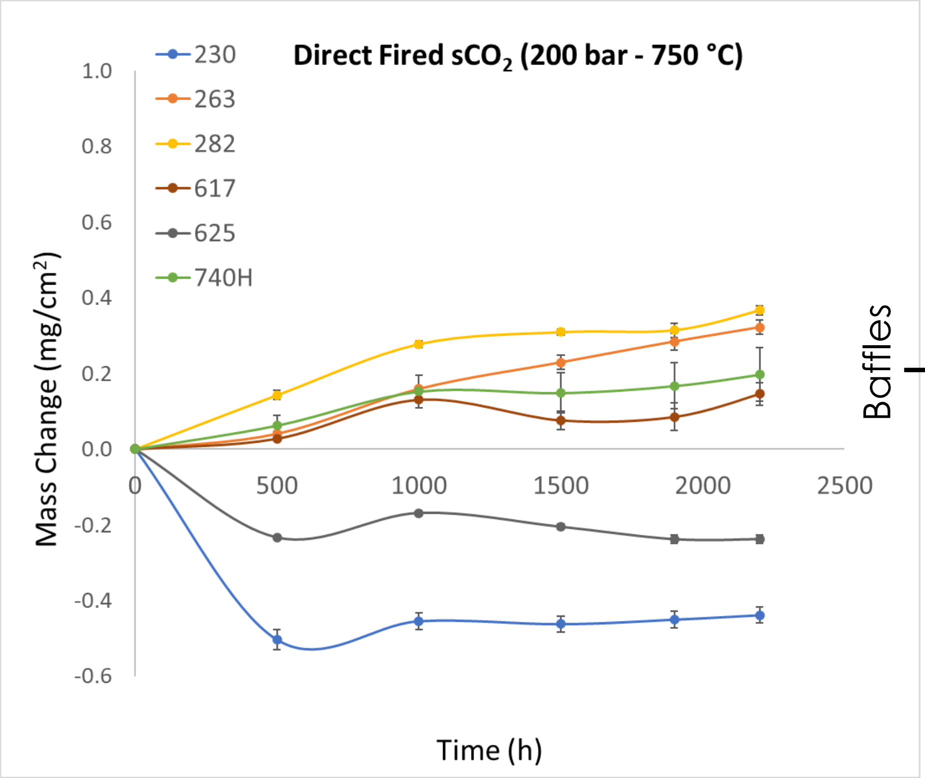
Surface Finished

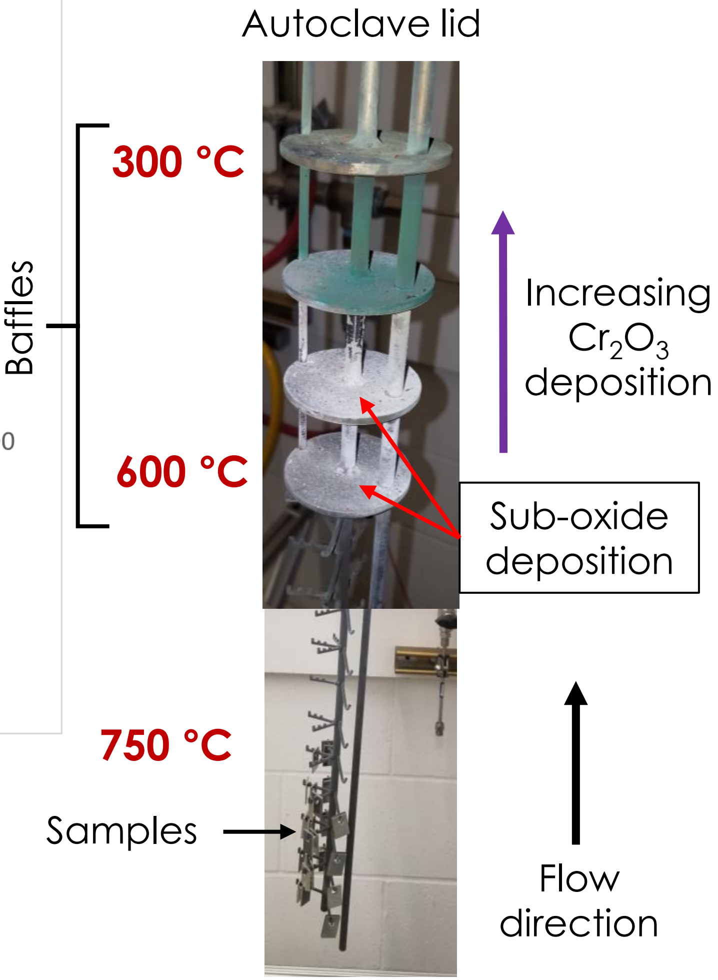


Internal oxidation

Chromia Volatilization vs. Pressure



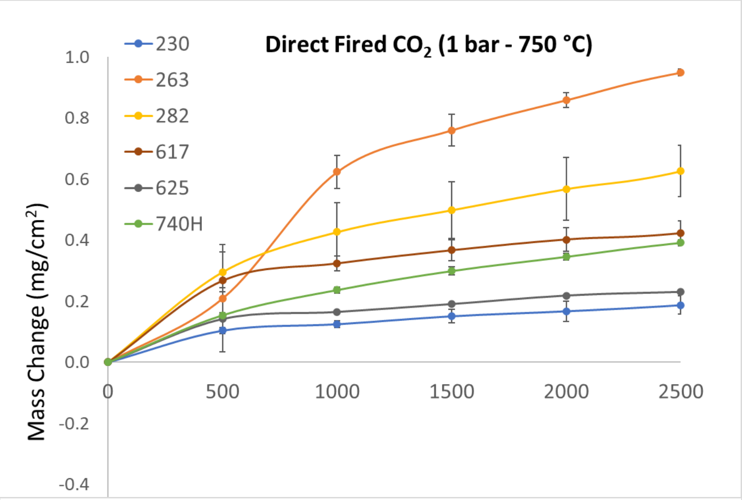


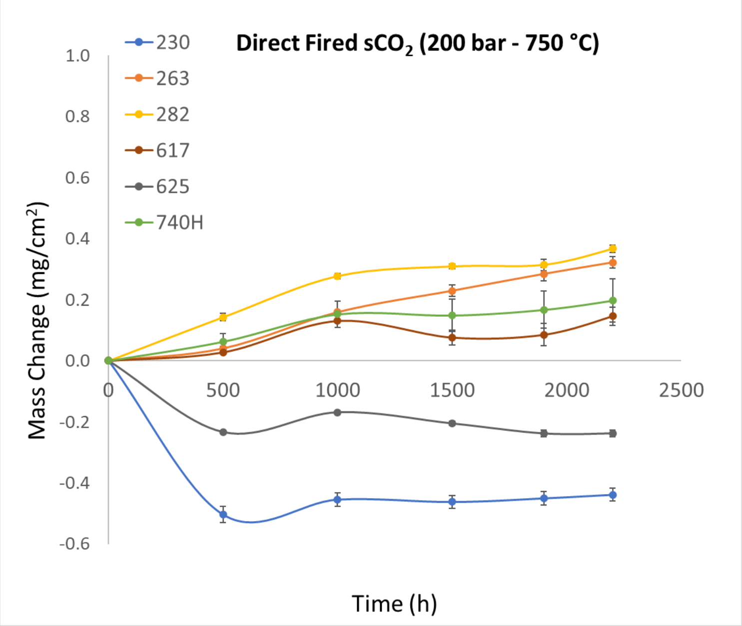


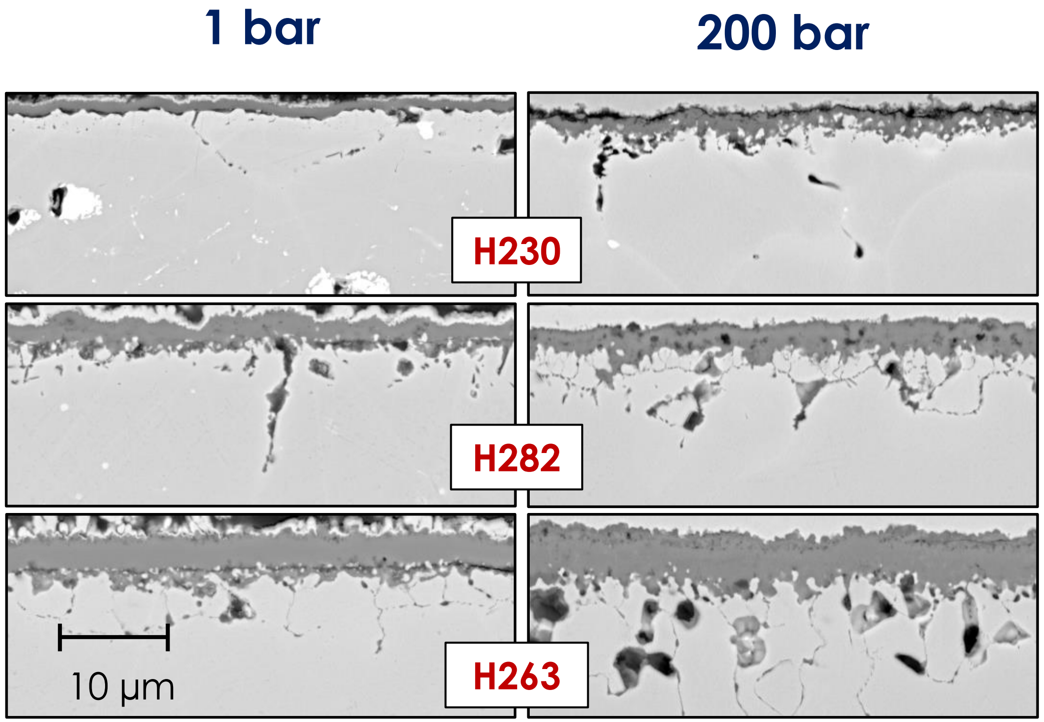
- Survey of Ni-based alloys in **Direct Fired** conditions vs. pressure
- Steady mass gains at ambient pressure
- Lower mass gains/losses at elevated pressures
- Increased downstream particulate collection

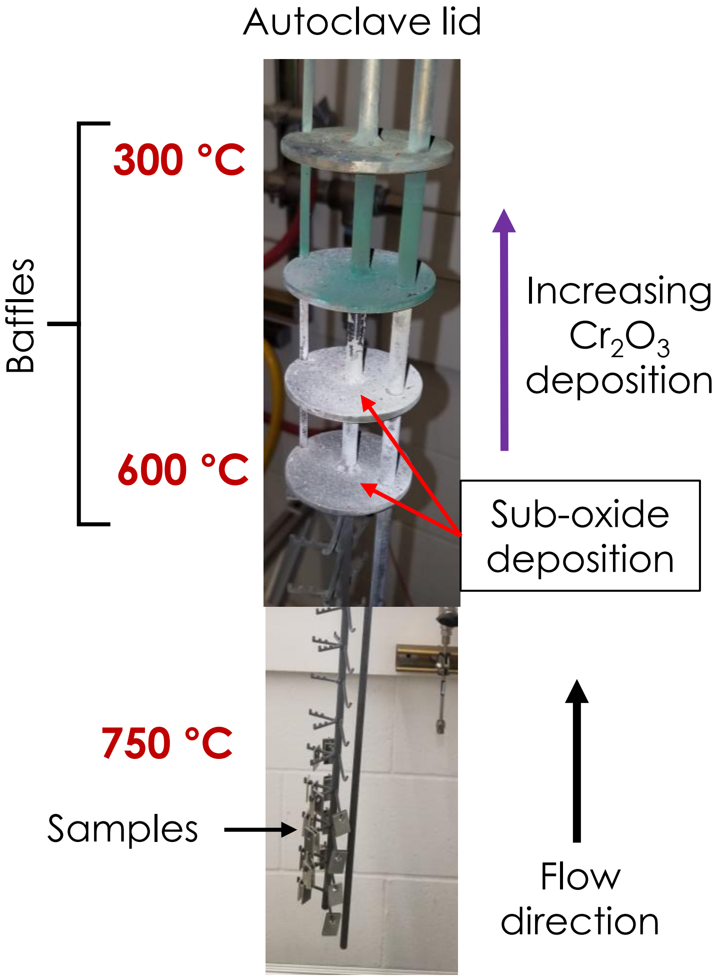
Oleksak, R.P., C.S. Carney, and O.N. Dogan, Effect of pressure on high-temperature oxidation of Ni alloys in supercritical CO_2 containing impurities. Corrosion Science **215**, 2023.

Chromia Volatilization vs. Pressure







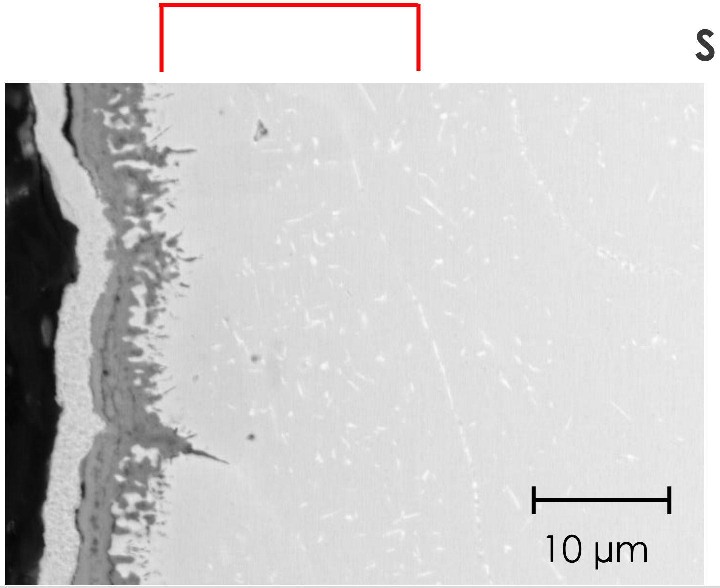


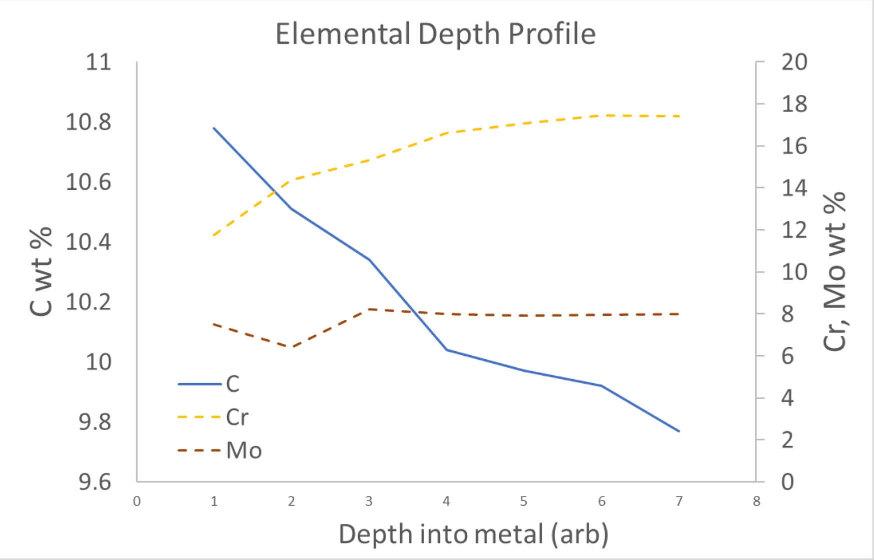
- Similar oxide scales between pressures
- Occurs only with water vapor at elevated pressure
- Volatilization can increase with fluid velocity

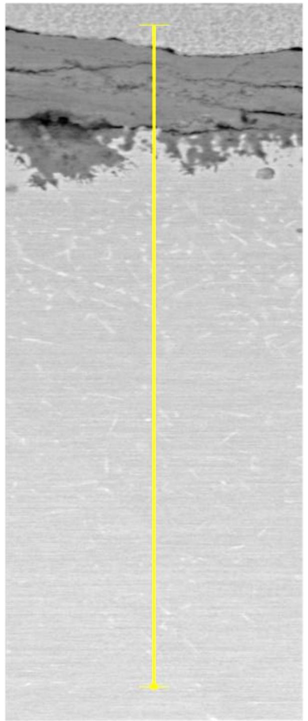
Oleksak, R.P., C.S. Carney, and O.N. Dogan, Effect of pressure on high-temperature oxidation of Ni alloys in supercritical CO_2 containing impurities. Corrosion Science **215**, 2023.

Carbide Formation Near Surface

S1 As Printed

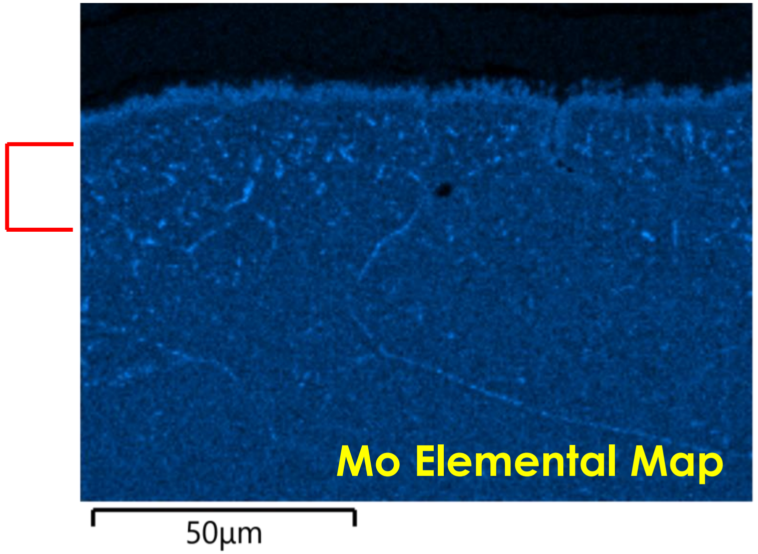






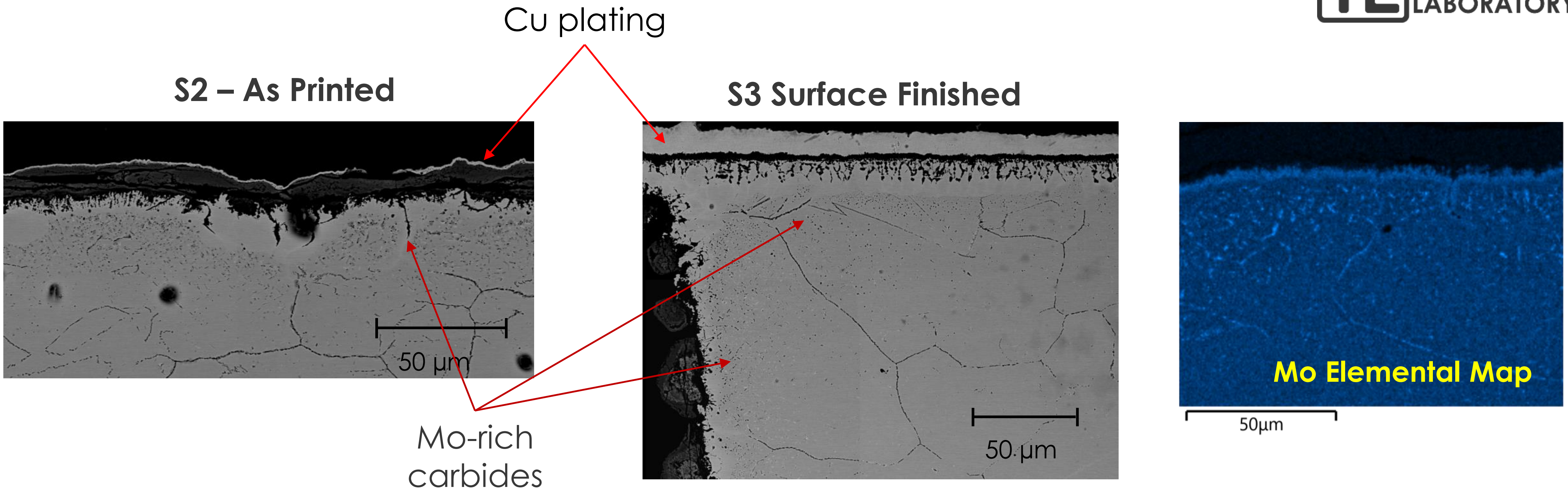
Mo-rich carbide region

S3 As Printed



- Mo-rich carbides sub-surface beneath recrystallization zone
- These structures found in greater concentration near surface
  - Suggestive of carburization during exposure

Sample Etching to Reveal Metal Carbides



Cu plating

S2 – As Printed

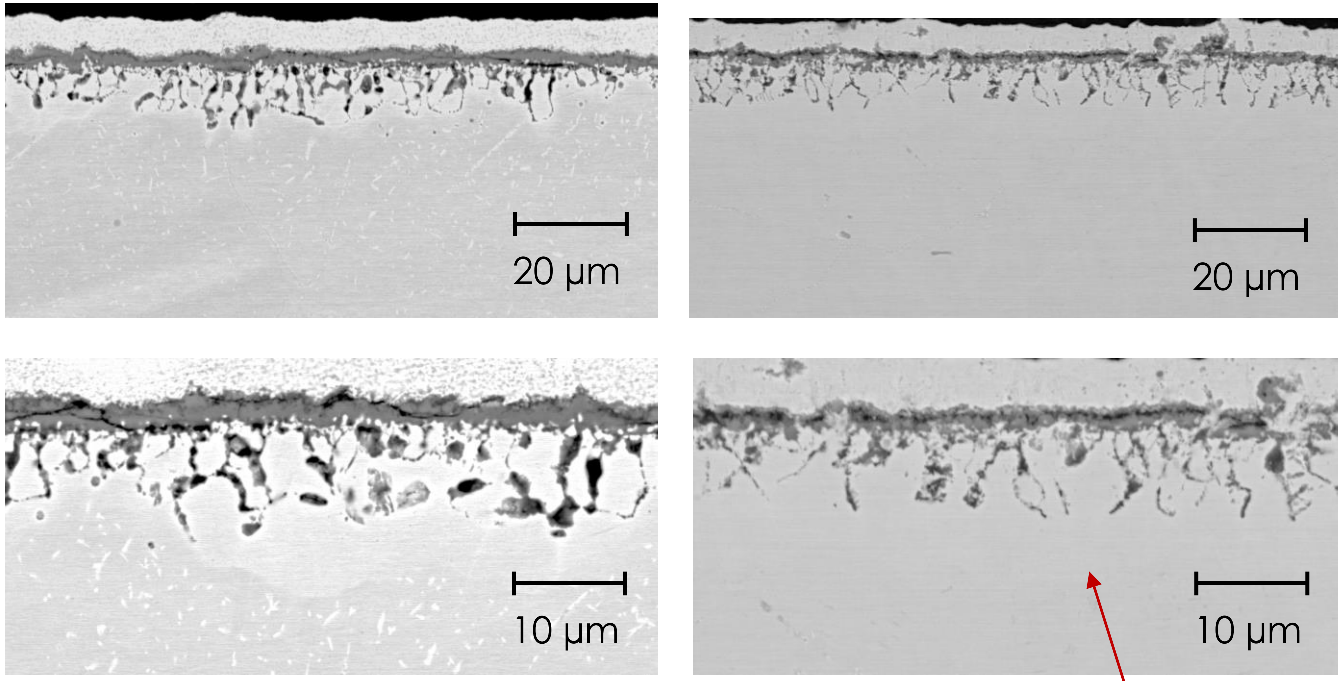
S3 Surface Finished

Mo-rich carbides

Mo Elemental Map

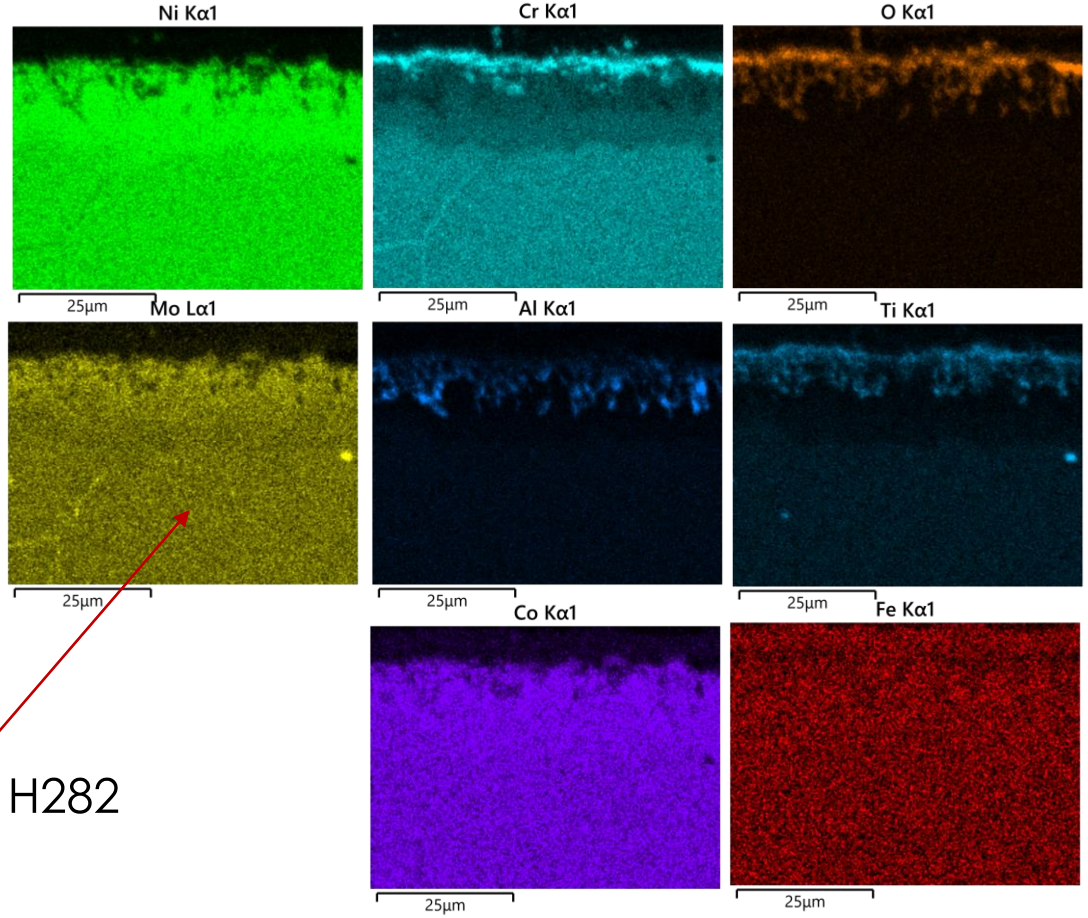
- Murkami’s reagent etchant used to reveal metal carbides
- Clearly present in As Printed samples
- Observed, but less prevalent when Surface Finished
- Also found along grain boundaries

Comparison to Wrought H282


S3 Surface Finished

Wrought H282

Wrought H282

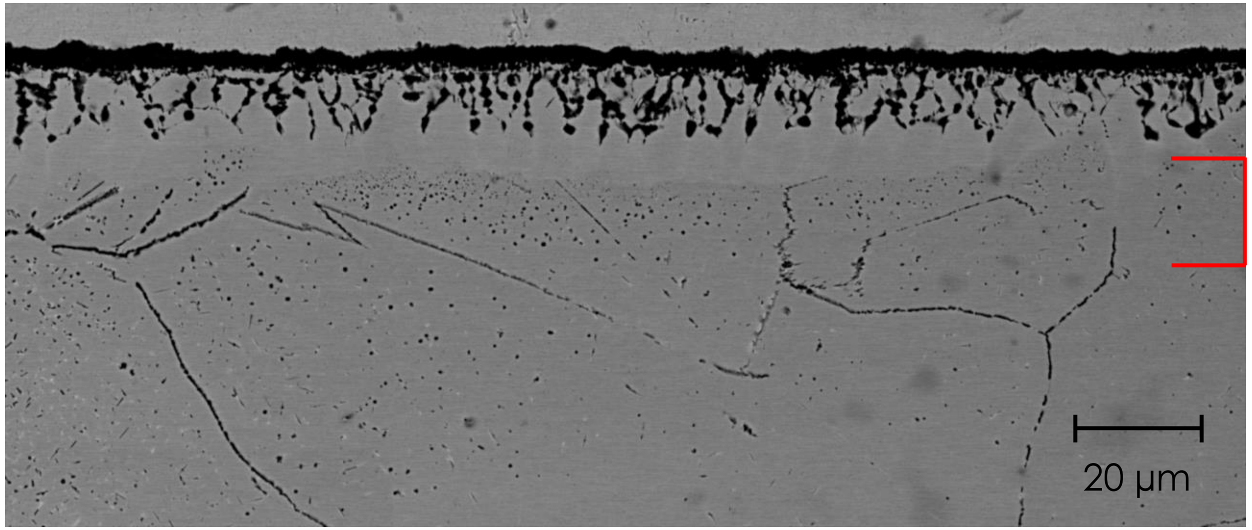


- AM Surface Finished has similar oxide scales to wrought H282
  - Thin, protective Cr-rich oxide layer
- Less indication of the Mo-rich carbides in wrought H282

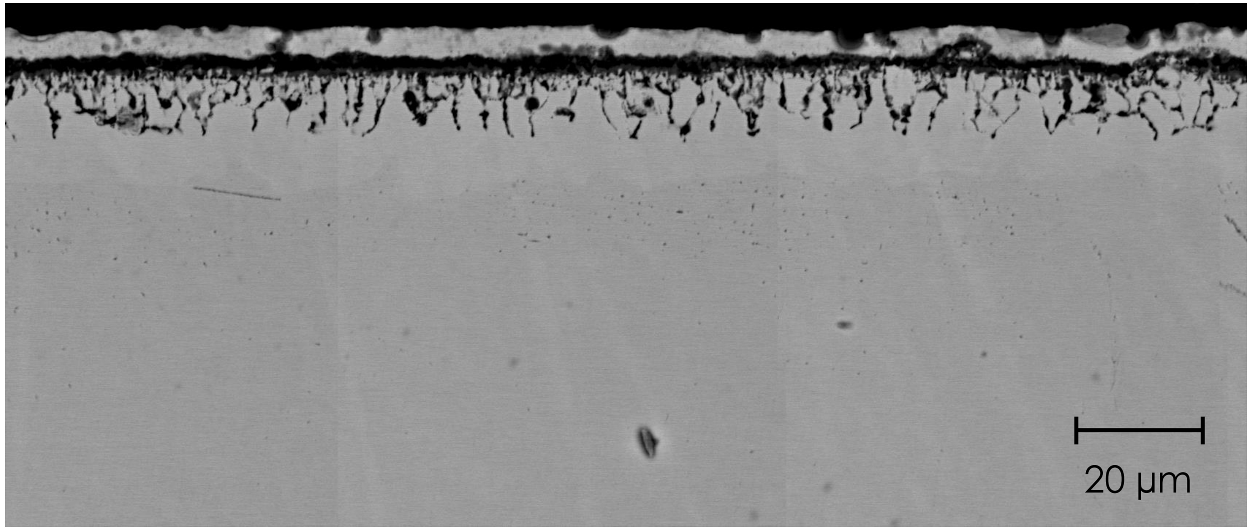
750 °C 200 bar, 95 CO_2 – 4 H_2O – 1 O_2

Etching Comparison to Wrought H282

S3 Surface Finished



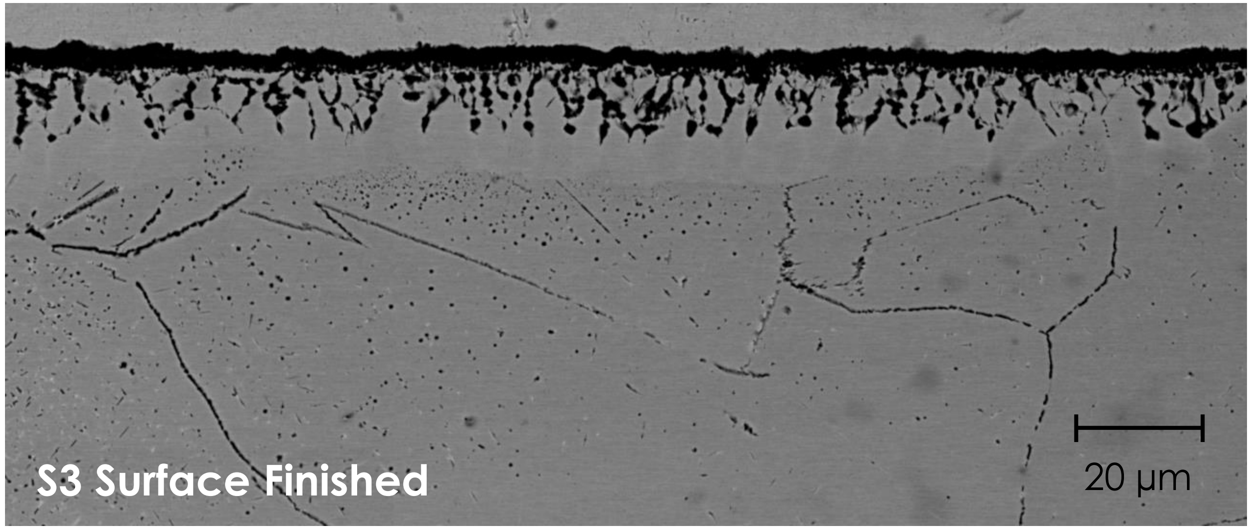
Wrought H282

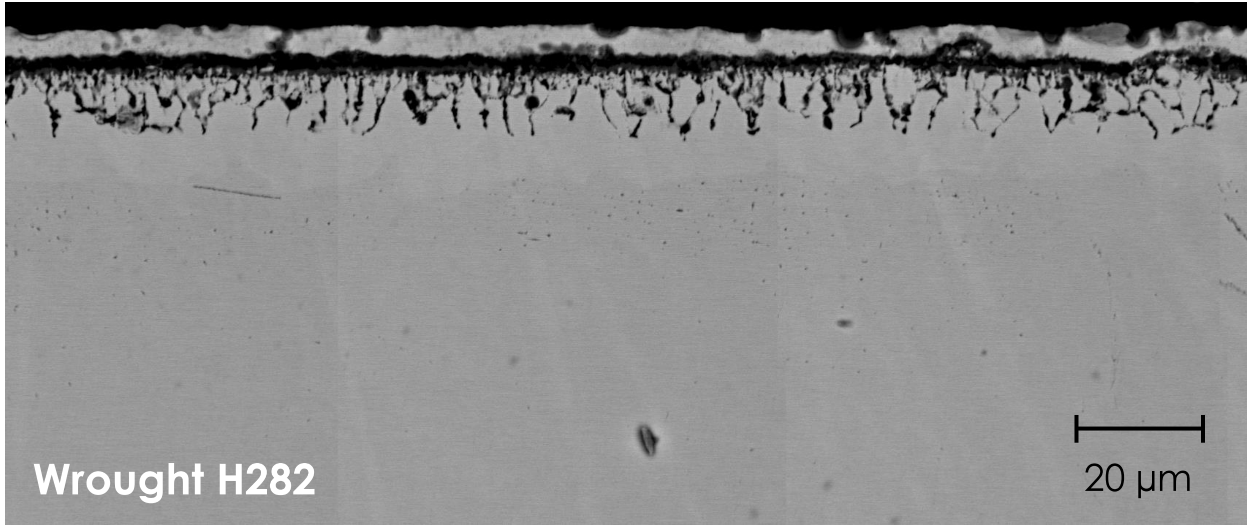


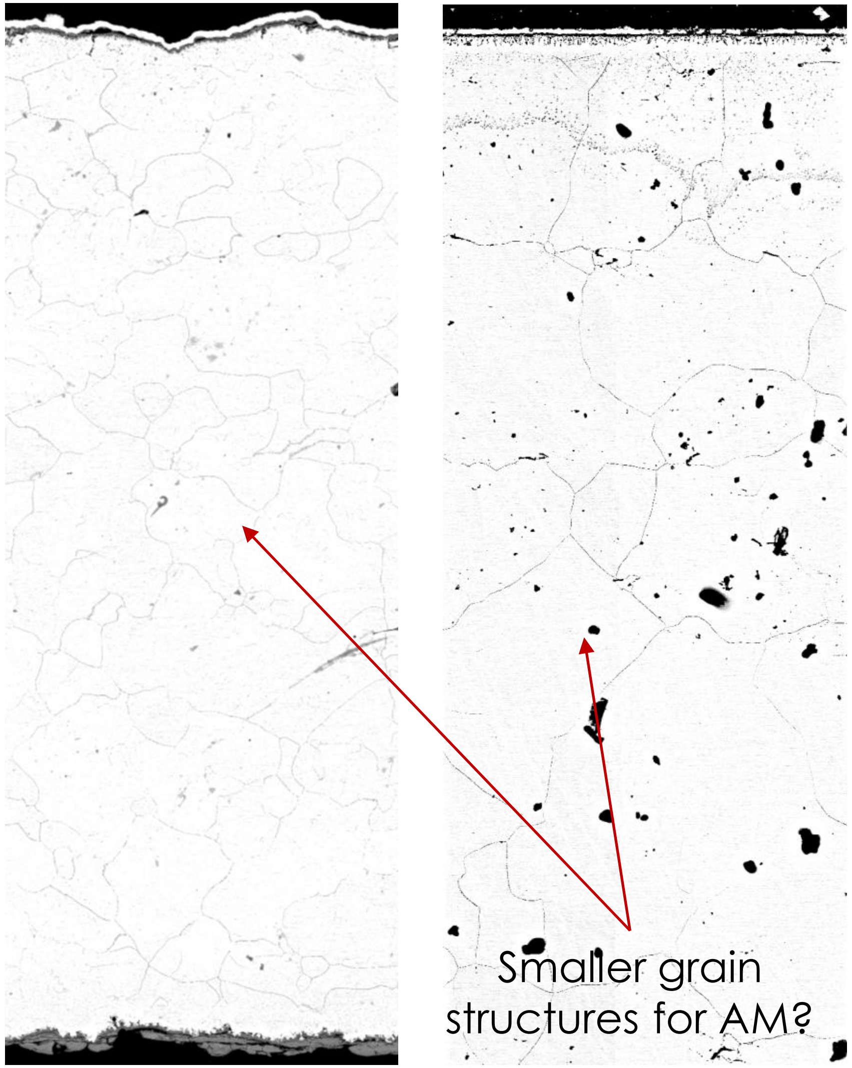
- Visible sub-surface carbides much less prevalent in wrought H282
- Different grain structure between AM vs. wrought?

750 °C 200 bar, 95 CO_2 – 4 H_2O – 1 O_2

Etching Comparison to Wrought H282






S3 As Printed

Wrought H282

Smaller grain structures for AM?

Grain boundary carburization throughout sample

Perhaps additional etching step to reveal grains

AM Alloys (H282) in Direct Fired Power Cycle Environments

Considerations for real systems

- Reduces water vapor assisted chromia scale volatilization
  - Thin channels less affected by downstream precipitation/deposition
  - Volatilization increases with higher fluid velocities
- Increases near surface carburization during exposure
  - What are the long-term mechanical effects
  - Perhaps magnified for thin-walled components
- Surface Finishing samples improved oxidation resistance
  - Alternate oxidation mechanism
  - How feasible for compact printed components

- Potential oxidation behavior dependence upon AM laser production scan rate

Acknowledgements

Additional NETL Co-Workers

Dennis Burkey, Matthew Fortner, James Willis, Dennis Funk, Jessica Habjam

Funding

This work was performed in support of the ARPA-E HITEMMP project titled "High Energy Density Modular Heat Exchangers through Design, Materials Processing, and Manufacturing Innovations."

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