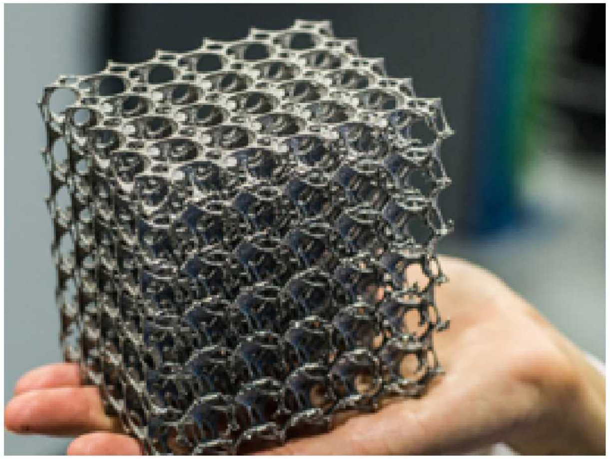
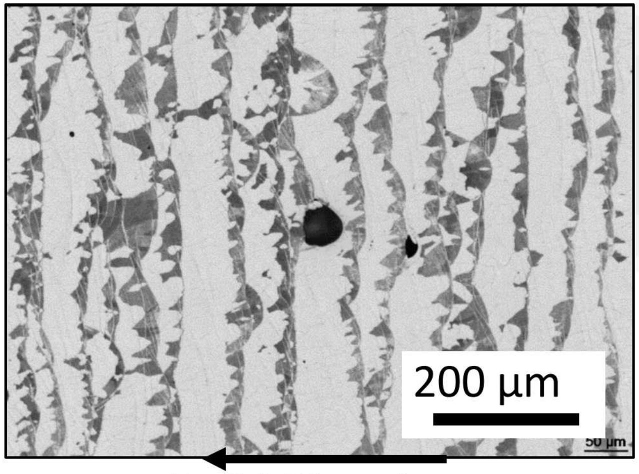
Corrosion of Selective Laser Melted Additive Stainless Steels

SAND2018-12749PE

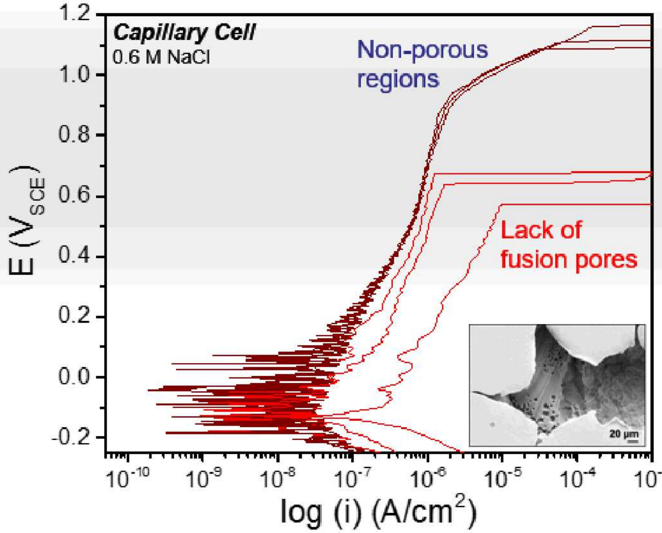
How Stainless Are They?

Eric J. Schindelholz
Sandia National Laboratories





Build Direction



University of Nevada, Reno
November 2, 2018

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Schindelholz Corrosion Group

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Jacob Carpenter, UNM undergrad intern

Jason Taylor, technologist

Sandia Collaborators

Jeff Rodelas (weld metallurgy)

Bradley Jared (AM process science)

Mike Abere (laser processing)

Katie Jungjohann (in-situ TEM)

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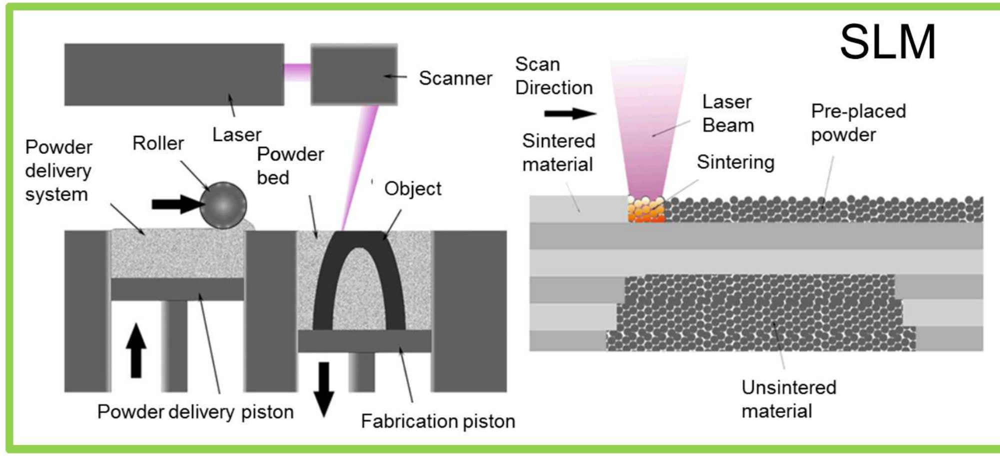
Outline

- **Motivation**: application, material, aging questions
- **What makes stainless steel stainless?**: passive film
- **Additive stainless steel:** unique microstructure and passivity
  - SLM 17-4 PH
  - SLM 304L
- **New Directions and Future Work**
  - In-situ Electrochemical TEM for microstructure-performance
  - Surface finishing strategties

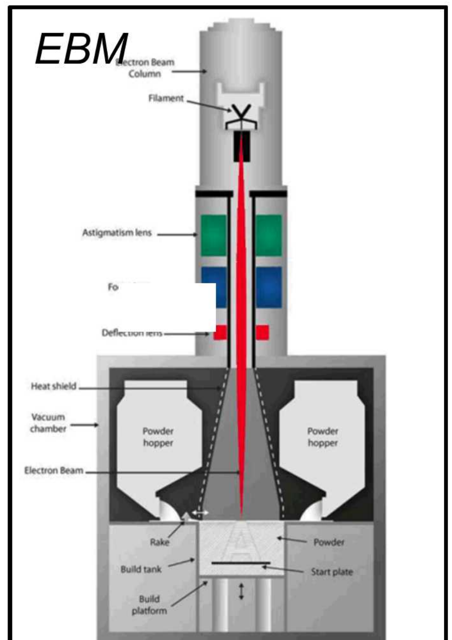
What is Additive Manufacturing?

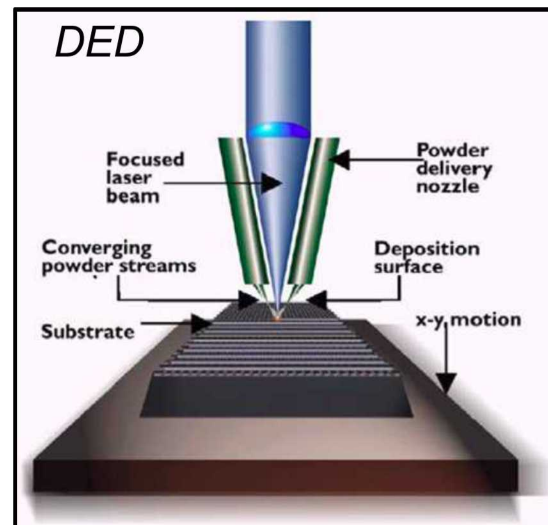
Process Categories:

- Binder Jetting
- Wire-Based Fusion
- Powder-Based Fusion
  - Selective Laser Melting (SLM)
  - Electron Beam Melting (EBM)
  - Directed Energy Deposition (DED)
- Sheet Lamination
  - Ultrasonic
- Vat Photopolymerization



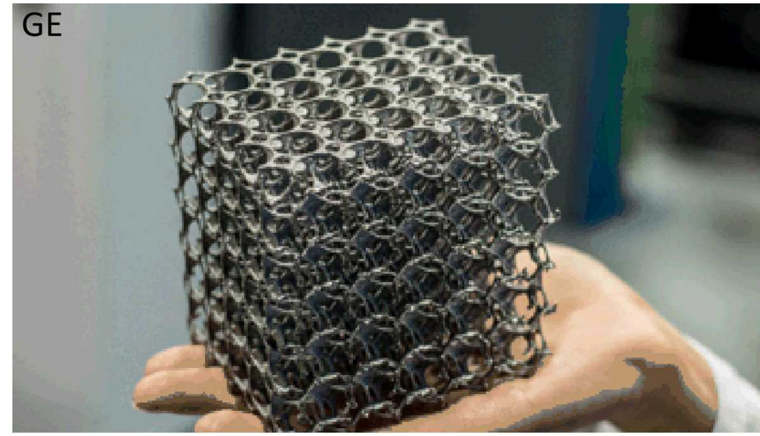
Wikipedia "selective laser sintering"





Why AM?

sophisticated, unconventional 3D geometries



lattice structure

heat exchanger

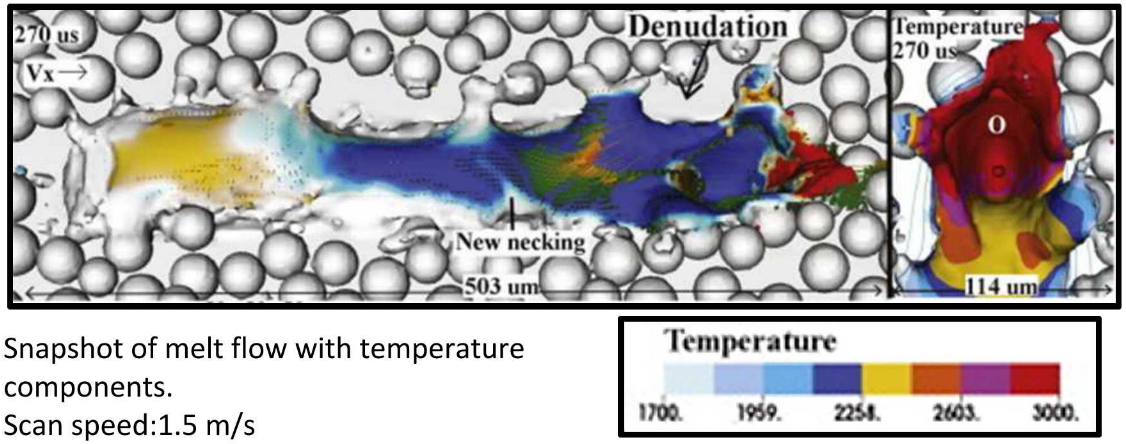
A design/process-pathway to lightweight-high strength parts

topology optimized design

Powder Bed SLM Processing and Material Characteristics

SLM Processing

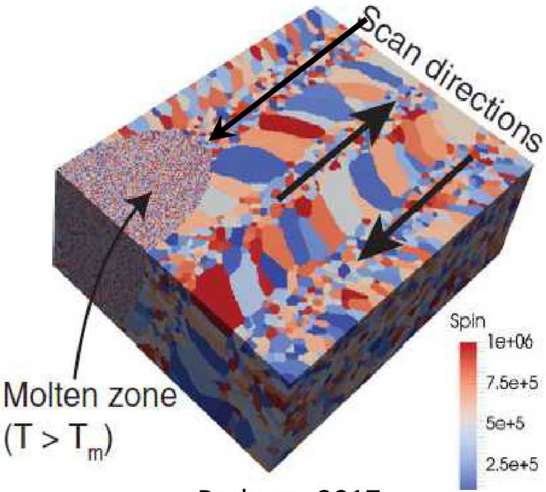
High thermal gradients, high cooling rates (up to 10^7 K/s), and high velocity growth vectors (directional solidification)



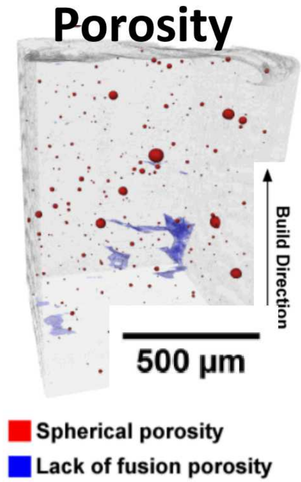
Snapshot of melt flow with temperature components.
Scan speed:1.5 m/s
Khairallah, 2016

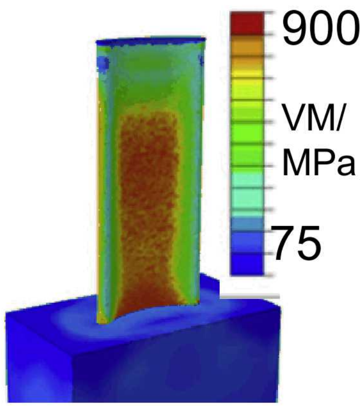
SLM Materials

Heterogenous mixture of elongated and equiaxed grains with periodicity



Rodgers, 2017





An, 2017

Stress

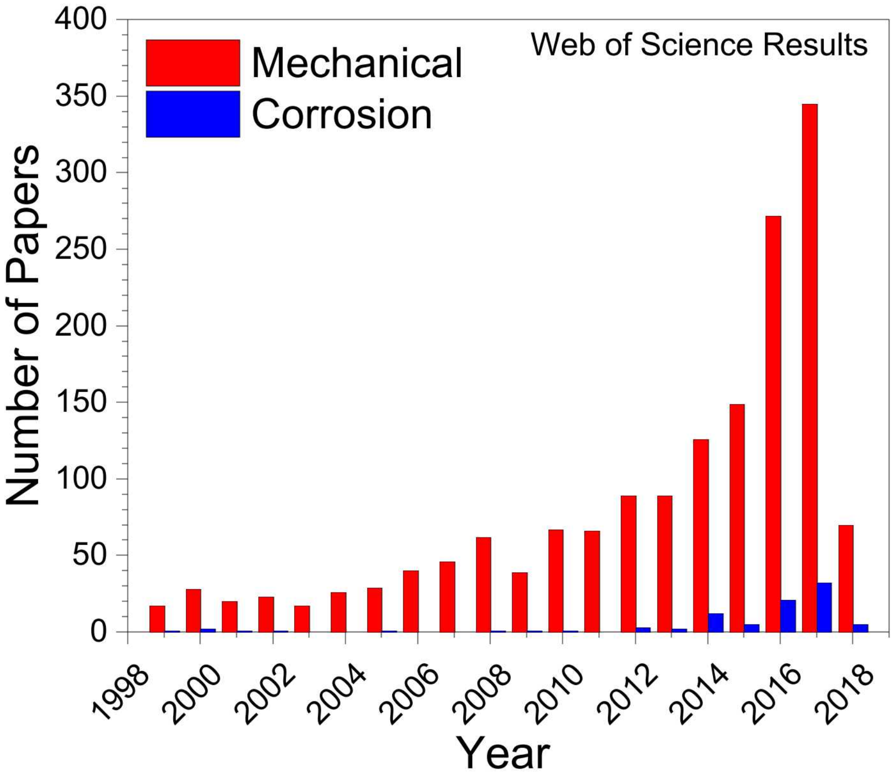
Corrosion of AM Metals: Needs and Knowledge

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



Motivating Questions

- How do the unique features of additive metals govern corrosion resistance relative to their conventionally processed counterparts?

- What is the impact of variance in alloy chemistry, AM processing and post-processing parameters on corrosion?

- Knowing this, how can we make materials to exceed both physical and corrosion resistance targets?

- How can we take advantage of AM to create new materials exceeding performance of conventional?

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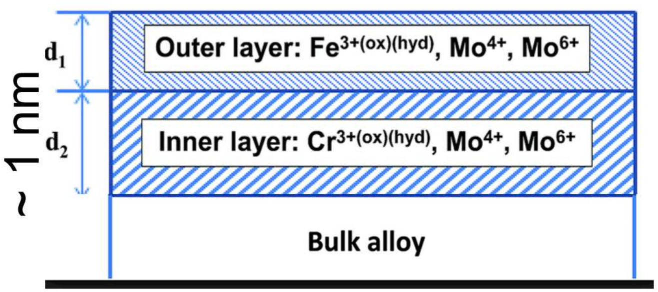
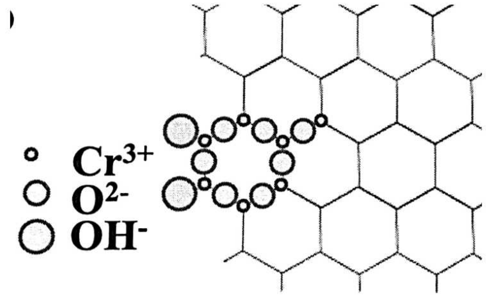
  - SLM 17-4 PH
  - SLM 304L
- **New Directions and Future Work**
  - In-situ Electrochemical TEM for microstructure-performance
  - Surface finishing strategies

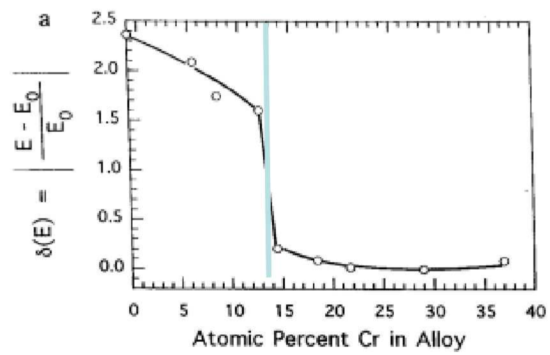
What Makes Stainless Steel Stainless? Passive Film…



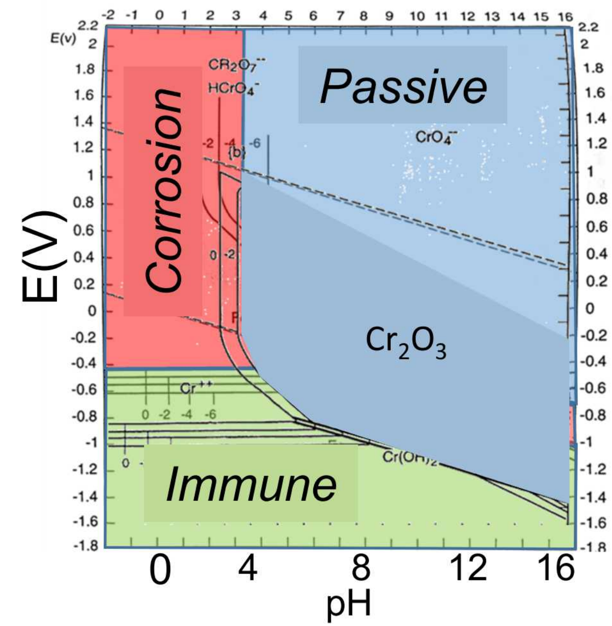
Fe-Cr-(Mo)-oxide films are charge and mass transfer barriers



Passivity relies on continuous Cr-(Mo) oxide film



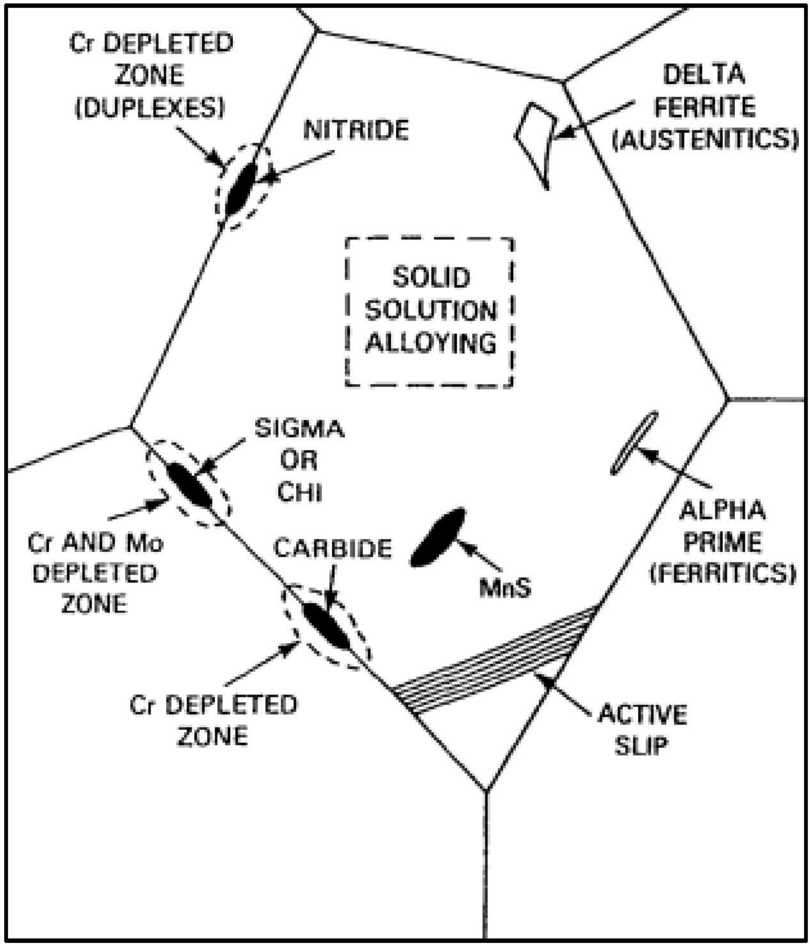
Critical [Cr] threshold to maintain continuity



Cr oxide film expands passivity environmental range

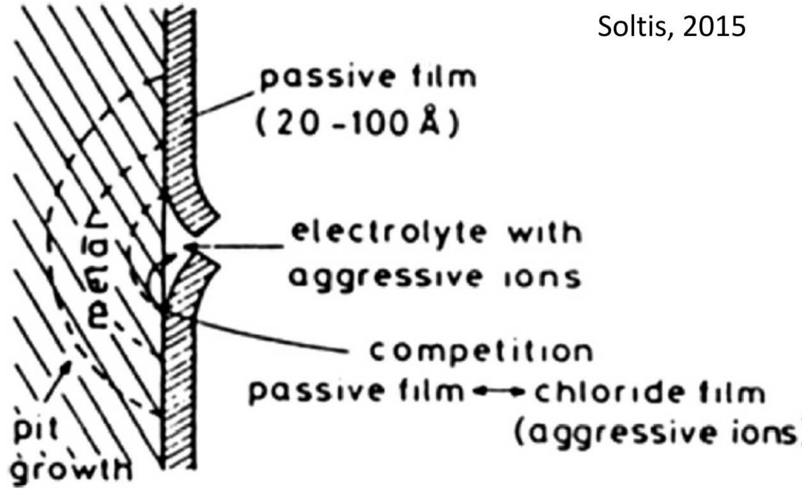
What Material Features are Conducive to Pitting? Pit Initiation

Sedricks, 1996



Microstructural Features Deleterious to Pitting Resistance

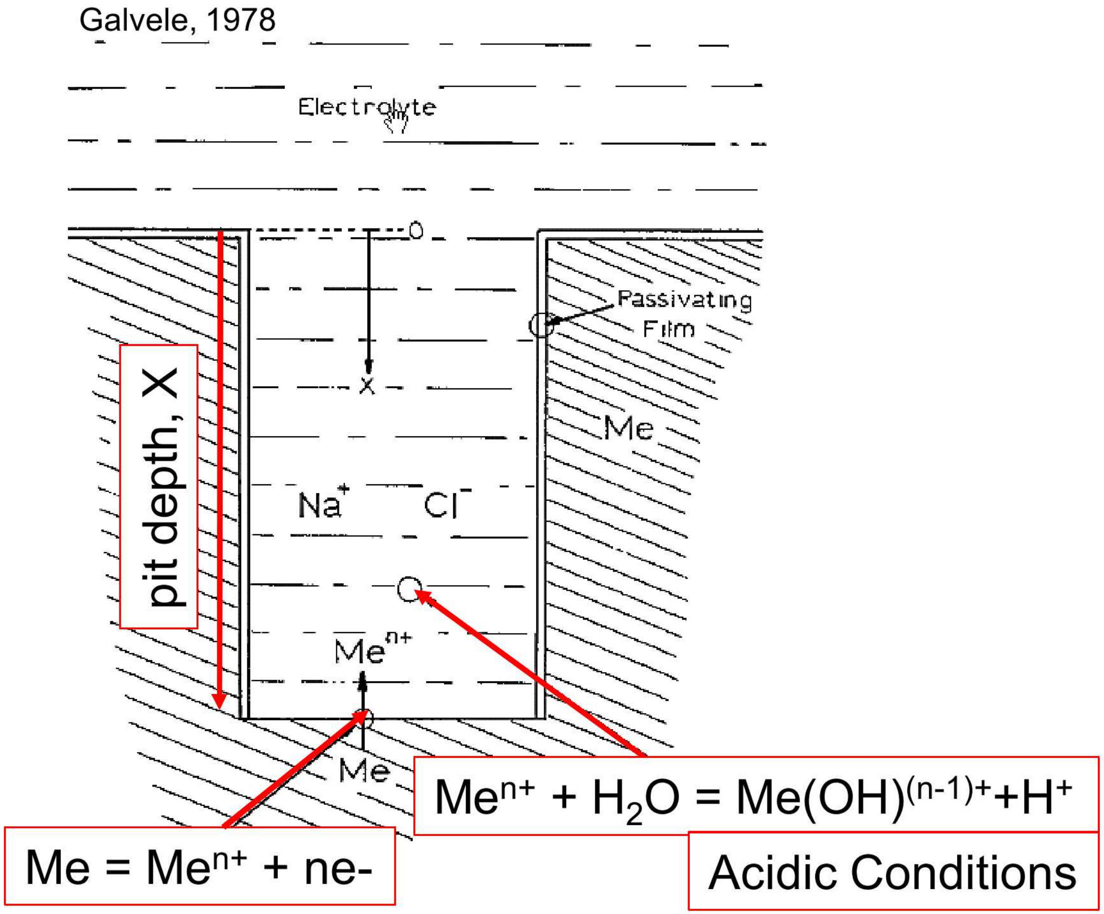
Soltis, 2015



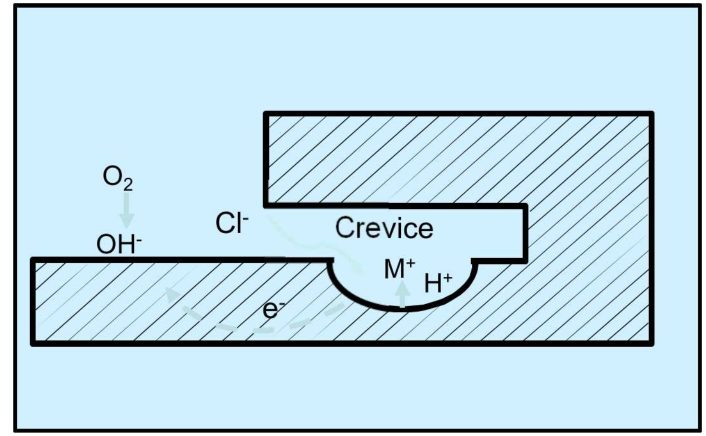
Film Breaking Mechanism:

- Breakdown at weak sites or flaws
- Electrostriction and surface tension
- Underlying salt film formation

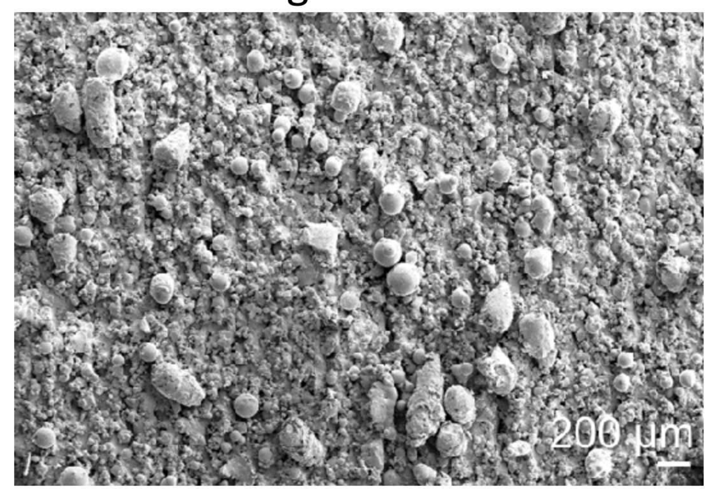
Propagation of Pitting



Extreme solution condition develops and maintained inside “occluded” area



Pre-existing Occluded Sites



As-Printed SLM 316 Surface

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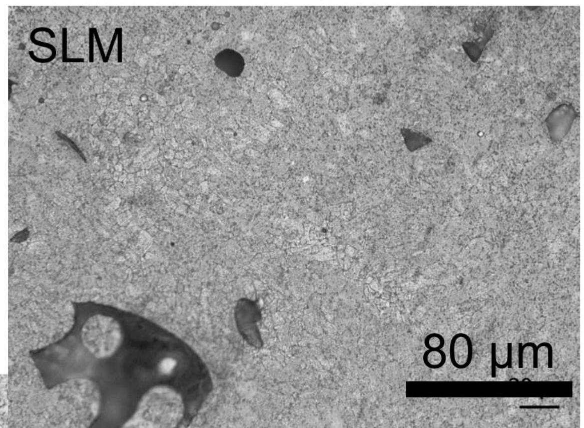
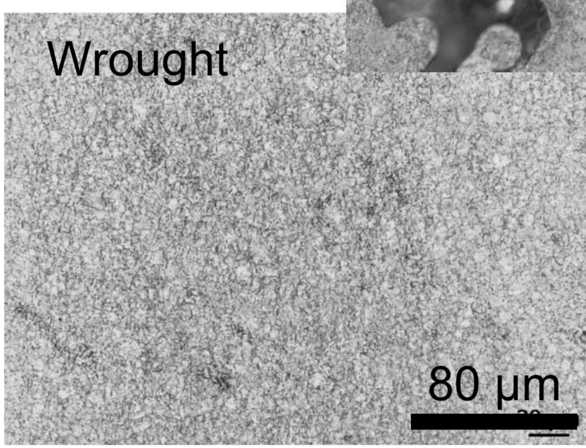
SLM 17-4PH, Material Characteristics

	C ±0.004	Cr	Cu	Nb	Ni	Mn	Mo ±0.011	P	Si	S	Fe	O ±0.008	N
Wrought	0.047	15.19	3.21	0.23	4.54	0.53	0.230	0.022	0.17	<0.001	75.6	0.014	0.023
SLM	0.017	16.02	3.95	0.29	4.12	0.22	0.025	0.013	0.33	0.002	74.9	0.068	0.036





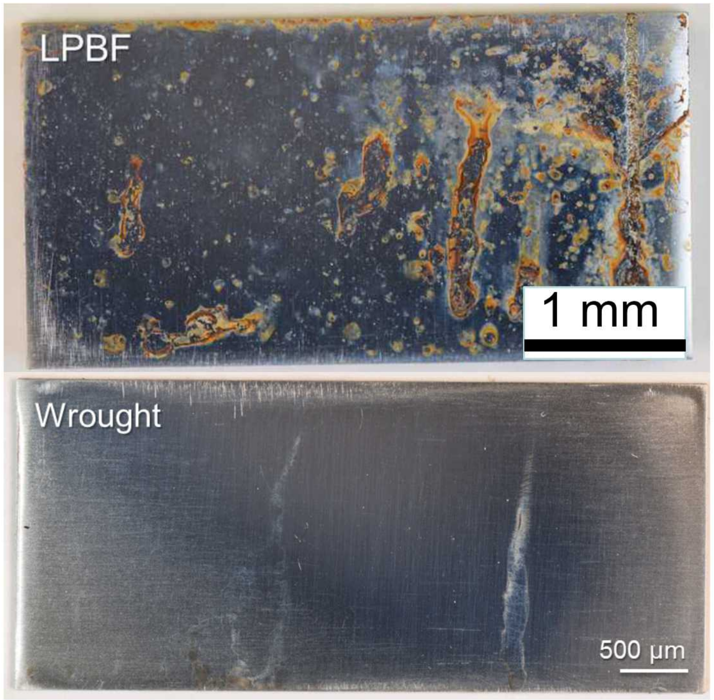
// Build Direction

- Solutionized, Peak Aged
  - AMS 5604:1050°C, 60 min in Ar, cooled to RT
  - Age hardened H900: 482°C 60 min in air
- No evidence of solidification substructure can be observed
- Solutionization heat treatment resulted in recrystallization and homogenization of solute micro segregation

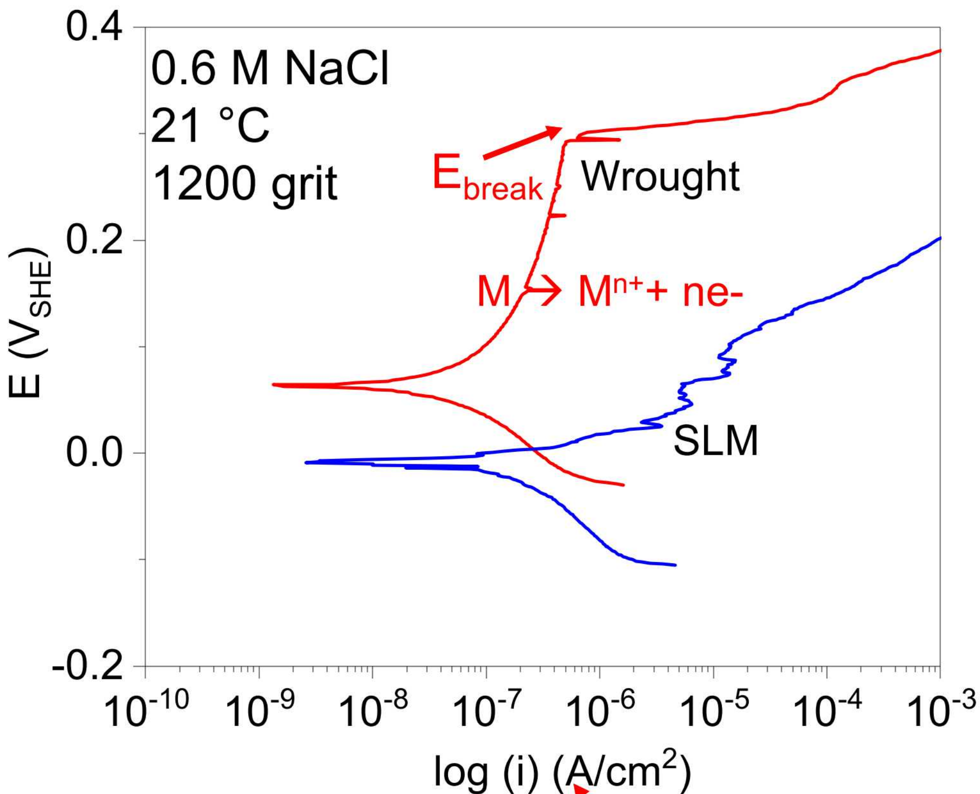
$PREN_{martensitics}$ = %Cr + 3.3%Mo + 16%N - 5%C → Wrought=16.1, SLM =16.6

Inferior Pitting Resistance of 17-4 PH SLM

Salt Fog Exposure



Pitting of SLM after 2 weeks in ASTM B117



<u>Reading the Graph</u>

Metal Dissolution Rate = i/nF ($mol*cm^{-2}*s^{-1}$)

Microscale Electrochemistry Reveals Controlling Role of Pores

Capillary Microcell

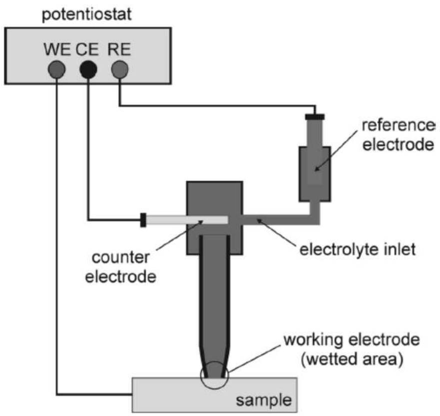
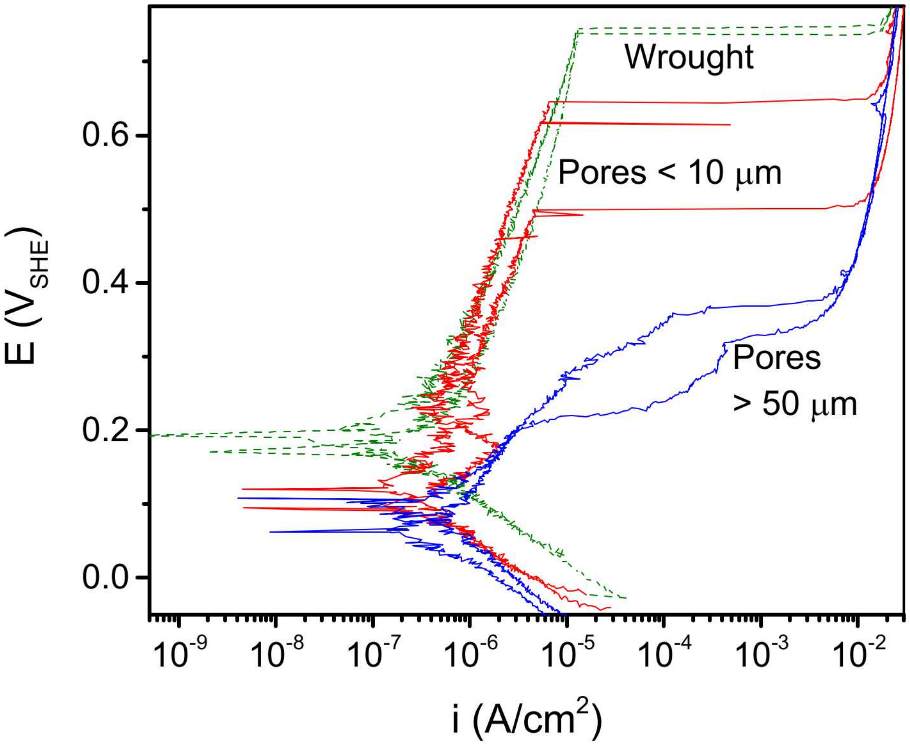


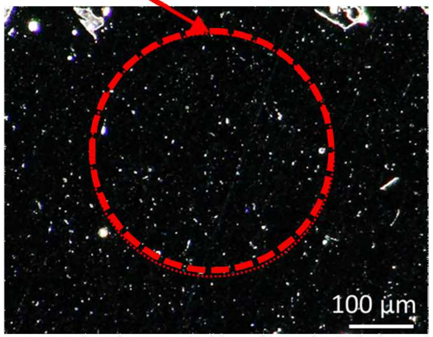
Fig. 3. Three-electrode setup of the electrochemical micro-cell.

Andreatta, 2016

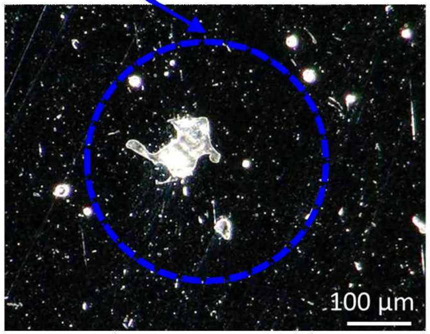


Schaller, Schindelholz, et al. 2017

Pores < 10 μm
Micro-electrochemical Cell Area

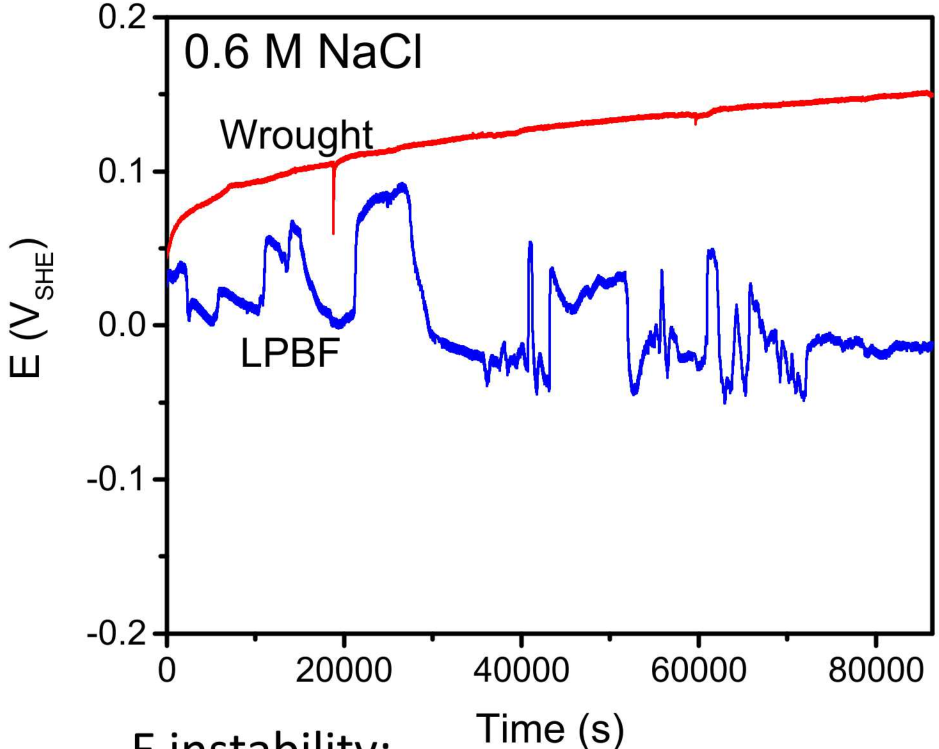


Pores > 50 μm
Micro-electrochemical Cell Area



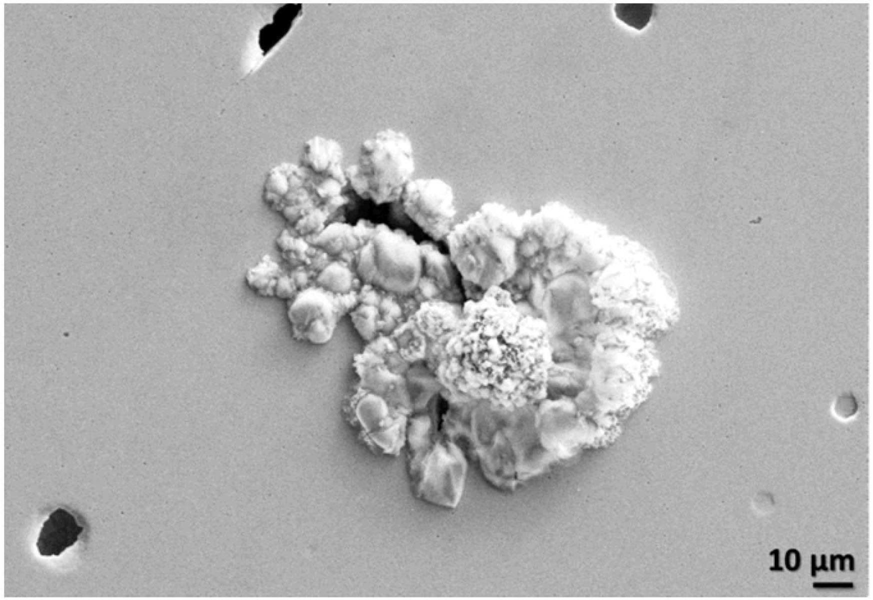
Primarily a geometry effect- crevice corrosion

Sustained Active Localized Corrosion in SLM Pores During Immersion



E instability:

- Active corrosion pitting
- Solution ingress into pores (EIS)



Corrosion product build-up after 7 day open circuit exposure in quiescent 0.6 M NaCl

17-4 PH Study Conclusions

- SLM exhibited inferior corrosion resistance relative to wrought in immersed and atmospheric tests (no passive region).
- Porosity is the most obvious differentiating feature of consequence to localized corrosion resistance relative to wrought material. Directly established this as primary cause.
- Secondary causes could be differences in passive characteristics film or underlying microstructure on lack of fusion surfaces.
- Pit/crevice stability as function of pore geometry could enable identification of most deleterious geometries -> processing target.

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SLM 304L: Material and Process Characteristics

Measured 304L Material Composition (Weight %)

	C	Cr	Co	Cu	Nb	Ni	Mn	Mo	P	Si	S	Fe	O	N
Wrought	**0.025±** 0.004	**18.16±** 0.363	**0.17±** 0.026	**0.49±** 0.074	**<0.05±** 0.008	**8.10±** 0.405	**1.73±** 0.173	**0.33±** 0.049	**0.034±** 0.005	**0.22±** 0.033	**<0.001±** 0.000	**70.5±** 0.353	**0.003±** 0.000	**0.076±** 0.011
AM	**0.013±** 0.002	**18.89±** 0.378	**<0.03±** 0.005	**<0.1±** 0.000	**<0.05±** 0.008	**10.74±** 0.537	**1.44±** 0.144	**0.014±** 0.002	**0.005±** 0.001	**0.50±** 0.075	**0.005±** 0.001	**68.3±** 0.342	**0.038±** 0.006	**0.011±** 0.002

Renishaw AM 250 Build Parameters

Parameter	Value
Laser power	200 W
Pulse time	75 µs
Pulse spacing	60 µm
Dwell time	1-3 µs
Hatch spacing	85 µm (Measured 82 ± 15 µm)
Layer thickness	50 µm (Measured 40 ± 10 µm)
Cover gas	Argon

Starting Powder

Ø = 15-45 µm, D50 = 29 µm

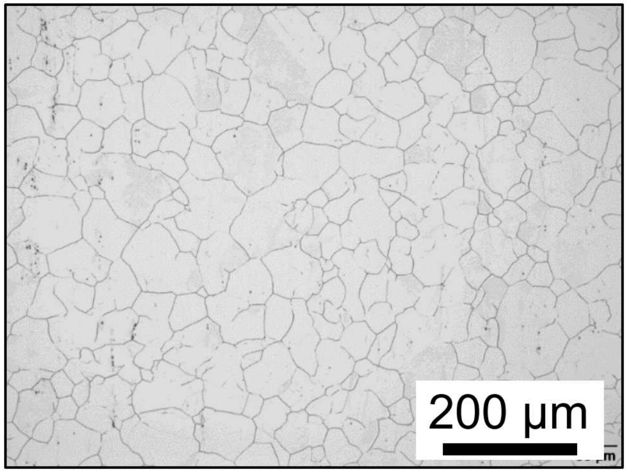
Ar-atomized

single use (not recycled)

$PREN_{austenitic}$ = %Cr + 3.3%Mo + 16%N → Wrought=20.3, SLM =19.1

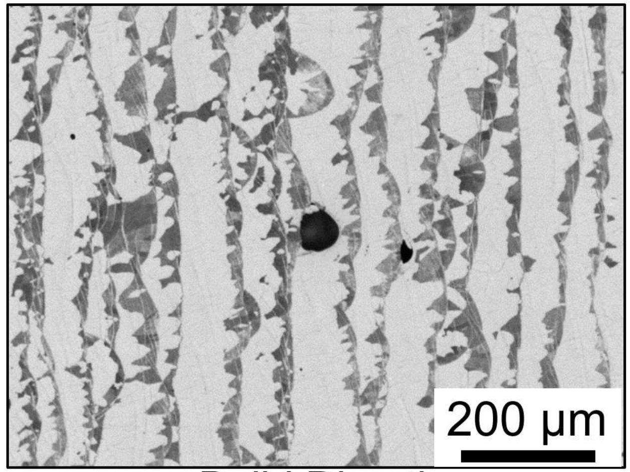
304L Microstructural Characteristics

Wrought 304L



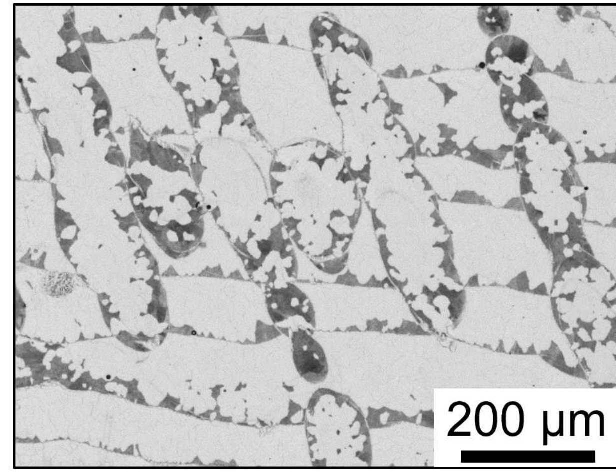
δ = 0.3 ± 0.1 vol%

SLM 304L
Parallel to Build



Build Direction ←

SLM 304L
Perpendicular to Build

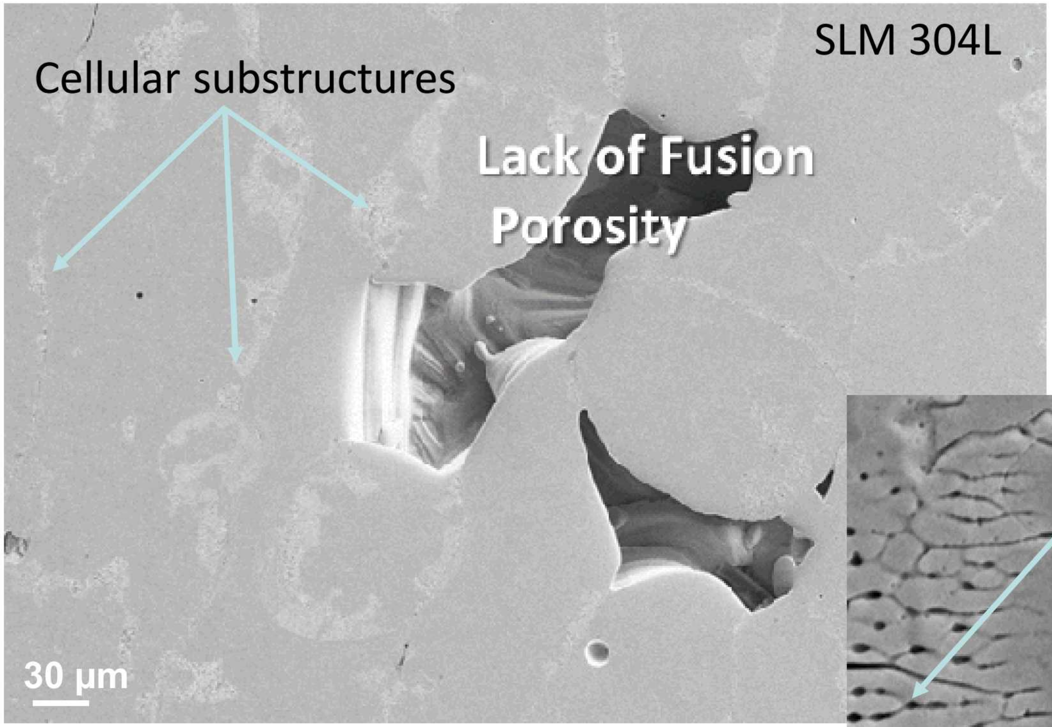


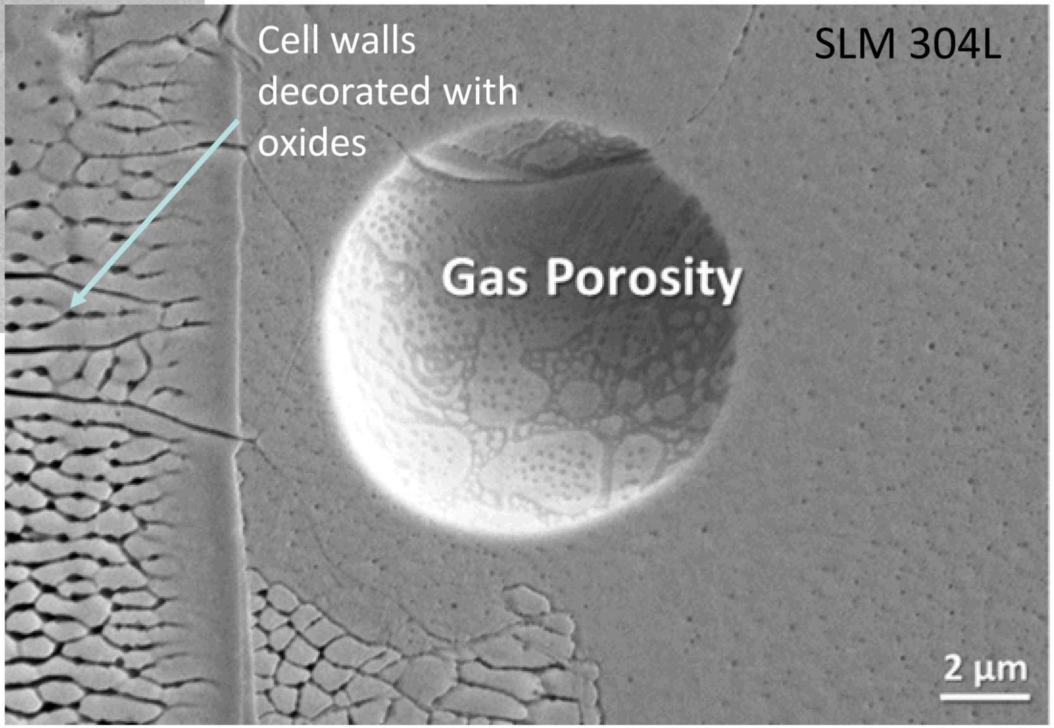
δ < 0.2 ± 0.1 vol%

SLM Differentiating Features:

- Periodic and directional microstructure
- Solidification substructure (primary γ)
- Porosity (both lack of fusion and gas porosity)

Solidification Structure and Porosity in SLM 304L

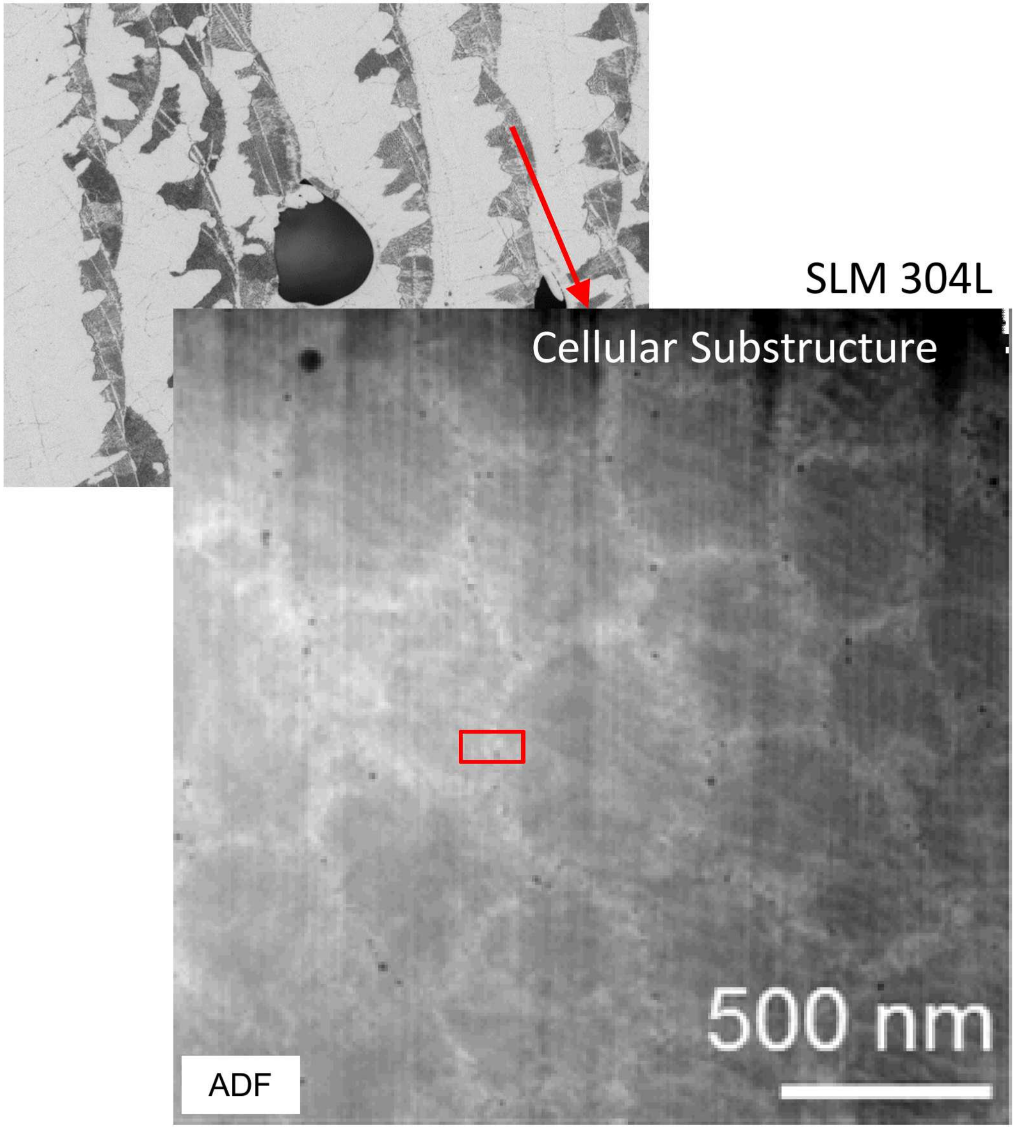




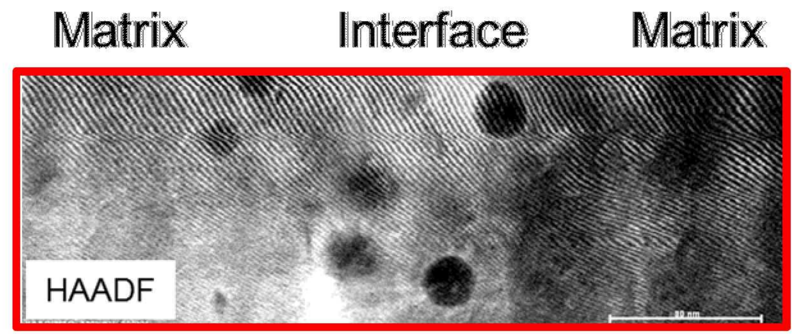
Lack of fusion pores vs. gas porosity:

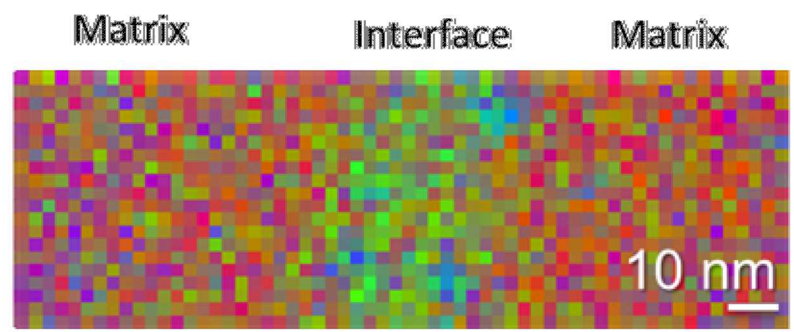
- tortuous vs. spherical

Substructure walls decorated with Si-Mn-O and Enriched in Cr



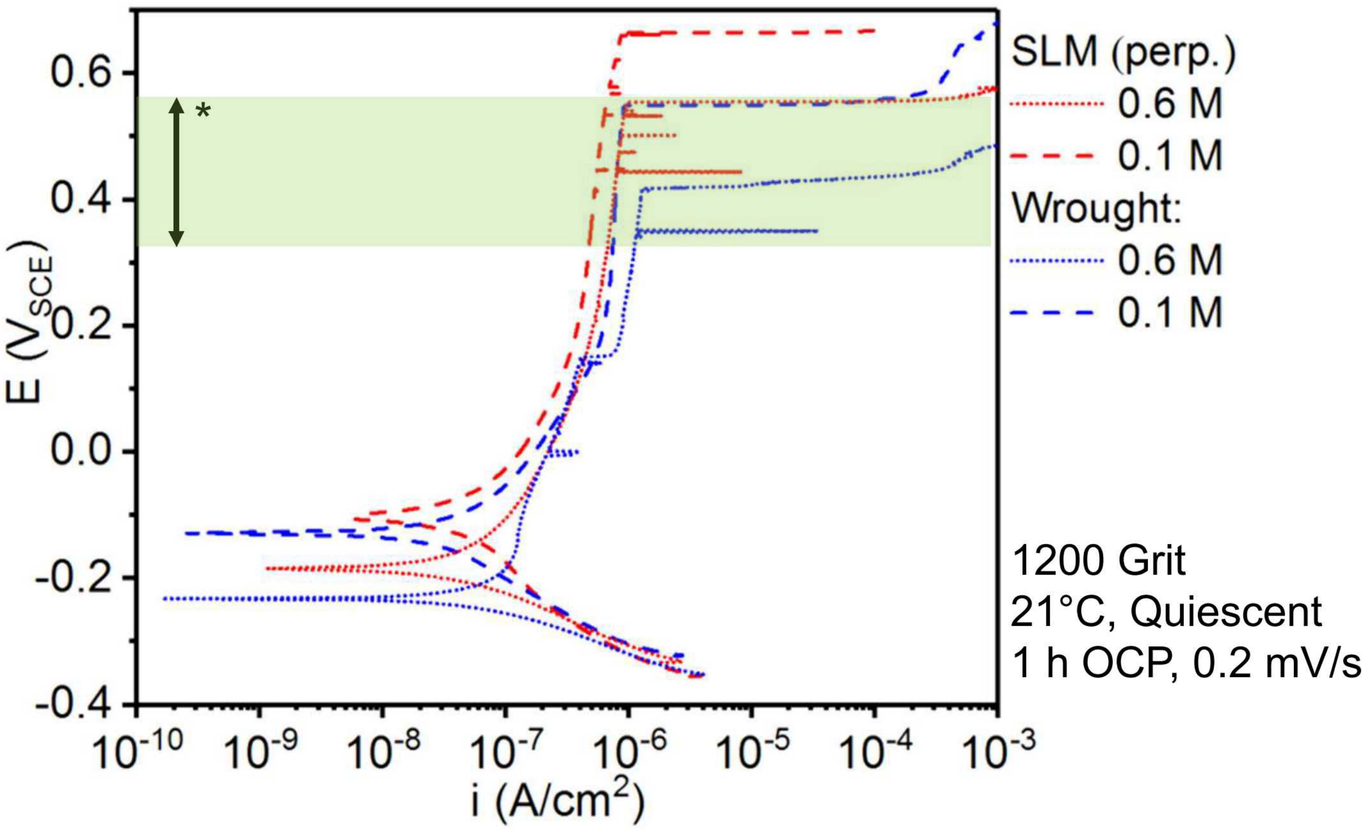
Segregation / Depletion





Increased Fe (+ 9%)
Increased Si
Increased Cr (+ 4%)

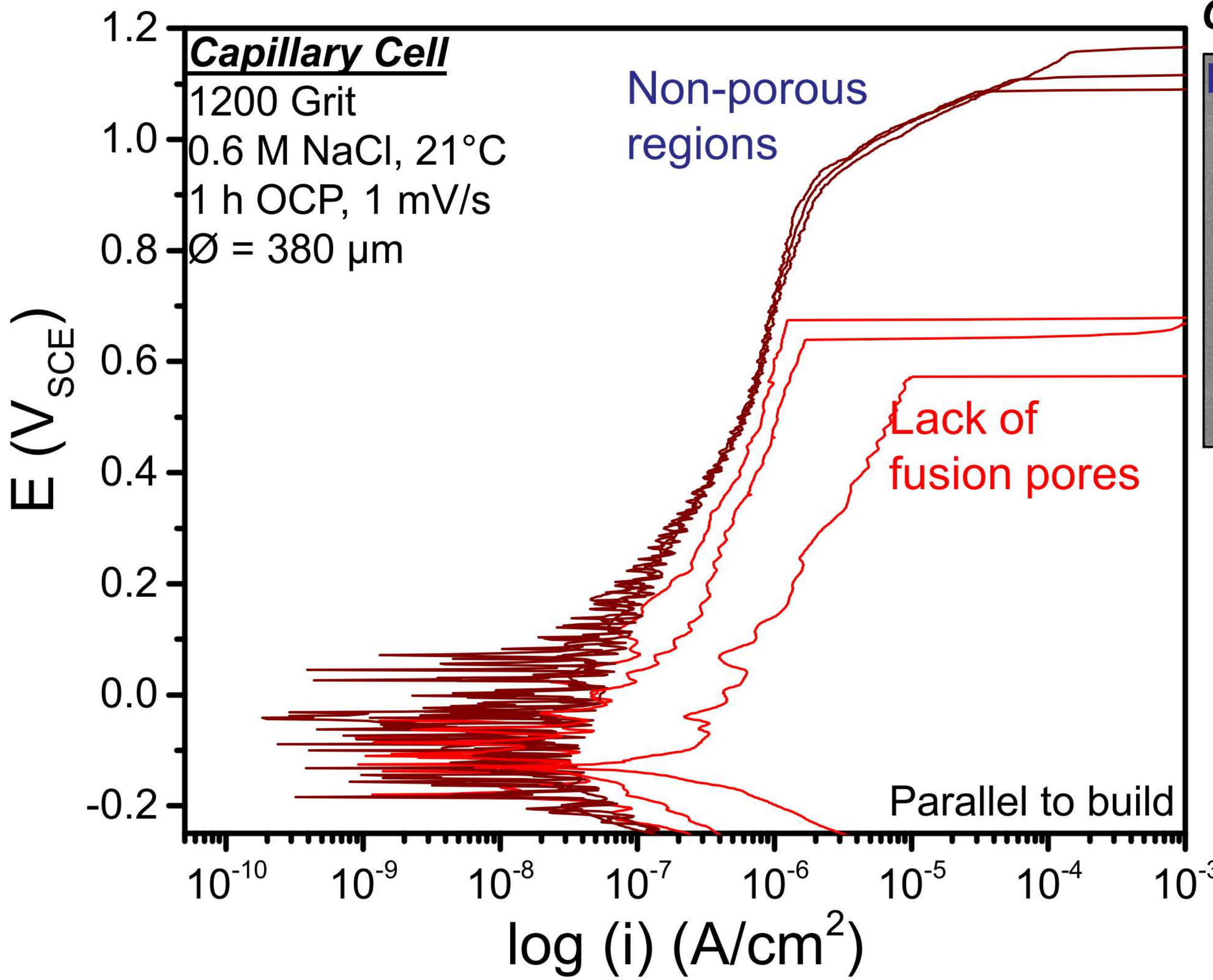
Superior Pitting Resistance of SLM 304L in NaCl Solutions



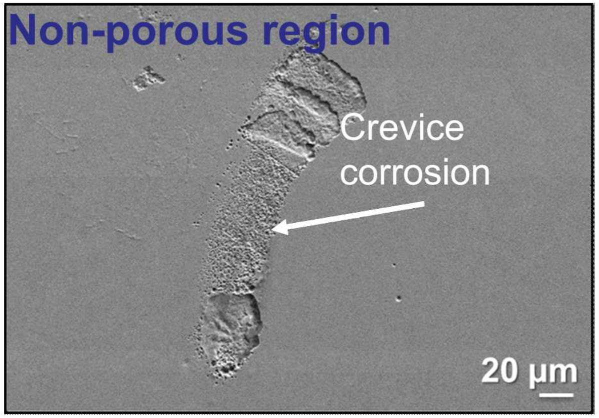
E_b of SLM > 0.12 V versus wrought (n= 20) in NaCl test solutions (0.1 to 1M) independent of build direction

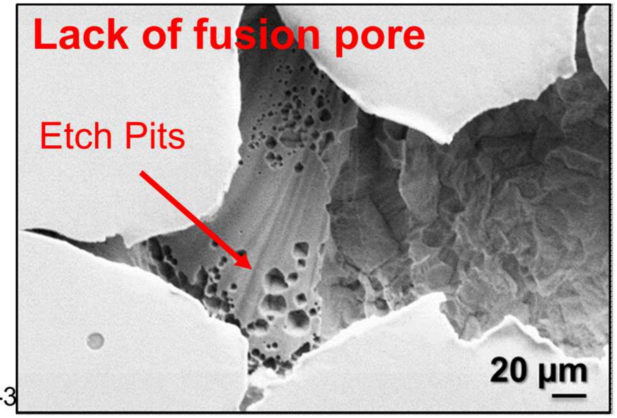
*E_b range for 0.1M NaCl, wrought 304L, Kumar et al, *Materials Characterization*, *54*(2), 141-147, 2005

Porosity Controls Breakdown Potential to First Order



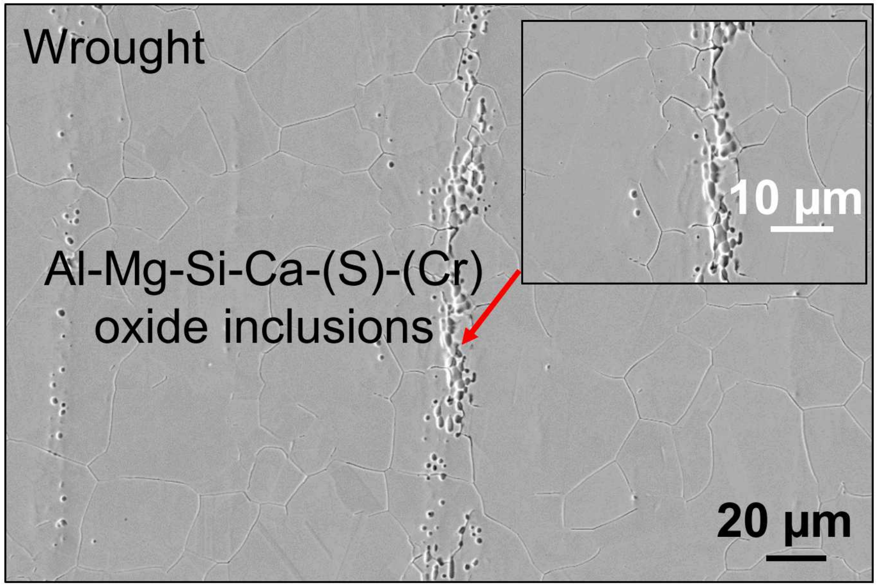
Corrosion damage post-scan



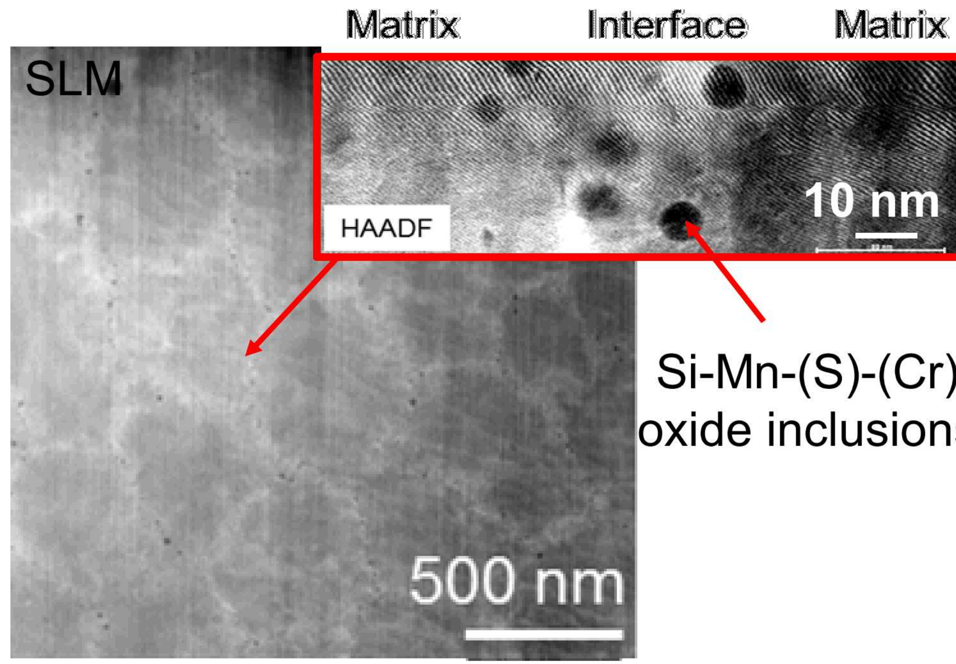


Excluding Lack of Fusion Pores Considerably Increases Pitting Resistance

What are preferential precursor pitting sites outside of lack of fusion features?



Breakdown at Si-O-X inclusions typical in wrought 300 series SS

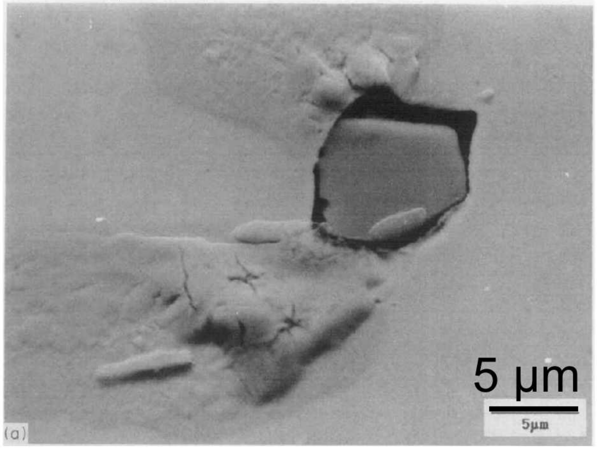


inclusion diameter x10 smaller in Cr-enriched boundaries

10x more oxygen in SLM than in wrought (0.03 vs 0.003 wt%)

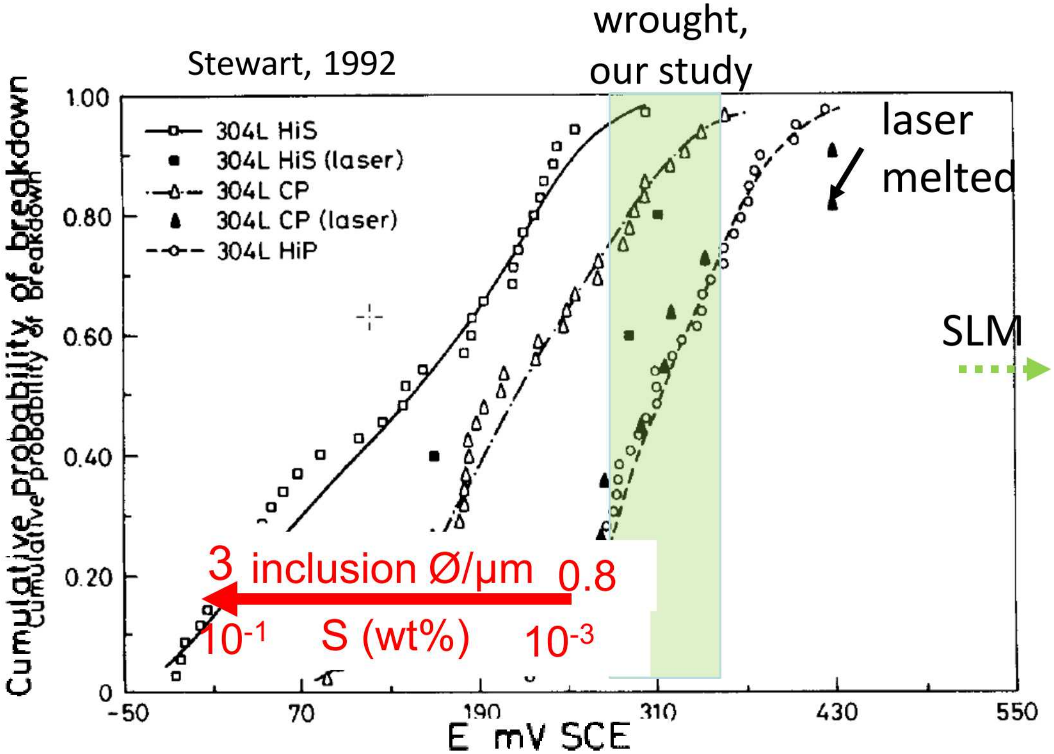
Pit Propagation at Oxide Inclusions

Baker, 1992



Undercutting of Ti-Cr-Al-O in wrought 316L

Stewart, 1992

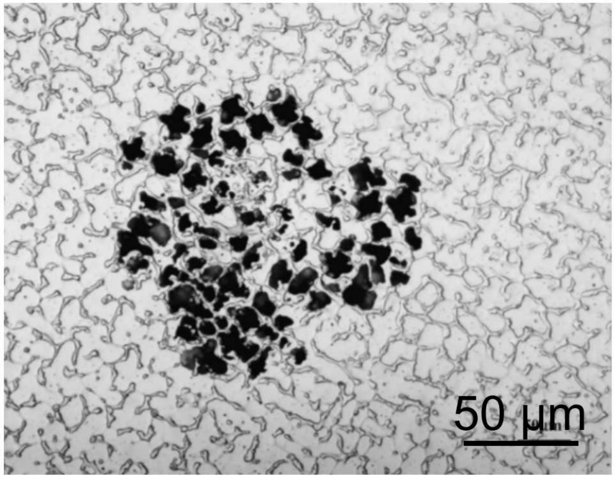


"it seems that below a certain size (as yet undetermined)….are too small to nucleate a damaging pit"

Pit stability model (Galvele, 1978)
with typical experimental pit current densities (Srinivasan, 2015) suggest
hemispherical pit growth favorable at r ≥ 1 µm

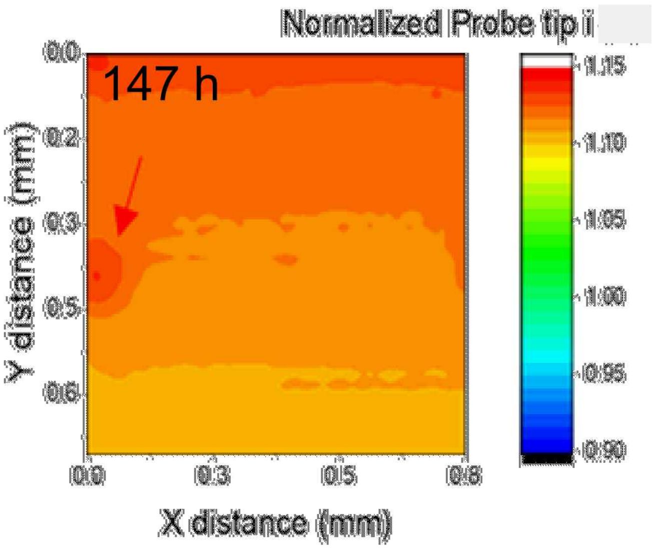
What are preferential breakdown sites outside of lack of fusion features?

Cui, Lundin, 2007

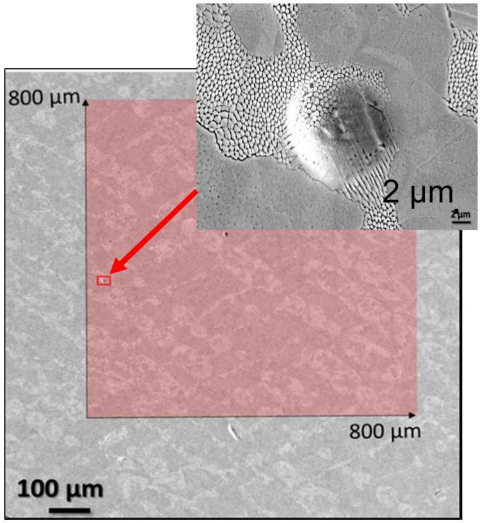


316L laser weld w/ preferential attack of γ

γ cores surrounded by δ: Cr and Ni depletion in γ

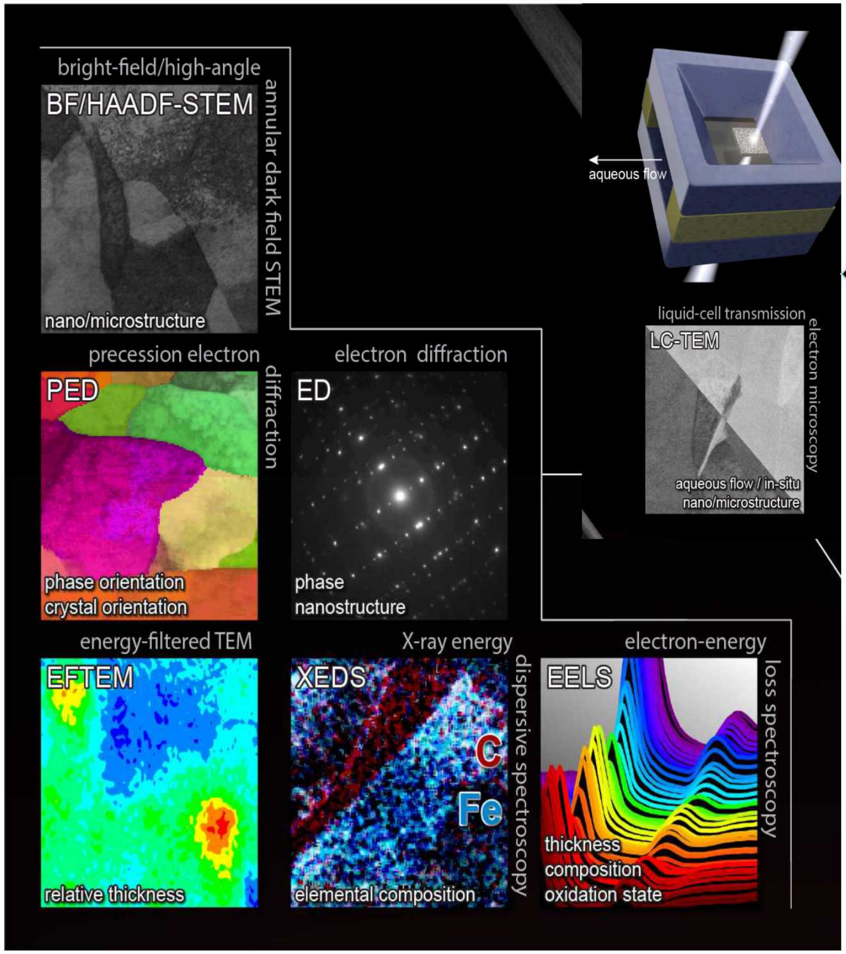


Positive Feedback SECM
0.001 KI + 0.01 M KCl, $21^{o}C$, OCP

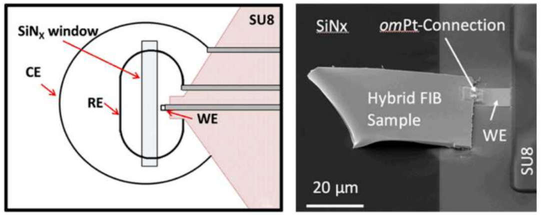


After SECM and etch
no preferential attack of substructure (primary γ) versus (primary δ)

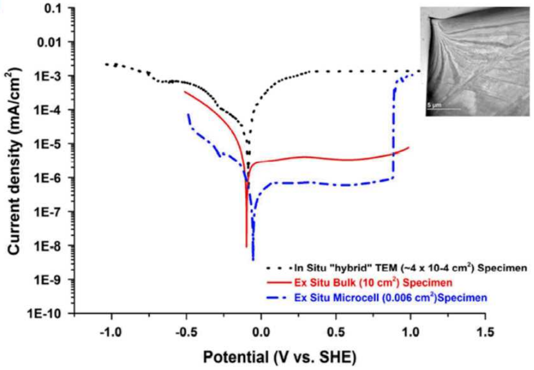
Electrochemical TEM: an Emergent Tool to Explore Nanoscale Corrosion Processes



DOE Center for Integrated NanoSciences, Jungjohann



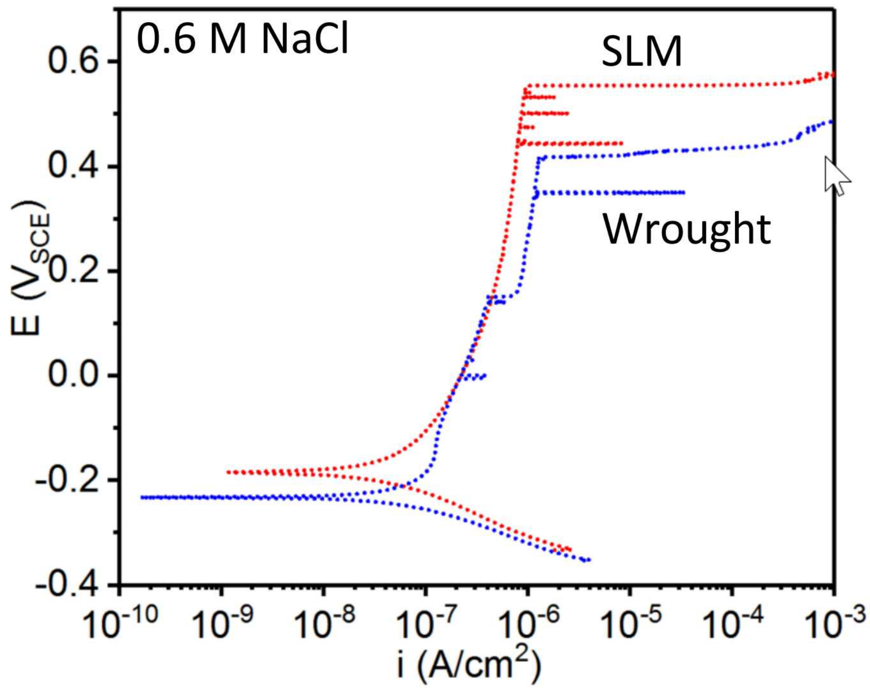
Schilling, 2017



<u>Some of the Challenges</u>

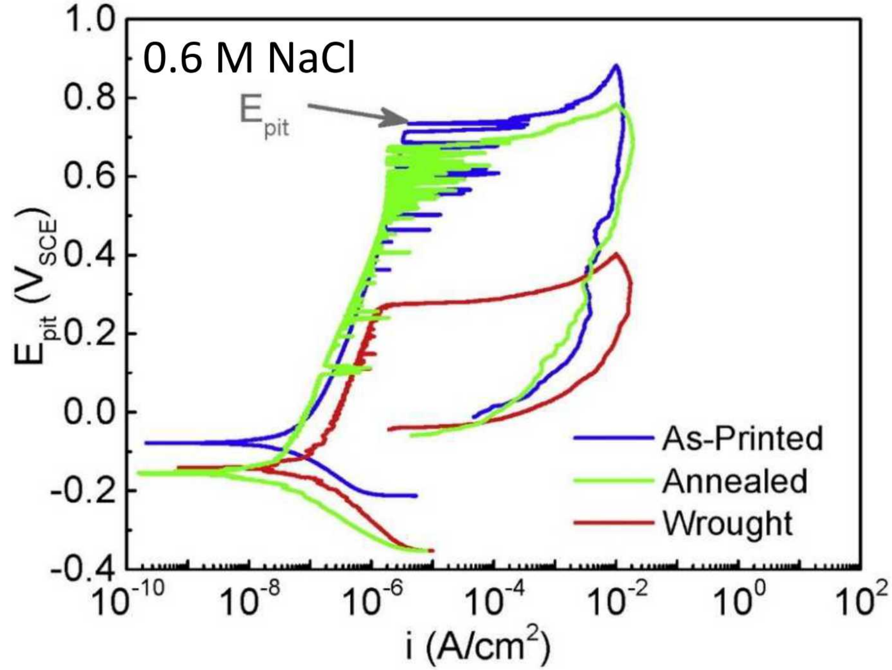
Echem dependence on ebeam current distribution, fluid flow sample preparation effects

Why the Higher Pitting Potential of SLM?



SLM 304L

Schaller, Schindelholz, et al., *Journal Electrochemical Society, 165:5 (2018) C234-C242*



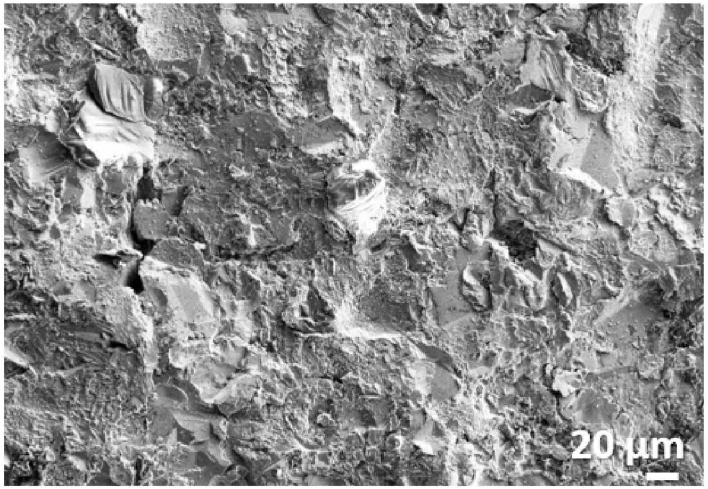
SLM 316L

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

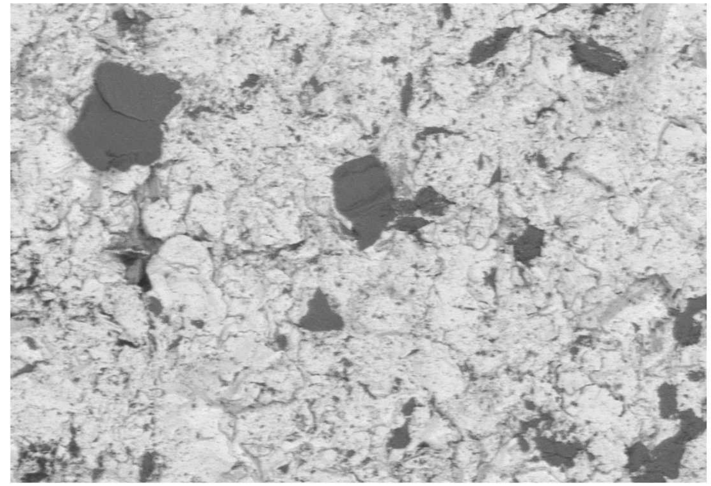
fine scale features ←→ superior* corrosion resistance to wrought

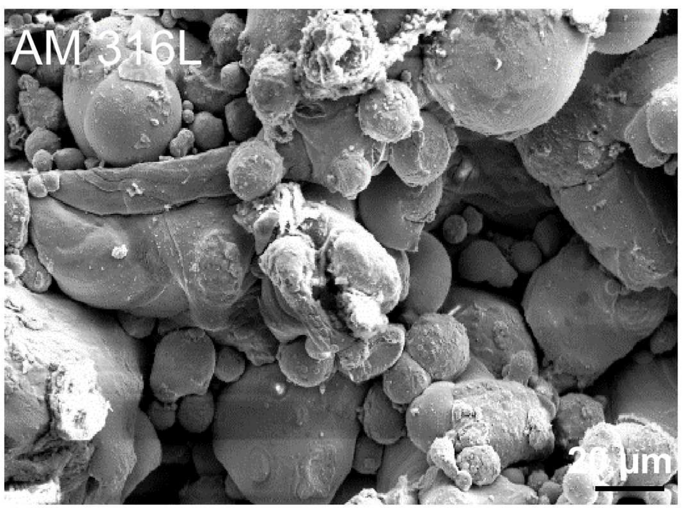
Surface Finish: A Differentiating Factor in SLM Metals

AM 304L Grit Blasted, SE

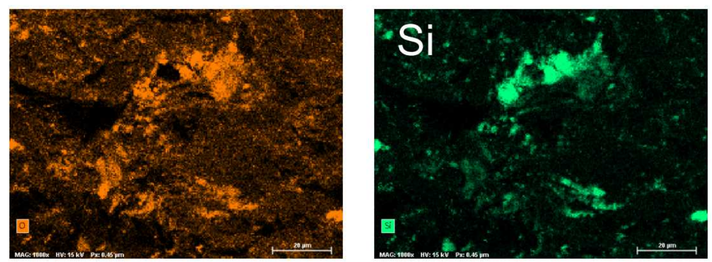


AM 304L Grit Blasted, BSE



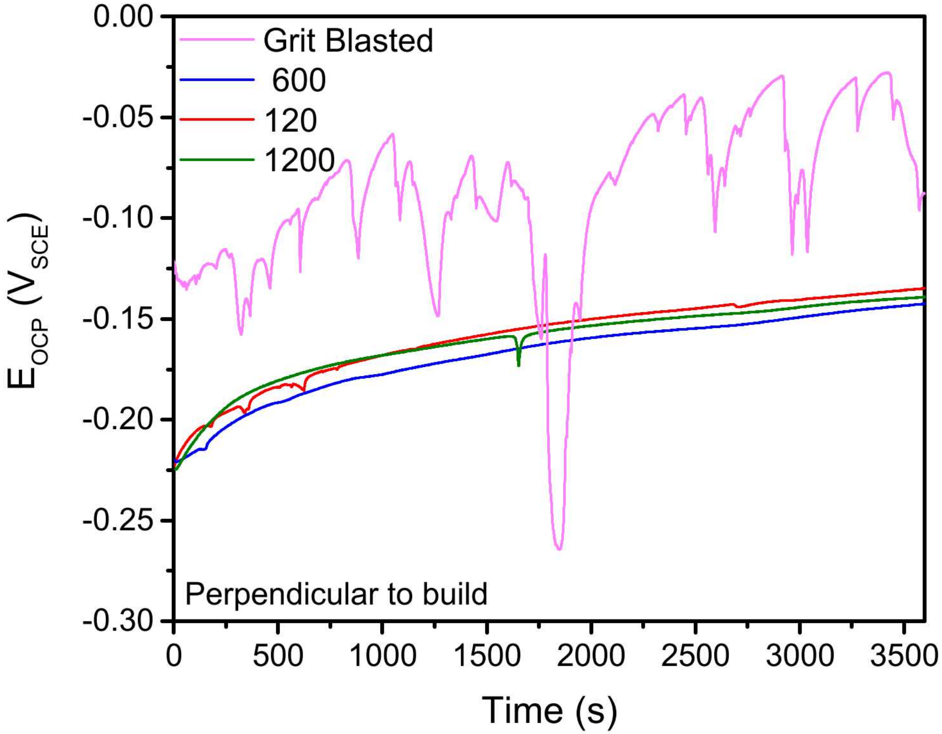


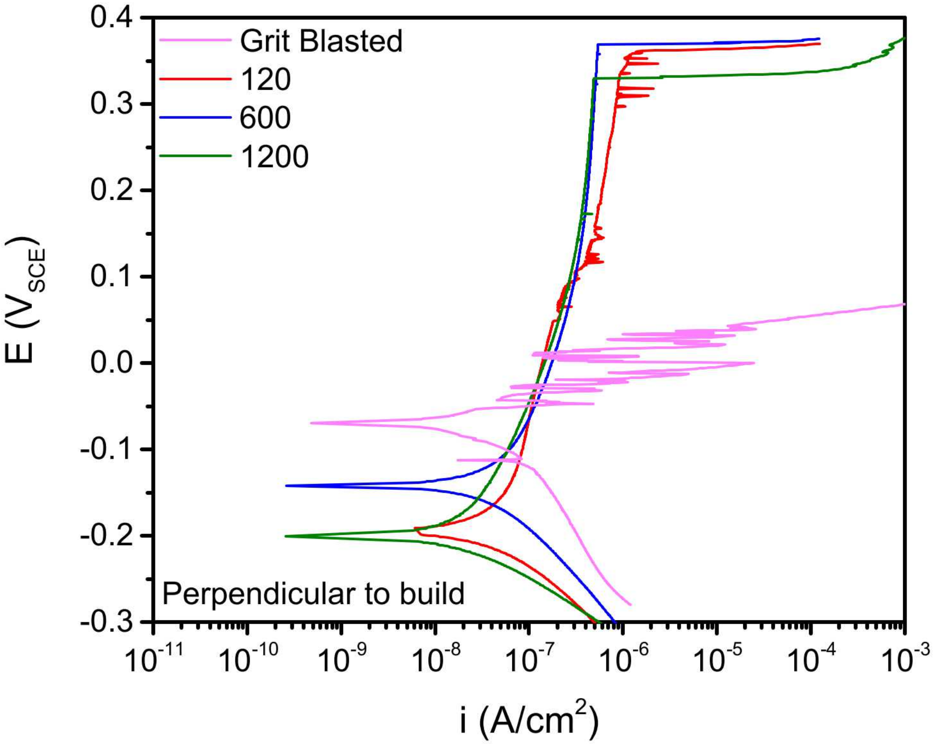
EDS of Grit Blasted Surface



Residual particles can be introduced/ embedded into the surface
→ possible crevice formers

Grit-Blasted Surface Finish Eliminates Resistance

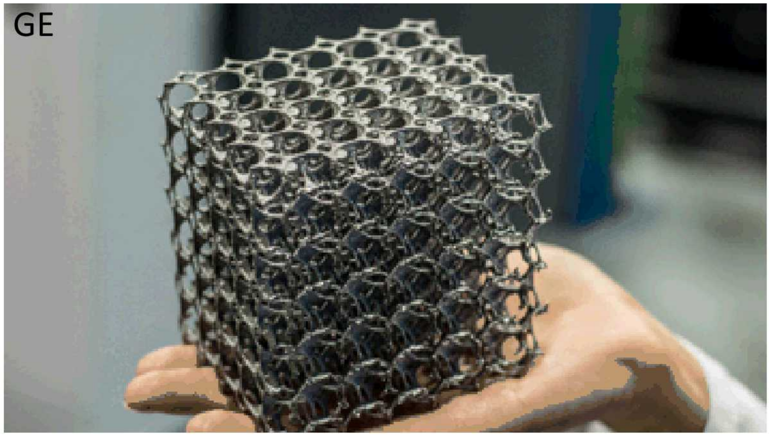




Corrosion susceptibility of AM material dependent on surface finish, grinding or polishing enhances resistance but not always applicable.

The Challenge of Surface Finish

sophisticated, unconventional 3D geometries



lattice structure

heat exchanger

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

topology optimized design

Conclusion: Some Answers… More Questions

- How do the unique features of additive metals govern corrosion resistance relative to their conventionally processed counterparts?
  - **Lack of fusion defects control E_b to first order (crevice former)**
  - **SLM 304L E_b > Wrought E_b → attribute to fine scale microstructure of SLM**
  - **Corrosion propagation from typical 304L pit initiation features not observed**
  - How does pit initiation and propagation behavior scale with nano-sized oxide, MnS and solidification subgrain features?
  - What are preferential long-term attack pathways WRT anisotropic microstructure?
  - What is environmental cracking (e.g. SCC) behavior WRT residual/applied stress?
  - Behavior in other in environments?
- What is impact of variance in alloy chemistry, AM processing and post-processing parameters on corrosion?
  - **SLM 17-4 PH – solutionizing and heat treatment erased build microstructure**
  - **304L – fast cooling rates (10^5-10^7 K/s) result in ultrafine microstructure**
  - Scan strategy, laser power, build atmosphere, powder reuse?
  - Residual stress?
- How can we take advantage of AM to create new materials exceeding performance of conventional?

Conclusion: Some Answers… More Questions

- How do the unique features of additive metals govern corrosion resistance relative to their conventionally processed counterparts?
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Extras

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 propagate relative to the highly anisotropic microstructure?
  - Preferential dissolution analogous to intergranular attack on HAZ?
  - How does it relate to SCC?