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Investigations on the corrosion behavior of additively manufactured stainless steel

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DOD/DOE Joint Munitions Program

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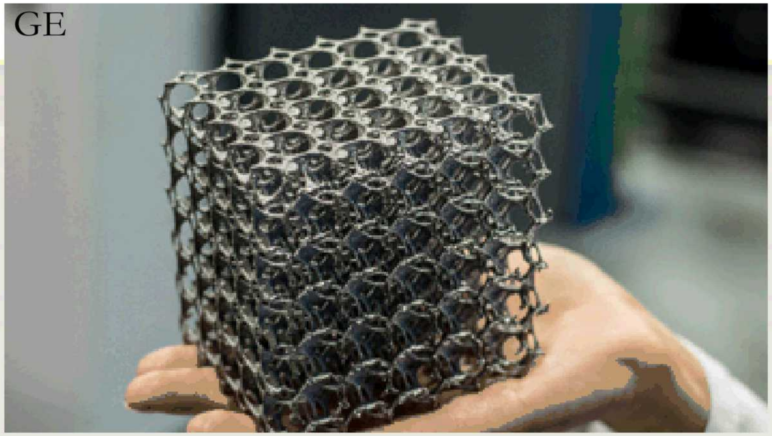
Why additive manufacturing (AM)?

Sophisticated, unconventional 3D geometries; small lot production



Lattice structure

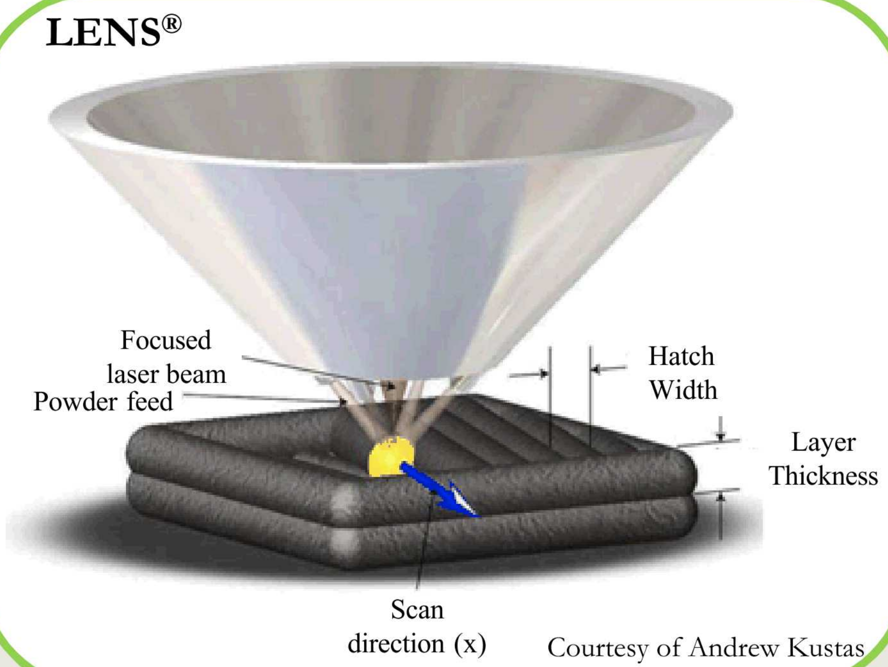
Heat exchanger

A design/process-pathway to lightweight-high strength parts

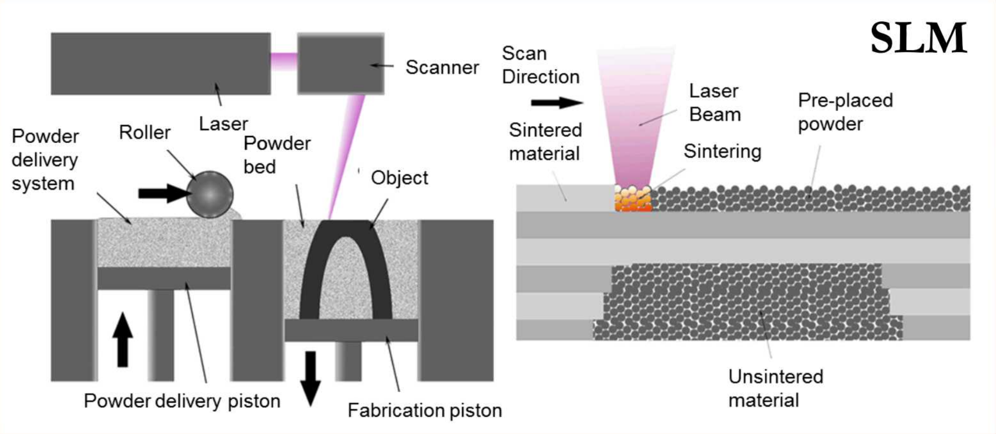
Topology optimized design

Common AM Processes

- Binder Jetting
- Wire-Based Fusion
- Powder-Based Fusion
  - Selective Laser Melting (SLM)
  - Direct energy deposition (DED – such as LENS ®)
  - Electron Beam Melting (EBM)
- Sheet Lamination
  - Ultrasonic
- Vat Photopolymerization
- Fused Deposition Modeling (FDM)



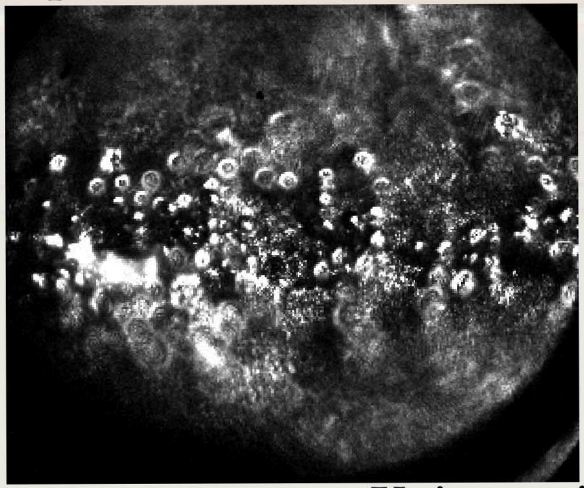
Courtesy of Andrew Kustas



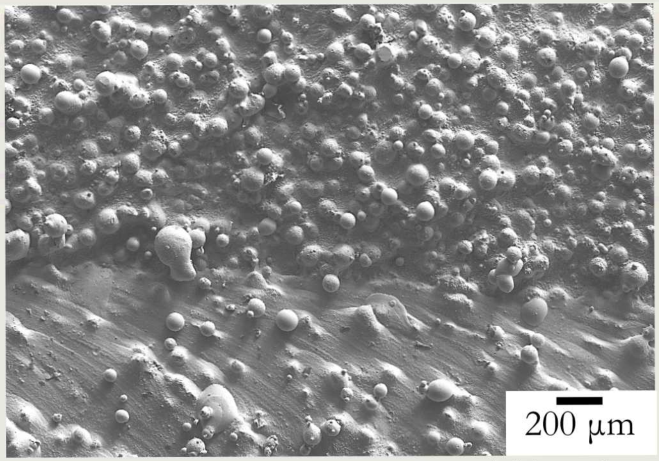
Wikipedia "selective laser sintering"

Powder AM processing of metals and there material characteristics

Imperfect melting and fusion at powder/liquid interface

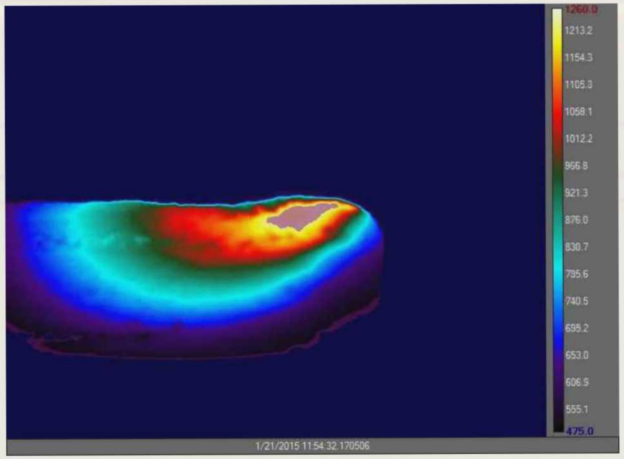


Matthews, 2016



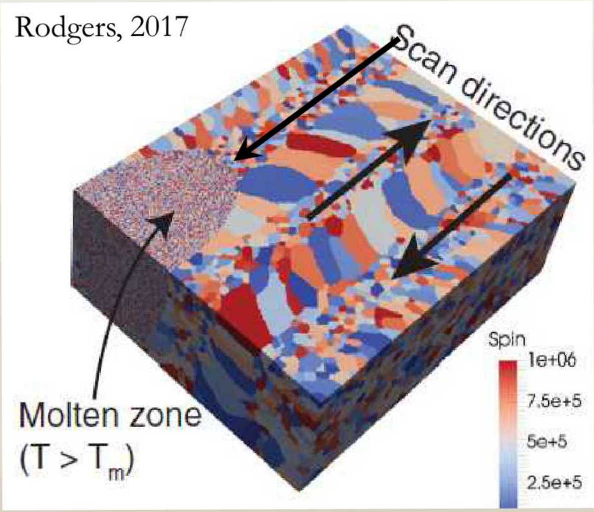
This study

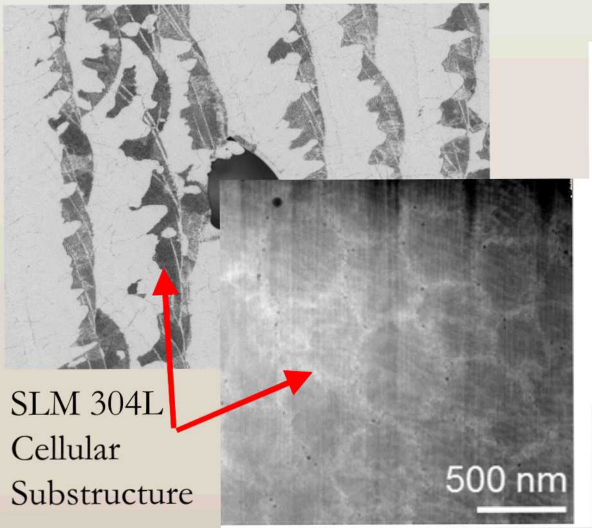
Thermal history during bi-directional metal deposition



Courtesy of Andrew Kustas

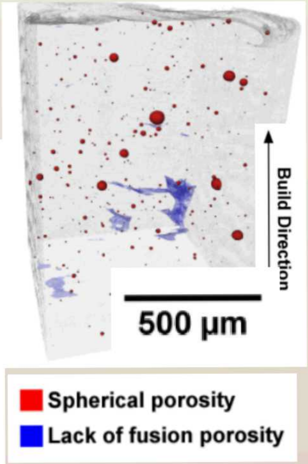
Unique microstructures



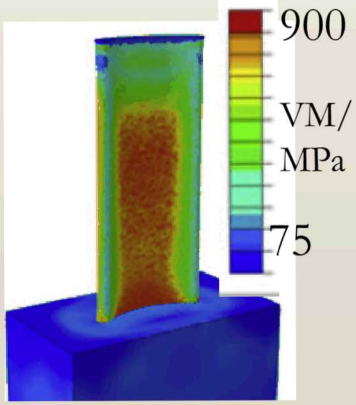


Schaller, 2018

Porosity

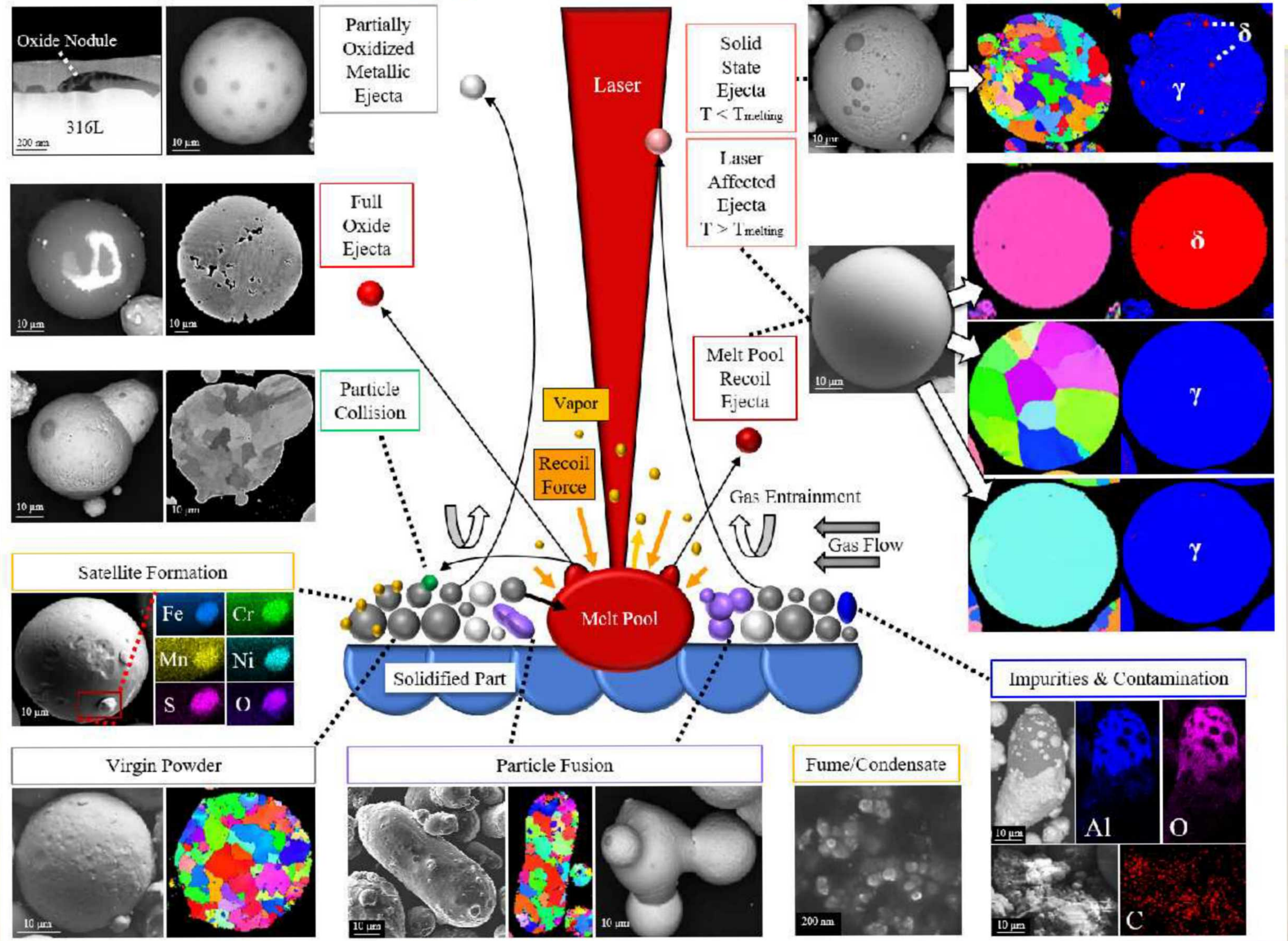


Residual Stresses



An, 2017

What else can happen during AM processing?

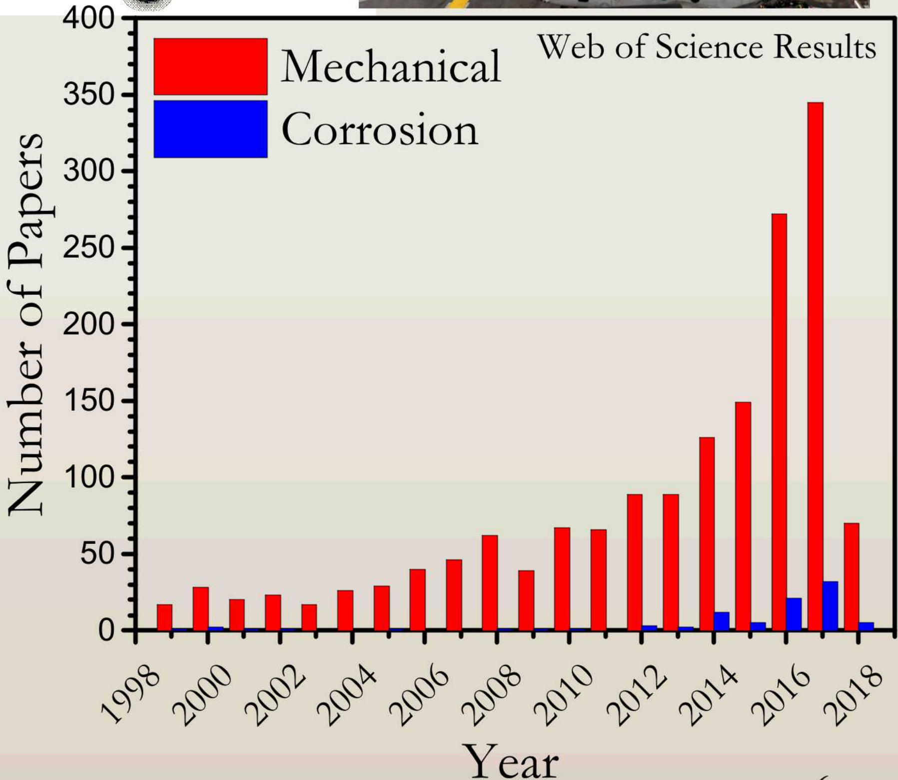


M. Heiden, L. Deibler, J. Rodelas, J. Koepke, D. Tung, D. Saiz, B. Jared. Evolution of 316L Stainless Steel Feedstock Due to Laser Powder Bed Fusion Process. *Manuscript submitted for publication.*

Corrosion of AM Metals: Needs and Knowledge

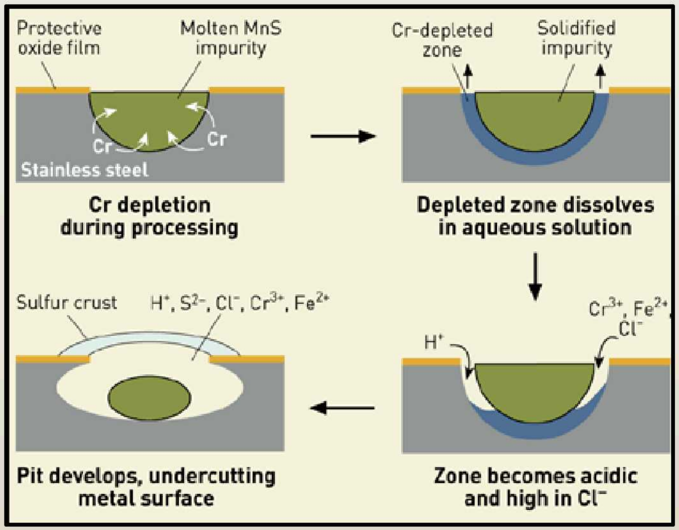
Aging and reliability of AM metals:

- Mechanical properties are primary performance metric.
- Understanding corrosion behavior critical for high-reliability, long life systems.
- Existing corrosion knowledge from laser-welding and powder metallurgy as closest analogs provides a starting point.

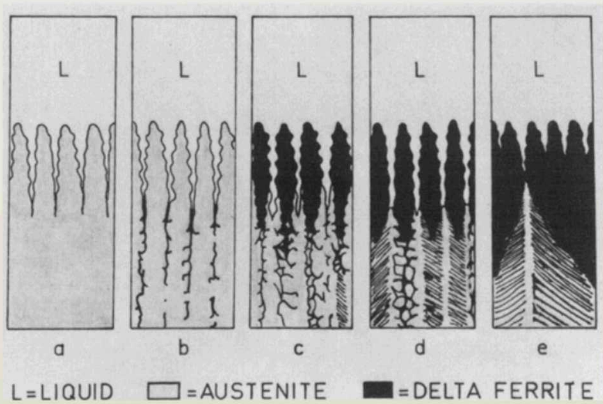


Microstructure Impacts on Corrosion

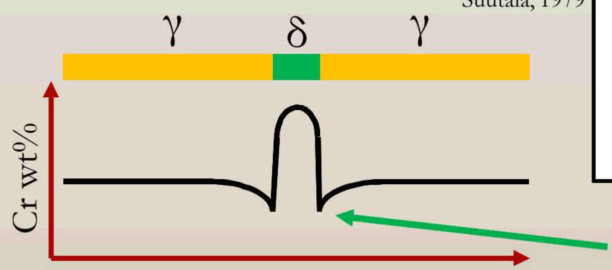
- Passive layer (chromium) provides corrosion protection
- AM microstructure could effect breakdown of the passive layer due to
  - Crevice Corrosion
  - Metallurgical Variables
  - Chromium Depletion and Pitting



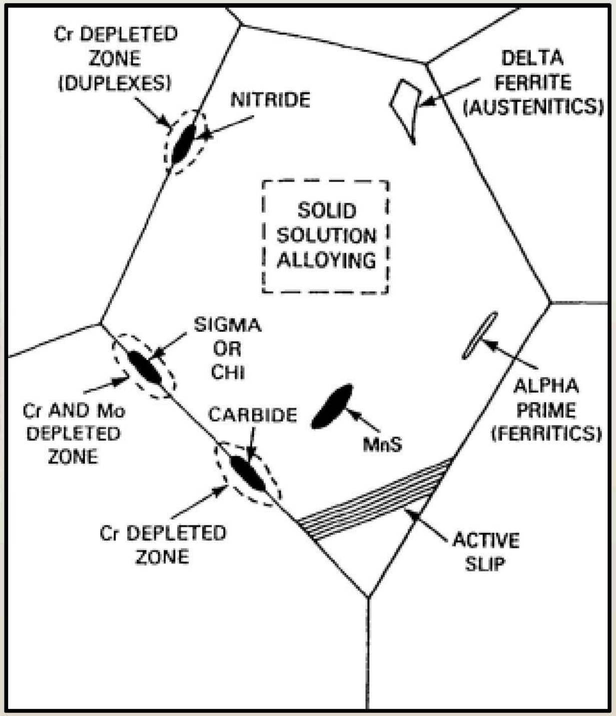
Ryan, 2002



Suutala, 1979



Dependent on cooling rate.



Sedricks, 1986

Questions when using AM, specifically DED

- How will the microstructural differences between stainless steel formed using wrought and DED processes govern its local corrosion responses?
  - What is the impact of variance in alloy chemistry (local chemical segregation) generated by AM processes on corrosion?
  - How will the common defects generated during AM (lack of fusion pores, gas pores, etc.) influence local corrosion of these materials?
  - Will the initiation and propagation of pits in NaCl solutions be altered on the AM materials?
- What can we do to further improve the as-printed materials response?

Material and Process Characteristics

Measured 304L Material Composition (Weight %)

Composition (wt%)	Cr	Ni	Mn	Si	Mo	Cu	N	P	C	S	O	PREN
Starting powder	19.1	10.4	1.6	0.50	0.04	0.03	0.089	0.006	0.015	0.006	0.017	20.8
Low power (LP)	18.6	9.86	1.48	0.59	0.004	0.01	0.044	0.01	0.011	0.005	0.018	19.3
High power (HP)	19.2	10.1	1.45	0.57	0.042	0.034	0.087	0.008	0.012	0.004	0.031	20.8
Wrought 304L	18.4	8.26	1.76	0.25	0.31	0.56	0.073	0.03	0.024	<0.001	0.009	20.6

DED Build Parameters

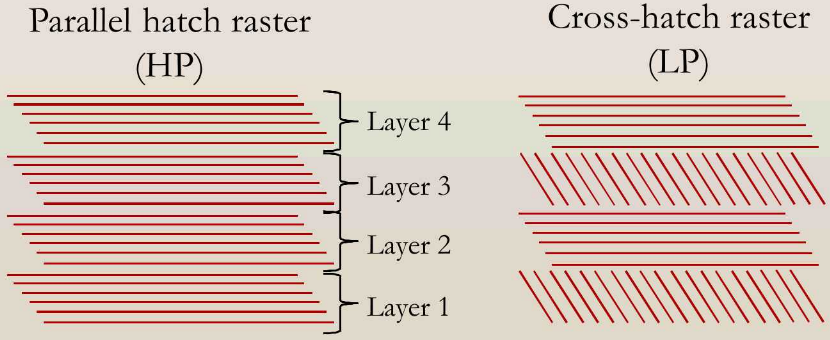
Laser Power (W)	380 (LP)	3800 (HP)
Travel Speed (mm/min)	762	508
Powder Feed Rate (g/min)	6.3	23
Hatch Spacing (mm)	0.46	2
Layer Thickness (mm)	0.3	1.25

$$PREN_{austenitic} = \%Cr + 3.3\%Mo + 16\%N$$

Starting Powder

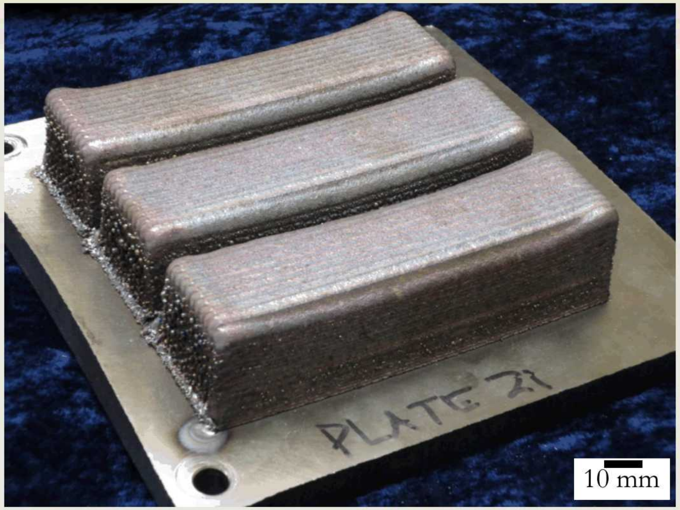
Ø = 45-90 μm

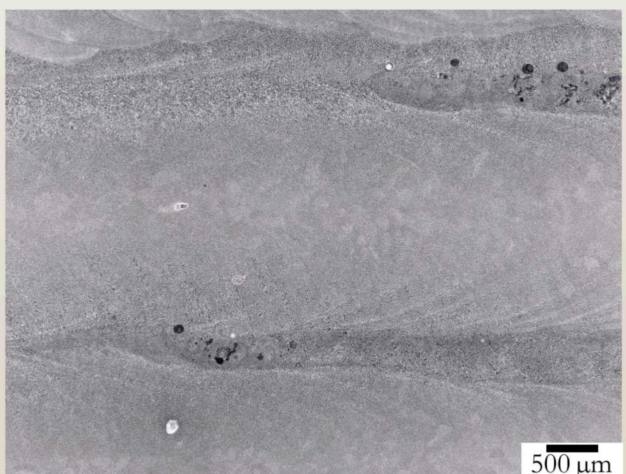
N_2-atomized single use **(not recycled)**



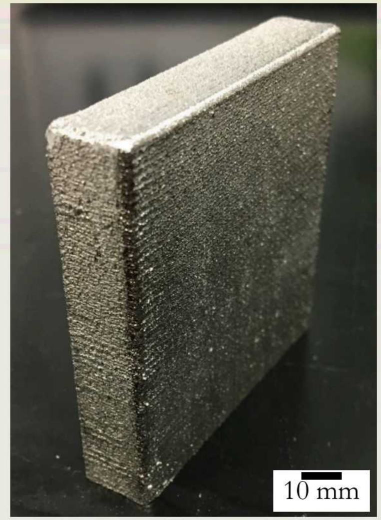
As built 304L DED materials

High power DED





Low power DED



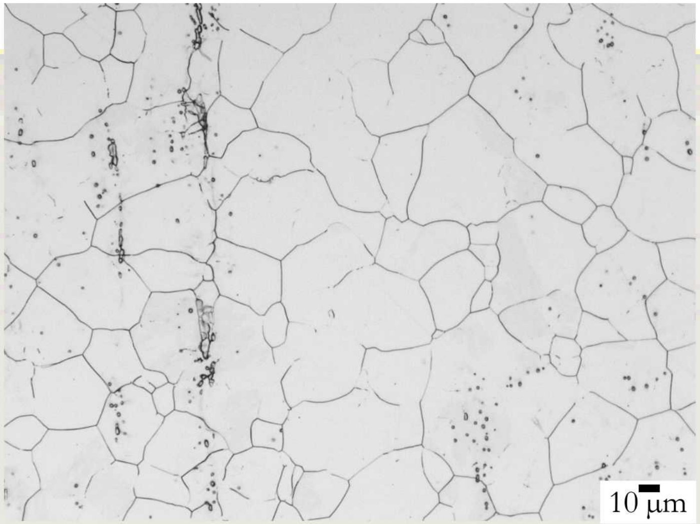
Powder bed SLM

Build direction
(parallel view)

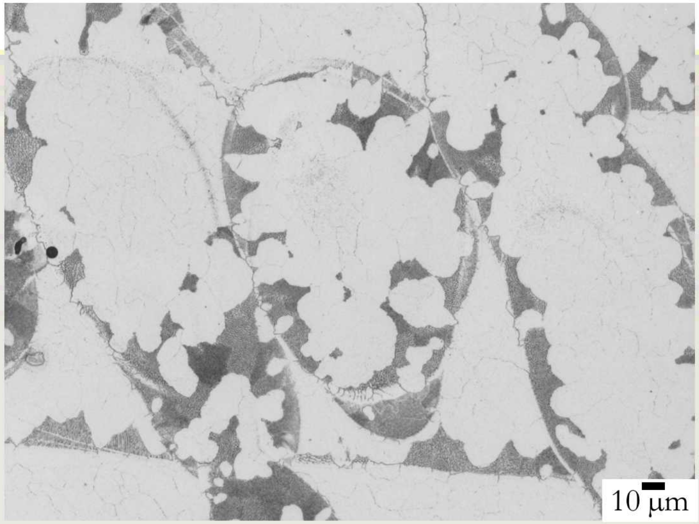
Cooling rates: SLM >> LP > HP

Wrought and AM 304L microstructure

Wrought δ = 0.43 vol%

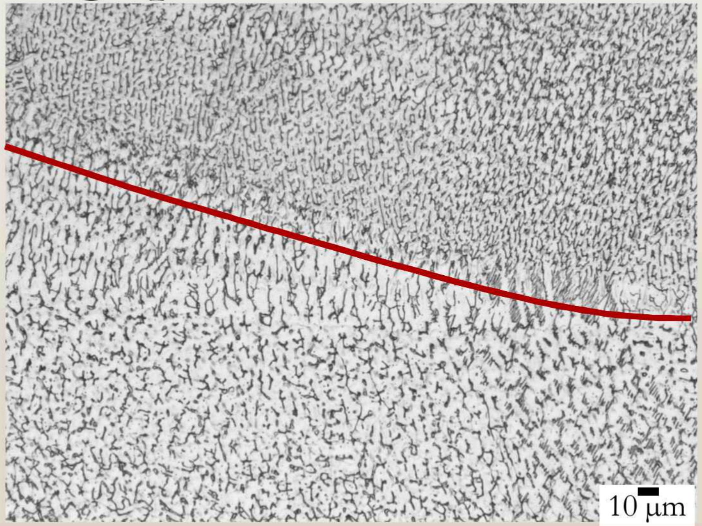


SLM δ < 0.01 vol%



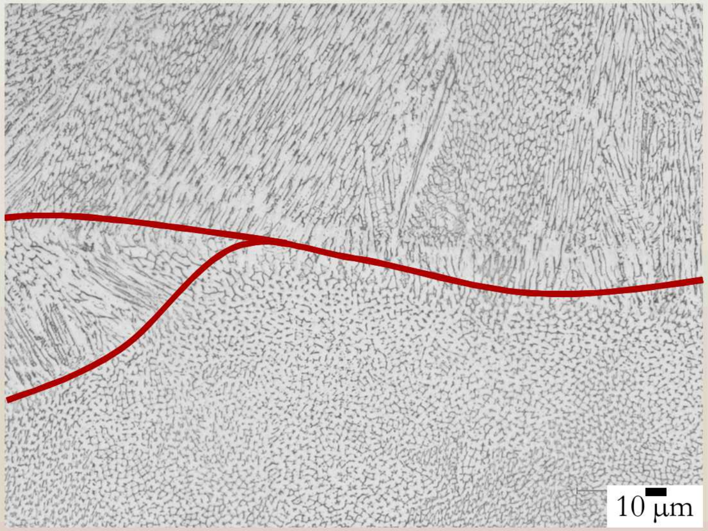
Build direction

High power DED δ = 2.0 vol%

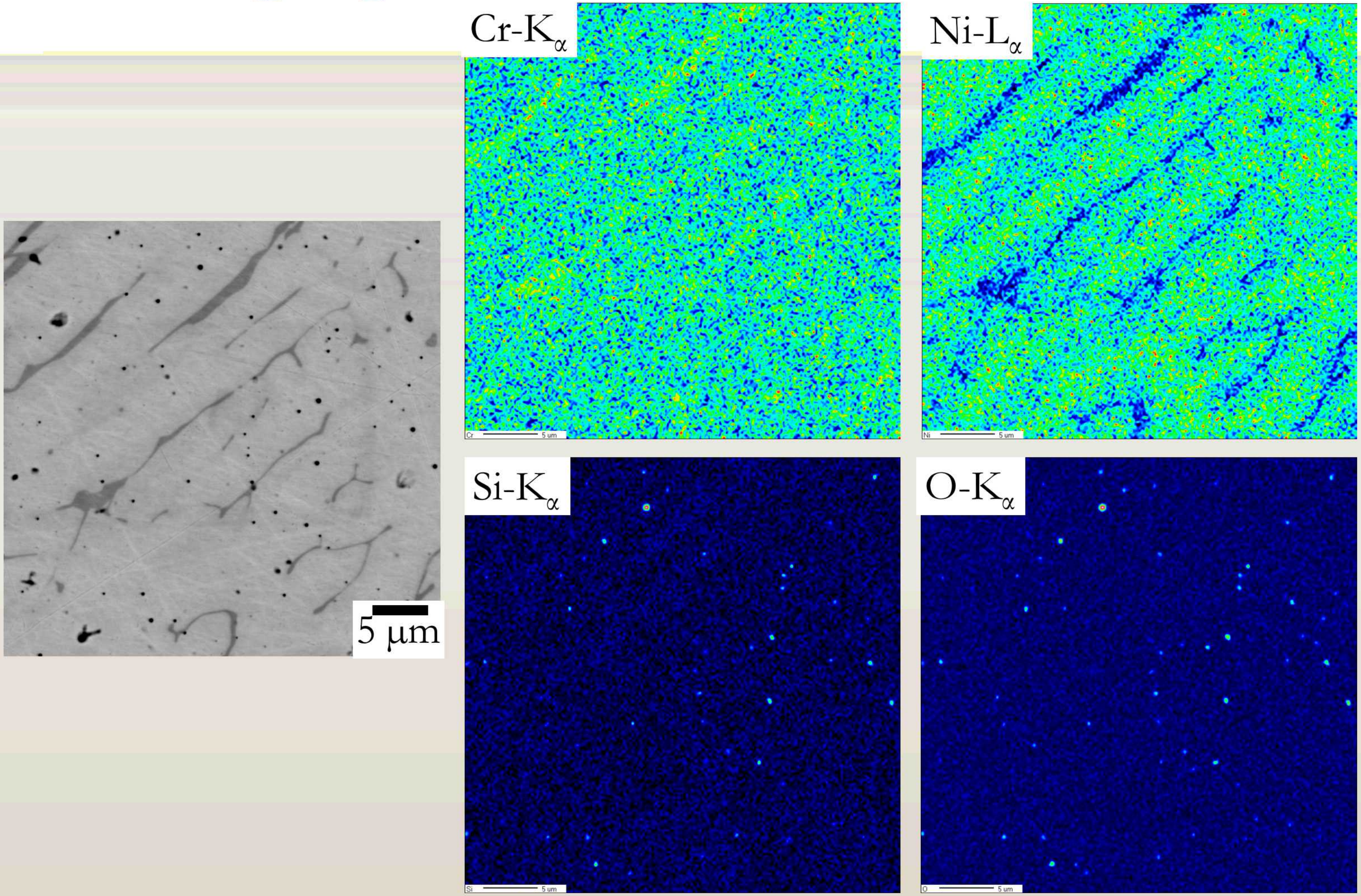


Build direction

Low power DED δ = 1.5 vol%



WDS of high power DED microstructure

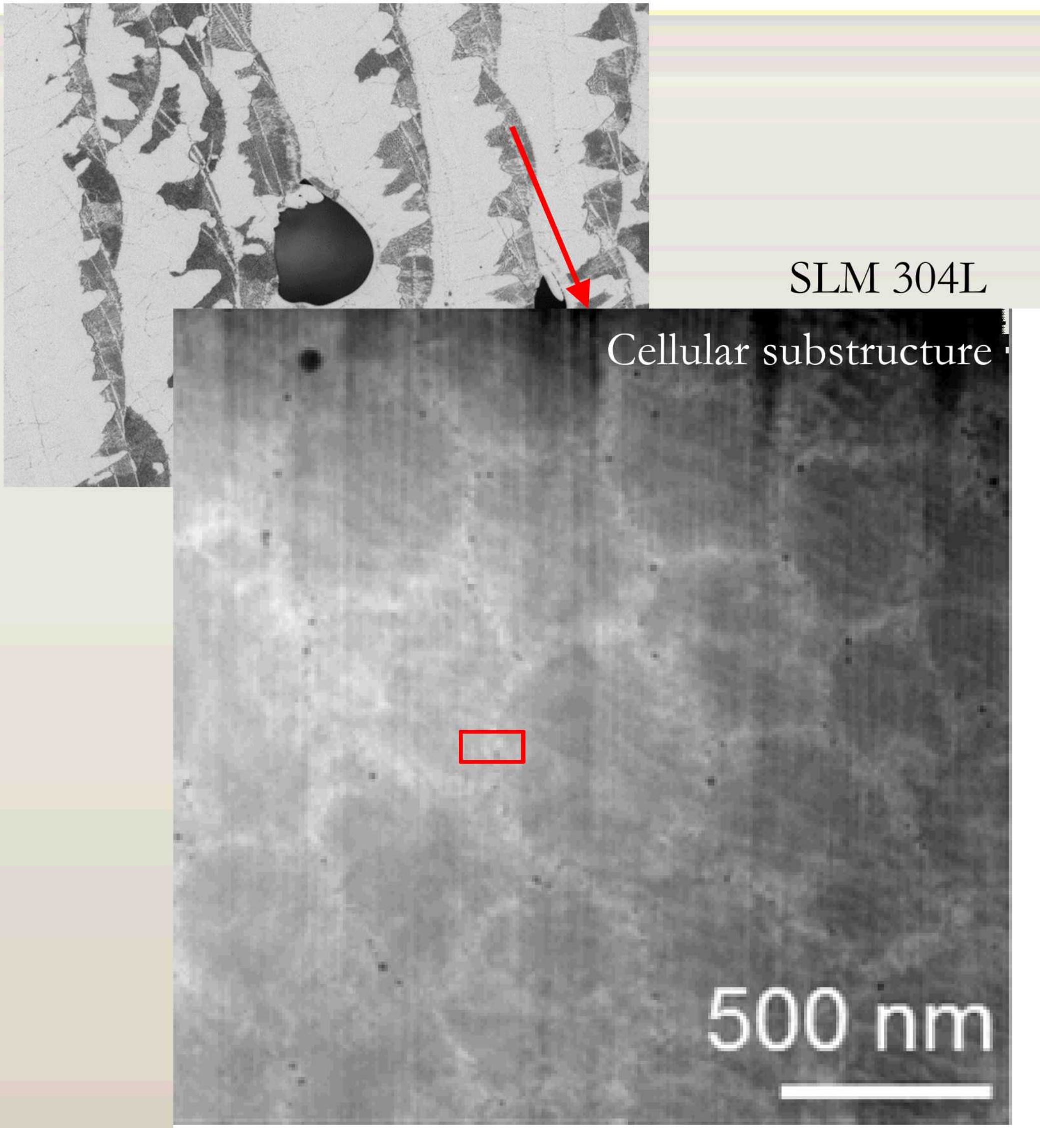


Cr segregates to δ-ferrite for HP and LP.

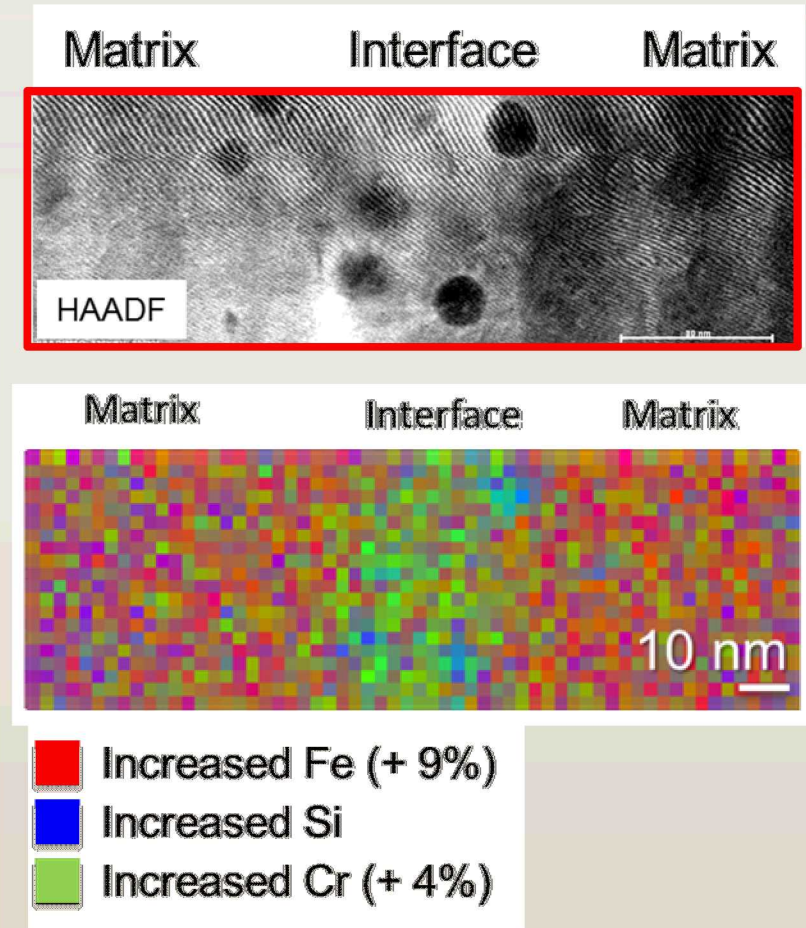
Many of the oxides formed are Si/Mn rich, typical for AM stainless materials.

Chemical segregation in SLM cellular substructure

SLM 304L

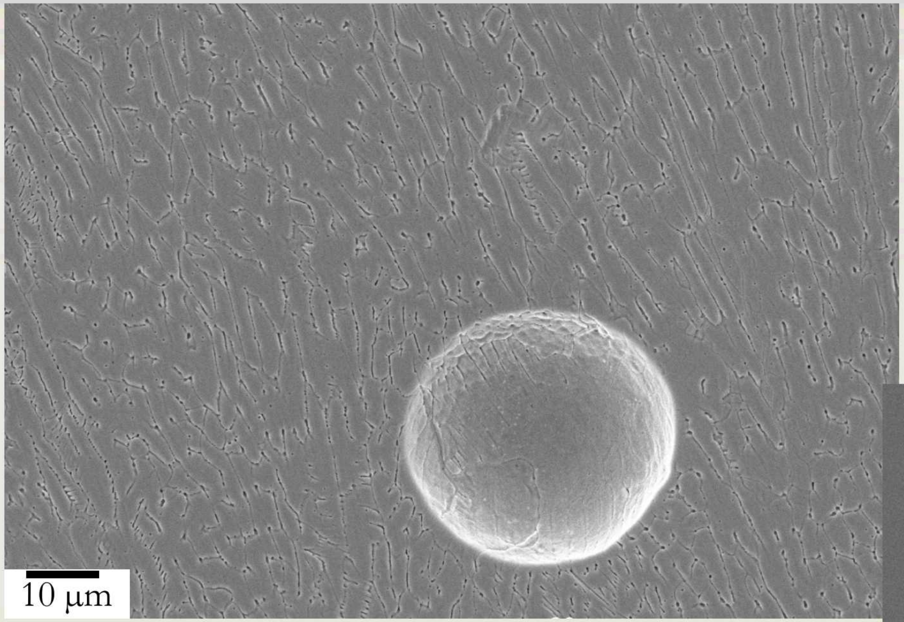


Segregation / Depletion



Common porosity in AM material

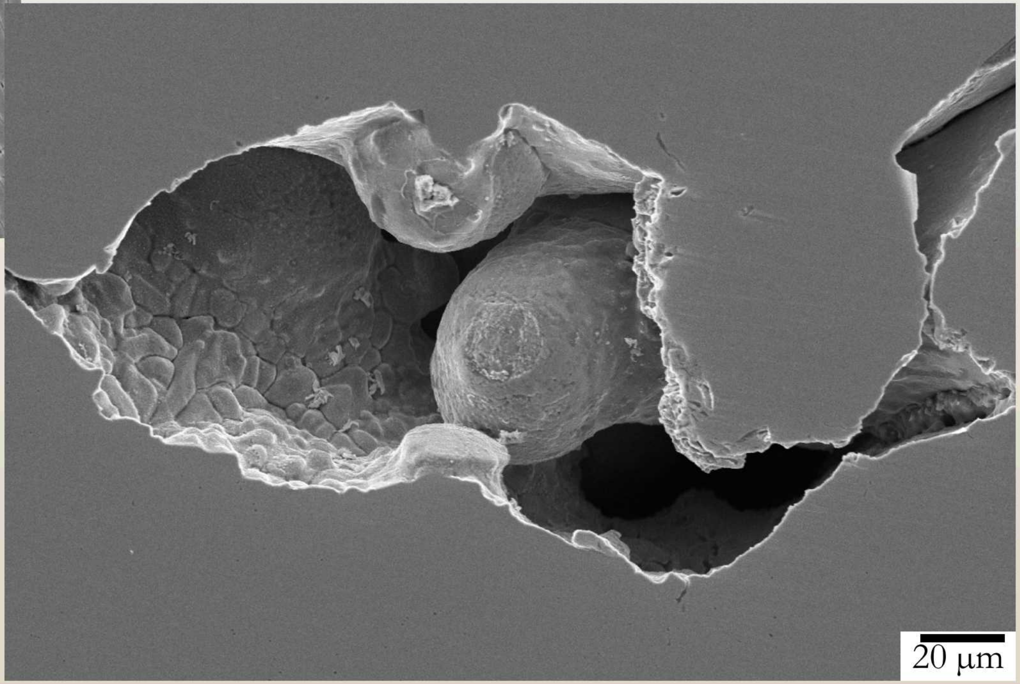
Low power DED – gas pore



Primarily gas pores observed in LP material.

Fusion pores in HP possibly from build path (parallel hatch raster).

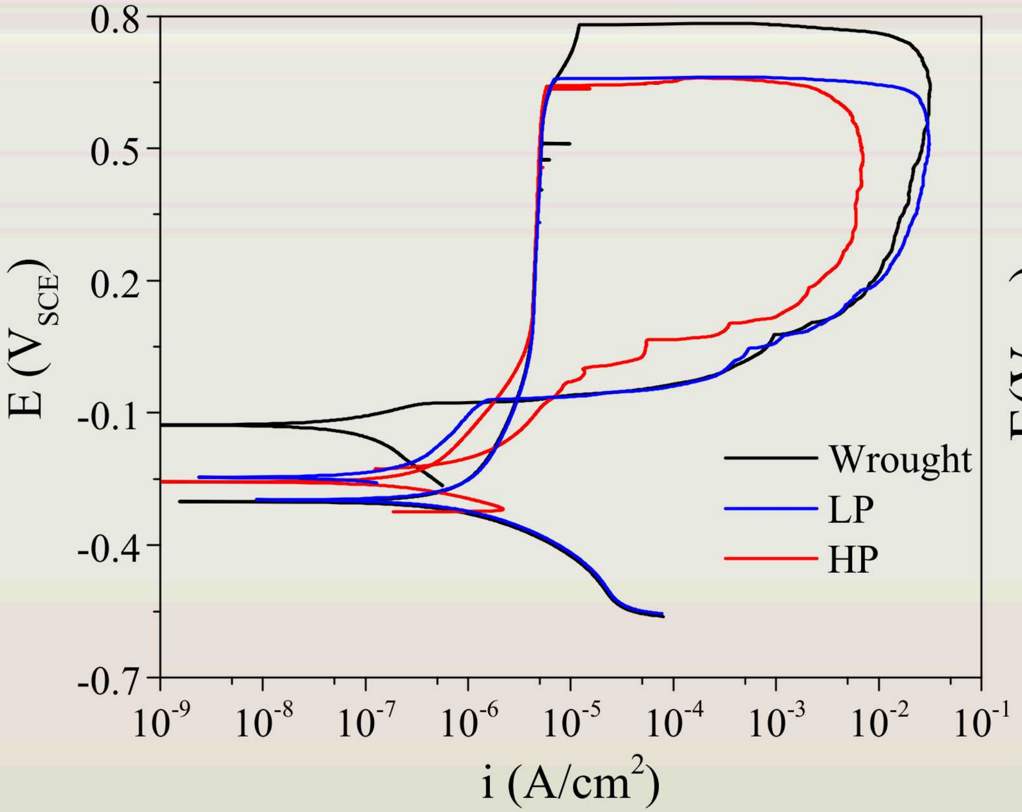
High power DED – lack of fusion pore

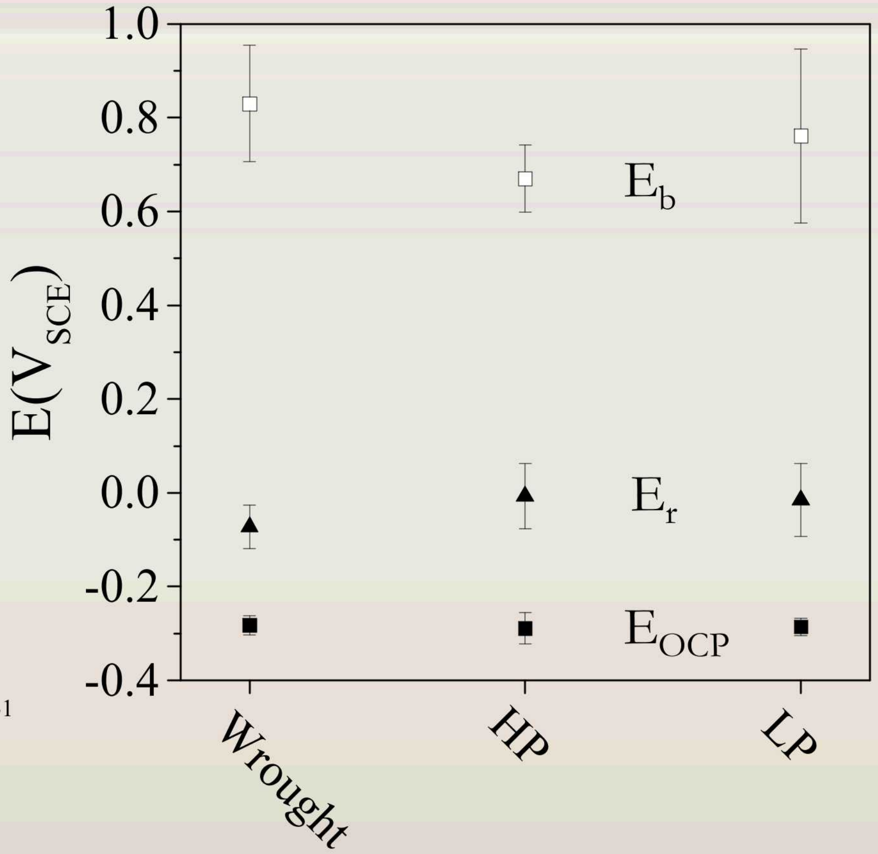


Corrosion considerations:

- Smooth hemispherical (gas porosity)
- Rough crevice-like (lack of fusion porosity).

Global Pitting Resistance of 304L in 0.6 M NaCl Solution





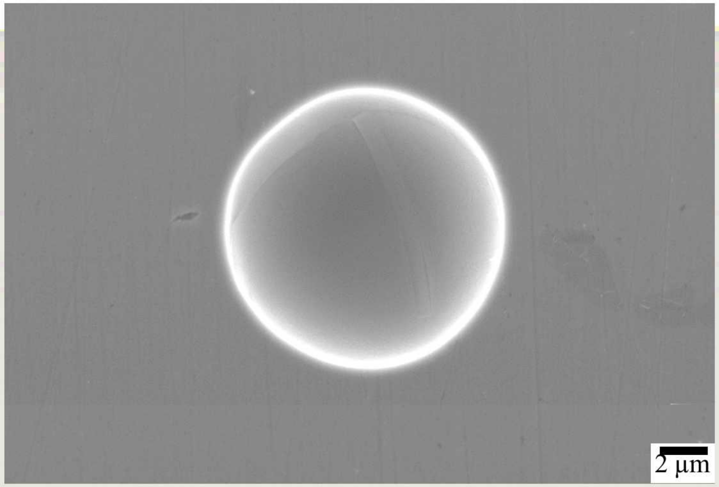
E_b of HP material significantly different than wrought in 0.6 M NaCl.

E_b of LP material similar to wrought, possibly due to faster cooling rates leading to less severe chemical segregation.

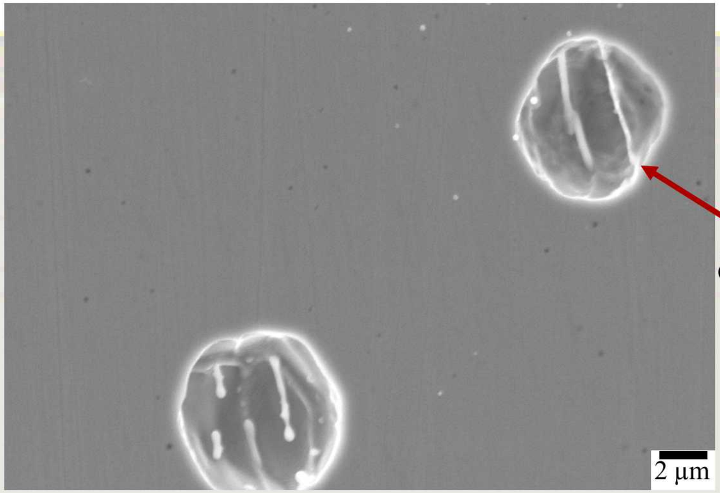
1200 Grit, 21°C, Quiescent, 1 h OCP, 1 mV/s

Pit initiation and propagation

Wrought

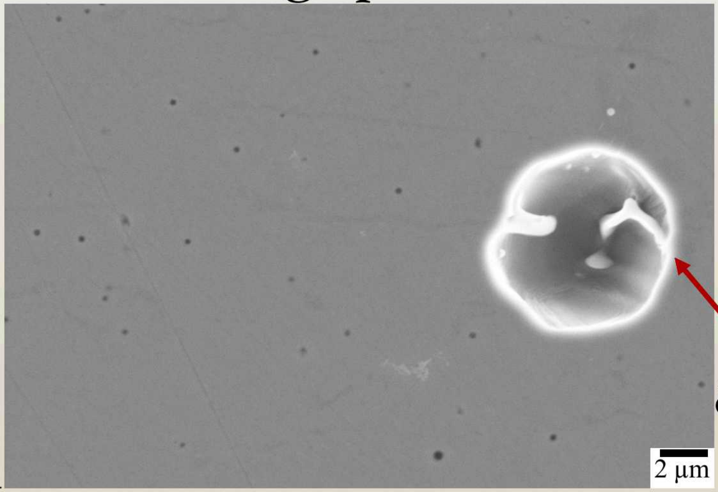


Low power



δ-ferrite

High power



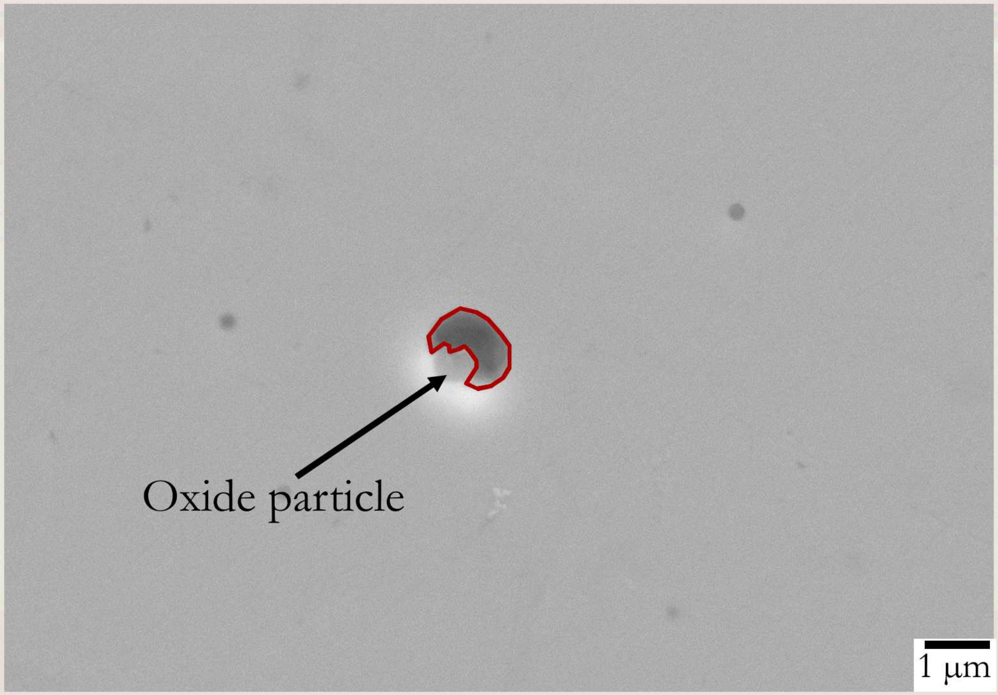
δ-ferrite

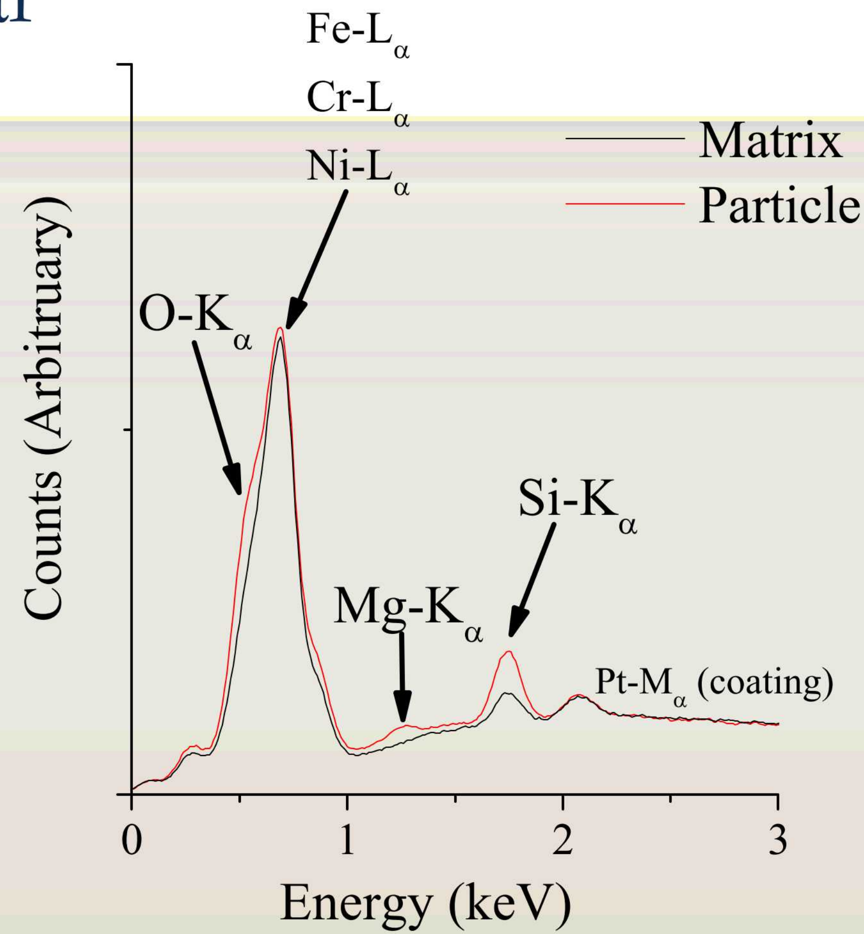
δ-ferrite corroded slower than the γ-austenite leading to irregular pit propagation.

Possibly reason for reduced E_b for HP material.

1200 Grit
0.6 M NaCl, 21°C
2 second potential hold at 0.6 V vs. Ag/AgCl

Pit initiation on HP material



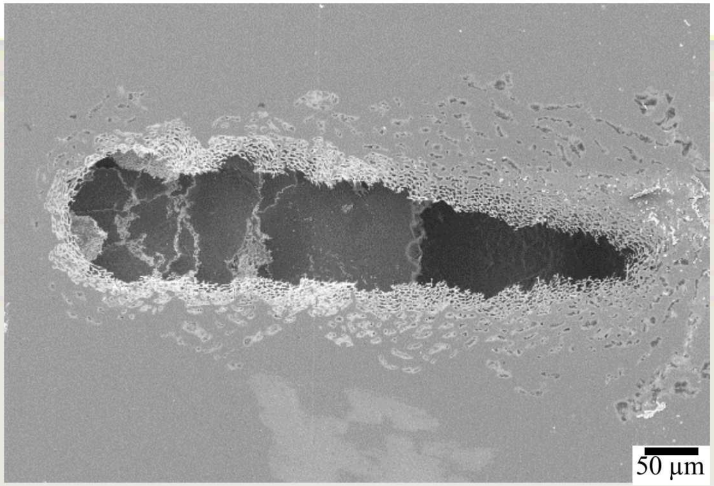


Initiation site observed at a Mg/Si rich oxide. Possibly similar mechanism as other pit initiations at oxides, however this normally involves preferred sulfur dissolution.

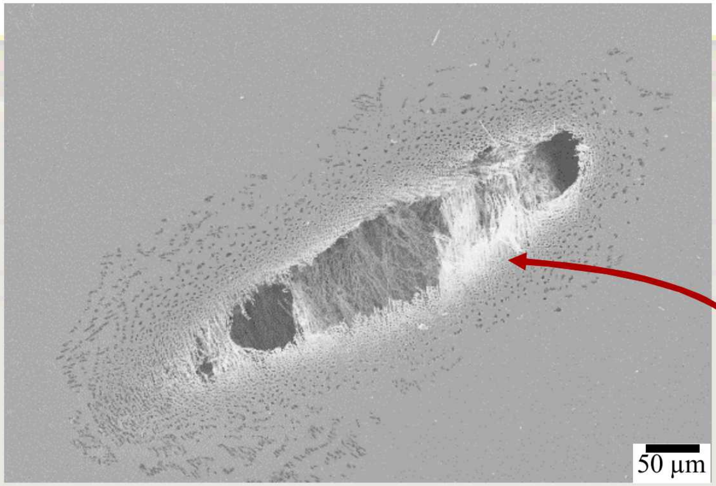
1200 Grit
0.6 M NaCl, 21°C
2 second potential hold at 0.6 V vs. Ag/AgCl

Typical pit propagation

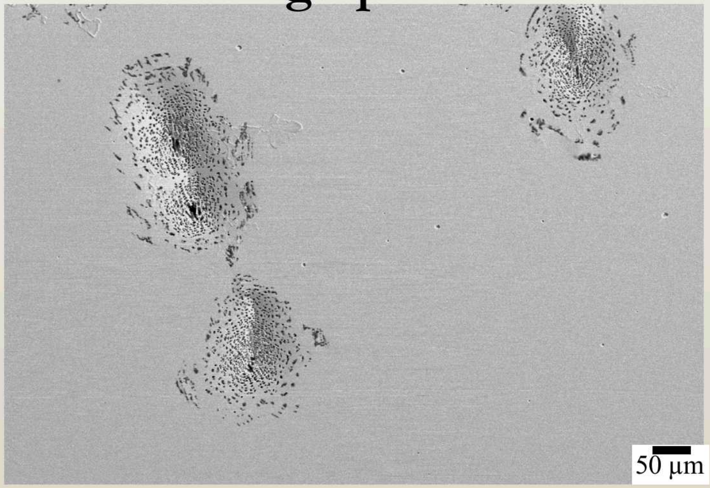
Wrought



Low power



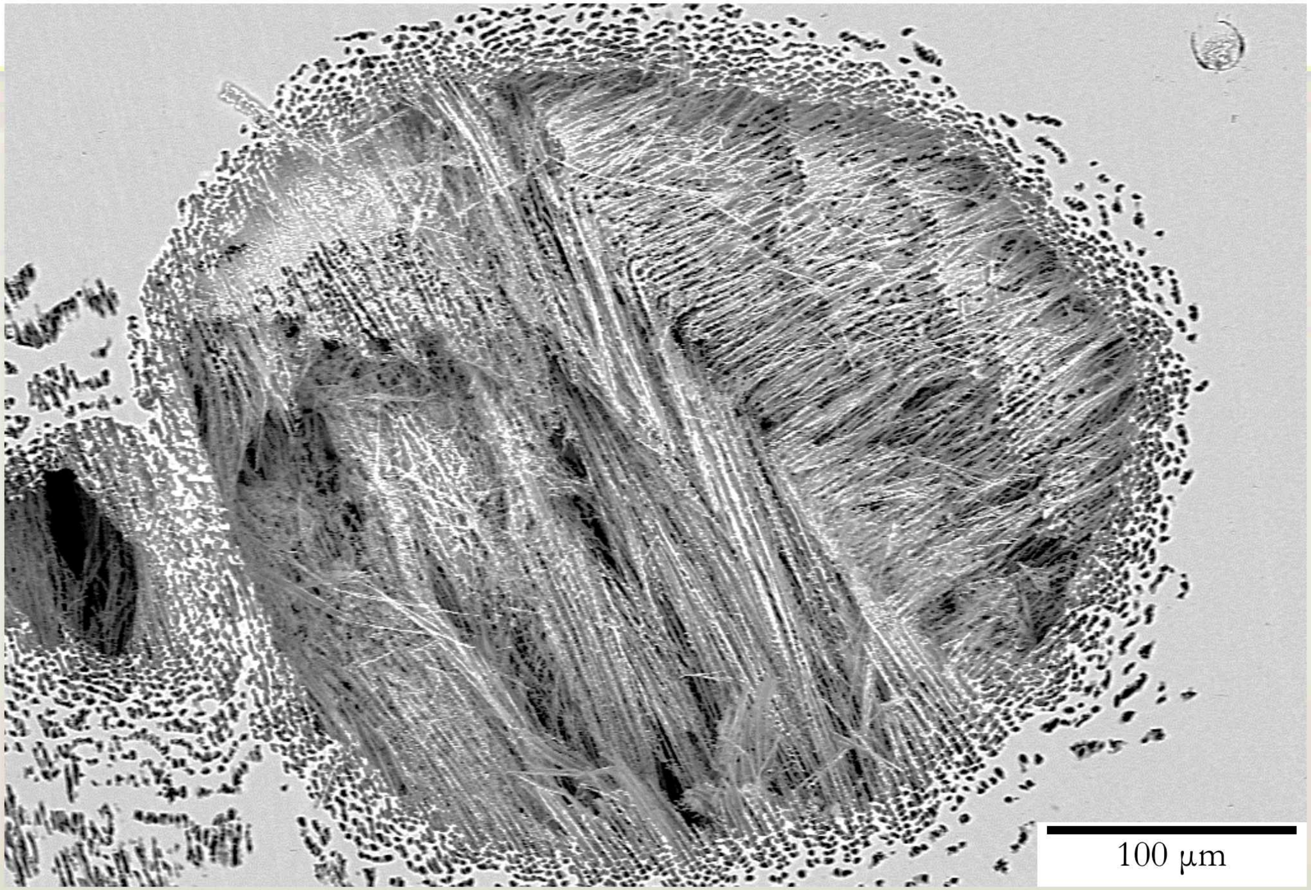
High power



Somewhat common lacy pit morphology for all pits after CPP experiment. δ-ferrite in DED materials can corrode much slower than austenite, leading to a "birds nest" of δ to remain in the pit.

1200 Grit
0.6 M NaCl, 21°C
After CPP measurement

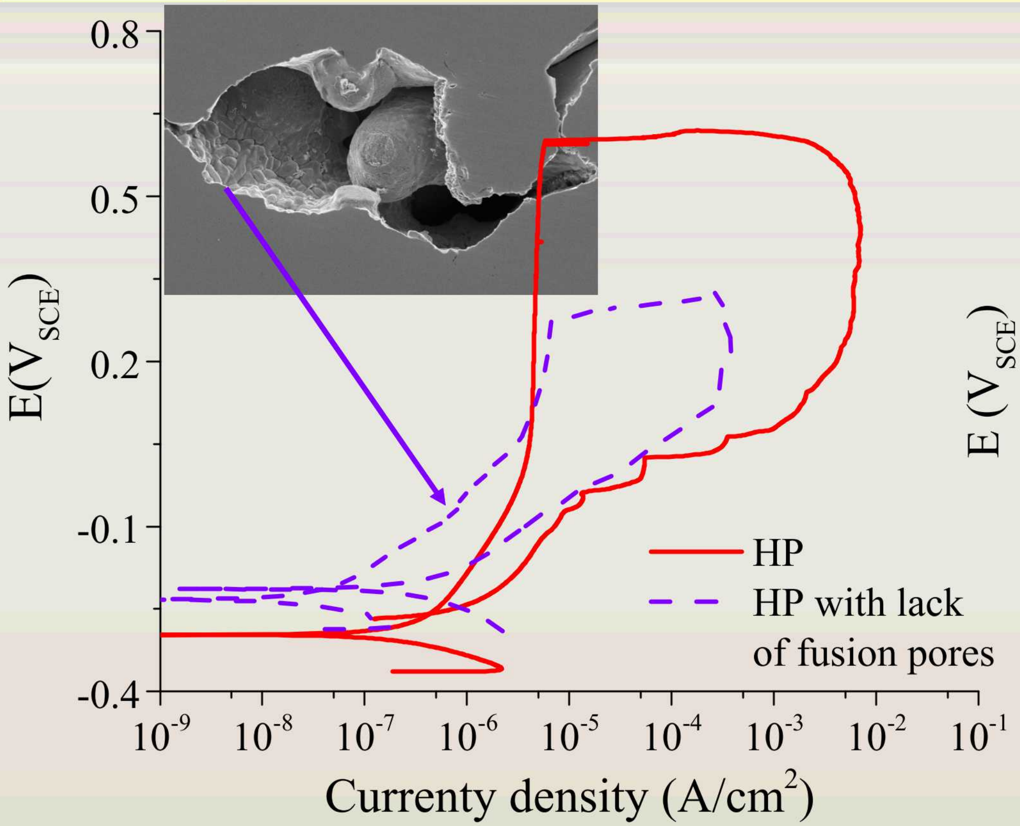
Pit propagation for LP DED materials

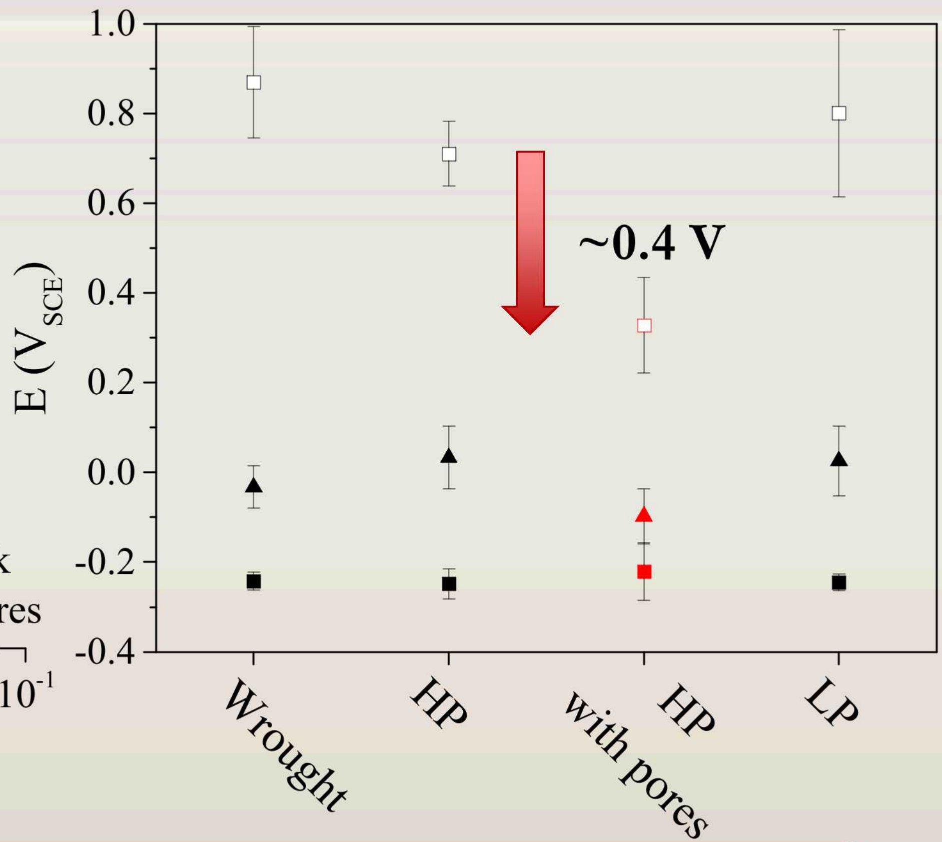


Pit on LP filled with δ-ferrite after CPP measurement.

1200 Grit
0.6 M NaCl, 21°C
After CPP measurement

Pitting resistance of DED material with lack of fusion pores

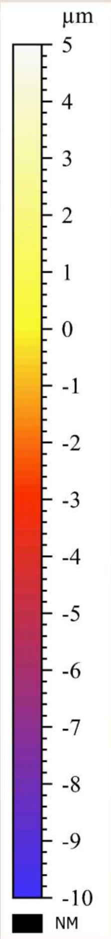




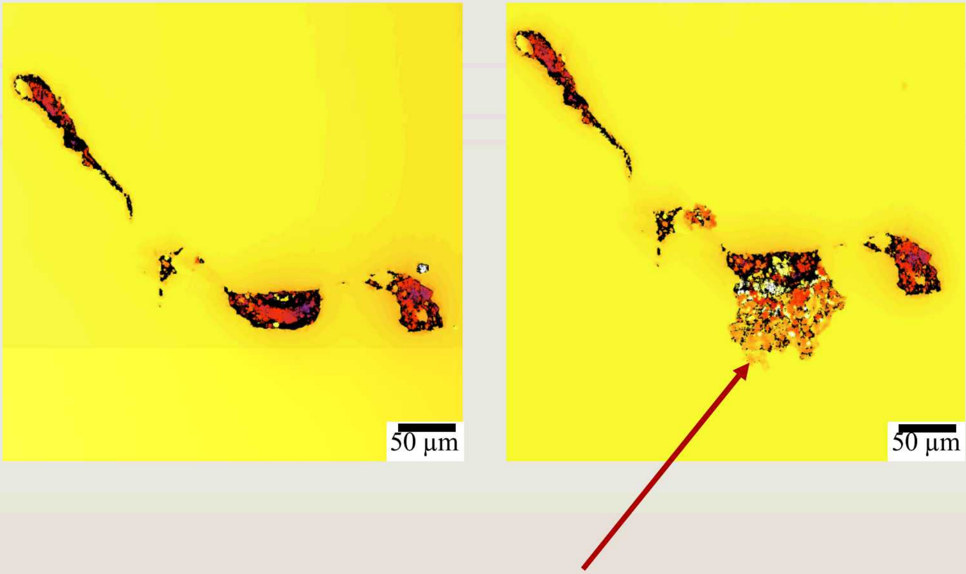
E_b of HP w/ fusion pores < 0.400 V versus wrought and HP without lack of fusion pores in 0.6 M NaCl.

1200 Grit, 21°C, Quiescent, 1 h OCP, 1 mV/s

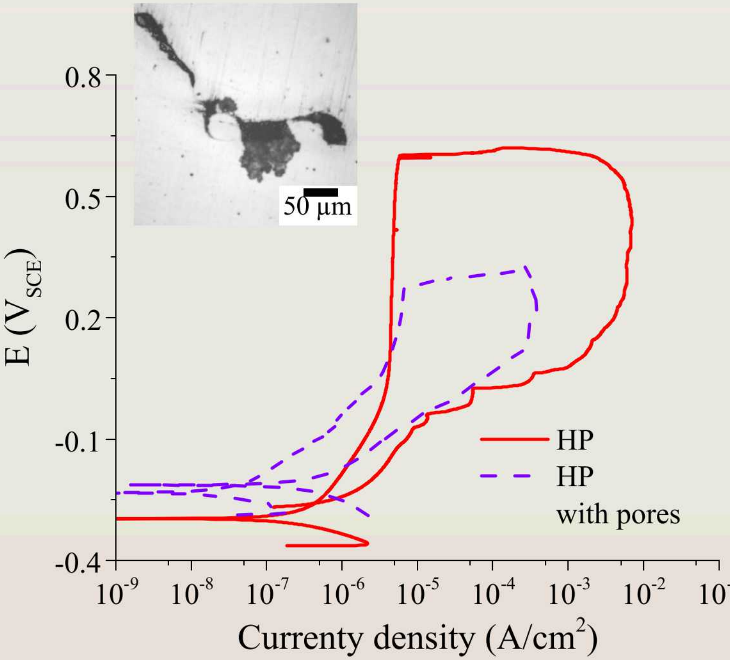
Pitting resistance of DED material with lack of fusion pores



Before **After**



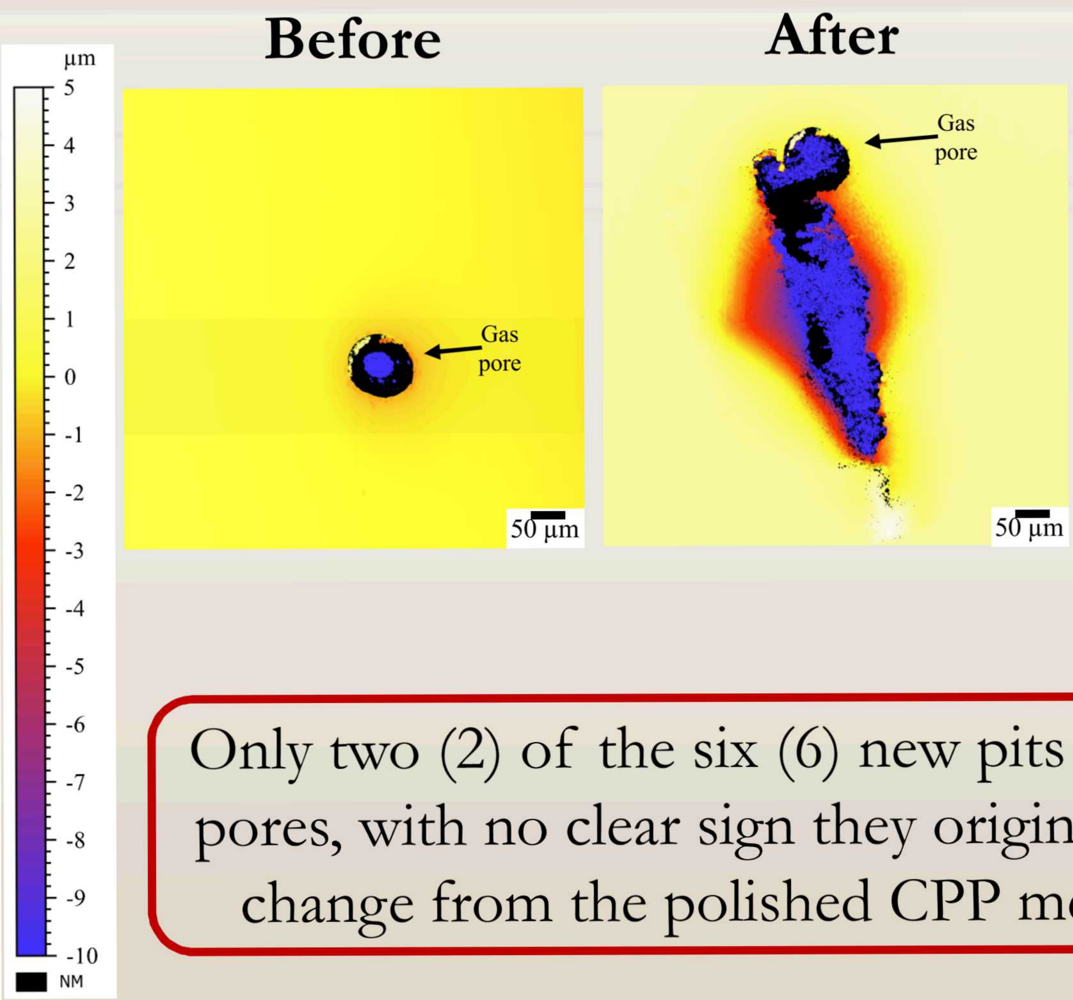
Corrosion growing from pore.

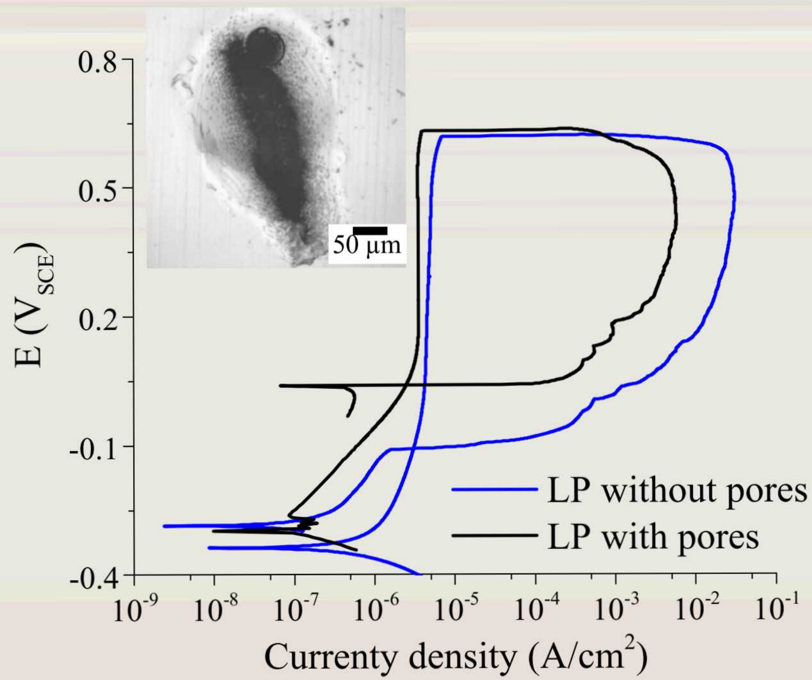


No new pits/pores open up on the HPLENS material however the E_b and E_r are substantially lower than normal.

1200 Grit, 21°C, Quiescent, 1 h OCP, 1 mV/s

Pitting resistance of DED material with gas pores

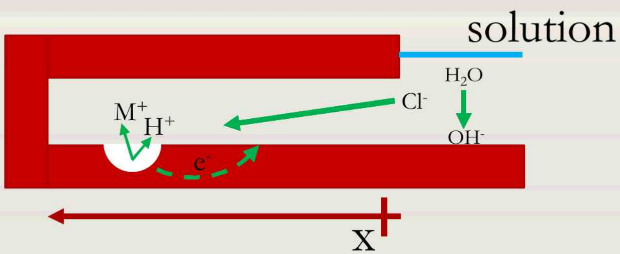




Only two (2) of the six (6) new pits occur in proximity to the gas pores, with no clear sign they originated from the pores. Also no change from the polished CPP measurements without pores.

1200 Grit, 21°C, Quiescent, 1 h OCP, 1 mV/s

Fusion pore acting as a crevice



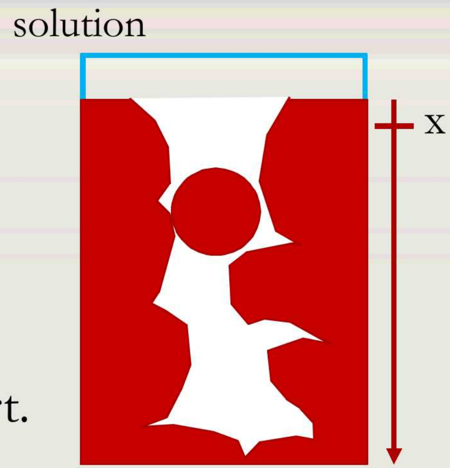
Typical crevice will have this geometry, leading to acidification at the deepest part.

The intensity of which is dictated by **crevice mouth width** and the **crevice depth**.

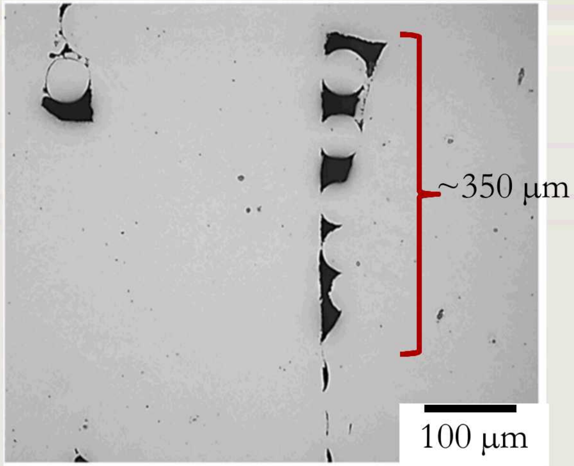
The smaller the width, the more intense the acidification.

The deeper into the crevice, the more intense the acidification.

Potential lack of fusion pore



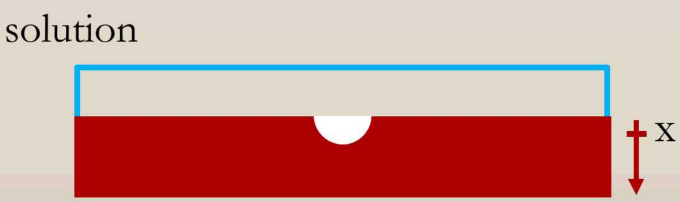
Real fusion pore in EBM Ti



Seifi, M., et al. (2016)

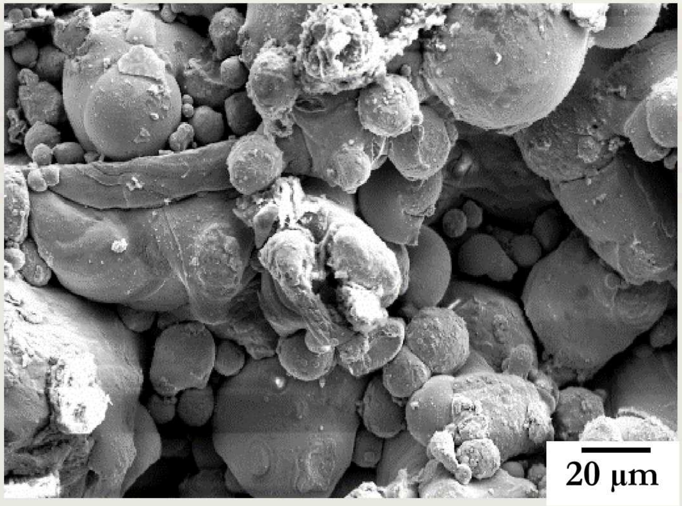
The fusion pores are more tortuous, usually have a small mouth and unknown depth (easily 500 µm).

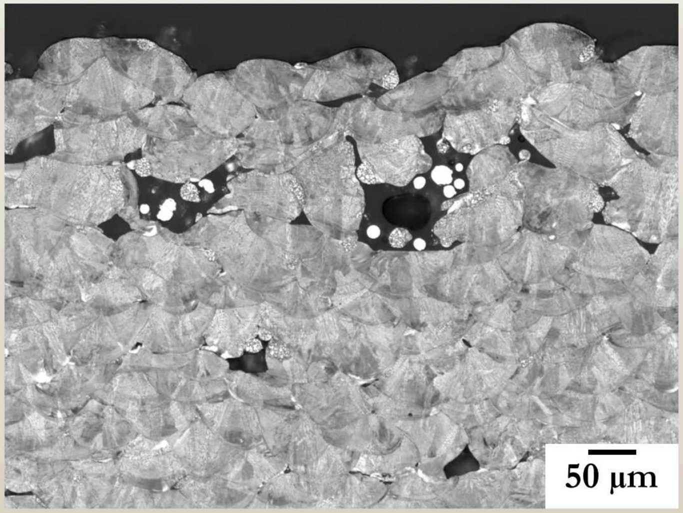
Potential lack of gas pore

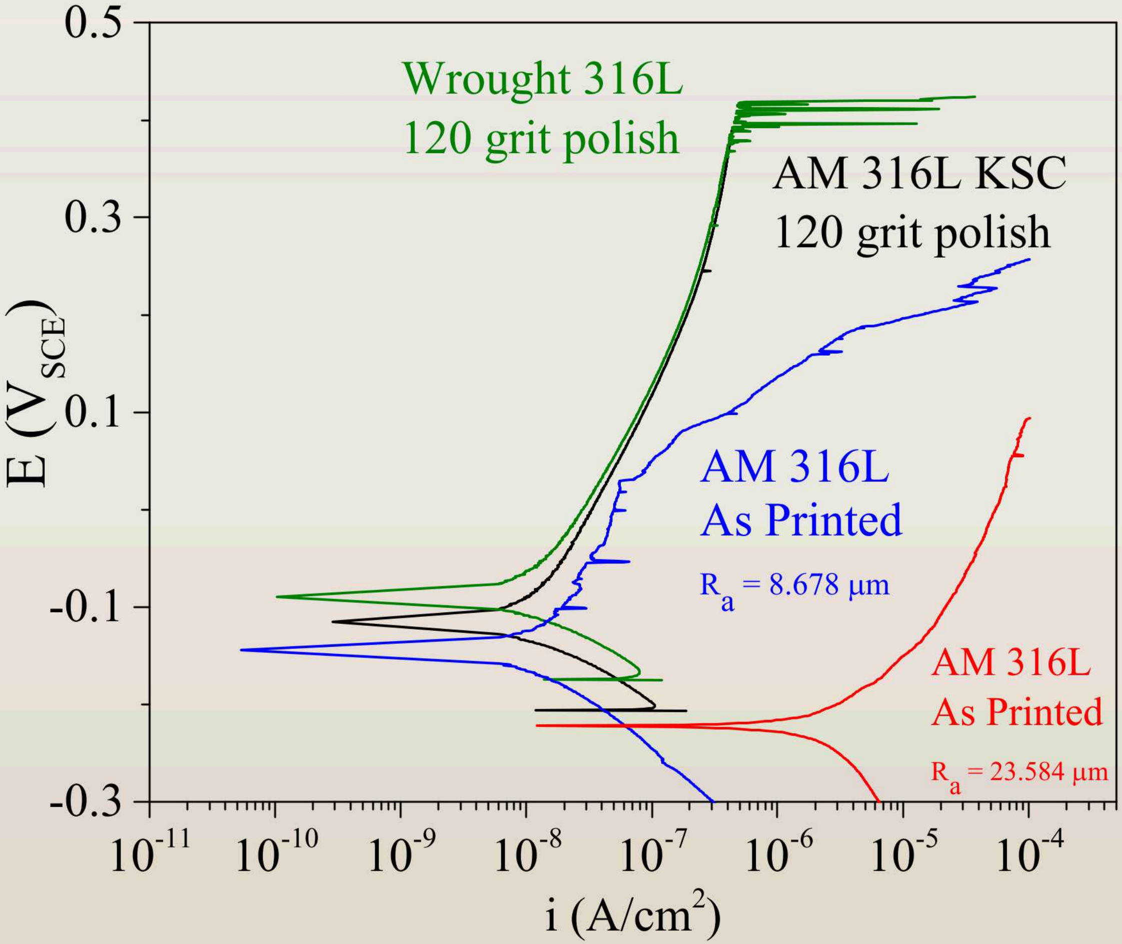


Surface finish: A differentiating factor in powder AM metals

As printed surface of AM 316L



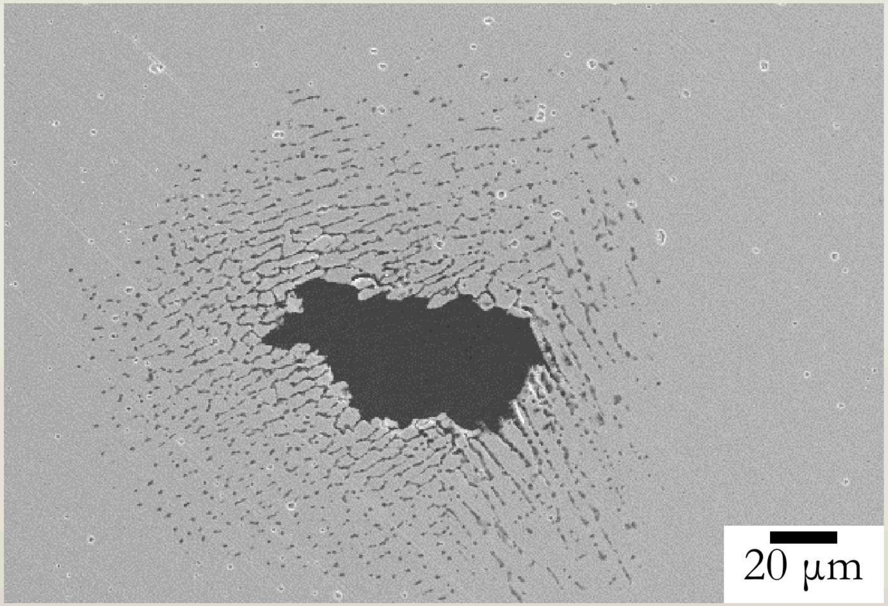


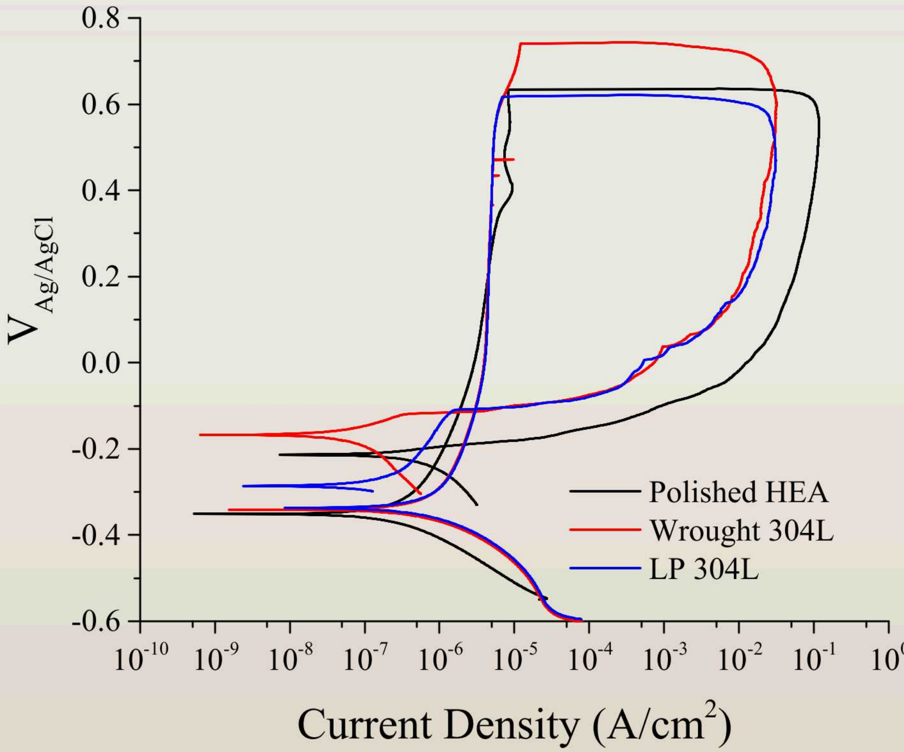


New alloys for AM processes

High entropy alloys (HEAs) should be less sensitive to chemical segregation when processed using AM techniques.

Investigating FeMnCrNiCo alloy – equal parts (20%) of each.





1200 Grit, 21°C, Quiescent, 1 h OCP, 1 mV/s

Conclusion

- Lack of fusion pores control E_b to first order (crevice former).
  - Should be used to predict lifetime of components made with AM.
- Gas pores have little influence on pit initiation in NaCl solution.
- DED materials without pores are on par with wrought 304L.
  - δ-ferrite likely the reason for lower E_b for HP material, slower cooling rates lead to more chemical/impurity segregation at ferrite/austenite interface.
  - **Will impact pit propagation.**
- Oxides in DED material may play a role in pit initiation, however not noticeably, similar to SLM.
- What is impact of variance in AM processing and post-processing parameters on corrosion?
  - Scan strategy, build atmosphere, powder reuse, surface finish, height of build?
  - Residual stress?

Questions?

EXTRAS

Figure #13: Double loop electrochemical potentiodynamic reativation (DLEPR)

Table 4: ISO12732 general interpretation of sensitization from DLEPR experiment.	
I_R/I_A value	**Degree of sensitization**
< 0.010	Unsensitized
0.01 to 0.05	Slightly sensitized
> 0.05	Sensitized

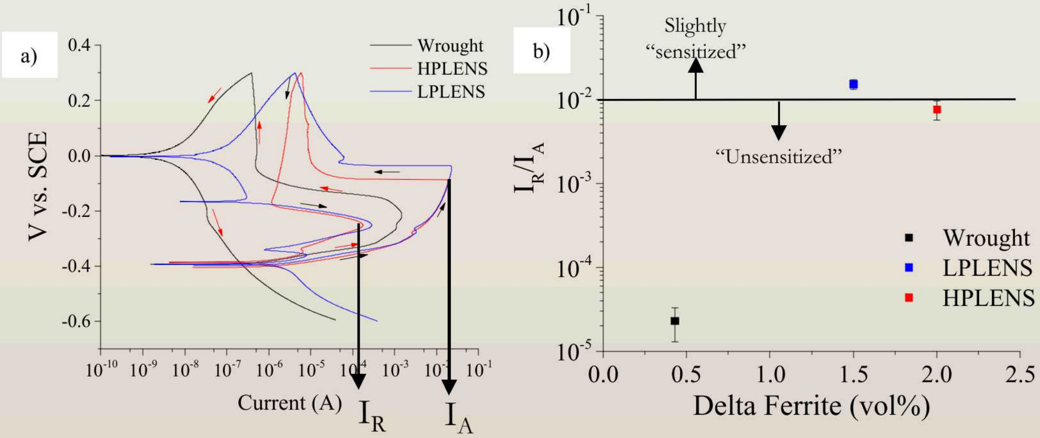


Figure 13: A typical response from a DLEPR measurement for each polished specimen fully immersed in stagnant 0.5 M H_2SO_4 + 0.005 M KSCN after 15 minutes at OCP in **a**), with the scan direction labelled and the activation (I_A) and reactivation (I_R) current labelled for the HPLENS scan. The ratio of I_A/I_R is plotted with respect to the volume % of delta ferrite in **b)**.

Figure #14: Images of DLEPR specimen after experiment

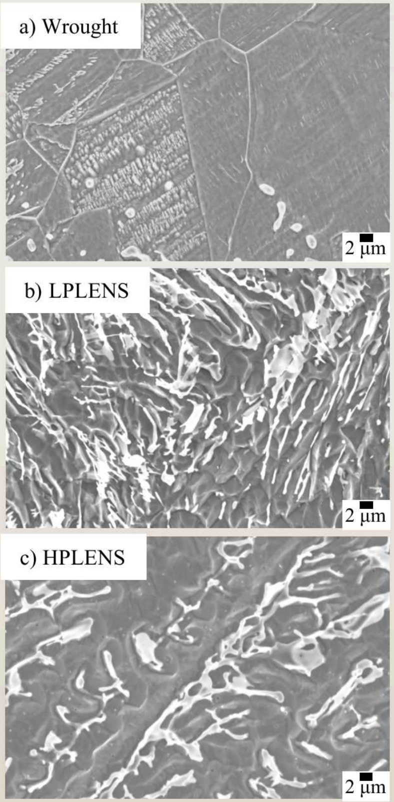
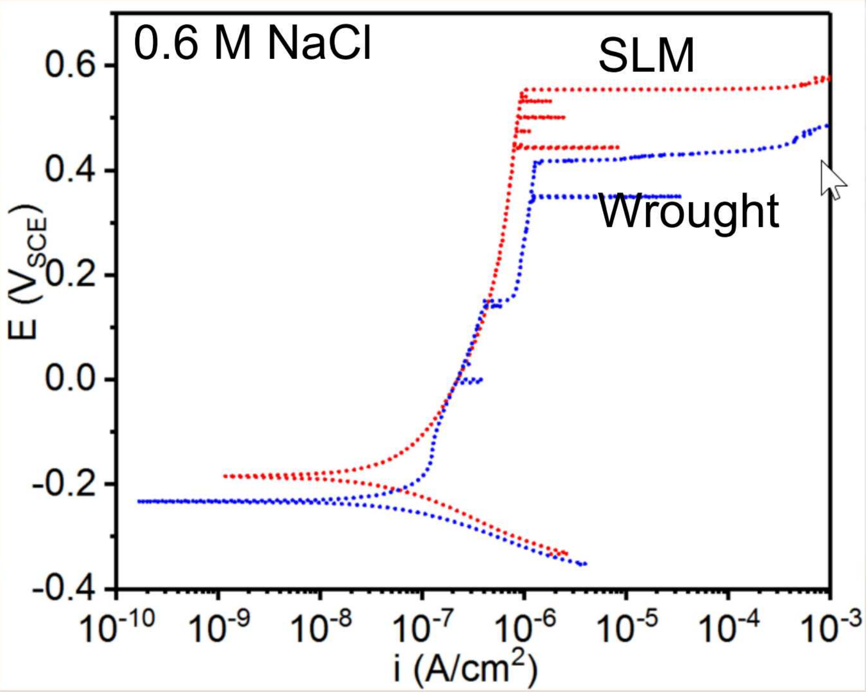


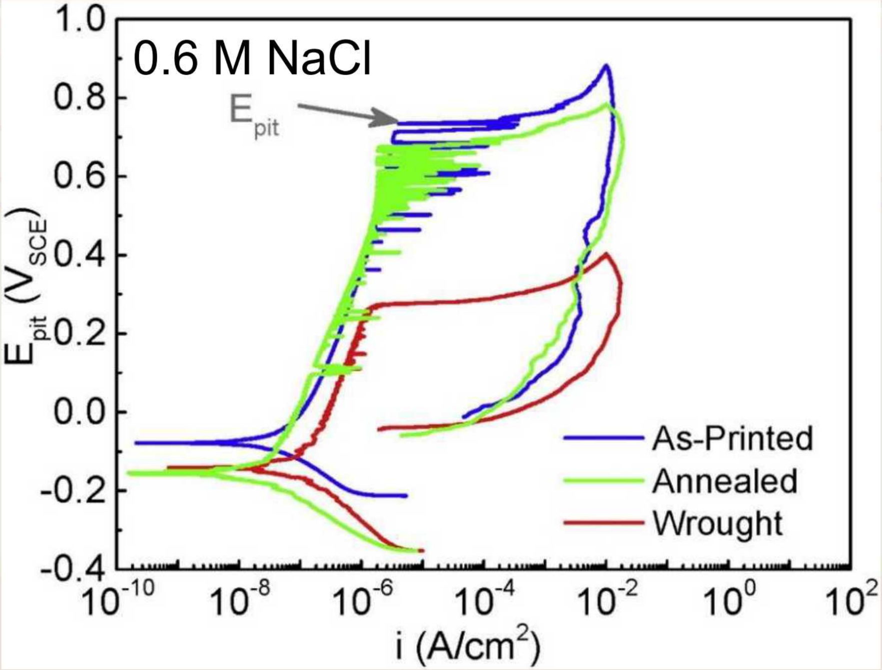
Figure 14: Secondary electron images of **a)** wrought, **b)** LPLENS, and **c)** HPLENS materials surface after the DLEPR measurement in stagnant 0.5 M H_2SO_4 + 0.005 M KSCN.

Why the Higher Pitting Potential of SLM?



SLM 304L

Schaller et al., *Journal of The Electrochemical Society* 165.5 (2018): C234-C242.

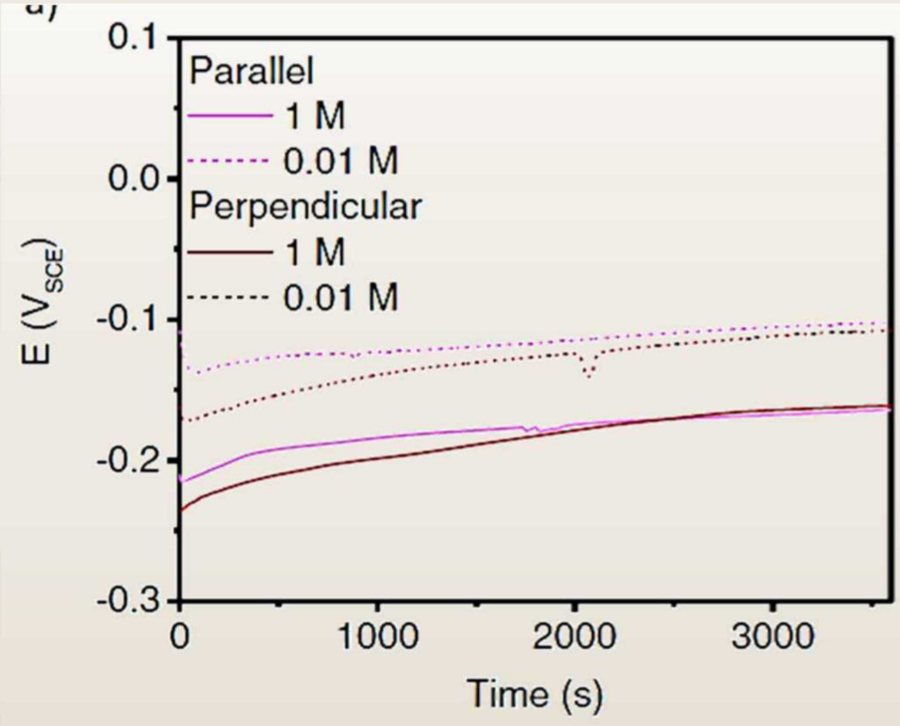


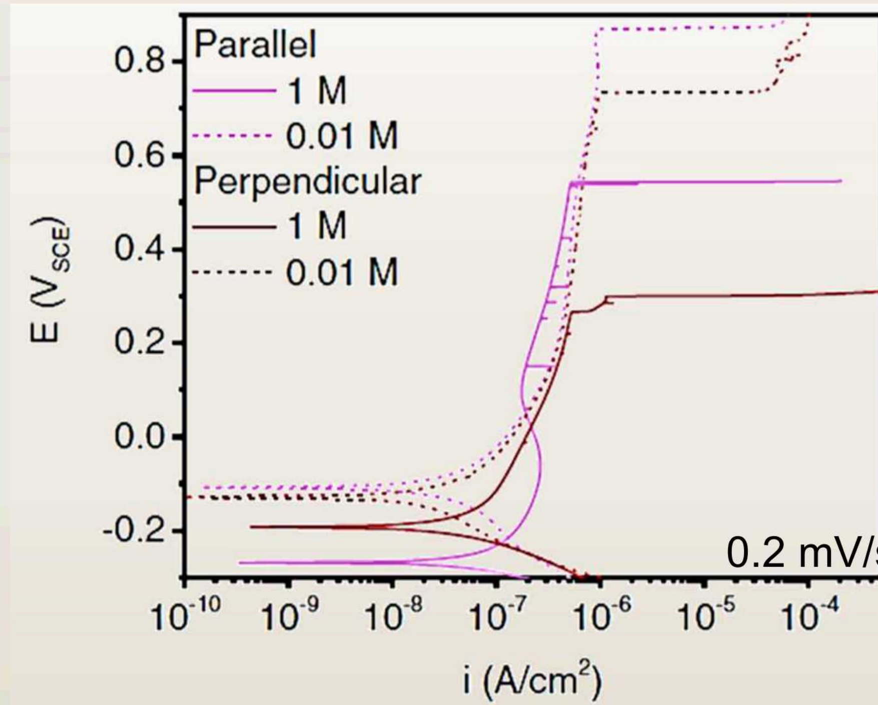
SLM 316L

Chao et al., *Scripta Materialia*141 (2017): 94-98.

fine scale features ←→ superior* corrosion resistance to wrought

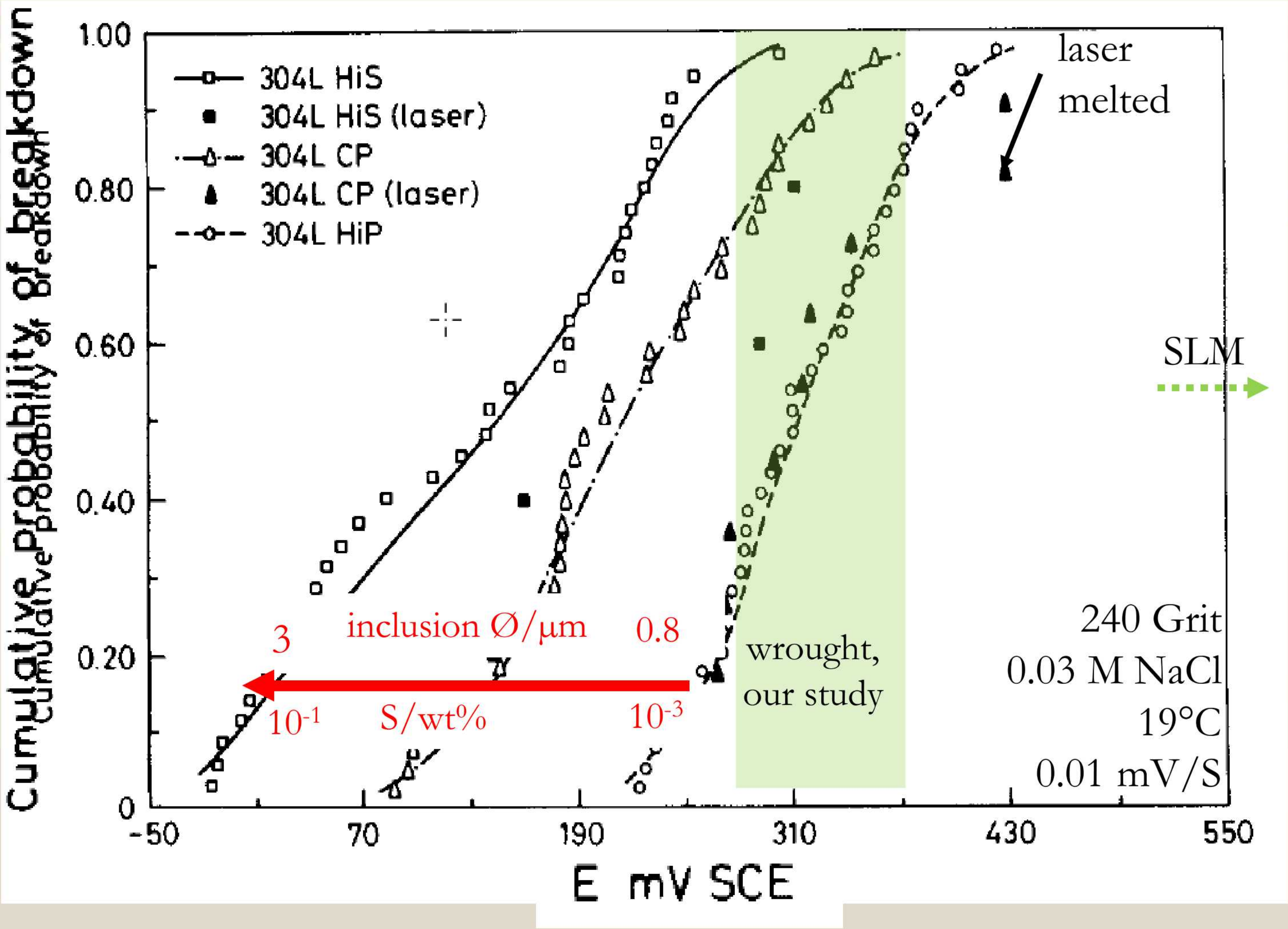
Pore Morphology May be Reason for Directional Difference





Direction	Pore Area Coverage (%)	Pore Cross-Sectional Area (µm)
Parallel	0.3 ± 0.1	1 ± 1
Perpindicular	0.2 ± 0.1	14 ± 7

Effect of Inclusion Size and S Content on Breakdown Potential



Stewart, Williams 1992

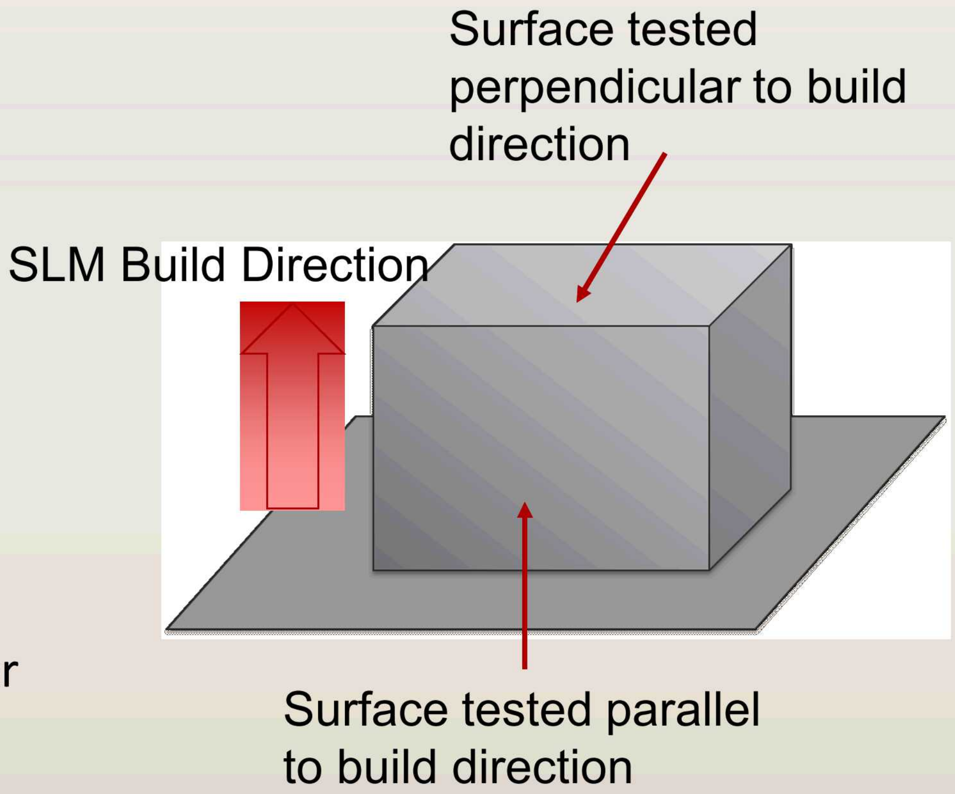
Ke, 1995
< 0.7 µm diameter MnS inclusions did not serve to initiate pits

Frankel, 2014

Sample Preparation: 304L

SLM Post-Build:

- Abrasive blasting: silicon oxide
- Electrochemical testing:
  - As received condition (grit blasted)
  - Abraded condition:
    - 60, 120, 600, or 1200 SiC paper
  - Both perpendicular and parallel surfaces tested



Open Questions

- Why and how does pit initiation and propagation behavior scale with feature size down to nano-sized oxide, MnS and solidification subgrains?
  - Requires adddressing some long-standing questions- e.g., why/how do pits initiate and propogate around MnS inclusions?
- What is the nature of the oxide film of SLM passive metals with fine-scale features and how does it relate?
  - Composition, structure and, electronic/defect characteristics of passive films relative to underlying microstructure?
- Once initiated, how does corrosion propogate relative to the highly anisotropic microstructure?
  - Preferential dissolution analogous to intergranular attack on HAZ?
  - How does it relate to SCC?
- What does long term behavior of material look like?
  - Preferential dissolution analogous to intergrajnular atacck?
  - SCC?”?