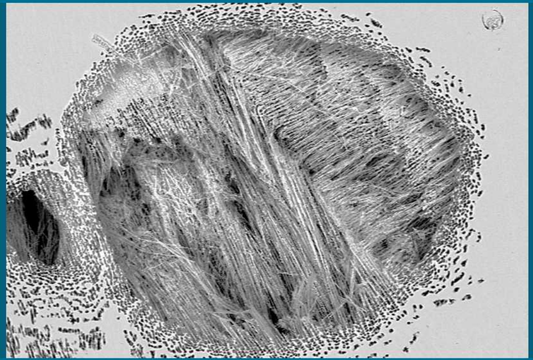
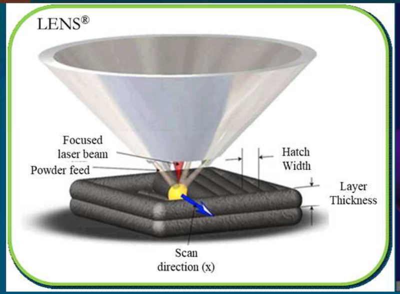
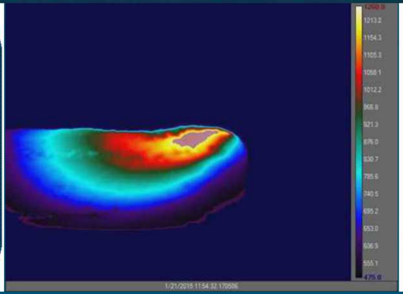
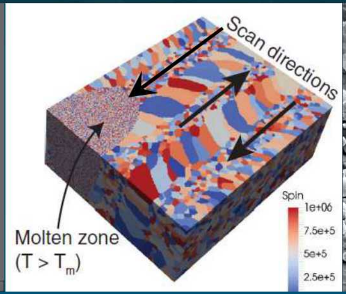
SAND2019-12250C

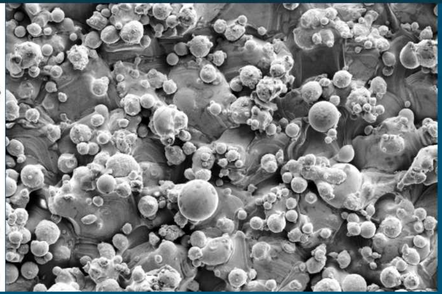
Corrosion and mechanical behavior of direct energy deposited high entropy alloys











PRESENTED BY

Presenter: Michael A. Melia

Co-authors: (SNL) Hai-duy Nguyen, Jay Carroll, Shaun R. Whetten, Michael Chandross, Nicolas Argibay, Eric Schindelholz, Andrew B. Kustas

(OSU) Saba Navabzadeh Esmaeely, Jenifer Locke

(Ames Lab) Emma White, Iver Anderson

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What is a High Entropy Alloy (HEA)?

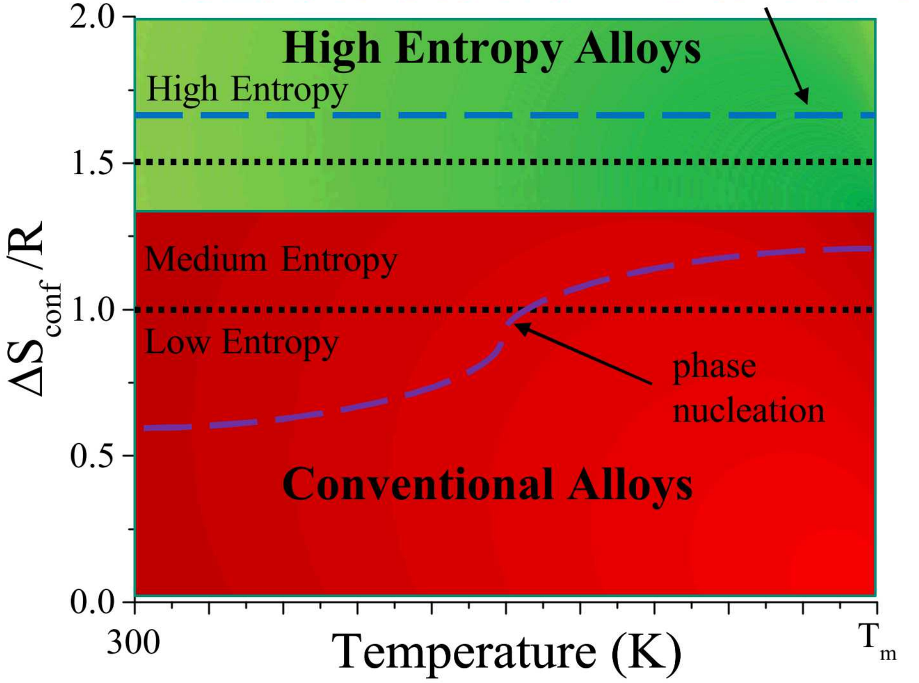
High Entropy Alloys: primarily **solid solutions** containing **5+ alloying constituents**, where the solutions have **high configurational entropy** ($\Delta S_{conf} > 1.4R$, approx. 12 J/mol-K).

High configurational entropy is believed to thermodynamically **suppresses phase separation**, a primary route for degradation of mechanical properties in conventional alloys.

Competition between Gibbs energy for solid solution and intermetallic formation.

$$\Delta G^{SS} < \Delta G^{IM} \quad \rightarrow \quad \Delta S^{SS} > \frac{\Delta H^{IM} - \Delta H^{SS}}{T}$$

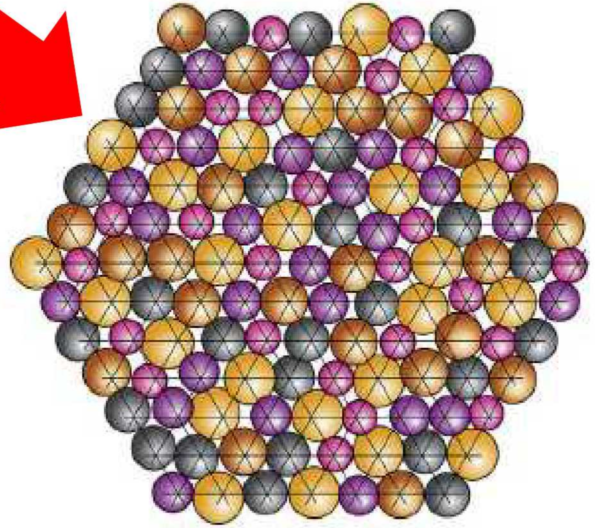
Stable solid solution microstructure



D. Miracle, 2014

$$\Delta S_{conf} = -R \sum_i X_i \ln(X_i)$$

Assuming regular/ideal solution.



Disordered solid solution

D. Miracle, 2017

Slide 2

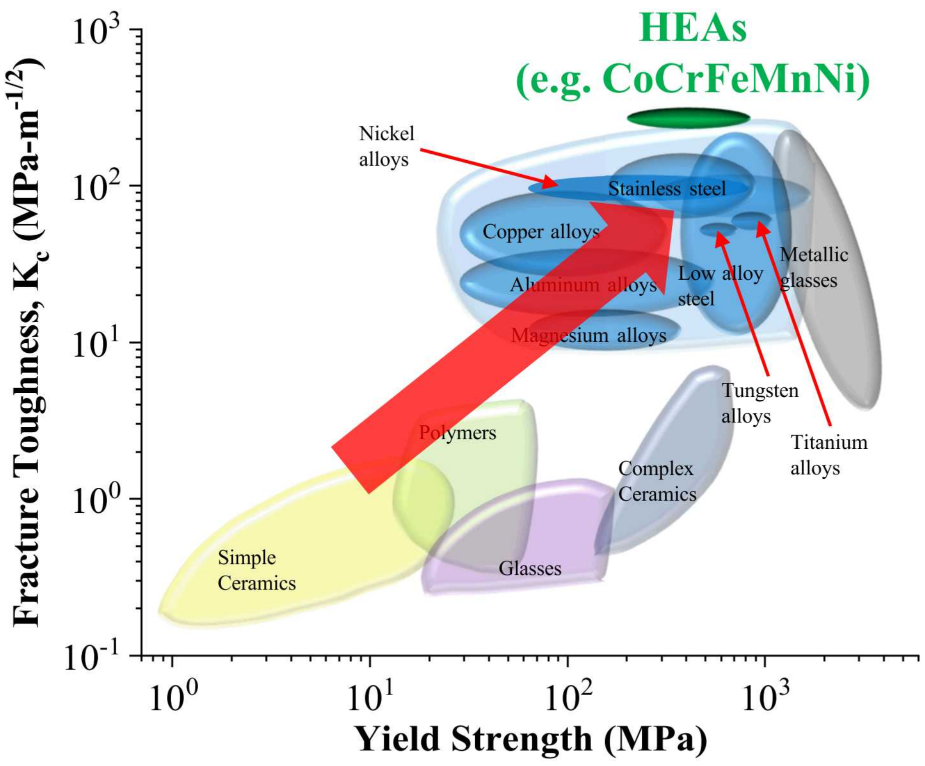
SEJ20 Title could be "What is a High Entropy Alloy?

Schindelholz, Eric John, 3/20/2019

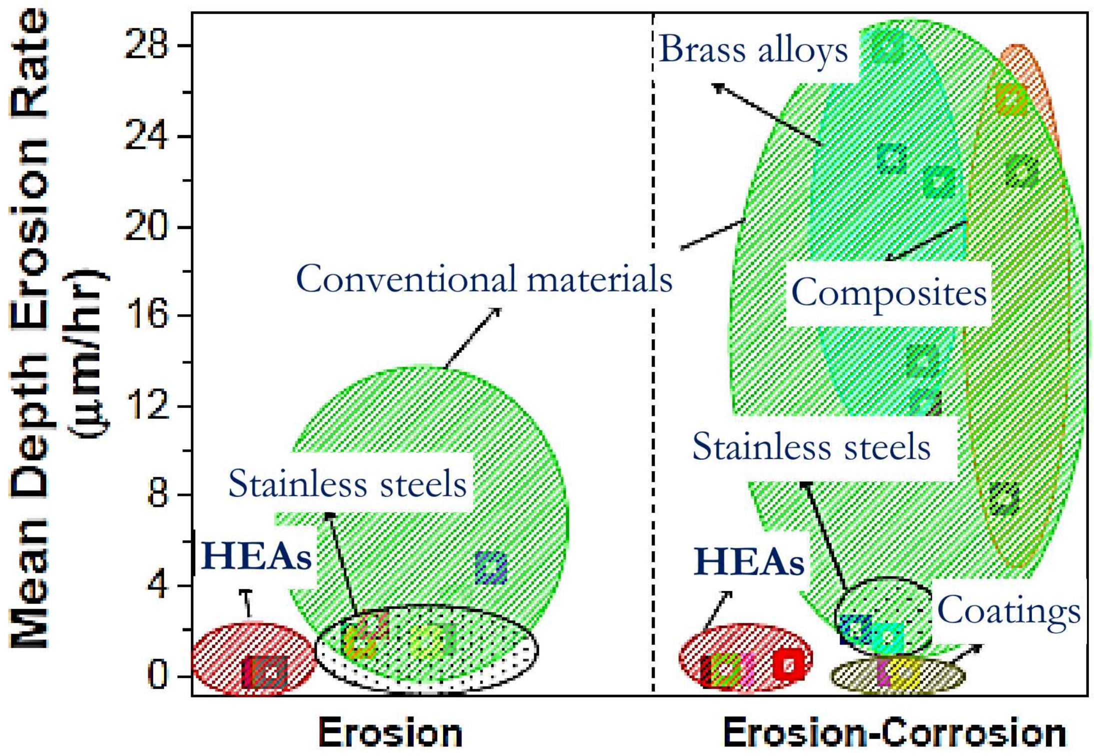
SEJ21 Also, why should we care about HEA for corrosion? What advantages over convetional alloys?

Schindelholz, Eric John, 3/20/2019

High Entropy Alloys (HEAs): Unusual mechanical properties



B. Gludovtaz, 2014



A. Ayyagari, 2018

Additive Manufacturing of HEAs

Why AM?

(1) Faster cooling rates promote single phase, (2) minimize waste of expensive material, (3) non-metallic inclusion size, (4) opportunity for combinatorial exploration of HEA compositions.

To date, AM studies have shown:

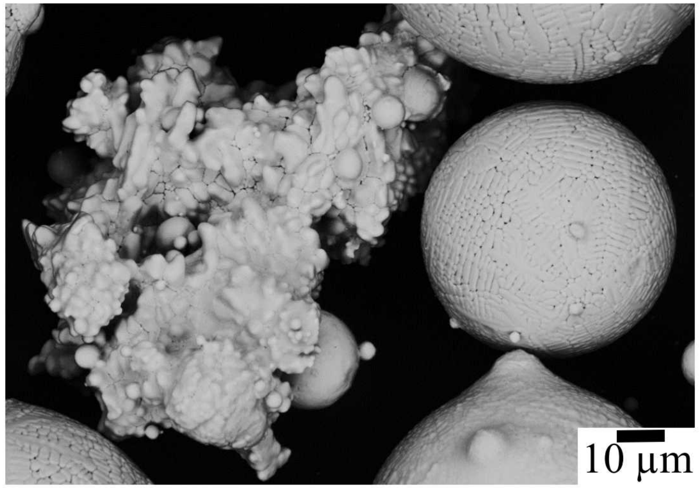
- Several studies on AM HEAs, specifically CoCrFeMnNi alloy looking at mechanical behavior.
- No work on corrosion of AM CoCrFeMnNi.

Study objectives

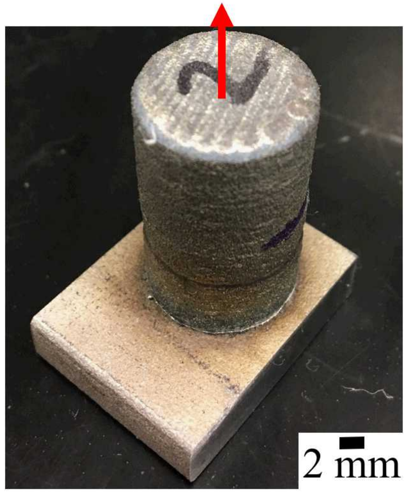
- Demonstrate feasibility of directed energy deposition (DED) for HEA processing low porosity, single phase part.
- Understand process-microstructure-mechanical, corrosion relationship.
  - CoCrFeMnNi as model alloy
    - Hypothesis - 20 at% Cr with Fe-Ni imparts passivity similar to SS 304.

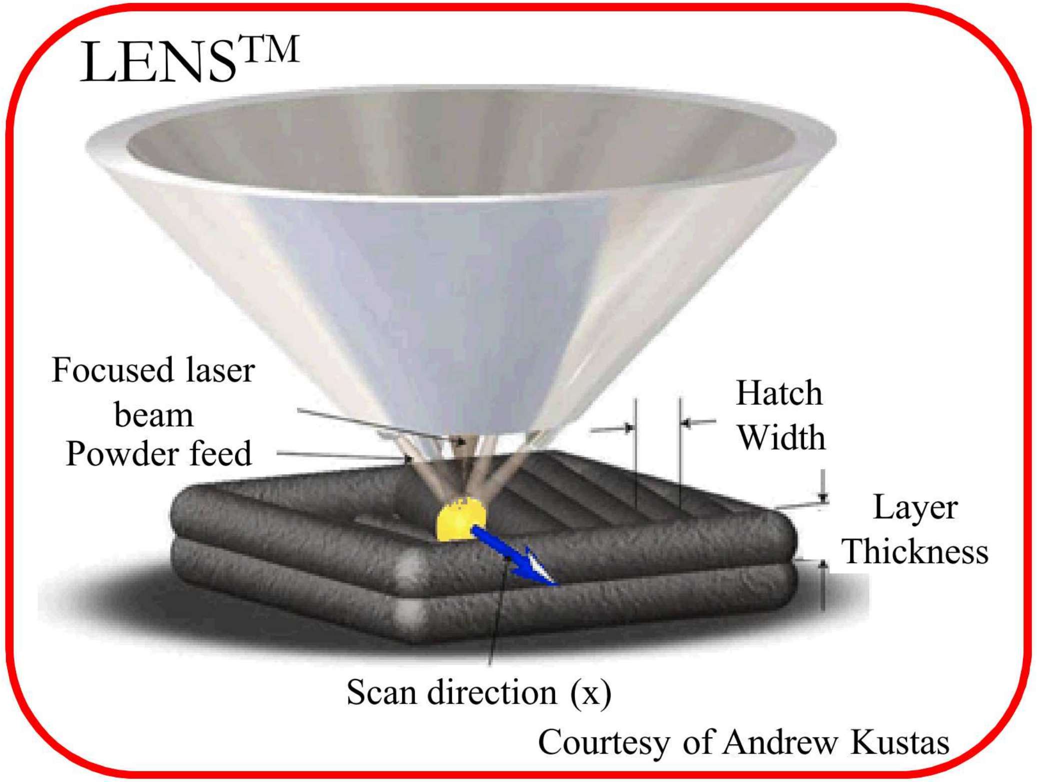
Powder and DED characteristics

Average powder diameter = 67 µm



Build direction





Open architecture Laser Engineered Net Shaping (LENS) system using a 2kW fiber laser (1064 nm):

- Inert atmosphere maintained at <50ppm O_2 and <10ppm H_2O by a continuously flowing Ar gas.
- Laser power: 350 – 400 W.
- Build velocity: 400 – 600 mm/min.
- A 90 degree cross hatch build pattern was employed, first material deposited each layer was the perimeter of the build.

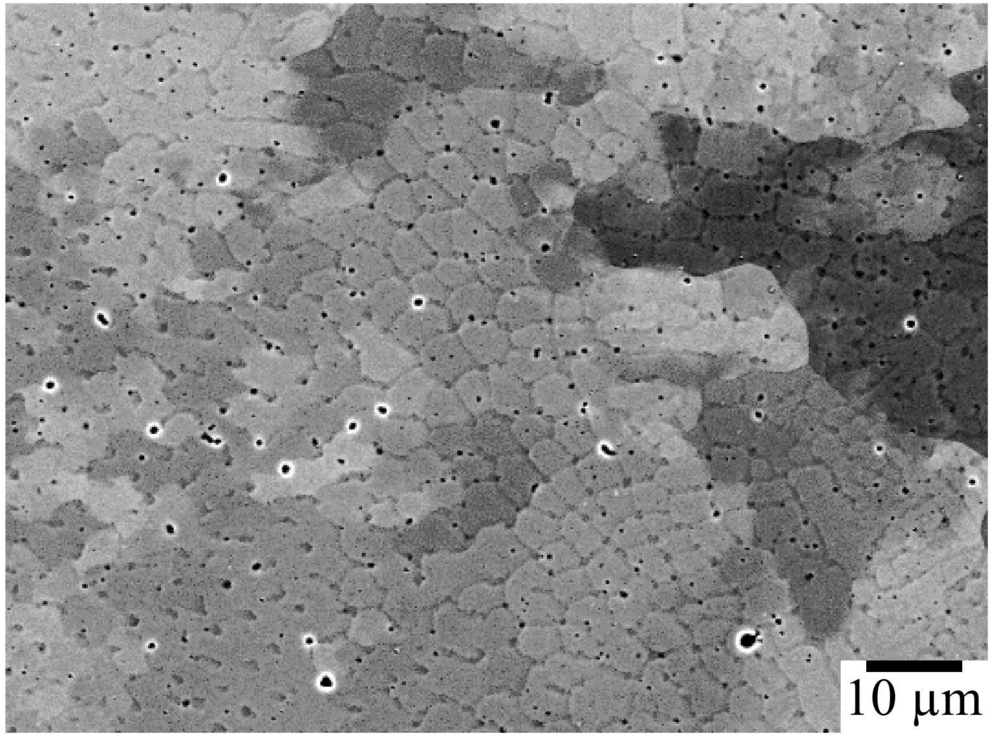
Composition (wt%)	Al	C	Co	Cr	Fe	Mn	Ni	N	O	S
Powder	0.003	0.005	20.91	18.46	20.14	19.06	21.34	0.002	0.064	0.008
As-built	0.006	0.005	21.3	18.2	20.5	18.5	21.5	0.0021	0.055	0.005

Powder from Ames Lab: Drs. Emma White and Iver Anderson

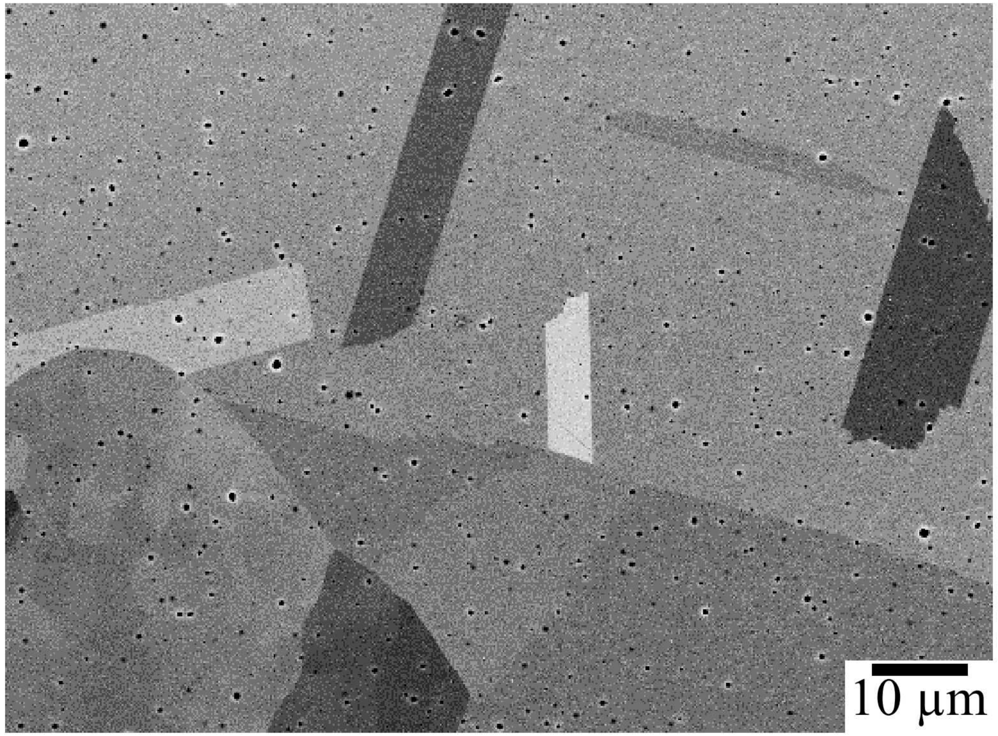
Chemical analysis by NSL Analytical.

Microstructural Characteristics

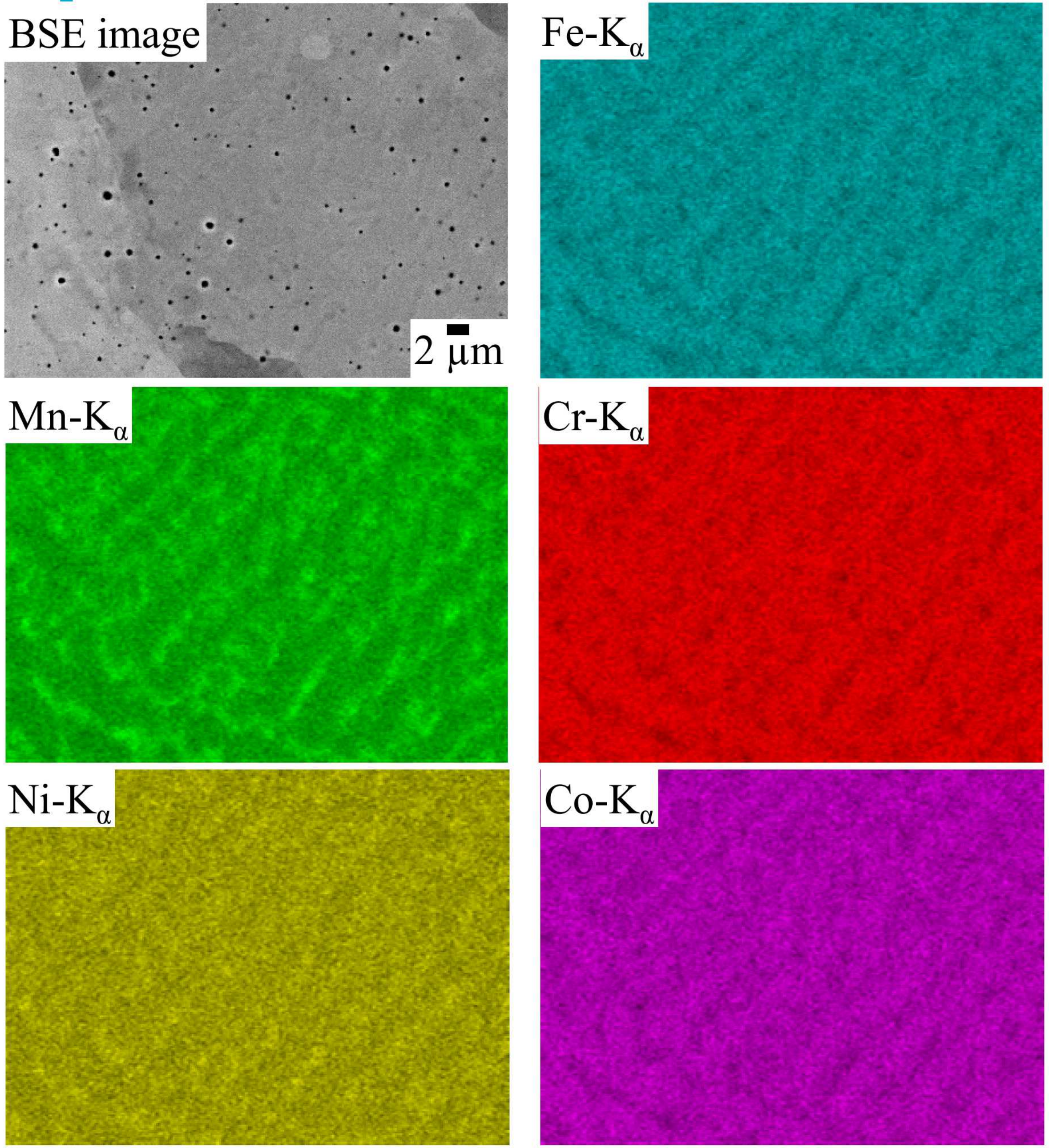
As-built

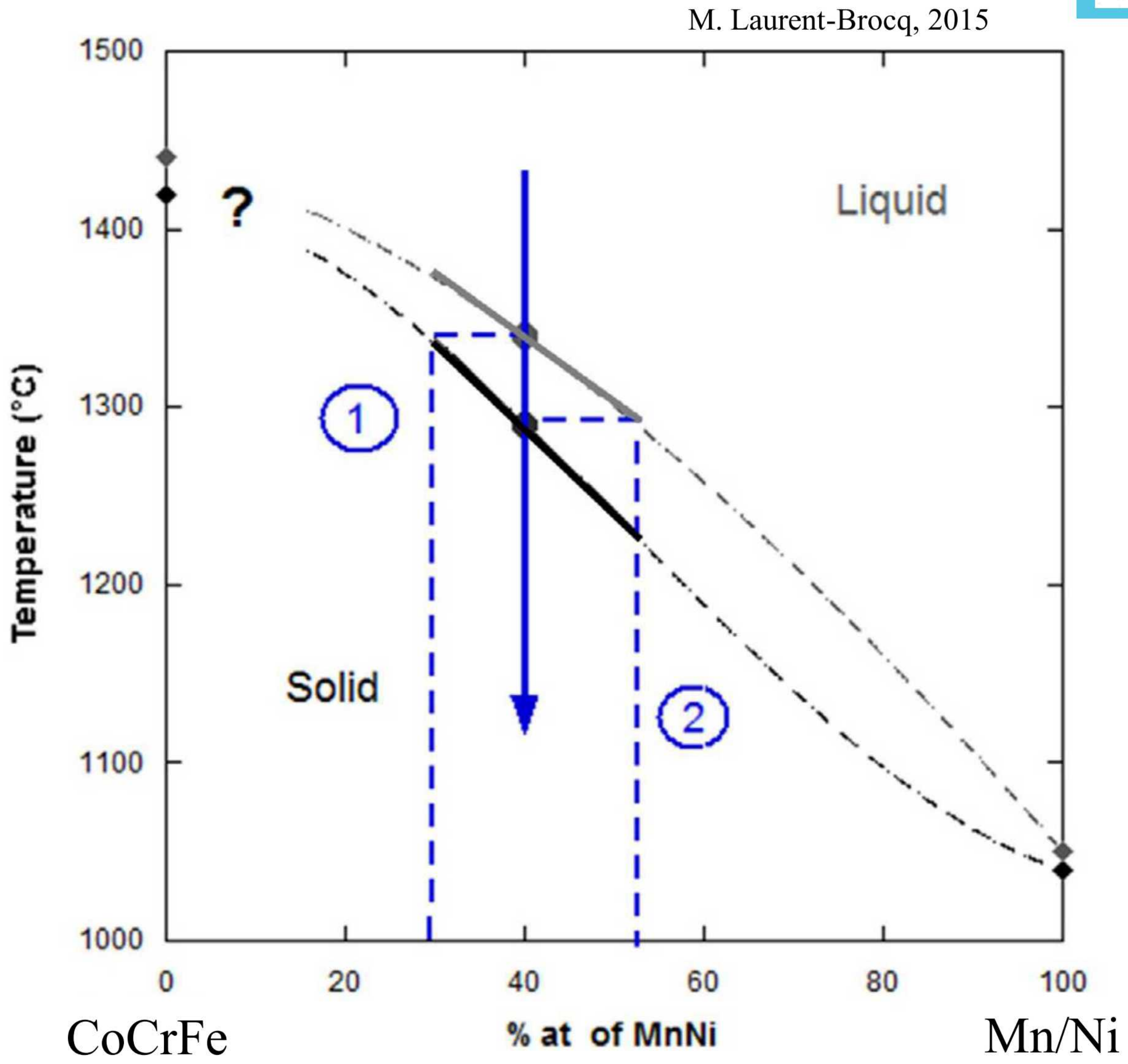


Annealed (1100C/1 hr)



Microstructural Characteristics: As-built



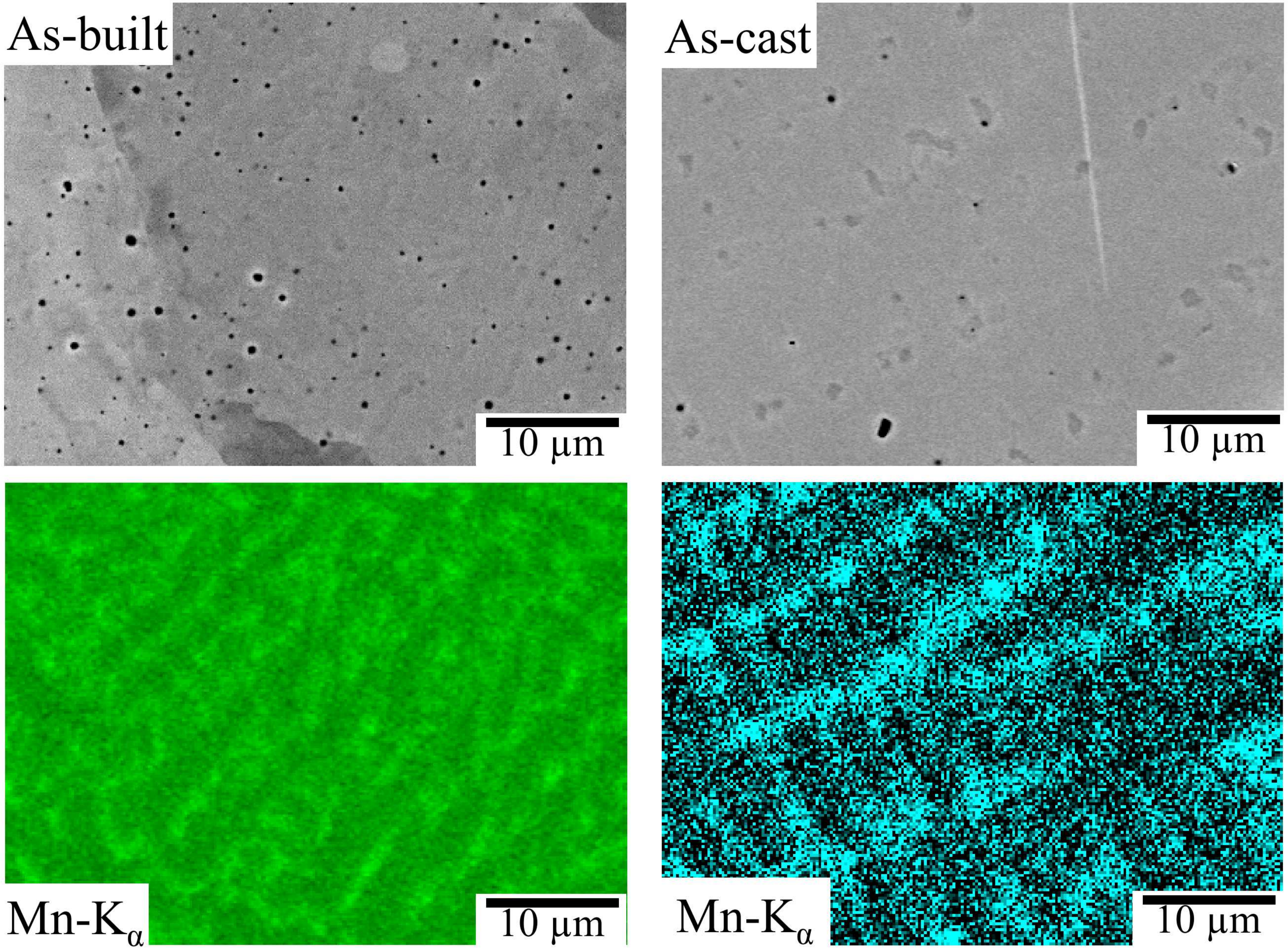


Mn/Ni enriched at interdendritic regions.

Microstructural Characteristics

Interdenrite thickness: 0.5 – 1 μm

Cooling rate: 10^3-10^4 K/s

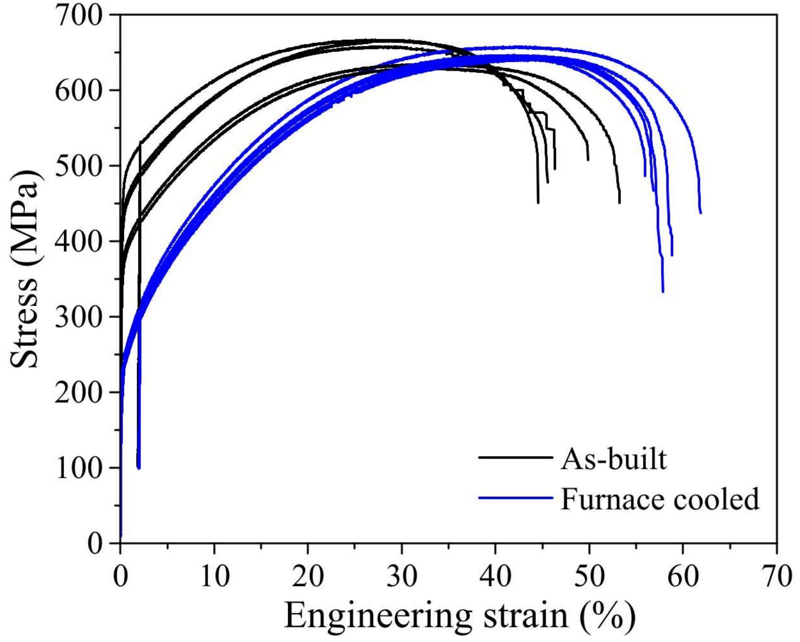


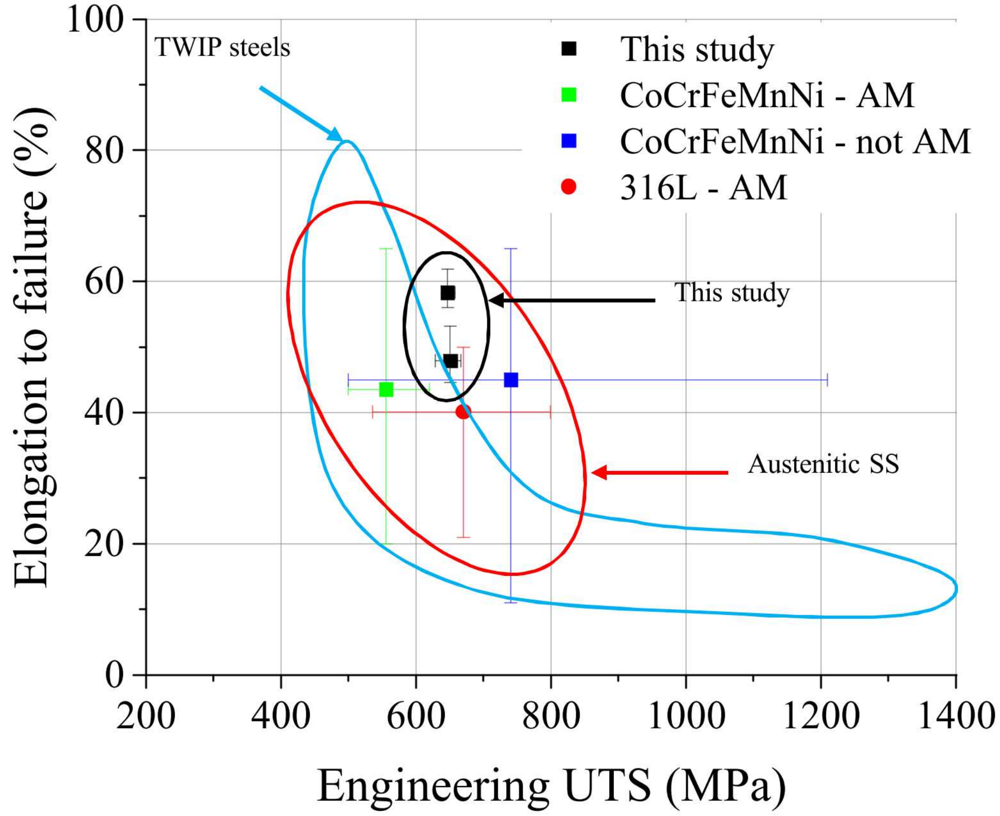
Courtesy of Bucknell University

Interdenrite thickness: ~ 5 μm

Cooling rate: 10^0-10^2 K/s

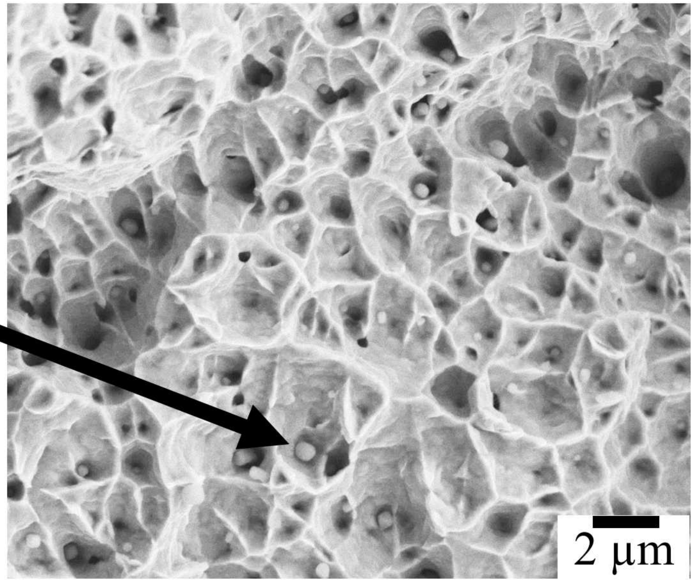
Mechanical properties of CoCrFeMnNi alloy





SEJ27
SEJ32
SEJ33
SEJ34

Oxides



Slide 9

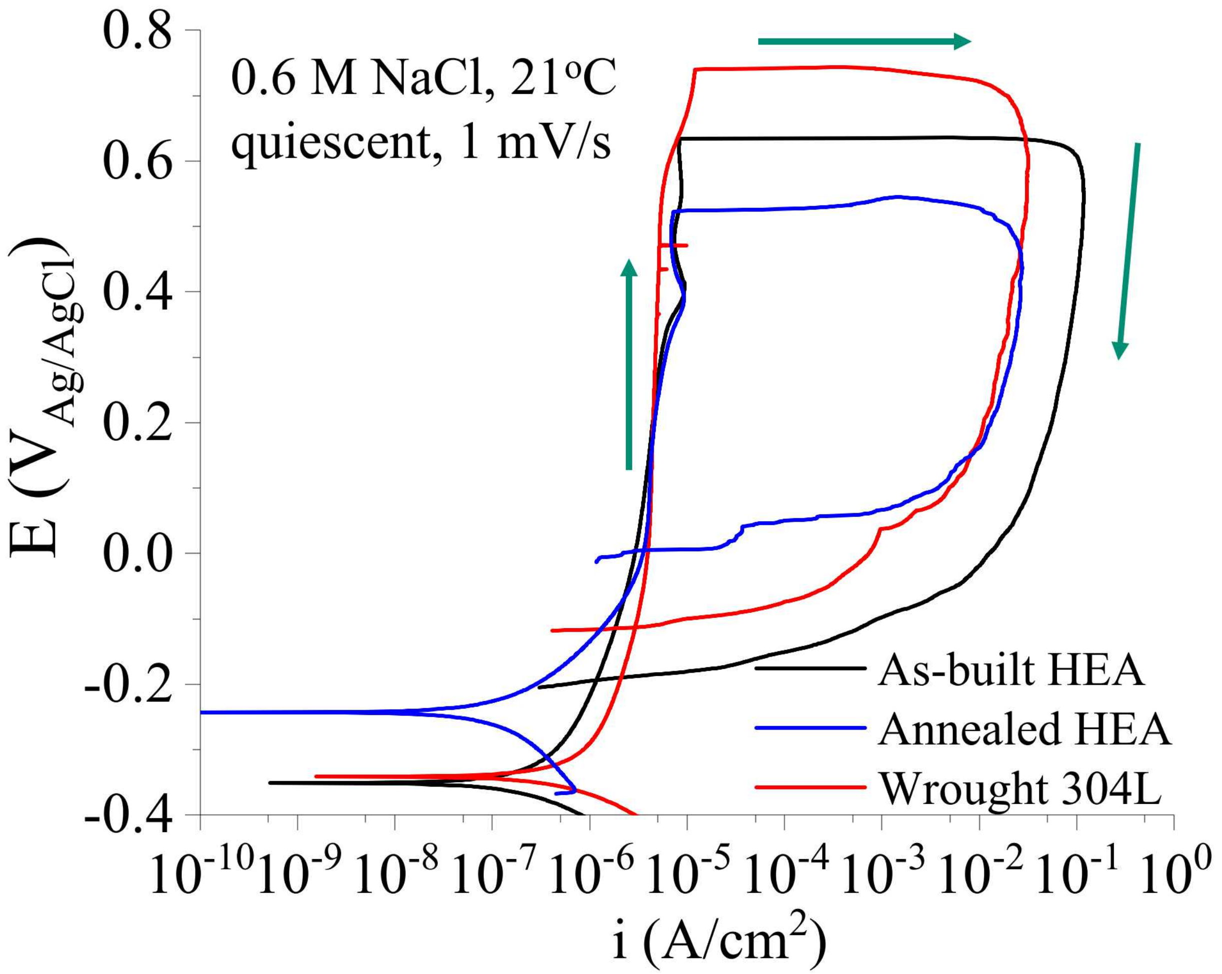
SEJ27 this plot is going to be really hard to read- font should be 18, but at the very least 16.
Schindelholz, Eric John, 3/21/2019

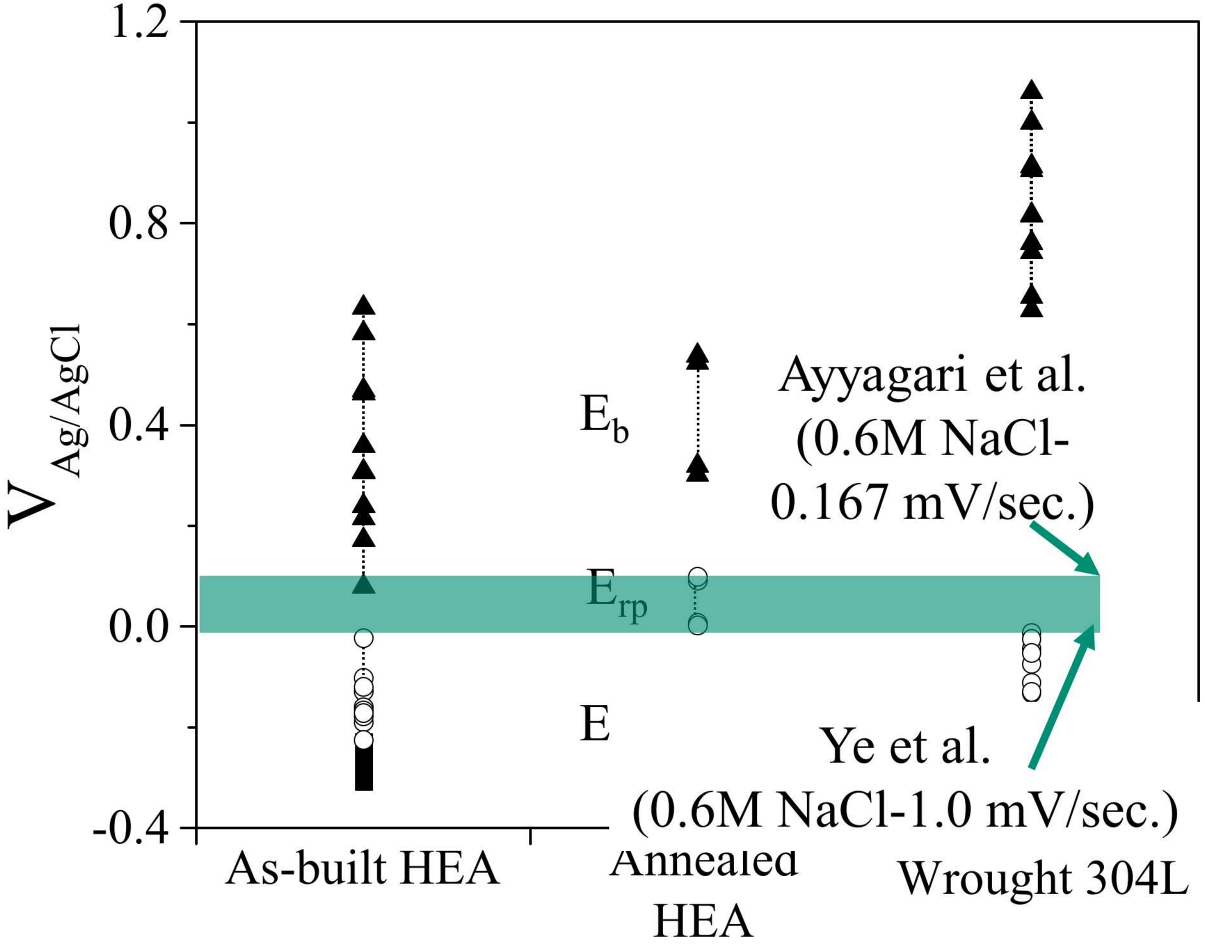
SEJ32 Be speciffci in descripttion. is "not AM" all just cast? If so, state "cast" instead.
Schindelholz, Eric John, 3/21/2019

SEJ33 Is green cantor alloy "AM" all SLM? or is there DED as well? State "SLM" or "SLM, DED". Same with 316L
Schindelholz, Eric John, 3/21/2019

SEJ34 Why are there two points for "this study" Annealed and As-built. If so, differentiate these in the plot.
Schindelholz, Eric John, 3/21/2019

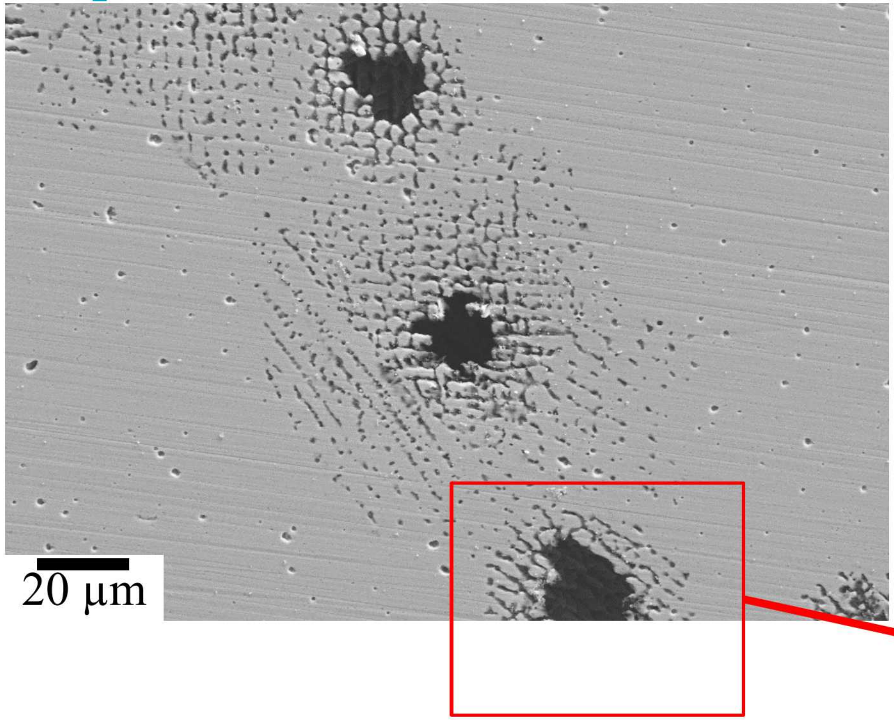
Anodic polarization behavior of CoCrFeMnNi alloy

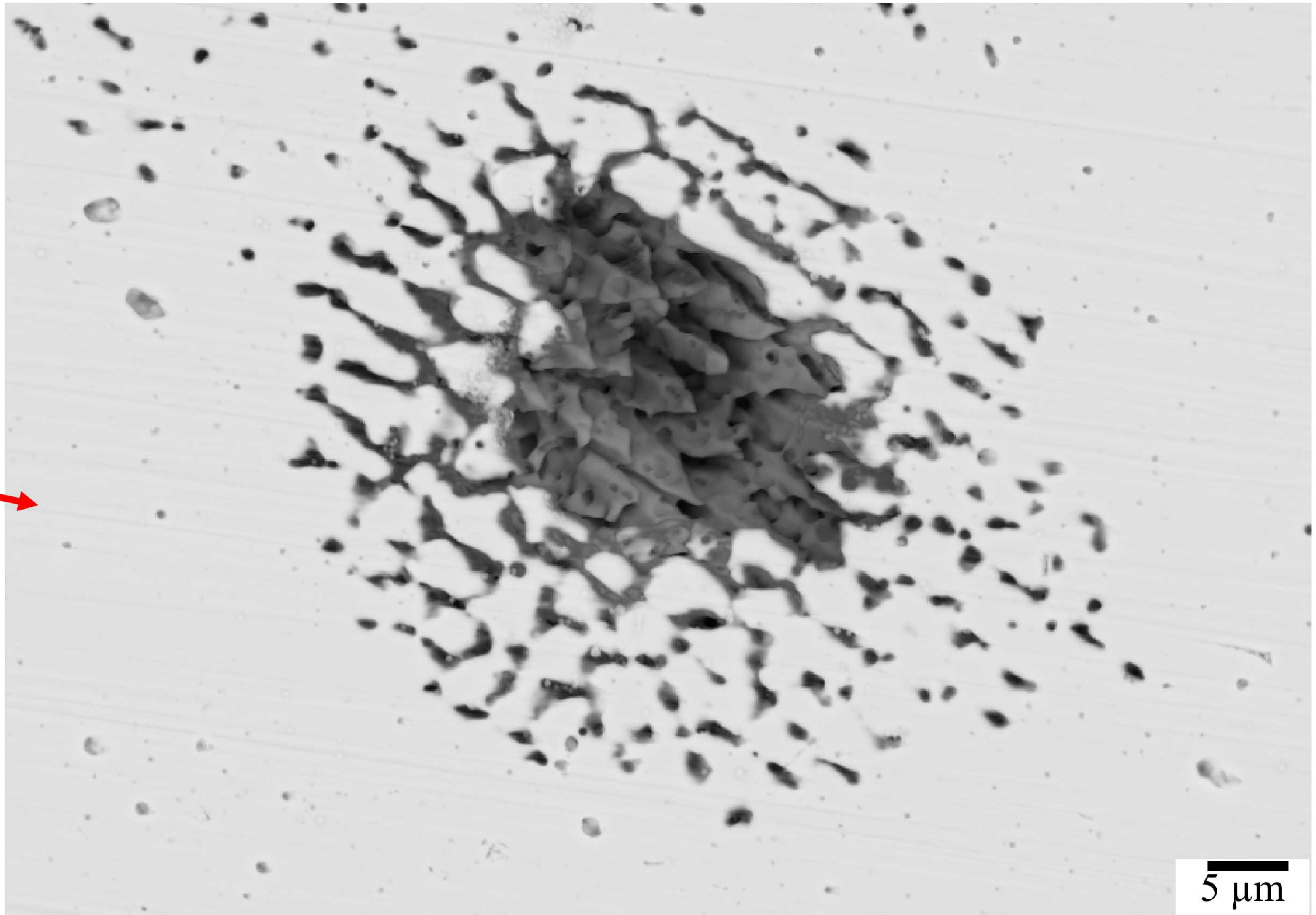




What is responsible for difference in E_b between CoCrFeMnNi and 304L?

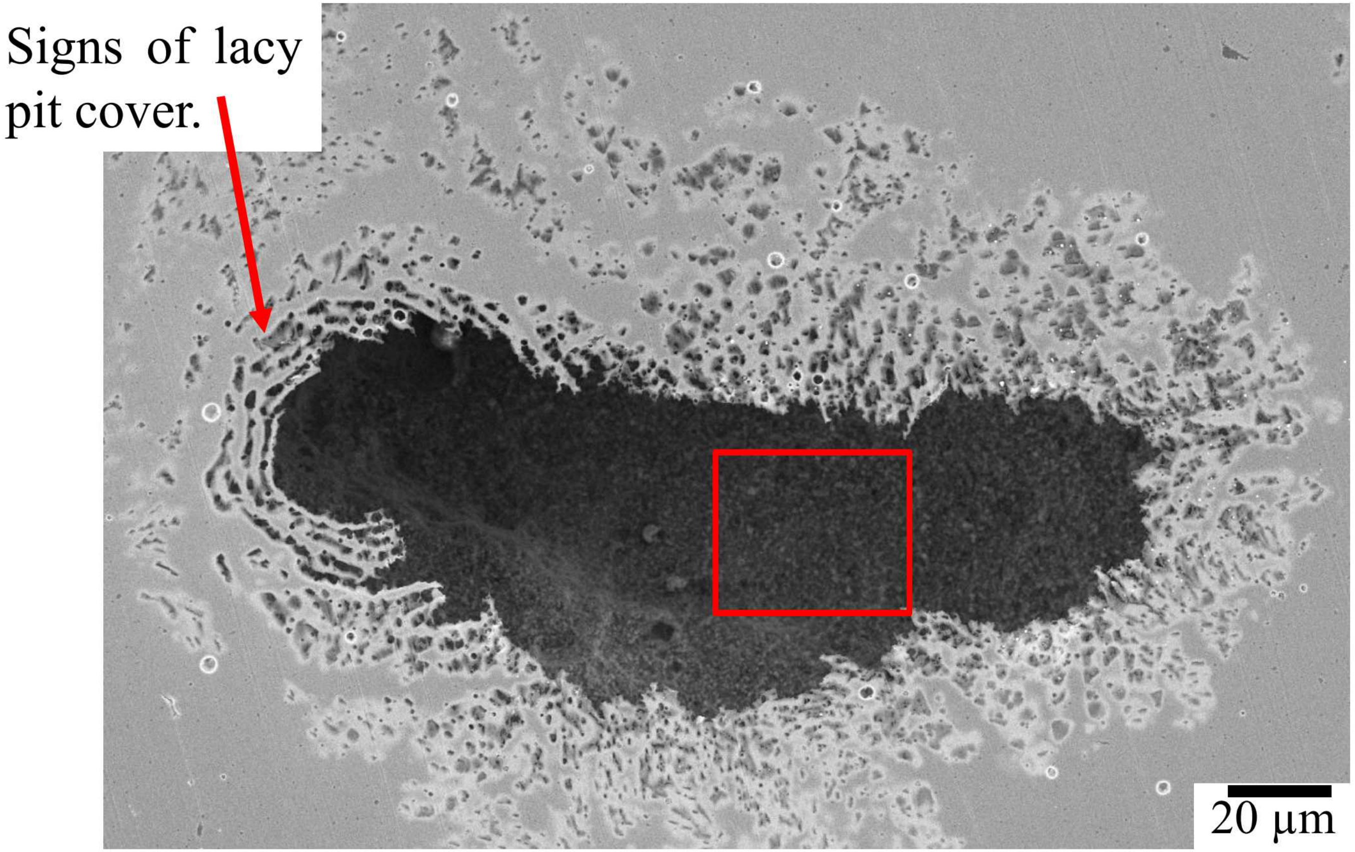
Pit morphology of CoCrFeMnNi alloy – **as-built**

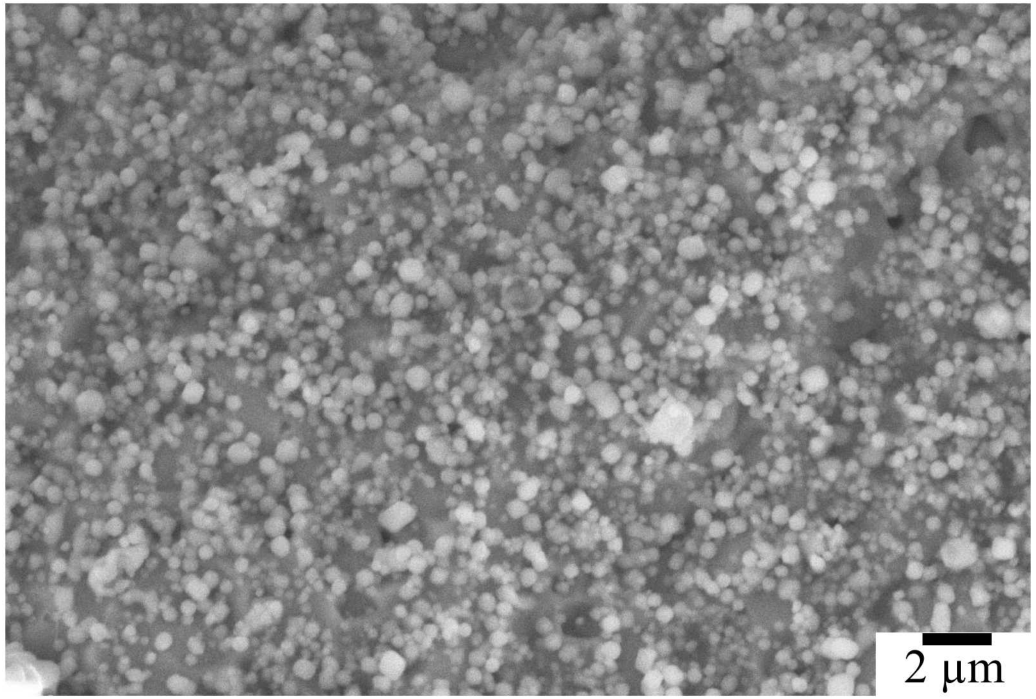




- Interdendrite regions are preferentially corroding
- Tortuous pitting morphology associated with interdendrite regions.

Pit morphology of CoCrFeMnNi alloy – **annealed**





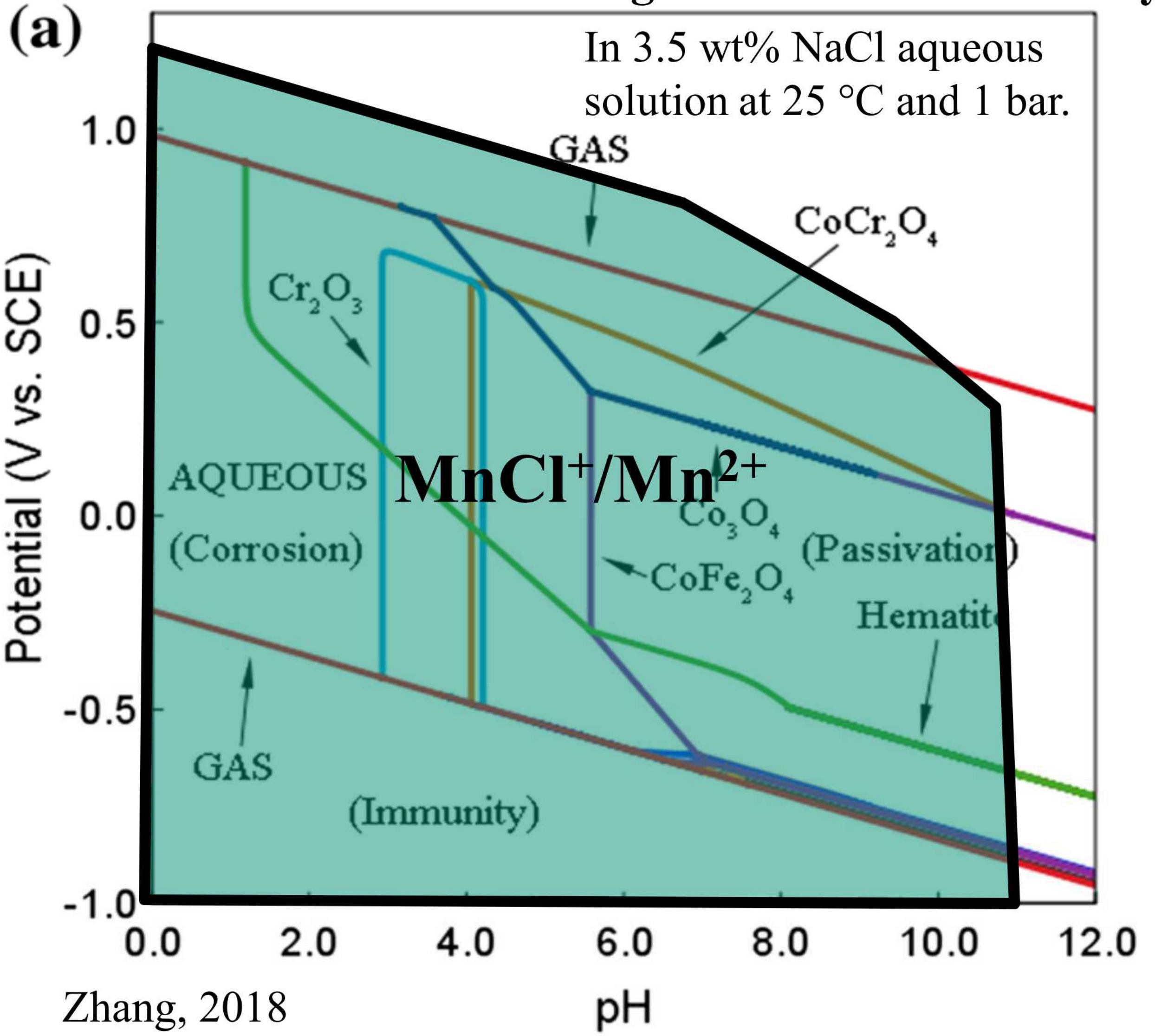
Particles at pit bottom.

Typically observed lower number of pits on the annealed specimen after a CPP measurement.

Pit bottom was smooth compared to as-built HEA. **Pit stability implications?**

Passive behavior of CoCrFeMnNi alloy

Calculated Pourbaix diagram for CoCrFeNi alloy

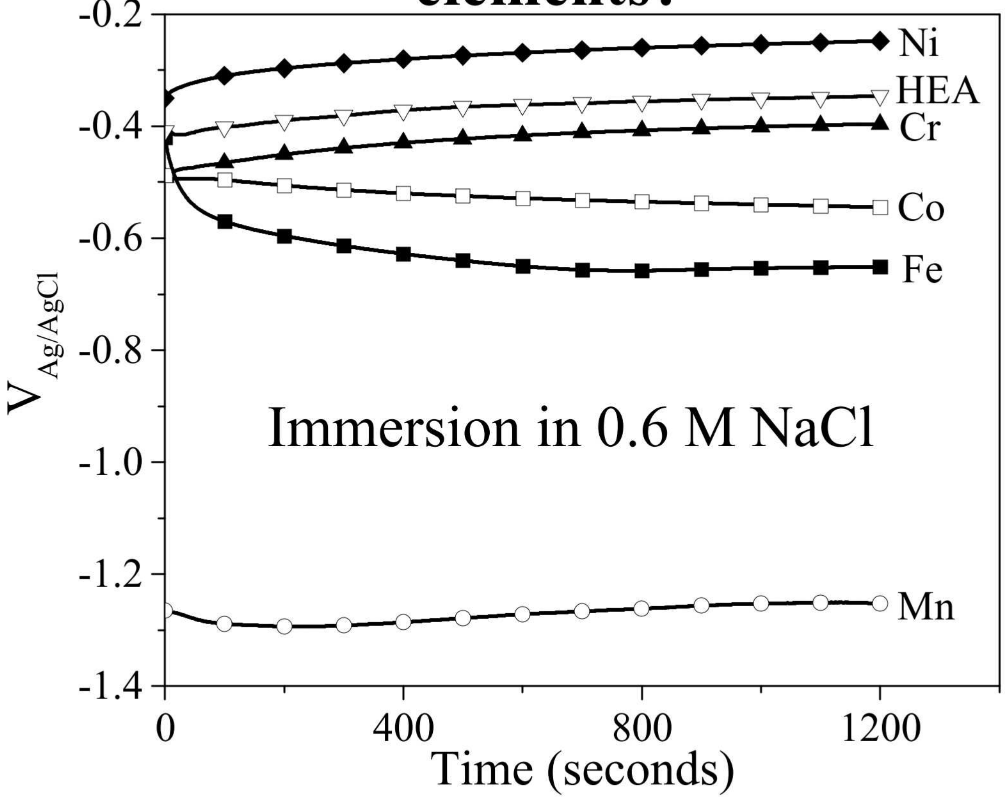


Zhang, 2018

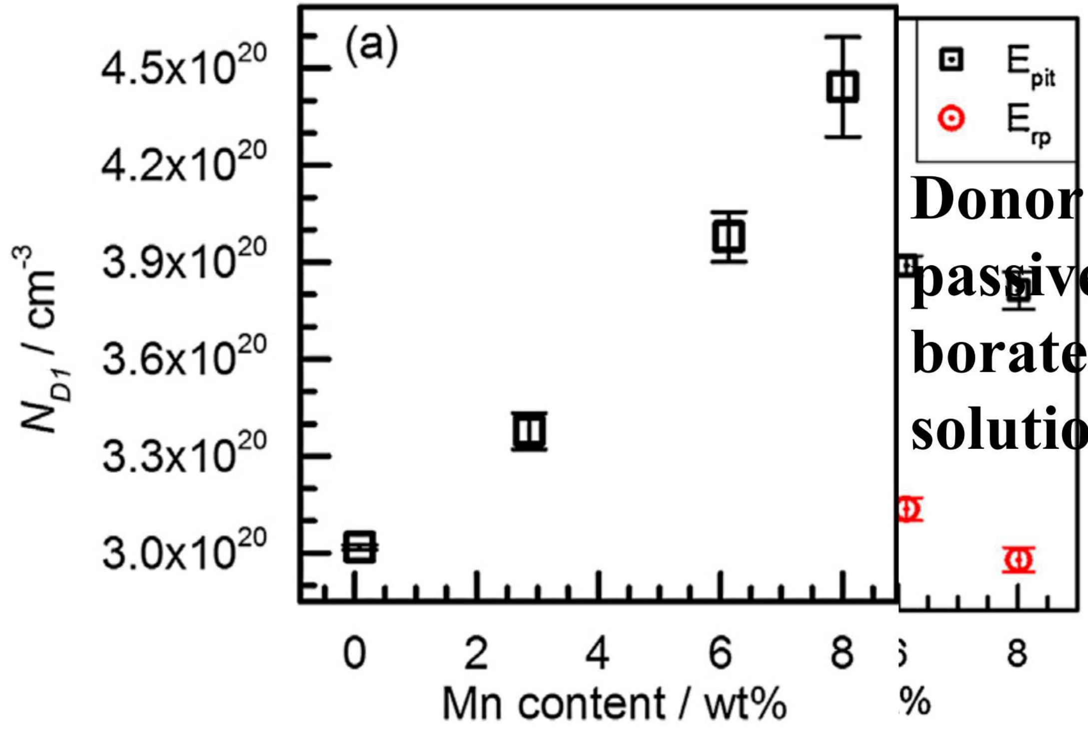
Anodic polarization behavior of CoCrFeMnNi alloy

What is responsible for difference in E_b between CoCrFeMnNi and 304L?

What about the additional alloying elements?



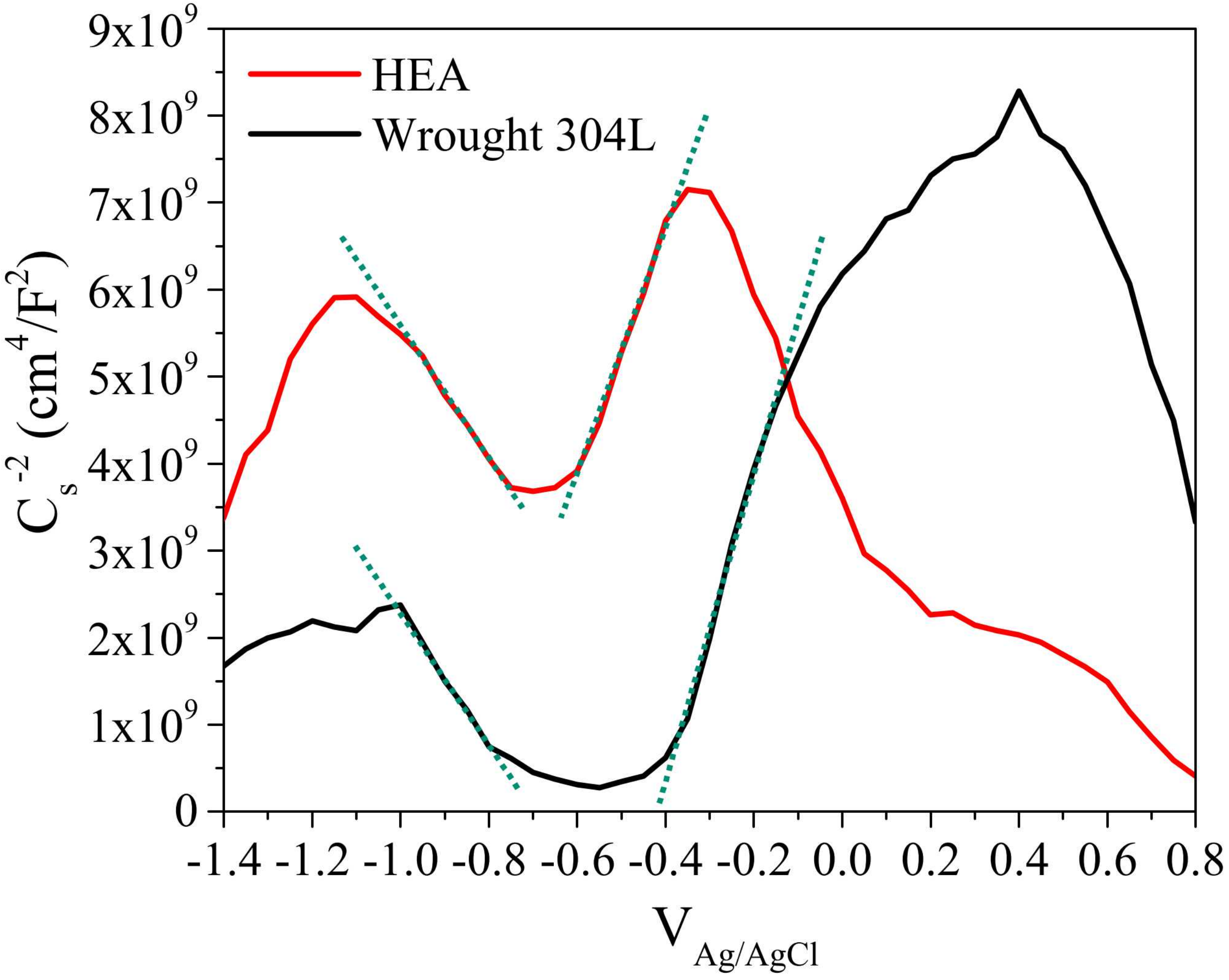
Few studies determined the fate of Mn, however observed/stated a reduction in stability of the passive film.



Donor density of passive film in borate buffer solution.

H.-Y. Ha, M.-H. Jang, T.-H. Lee, Influences of Mn in solid solution on the pitting corrosion behaviour of Fe-23 wt%Cr-based alloys, Electrochimica Acta, 191 (2016) 864-875.https://doi.org/10.1016/j.electacta.2016.01.118

Anodic polarization behavior of CoCrFeMnNi alloy



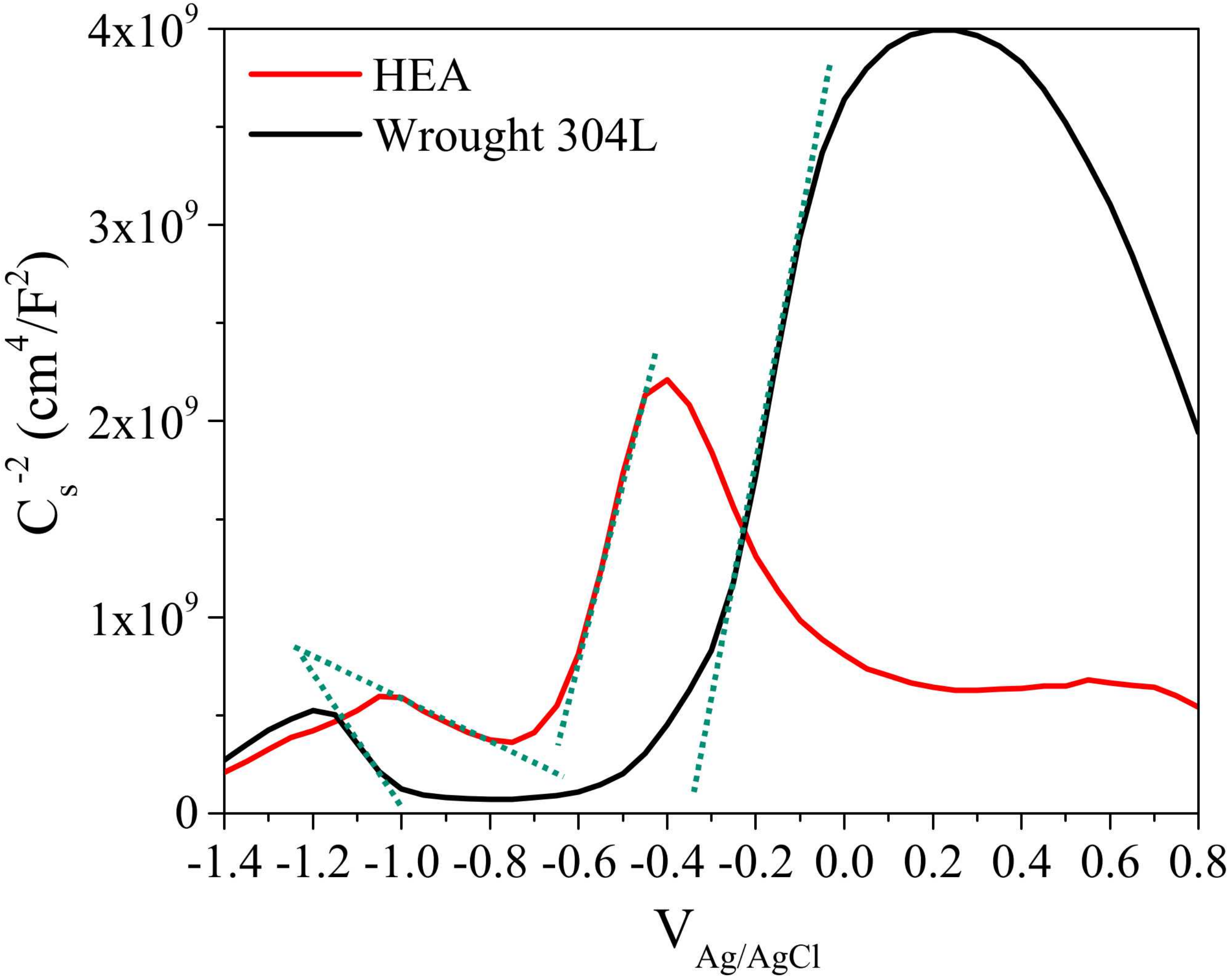
Mott-Schottky analysis of 304L and HEA.

- **Borate buffer solution (pH = 9.2).**
- Potential hold at 600 mV vs. Ag/AgCl for 1 hour.

Donor density for p-type (Cr oxide) and n-type (Fe oxide?) were similar.

$$dC^{-2}/dE = 2/\varepsilon\varepsilon_0 e N_D$$

Anodic polarization behavior of CoCrFeMnNi alloy



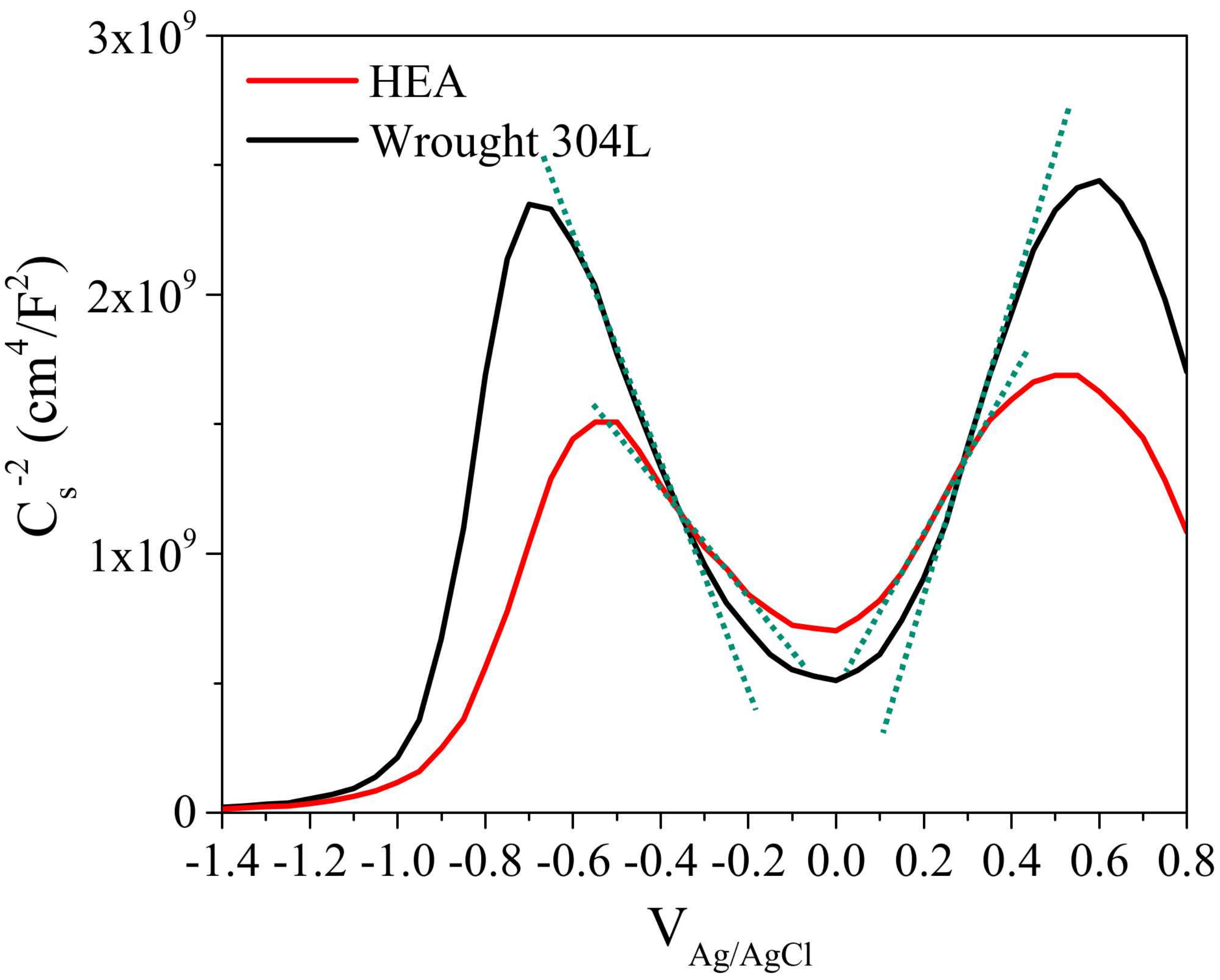
Mott-Schottky analysis of 304L and HEA.

- **1 M $NaSO_4$ solution (pH ~ 6).**
- Potential hold at 600 mV vs. Ag/AgCl for 1 hour.

Donor density for n-type was similar.
Donor density for p-type was larger for HEA.

smaller slope → larger donor density

Anodic polarization behavior of CoCrFeMnNi alloy



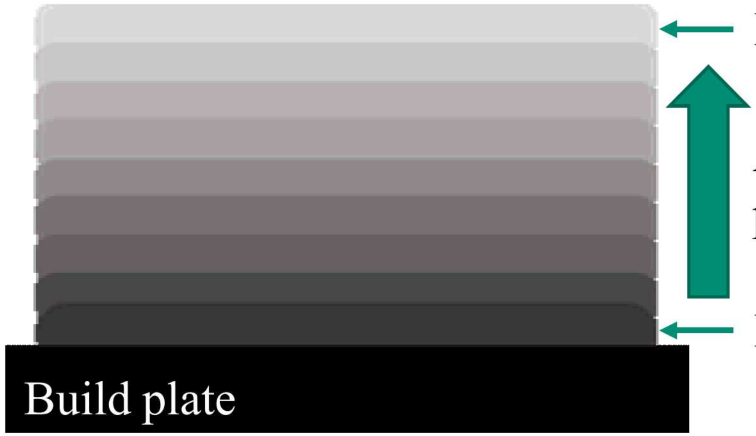
Mott-Schottky analysis of 304L and HEA.

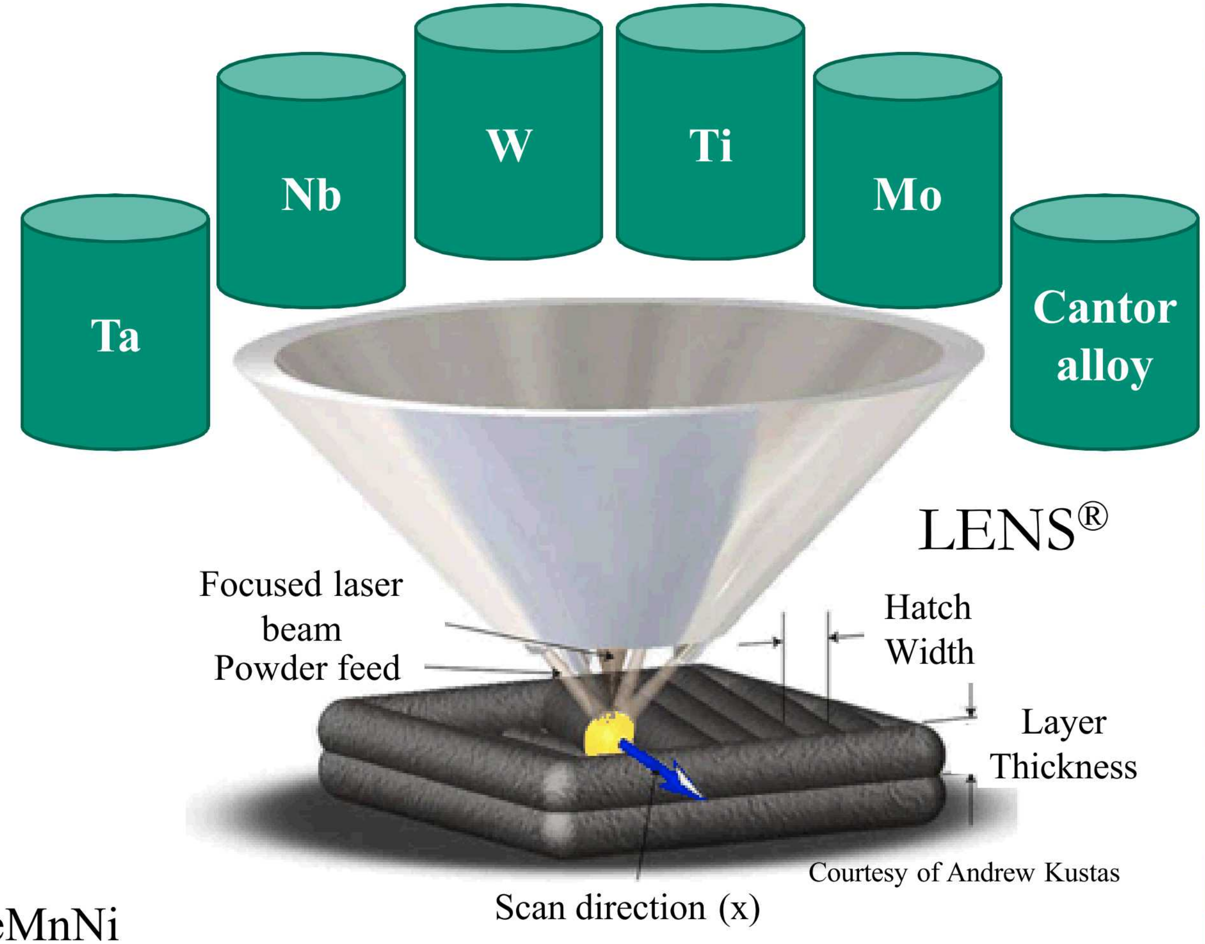
- **0.1 M H_2SO_4 solution (pH ~ 1).**
- Potential hold at 600 mV vs. Ag/AgCl for 1 hour.

Donor density for p-type and n-type were larger for HEA.

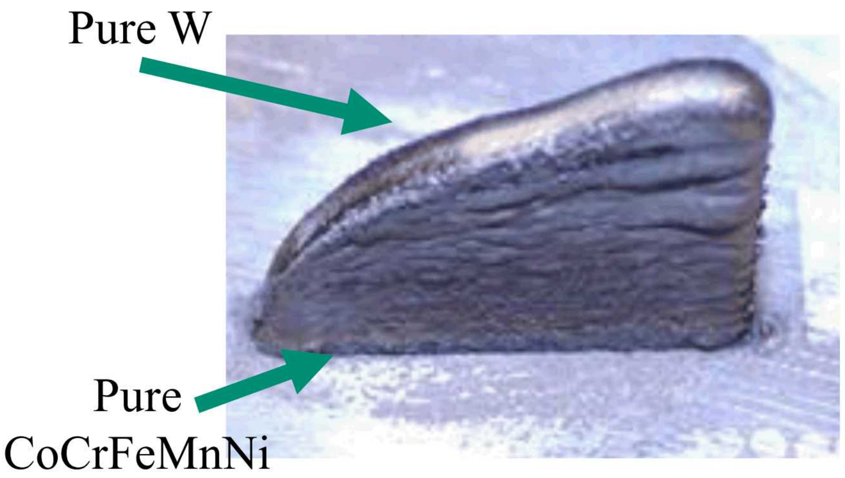
smaller slope → larger donor density

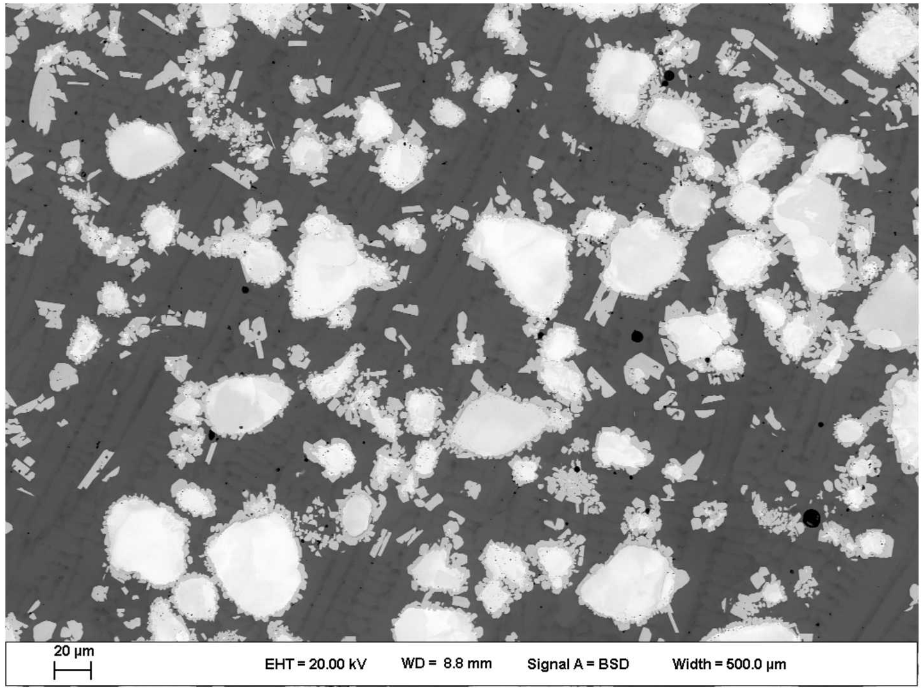
In situ mixing of powders with DED – rapid alloy screening

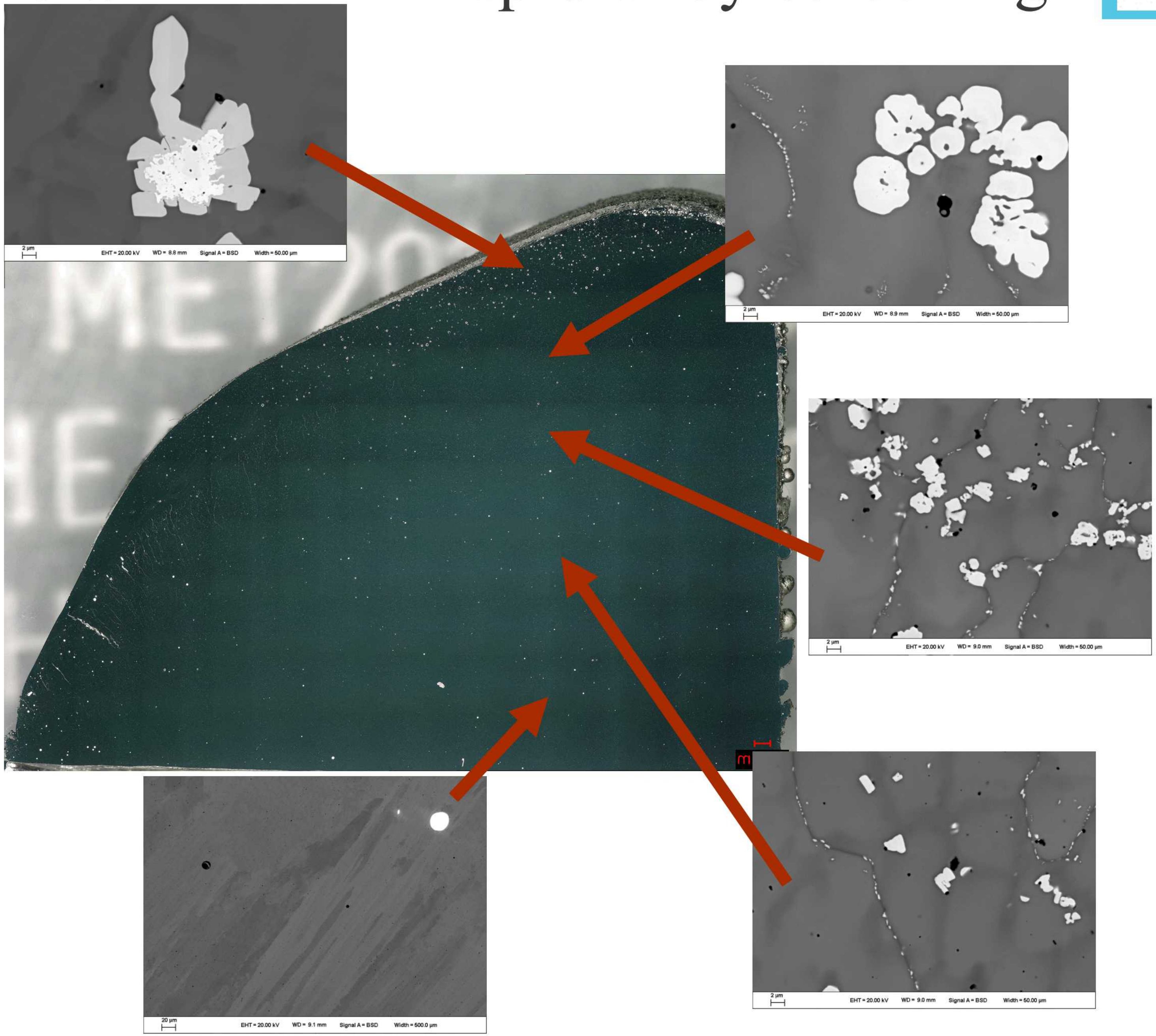




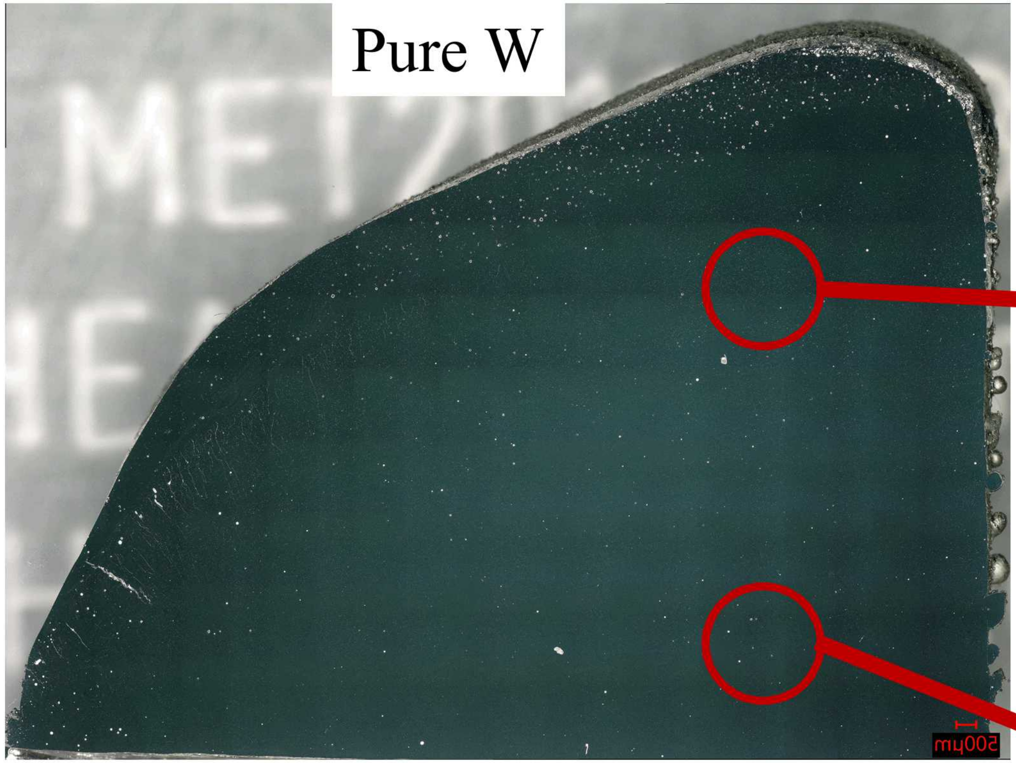
In situ mixing of powders with DED – rapid alloy screening



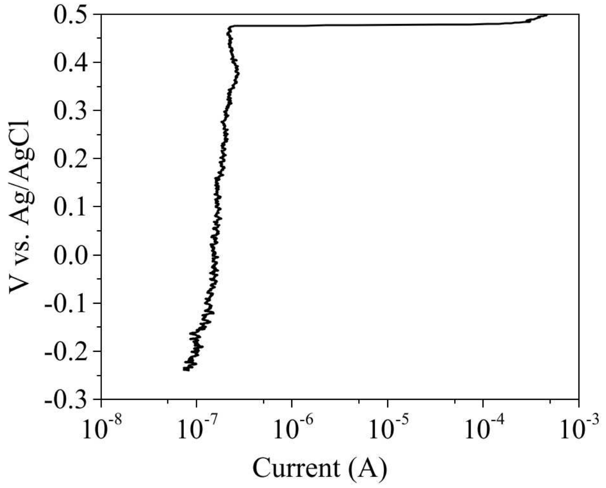


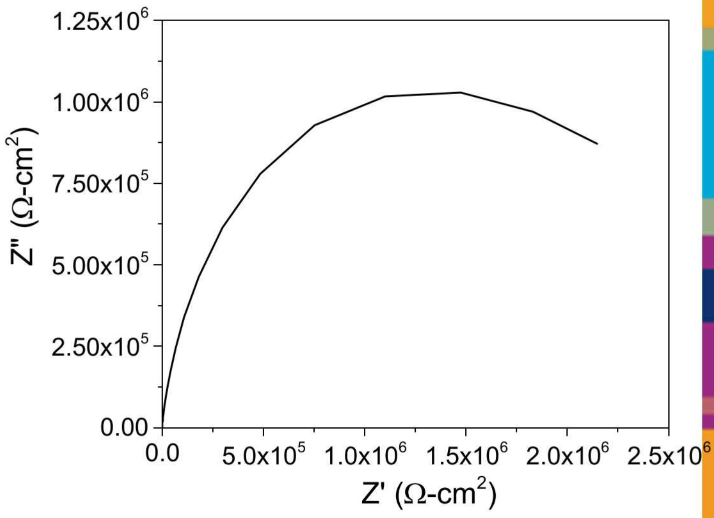


In situ mixing of powders with DED – rapid alloy screening

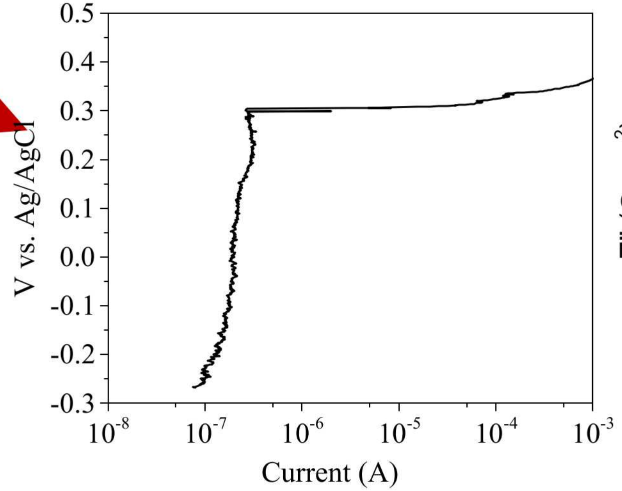


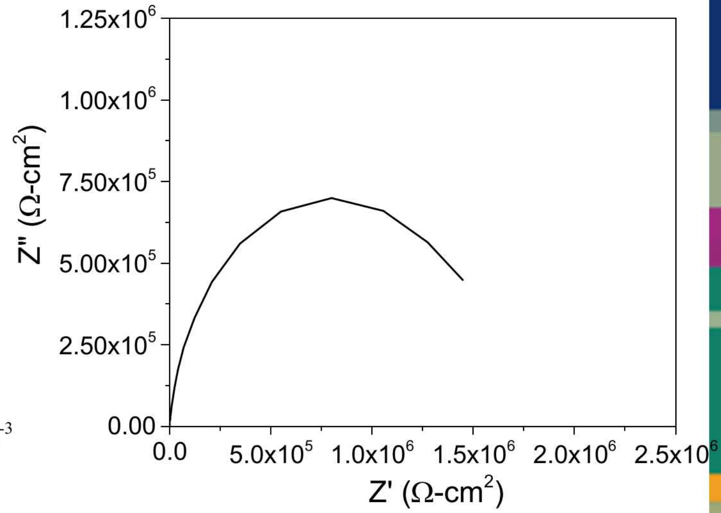
Pure CoCrFeMnNi





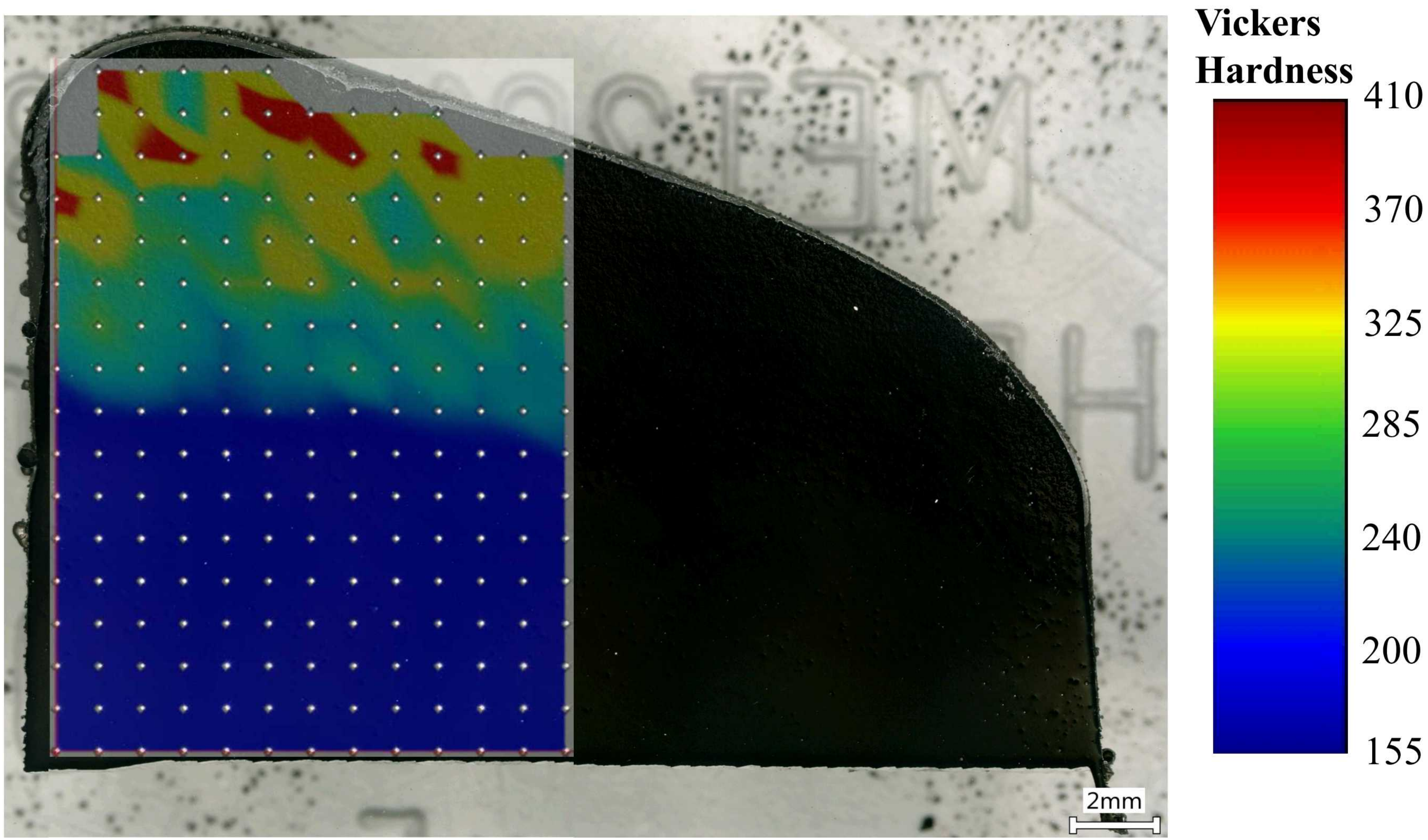
Corrosion in quiescent 0.6 M NaCl





Plan to start performing scanning electrochemical techniques (SKP, SECM, etc.) on these compositionally graded samples.

In situ mixing of powders with DED – rapid alloy screening



Hardness map overlay on sample.

Conclusions

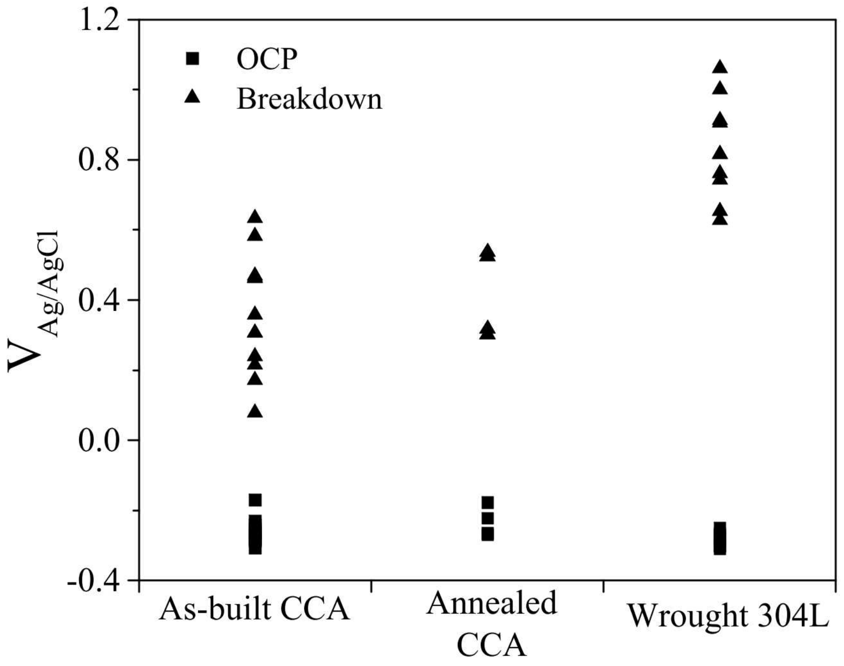
Demonstrated DED for manufacture of 99% dense, single phase CoCrFeMnNi with **high combination of ductility and strength.**

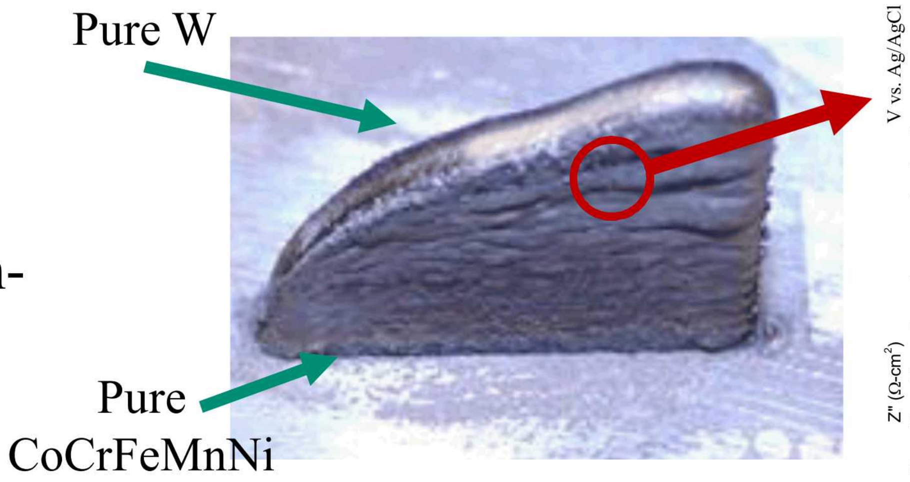
Preferential attack of Mn/Ni rich interdendrite regions during anodic polarization in 0.6 M NaCl:

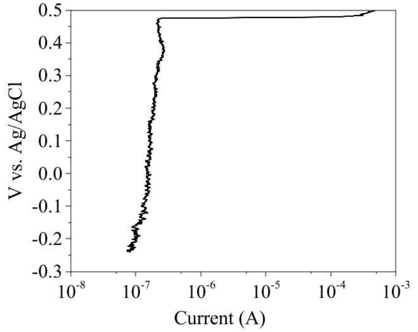
- discontinuity in Cr oxide film.
- galvanic effects.

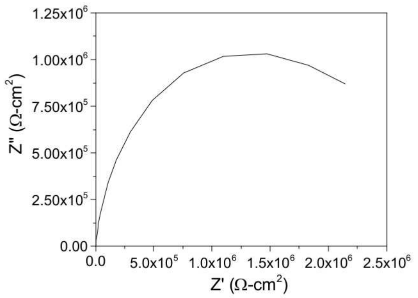
Large Mn content may be reducing stability of passive film on surface.

In situ DED elemental mixing will lead to high-throughput alloy screening.









Questions?

Extra slides

Additive manufacturing of HEAs

Why AM? Faster cooling rates, smaller non-metallic inclusion size, material waste, etc.

Low porosity, single phase parts can be built via DED. Metrics for success will be from:

- Fully dense part produced by DED.
- Single phase (FCC) microstructure with limited chemical segregation.
- Similar or superior **mechanical** behavior to HEA literature.
- Similar or superior **corrosion** behavior to HEA literature.
  Hypothesis that 20 at% Cr leads to similar corrosion behavior as 304L.

Project end goals: Use *in situ* mixing capabilities of DED to rapidly explore alloy space and design gradient materials.

Understand contribution of all elements to passivity of these alloys. Are single element contributions enough to make conclusions?

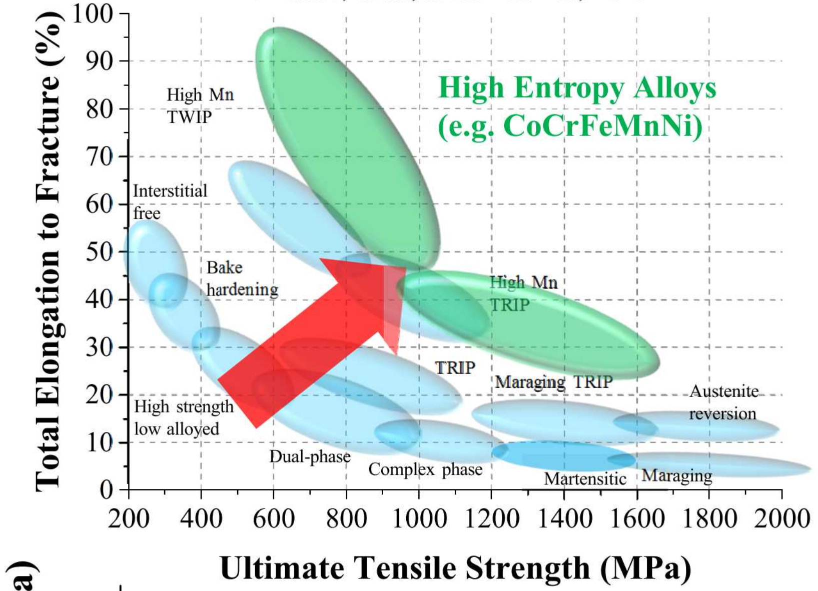
Slide 25

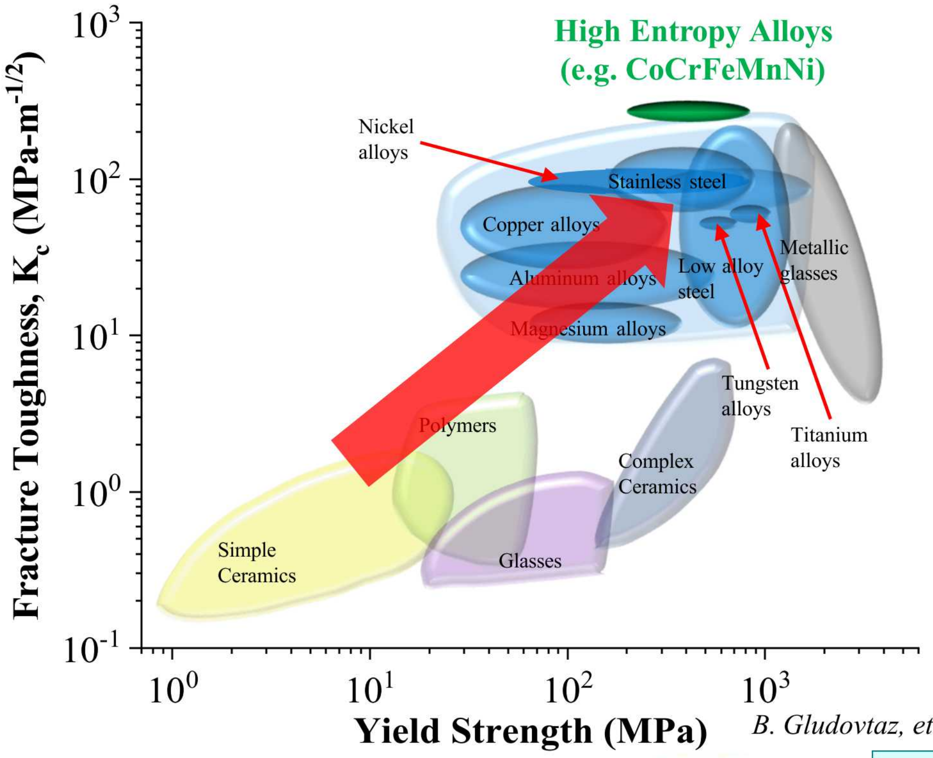
MMA12 Should I add a separate slide on this including literature?
Melia, Michael Anthony, 3/19/2019

SEJ35 See alternative slide below
Schindelholz, Eric John, 3/21/2019

High Entropy Alloys (HEAs): Unusual mechanical properties

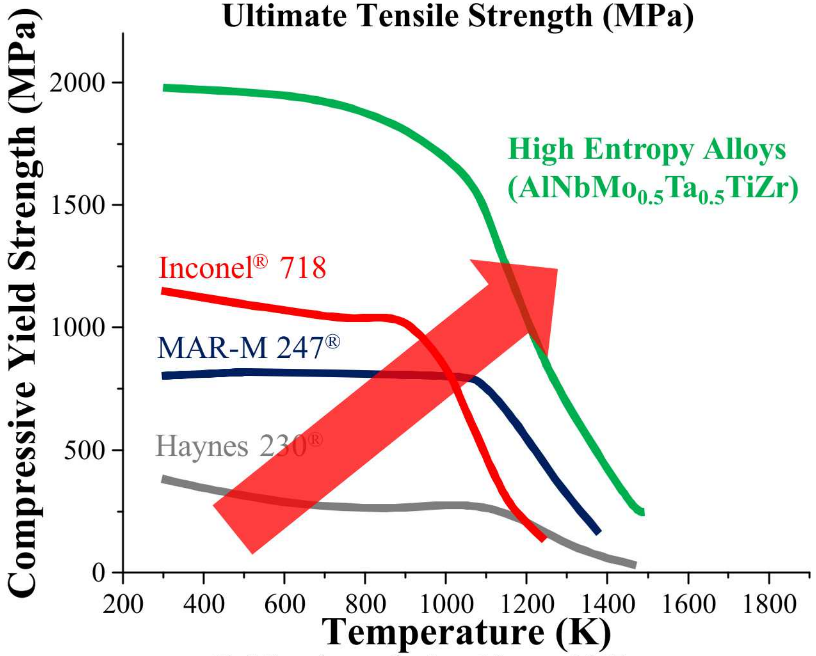
D. Raabe, et al., Steel Res. Int., 2015



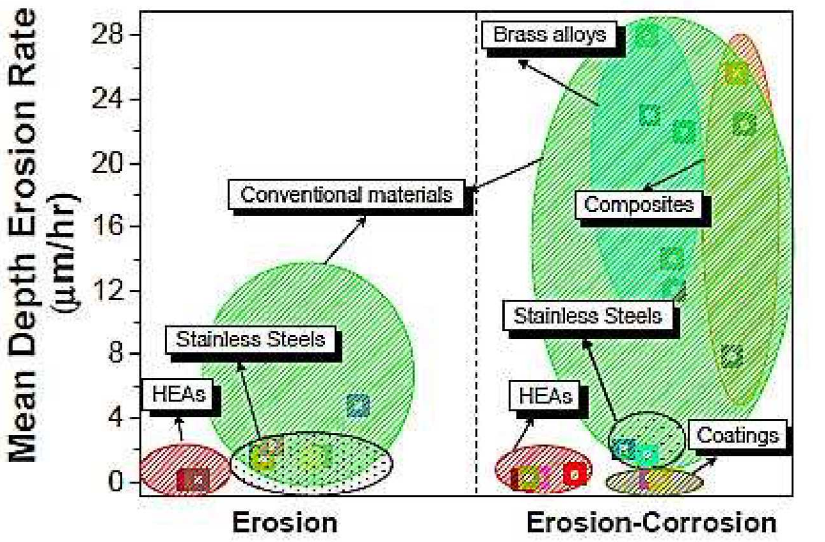


B. Gludovtaz, et al., Science., 2014

SEJ19



D. Miracle, et al., Acta Mater., 2017



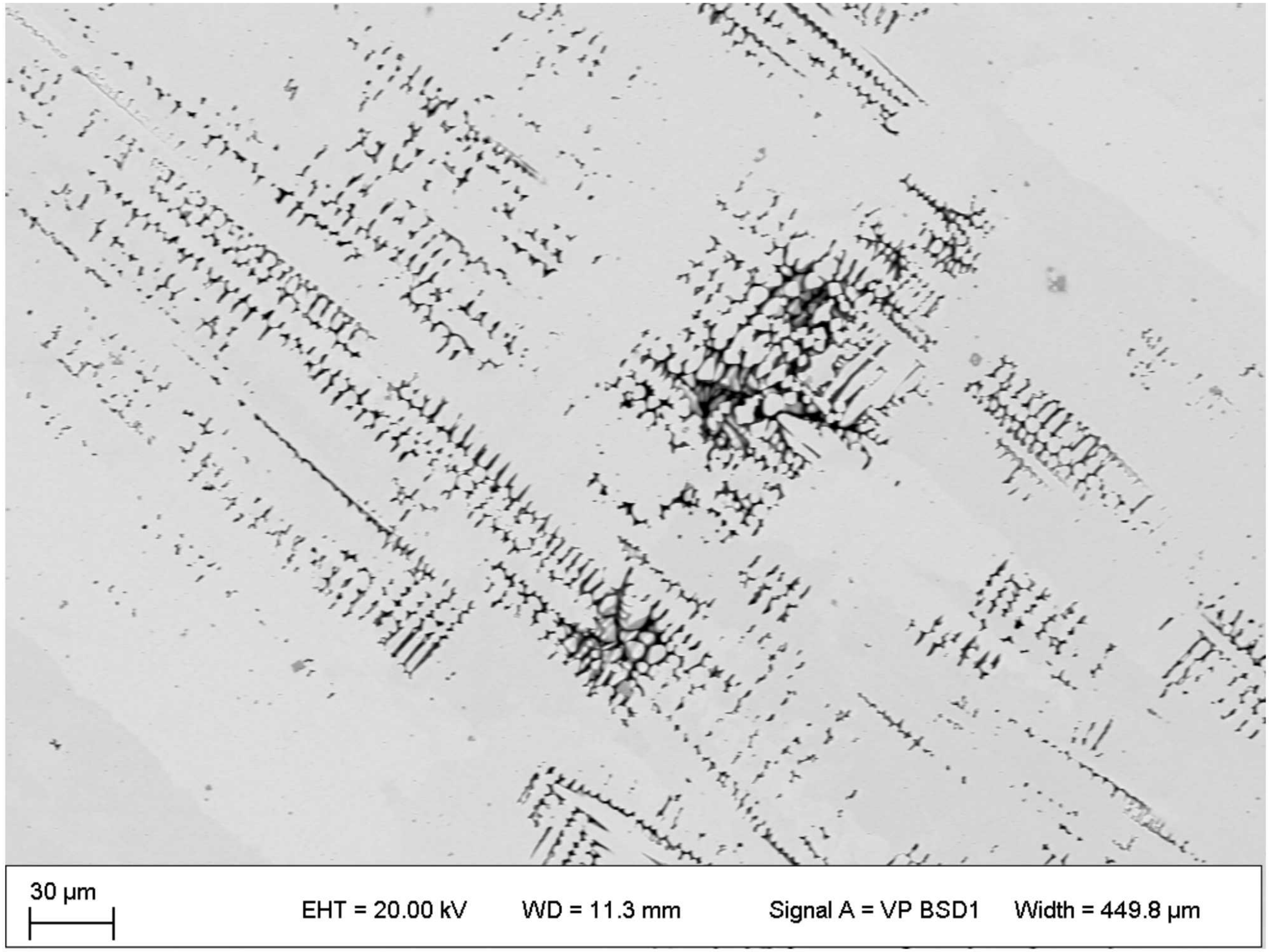
A. Ayyagari, et al., Metals, 2018

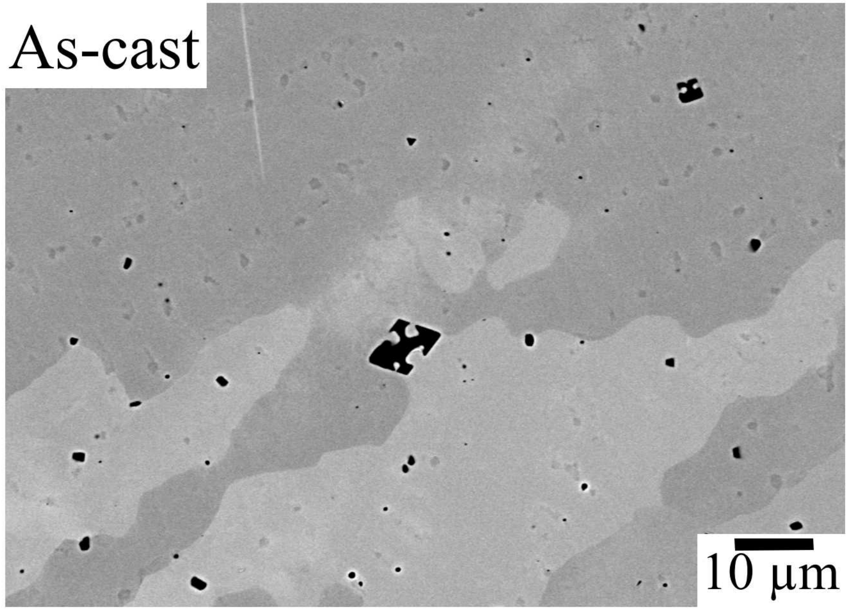
Slide 26

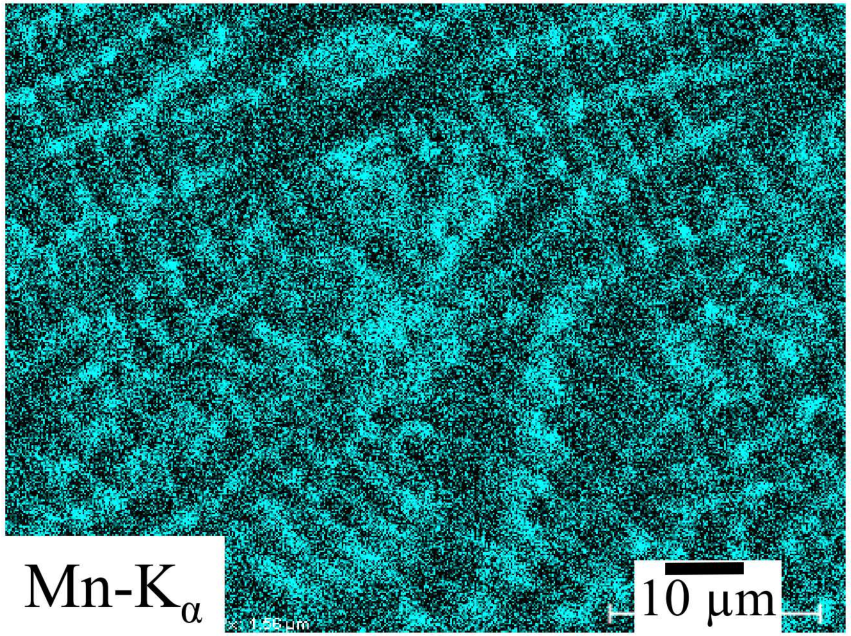
SEJ19 Your text in these should be at least 16 point font. Way too small.. Suggest just pick one or two plots and enlarge... Think this would make your poitn.

Schindelholz, Eric John, 3/20/2019

Cast microstructure of CoCrFeMnNi HEA

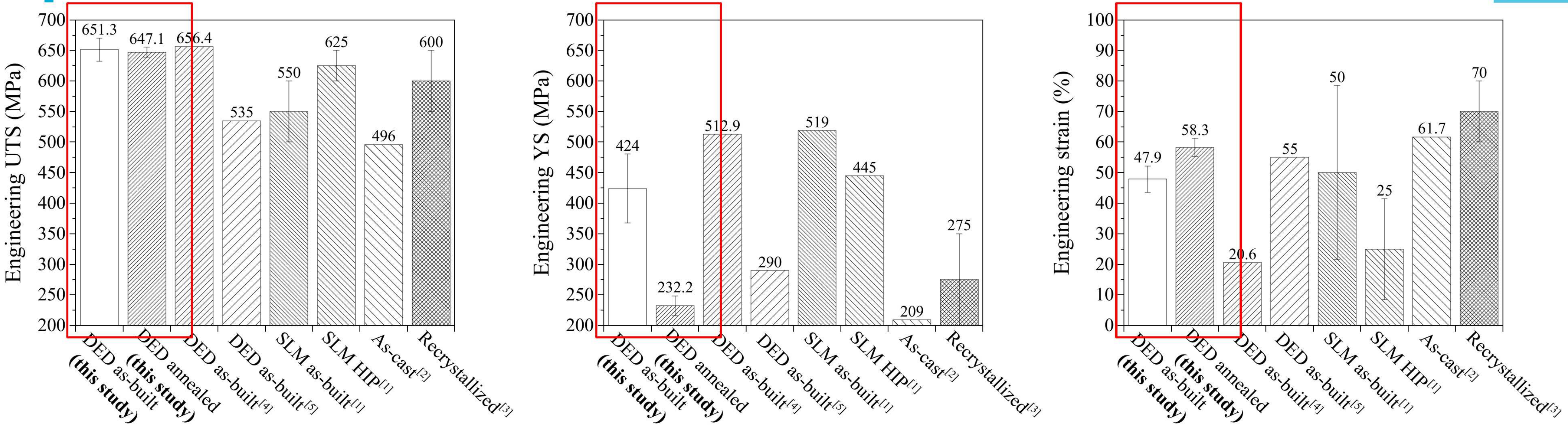






Courtesy of Bucknell University

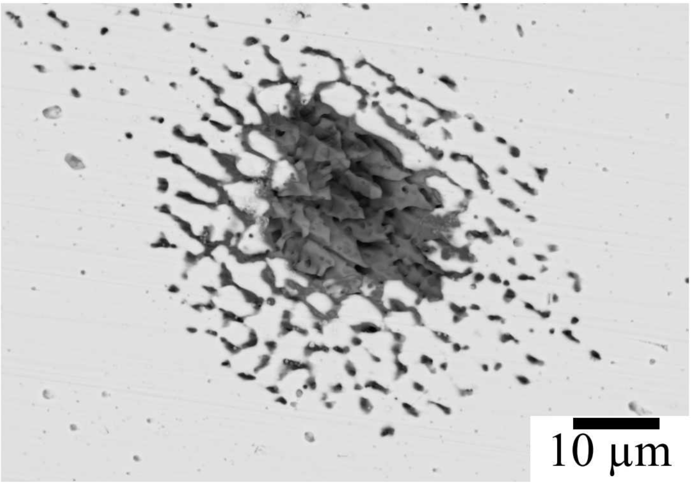
Mechanical properties of CoCrFeMnNi alloy



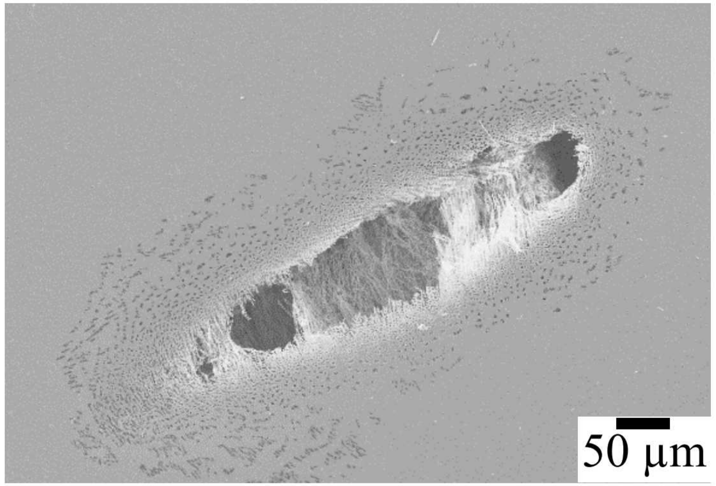
Include Tong and Wang data.

Pit morphology of CoCrFeMnNi alloy – **compared to 304L**

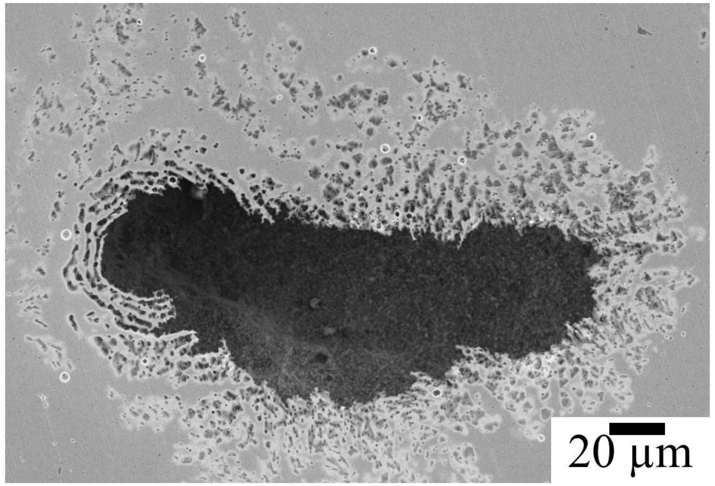
As-built HEA



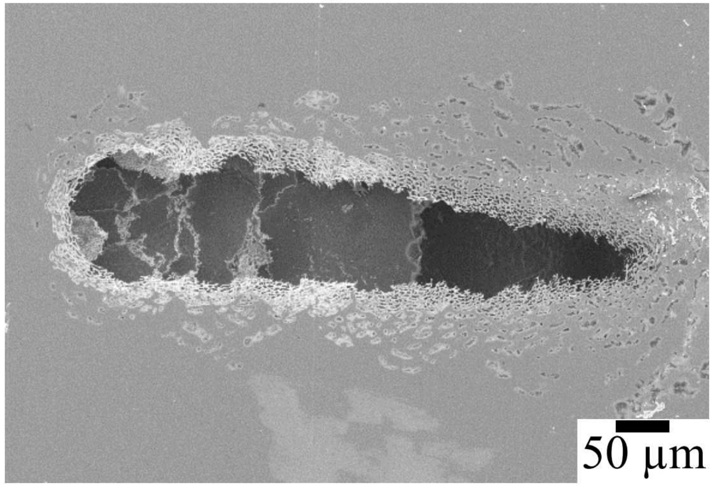
As-built 304L



Annealed HEA



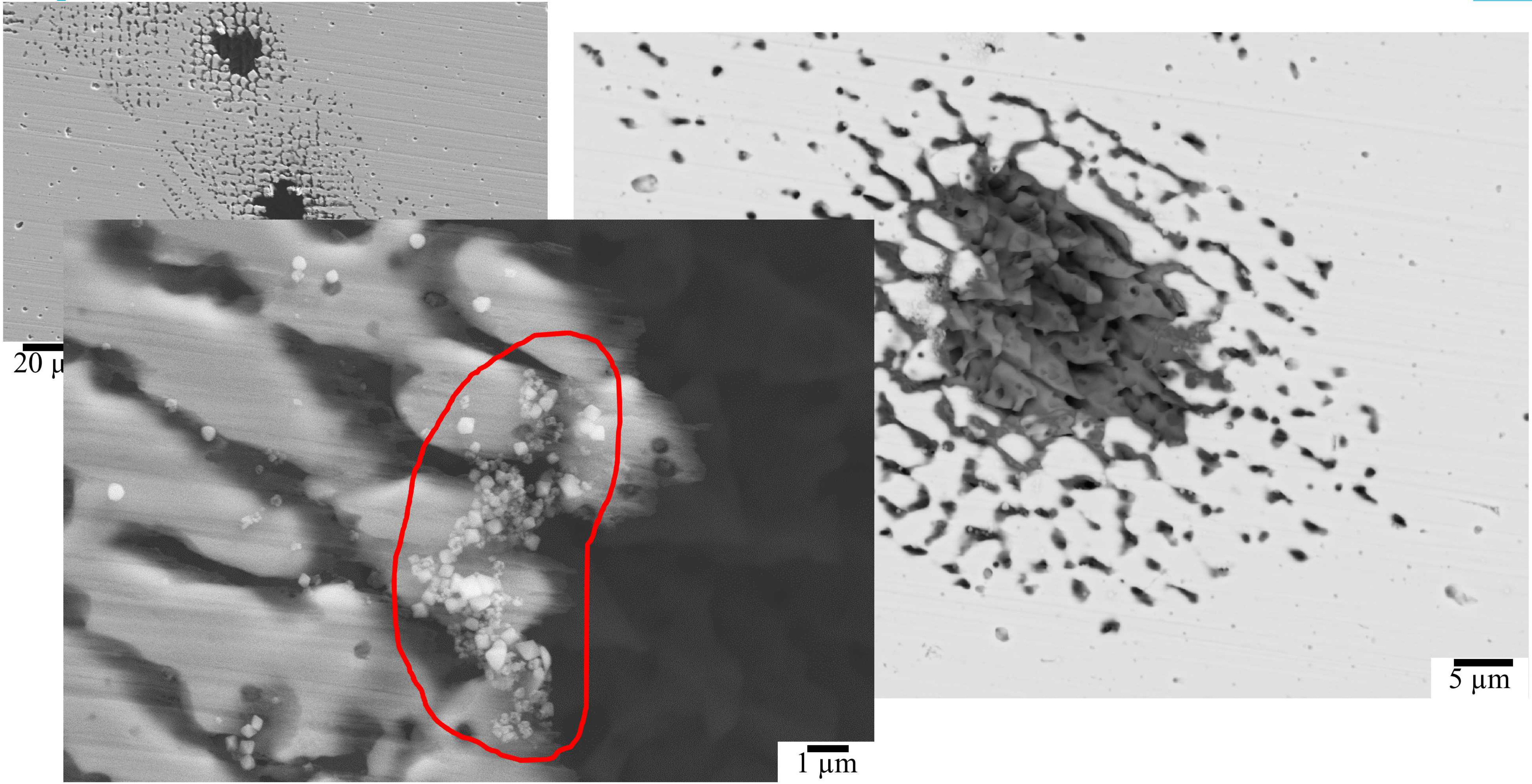
Wrought 304L



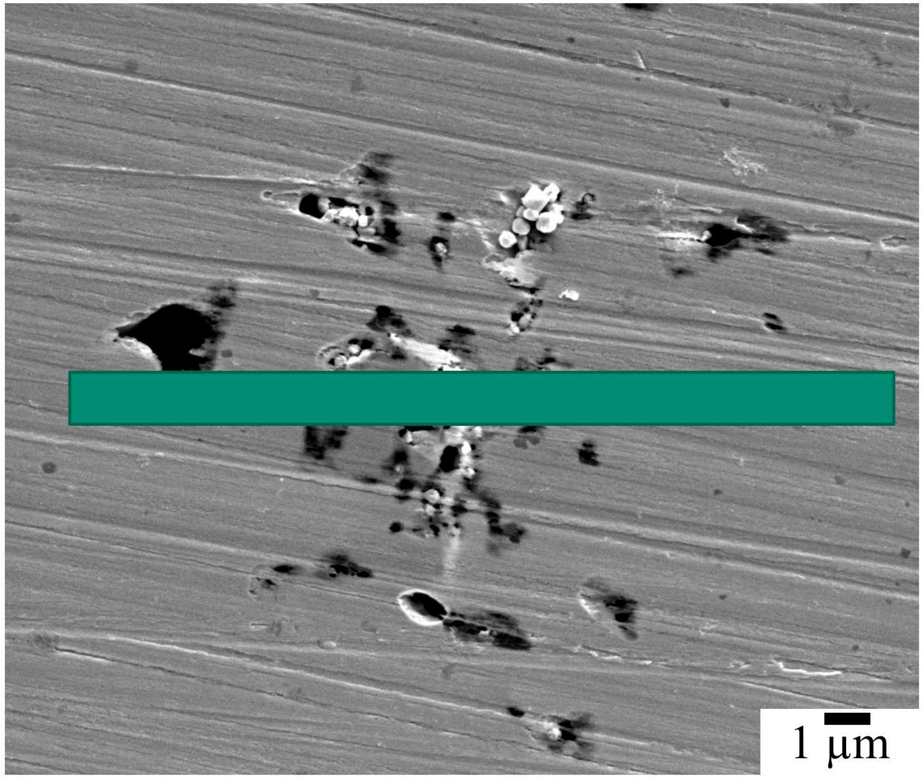
Annealed/wrought conditions show flat pit bottoms and lacy pit morphology.

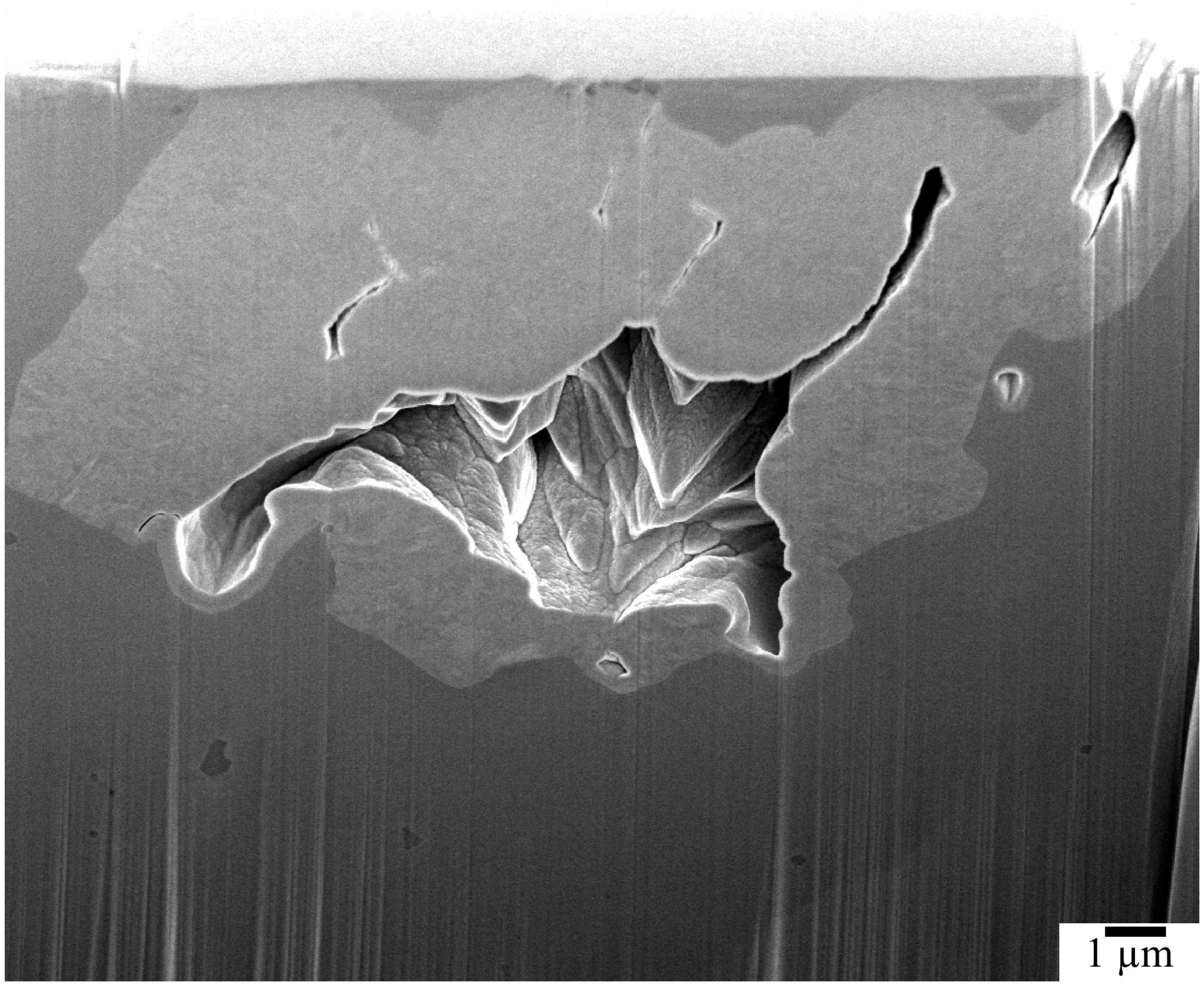
Inter/intra dendrite regions will have some control of pit morphology/propagation for as-built material.

Pit morphology of CoCrFeMnNi alloy – **as-built**



Pit morphology of CoCrFeMnNi alloy – **as-built**





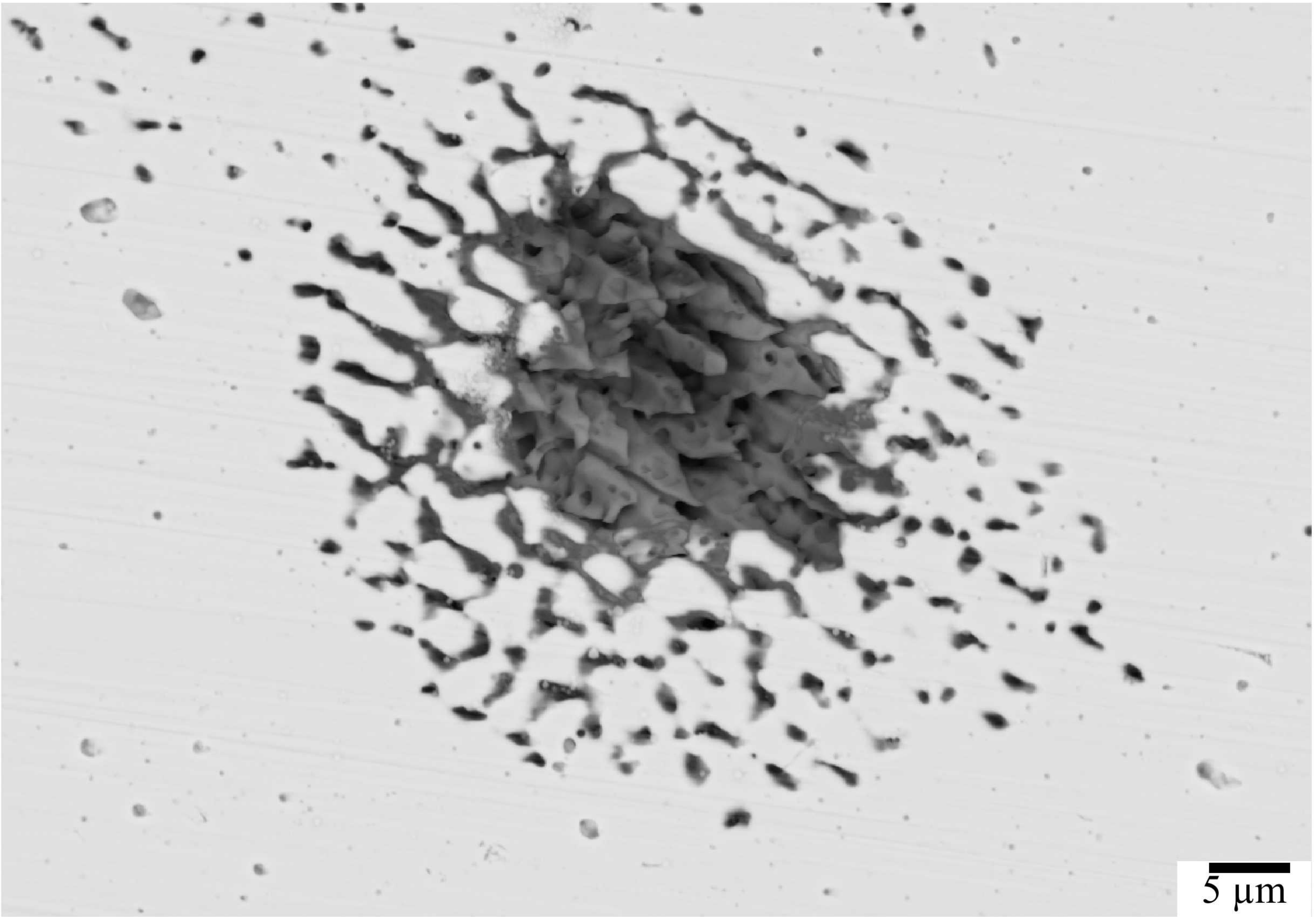
Early stages of pitting show propagation below surface can occur via this preferred interdendrite corrosion.

What causes this preferred interdendrite corrosion?

Short answer: chemical heterogeneity, specifically enriched areas of **Mn**.

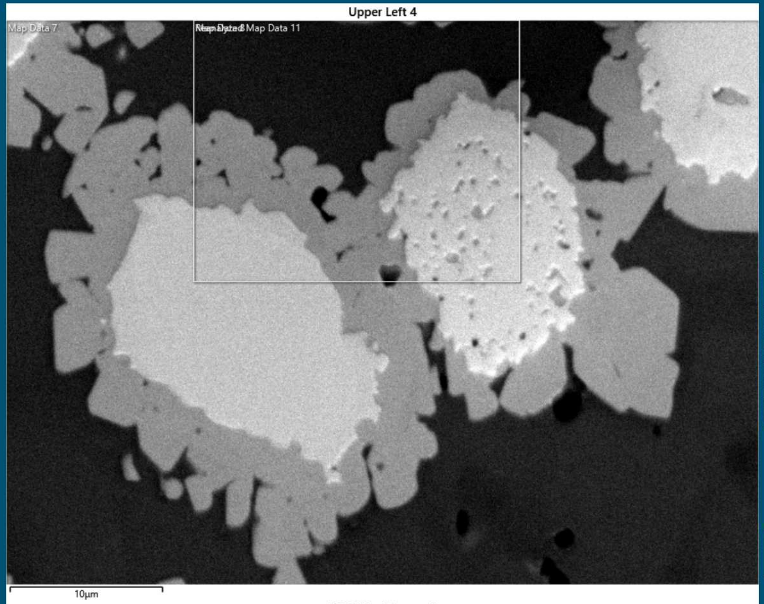
Long Answer: several factors involving how Mn impacts passivation locally:

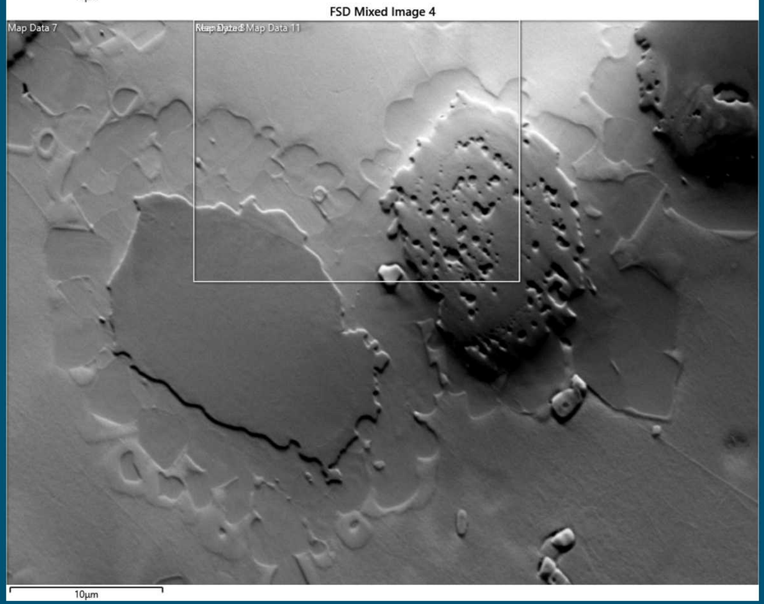
- Mn has the lowest Nernst potential of all major alloying elements, leading to galvanic coupling effect.
- Less stable passive corrosion product in areas enriched in Mn (possibly depleted in Cr).



What dominates?

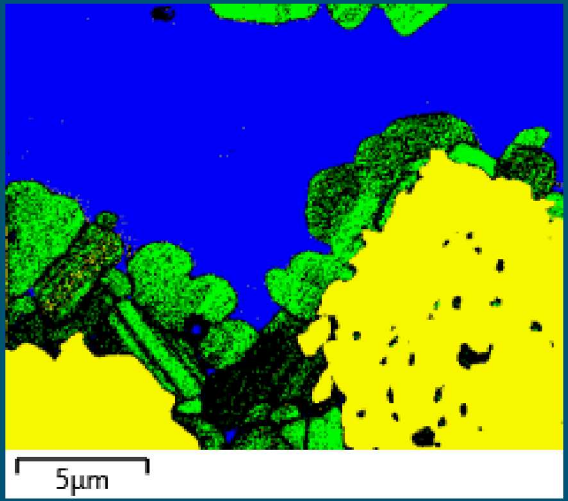
Cantor + W (Sample 5) – Near top





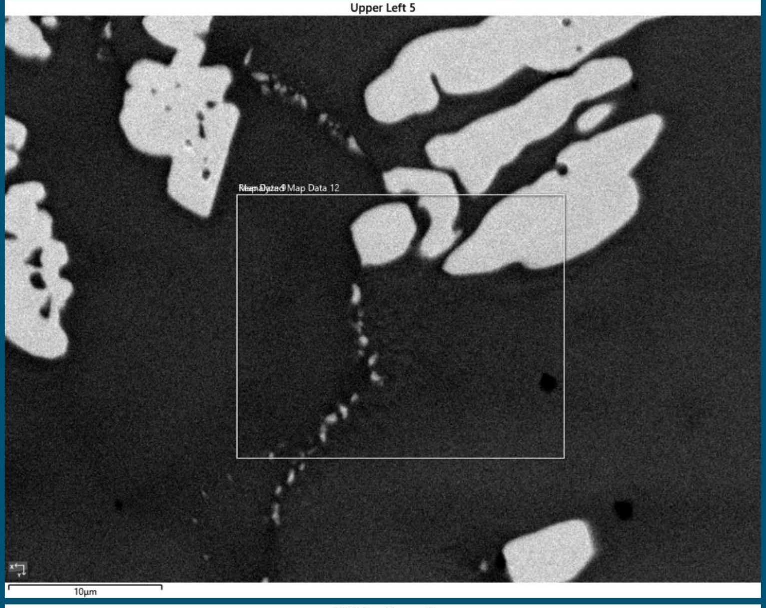
IPF map

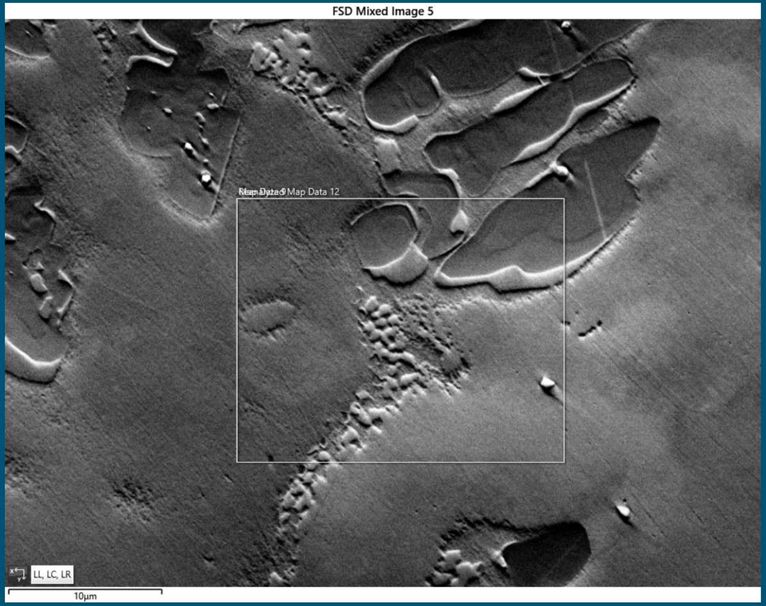
Phase map



	Fraction	Color
FCC - CoCrFeMnNi	41.3	
BCC – W	29.9	
Trigonal – µ-Fe_7W_6	12.3	

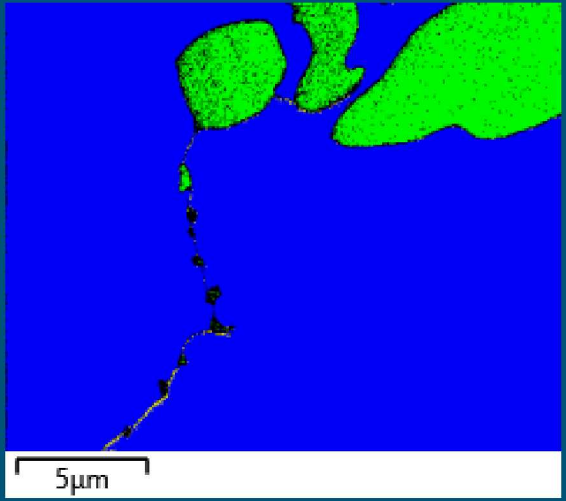
Cantor + W (Sample 5) – Middle





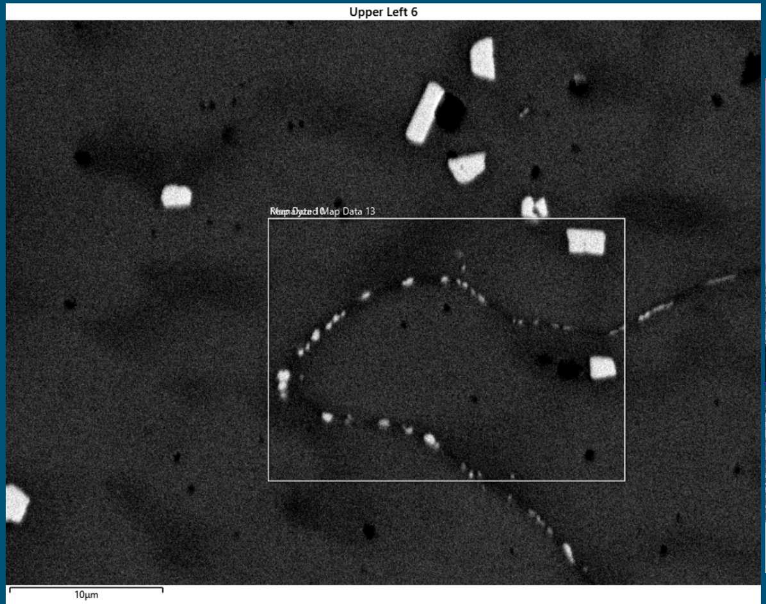
IPF map

Phase map

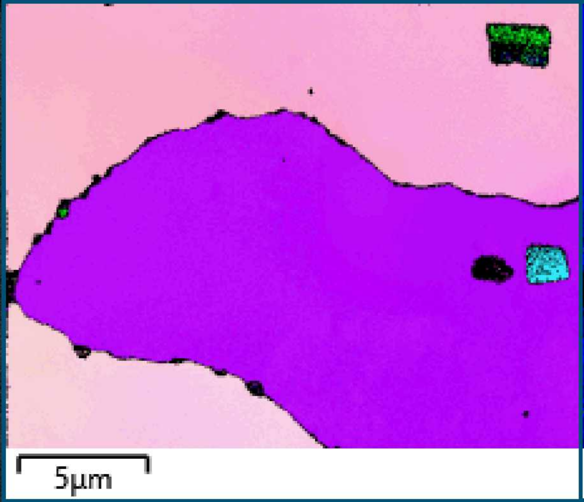


	Fraction	Color
FCC - CoCrFeMnNi	41.3	
BCC – W	29.9	
Trigonal – μ-Fe_7W_6	12.3	

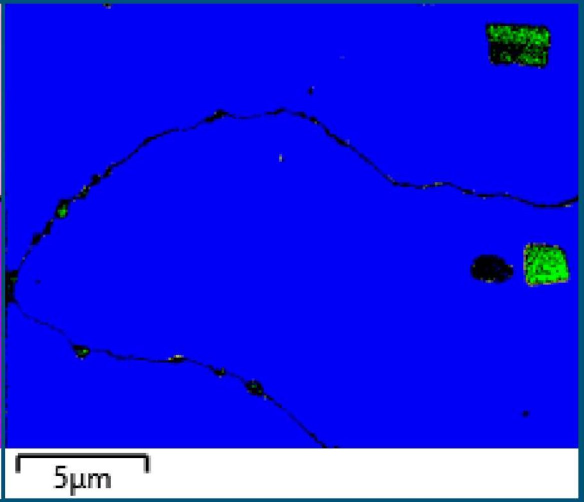
Cantor + W (Sample 5) – Near bottom



IPF map



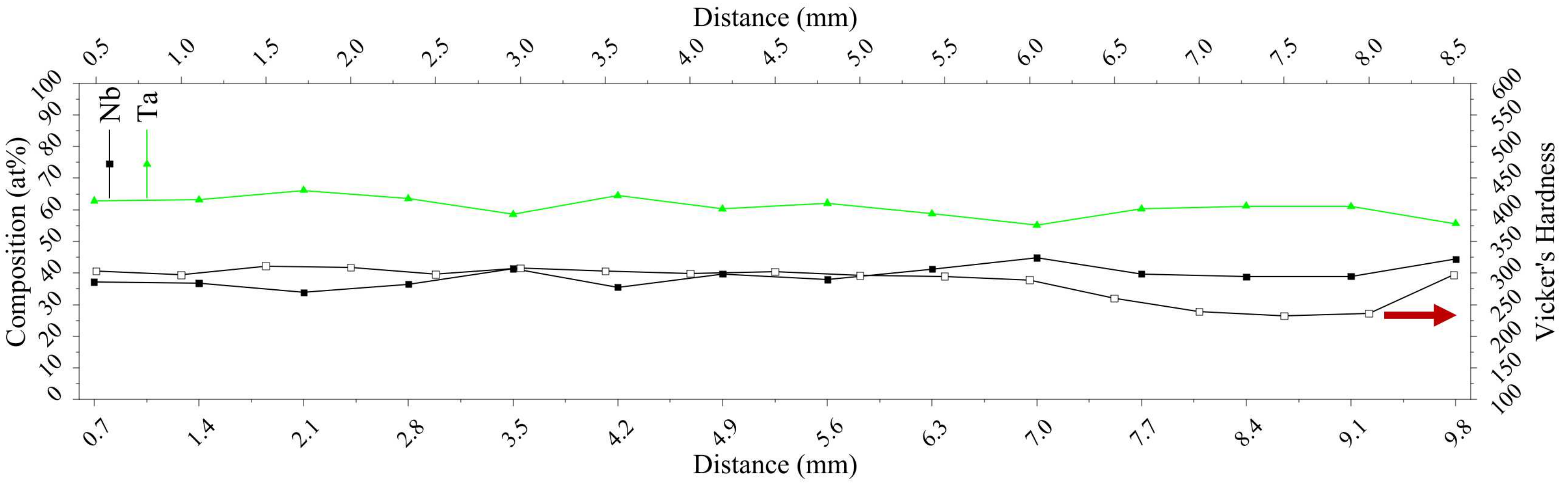
Phase map



	Fraction	Color
FCC - CoCrFeMnNi	41.3	
BCC – W	29.9	
Trigonal – µ-Fe_7W_6	12.3	

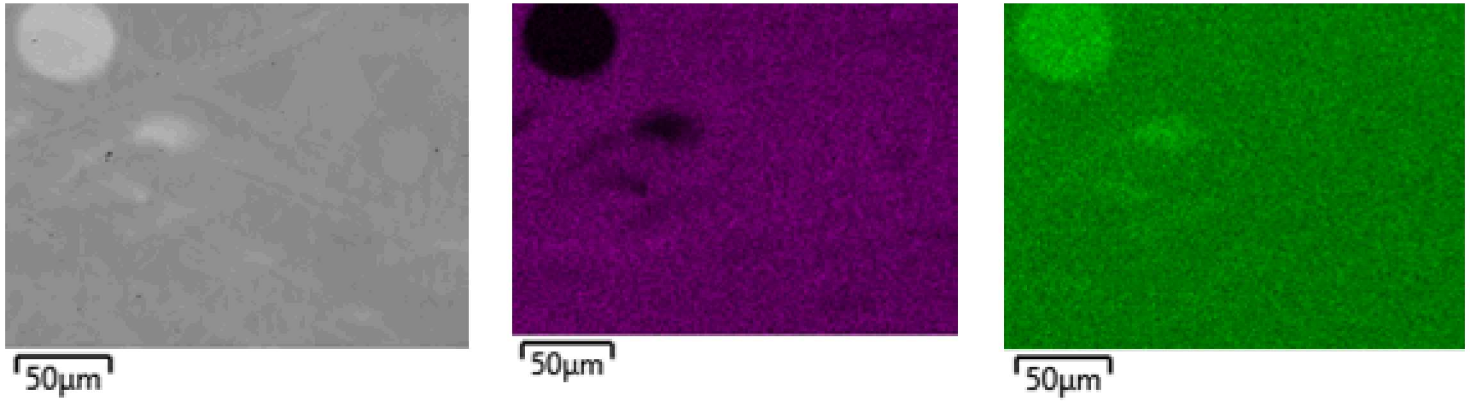
In situ mixing of powders with DED – rapid alloy screening

40 at% Nb – 60 at% Ta

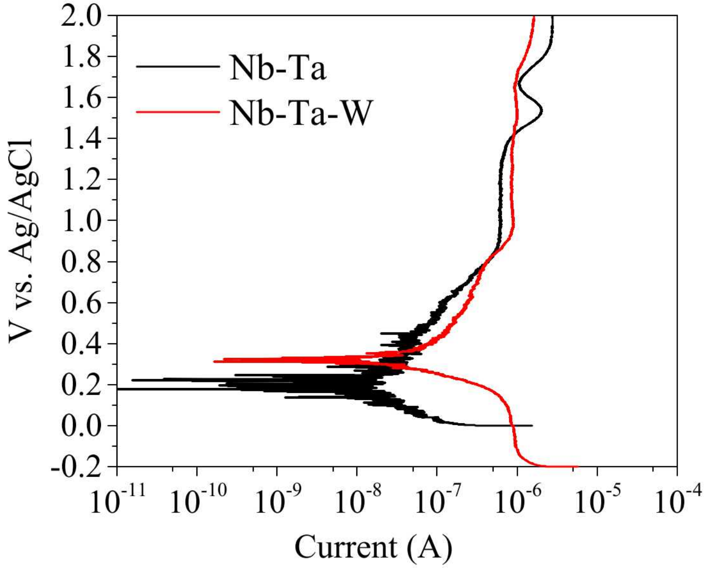


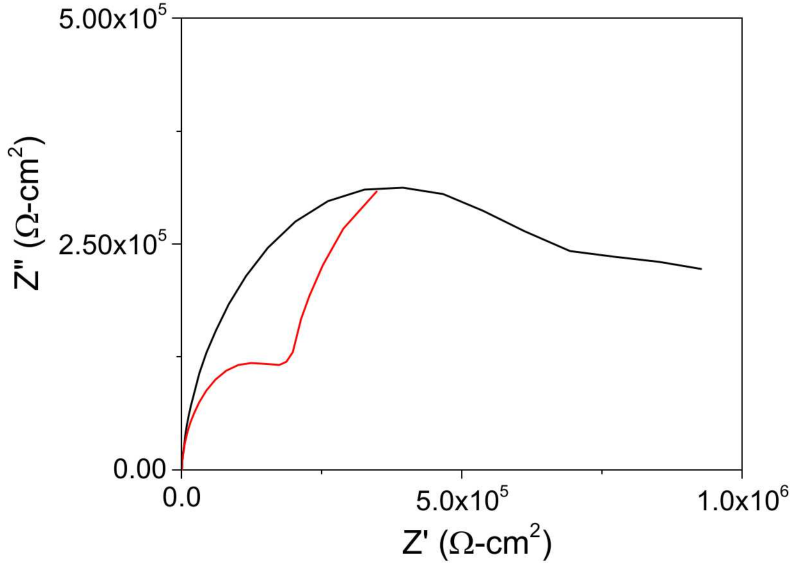
Nb-Lα

Ta-Lα



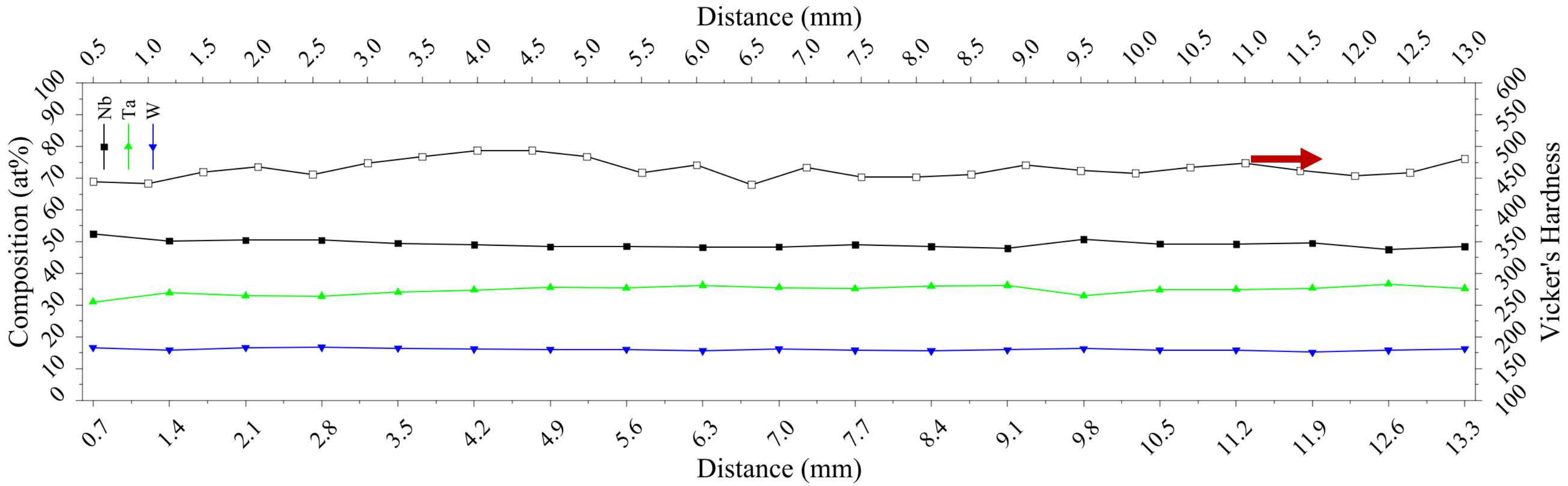
Corrosion in quiescent 1.0 M HCl



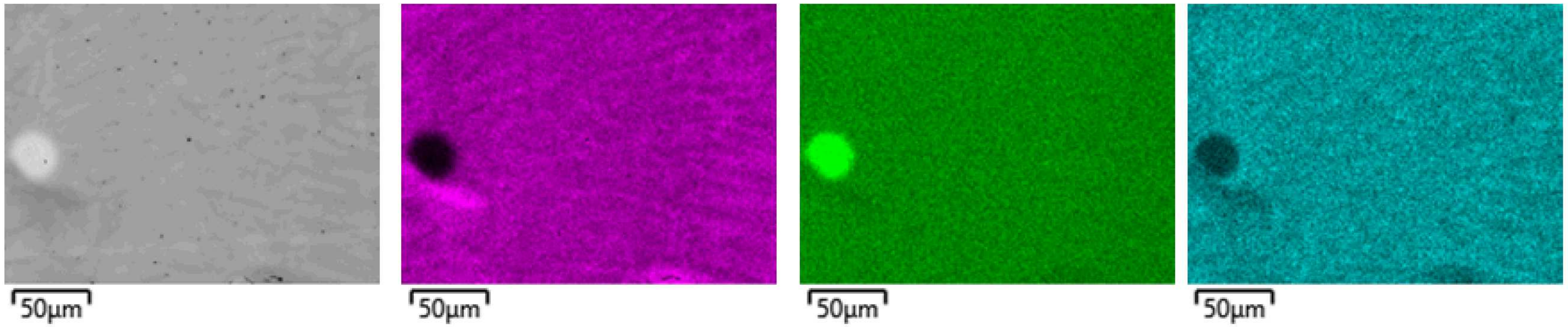


In situ mixing of powders with DED – rapid alloy screening

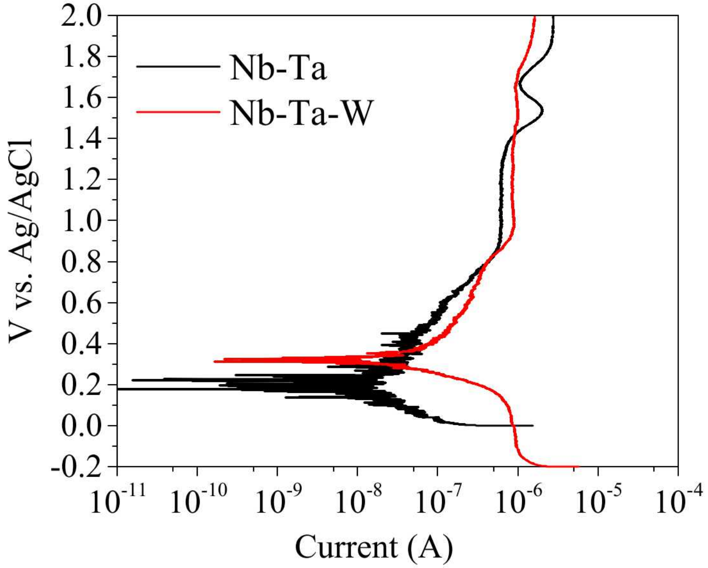
50 at% Nb - 35 at% Ta - 15 at% W

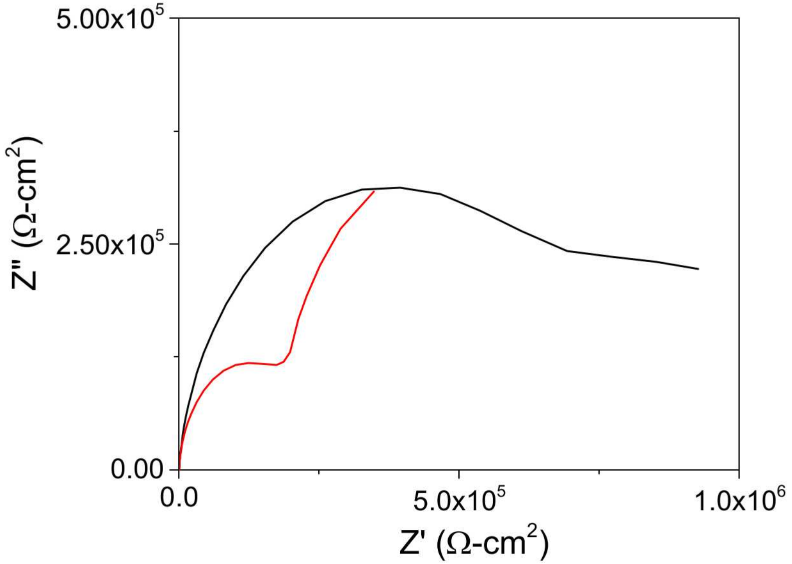


Nb-Lα　Ta-Lα　W-Lα

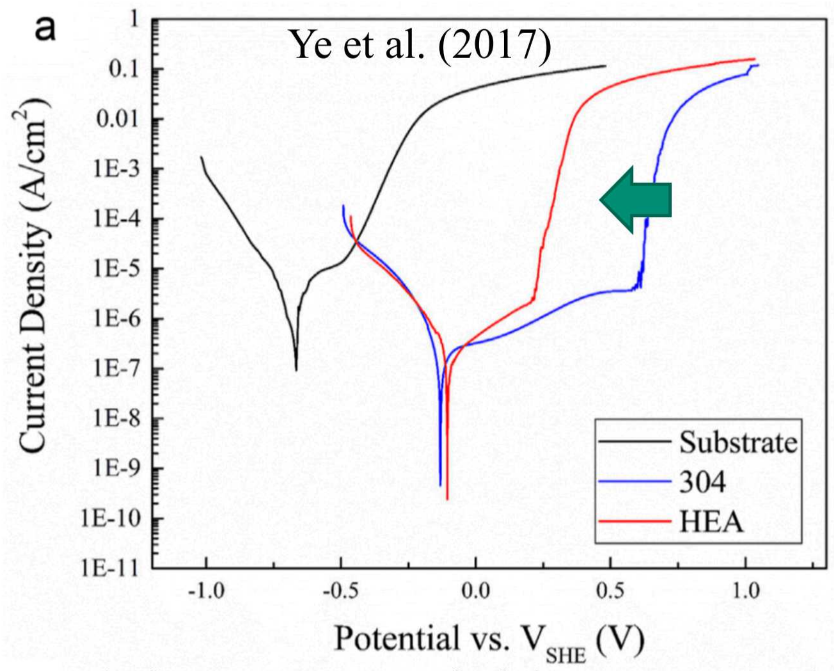


Corrosion in quiescent 1.0 M HCl

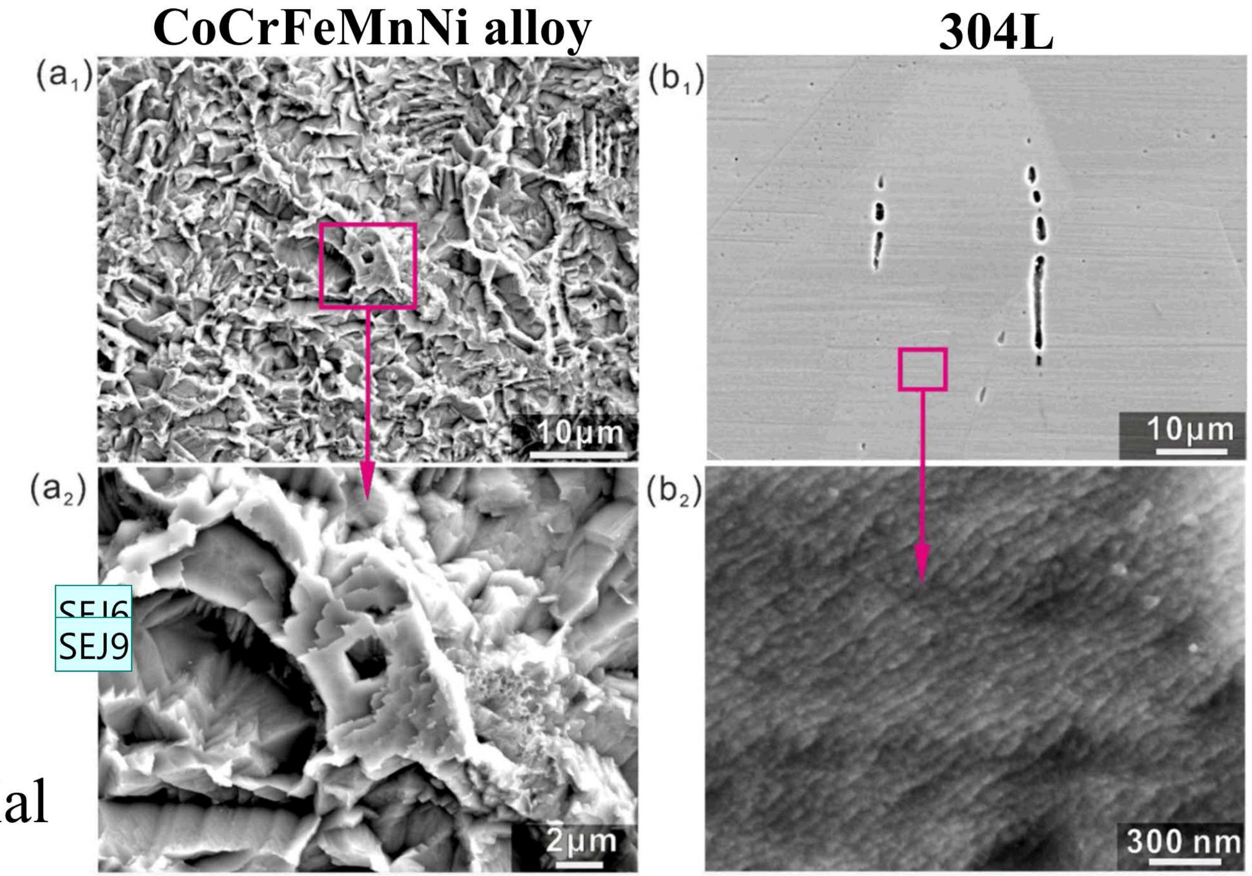




Anodic polarization behavior of CoCrFeMnNi alloy compared to 304L stainless steel



Breakdown potential is comparable ~2-300 mV reduction in breakdown potential from 304 to this HEA in NaCl solutions.



Luo et al. (2018)

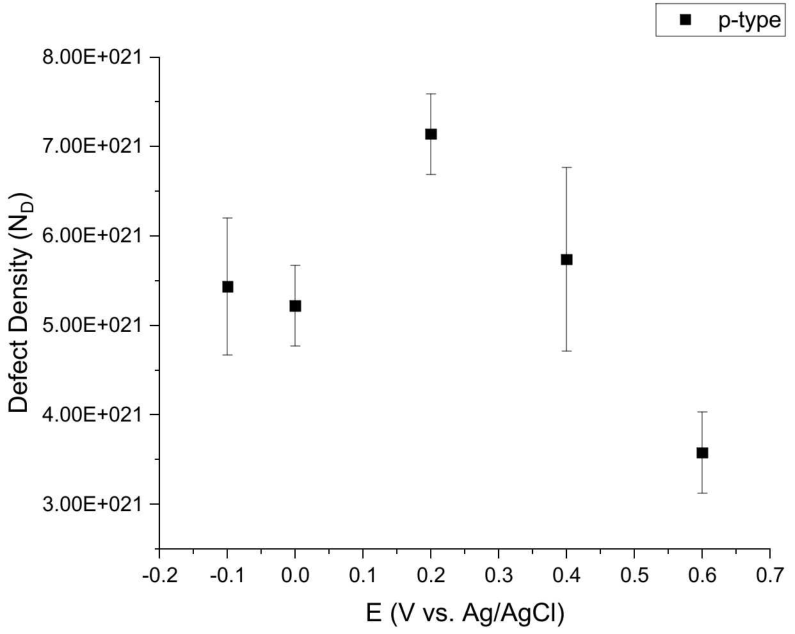
This study performed in 0.1 M H_2SO_4 shows significantly more corrosion of the HEA. Had concluded passive film was less stable than 304L because:

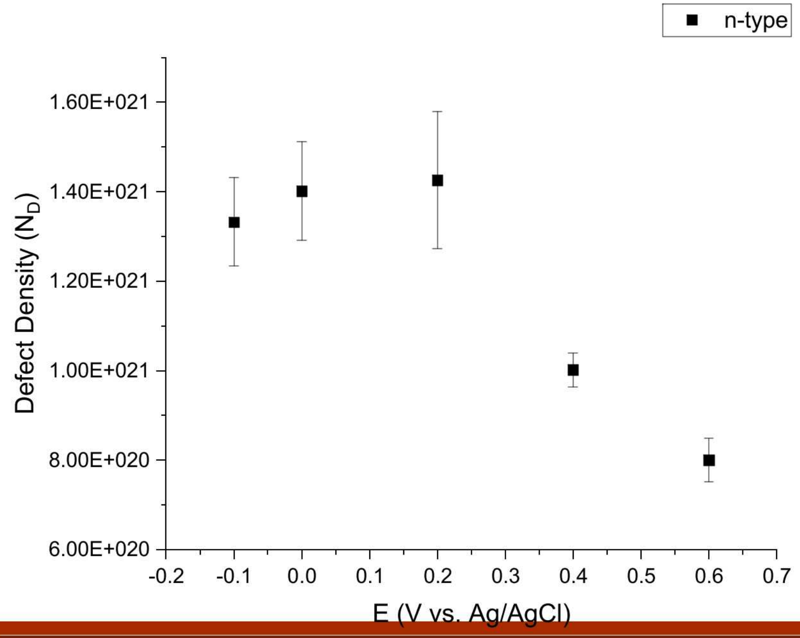
- **Less Cr was present in film.**
- **More hydroxide species than oxide.**

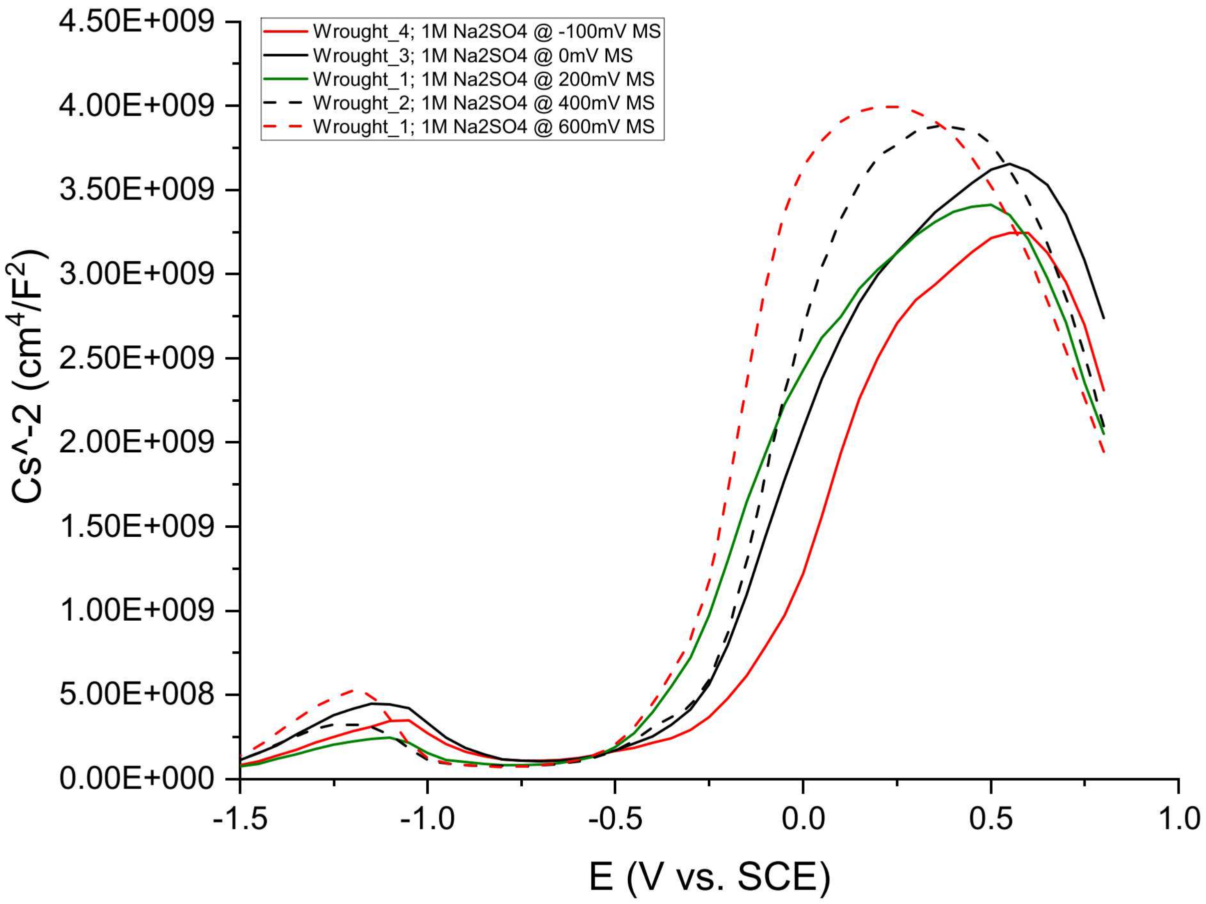
Slide 38

SEJ6 Why compare to 304L?
Schindelholz, Eric John, 3/20/2019

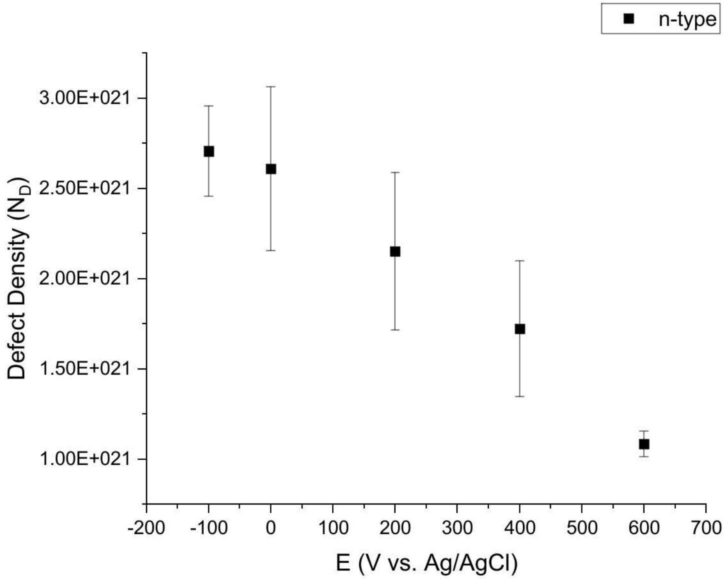
SEJ9 What is your key point in this slide?
Schindelholz, Eric John, 3/20/2019

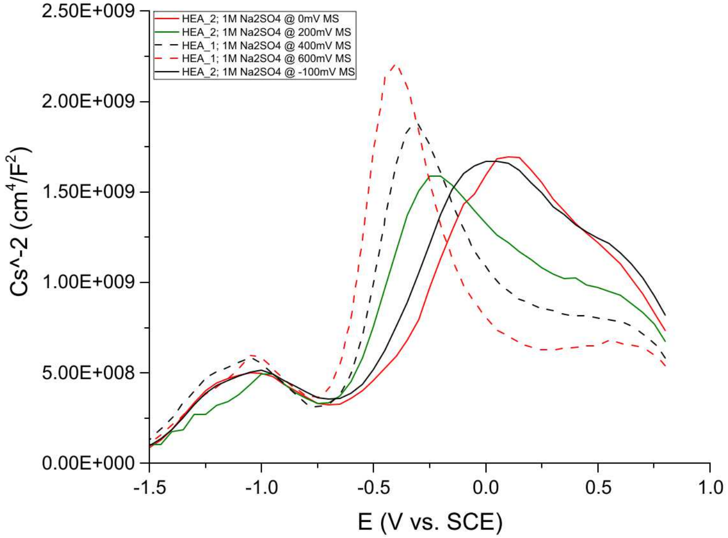




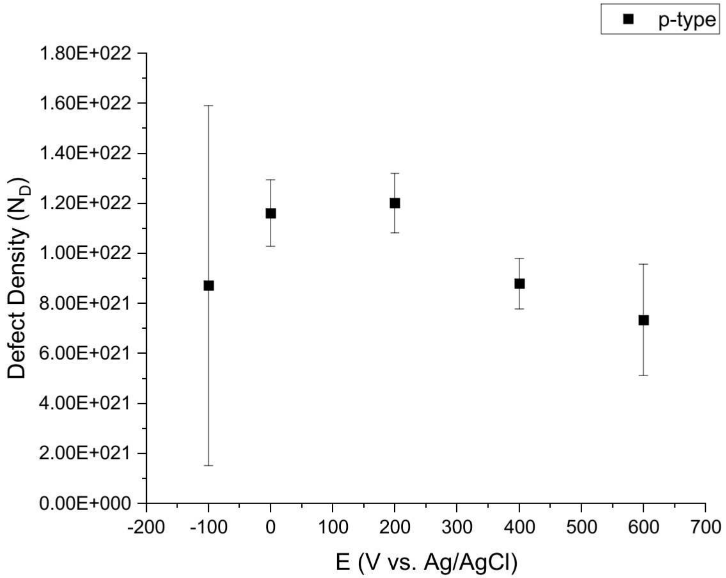


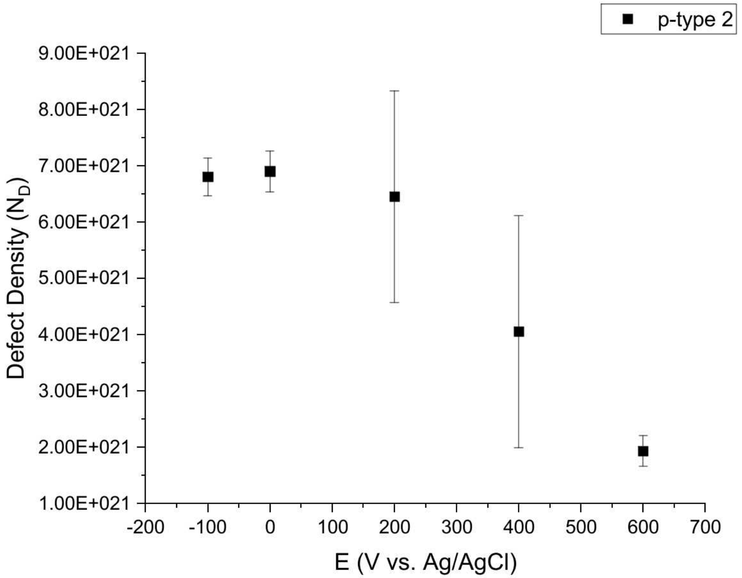
304L wrought – 1M Na_2SO_4

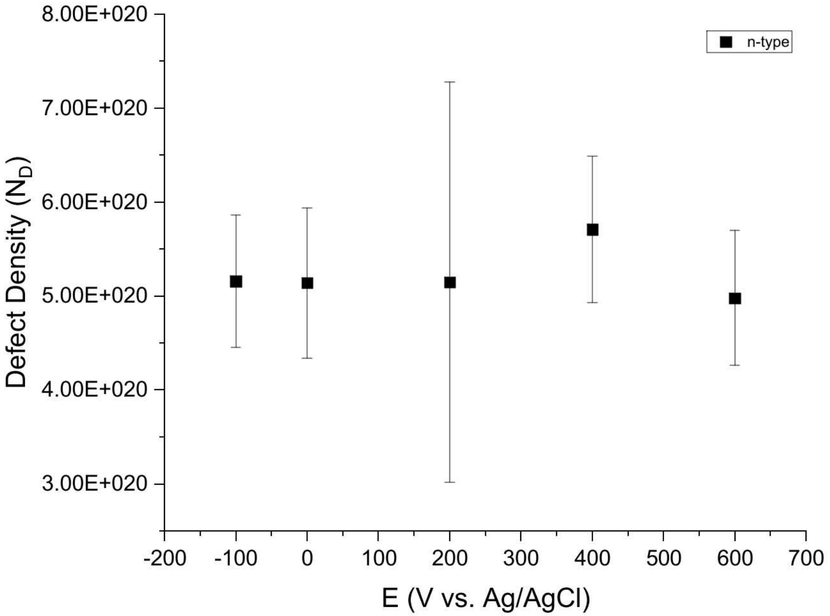


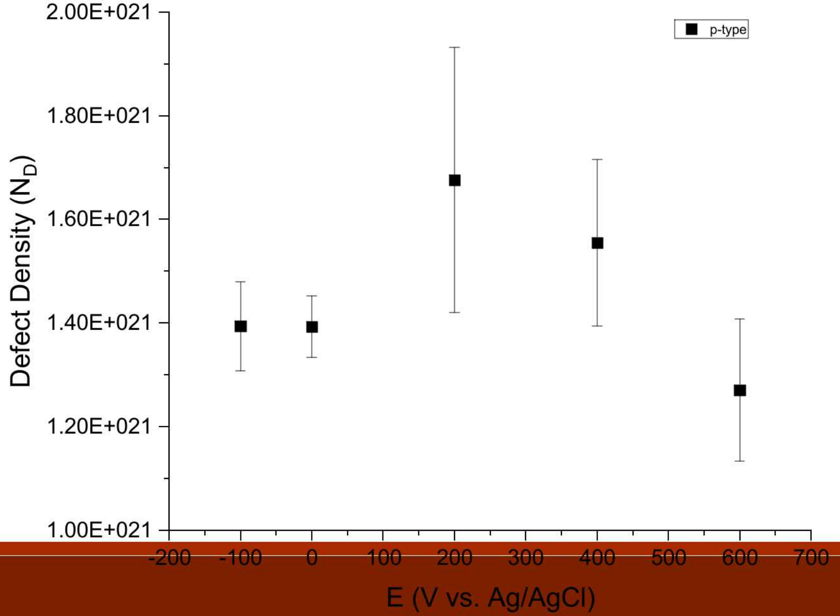


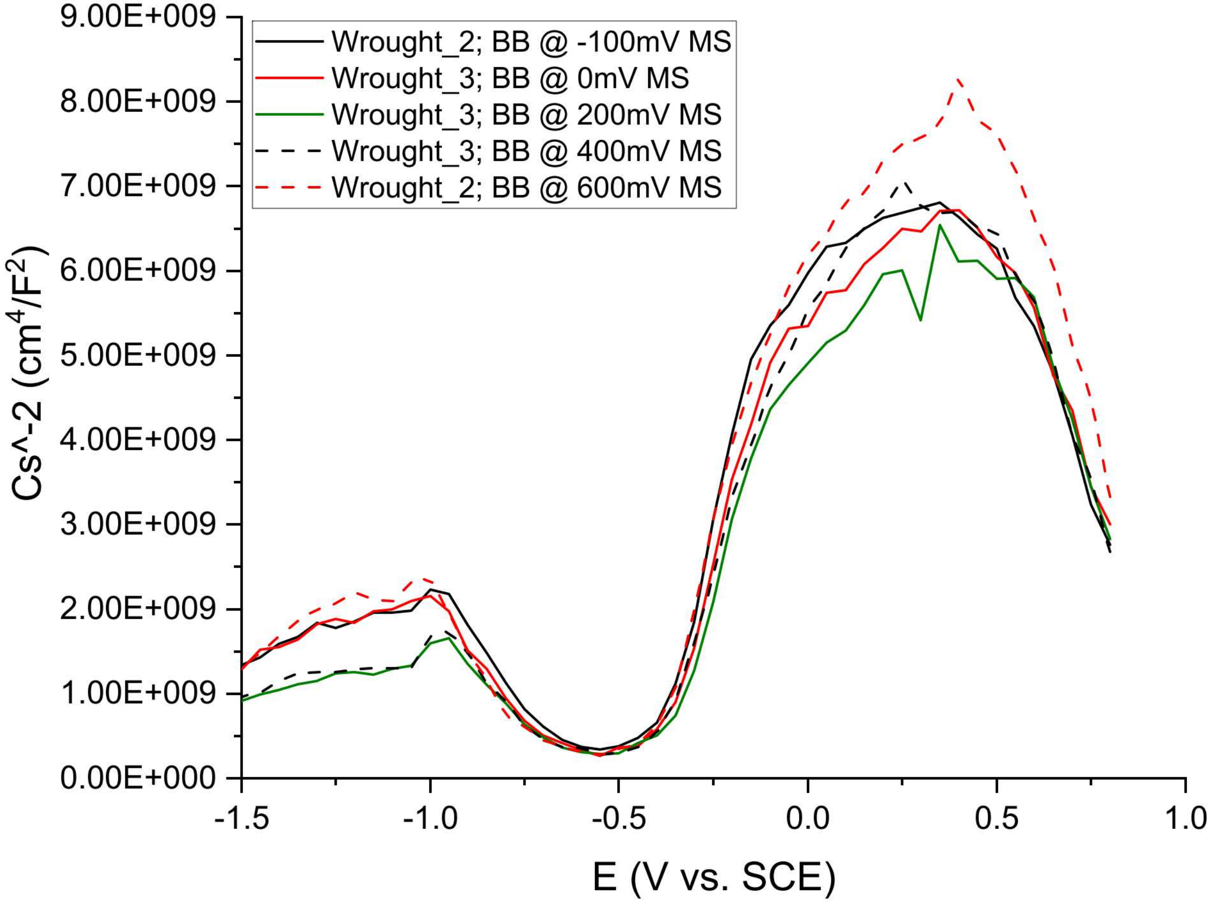
HEA LENS – 1M Na_2SO_4



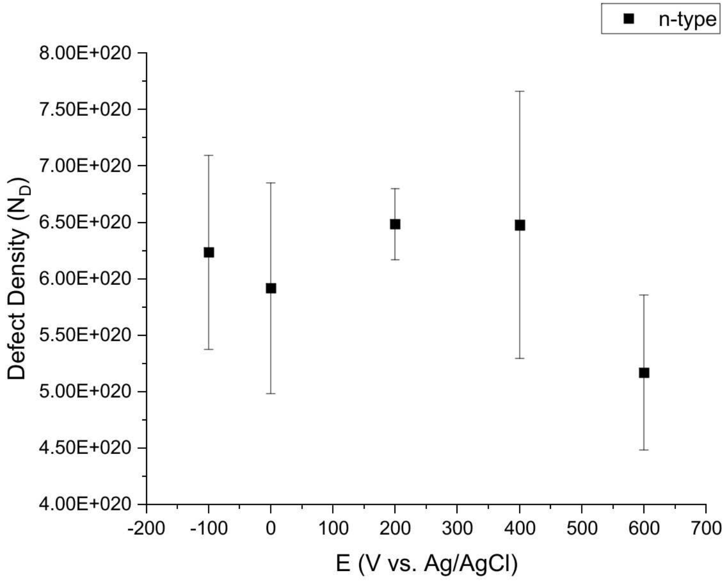


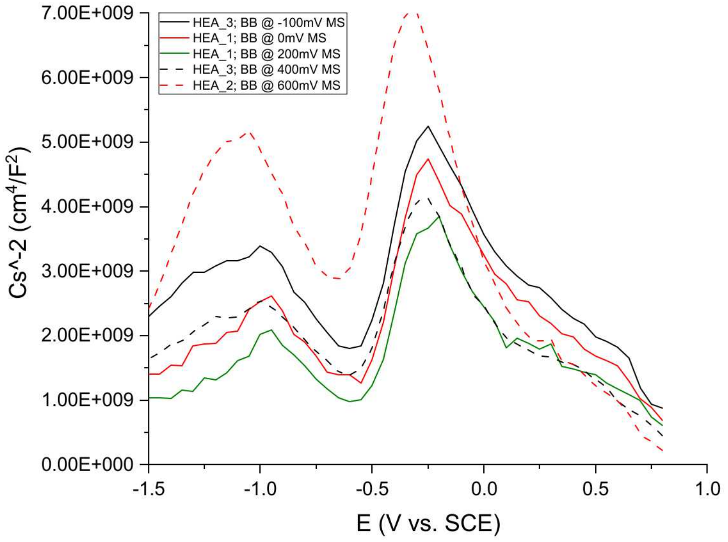




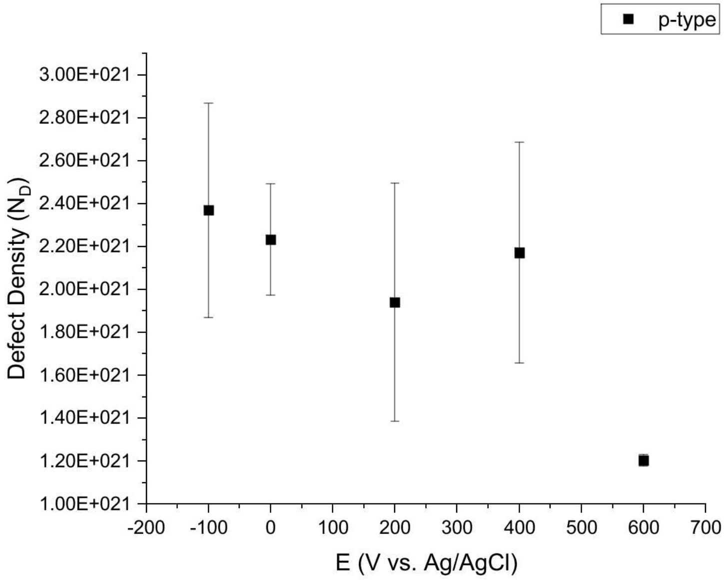


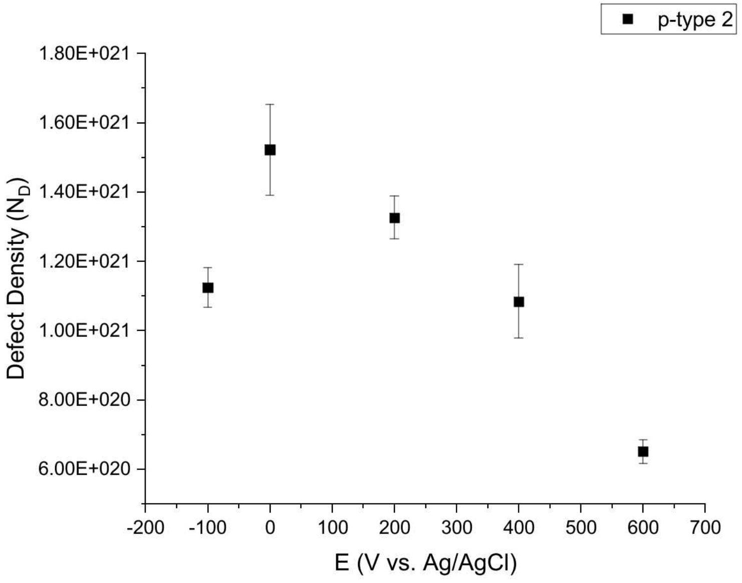
304L wrought – Borate Buffer

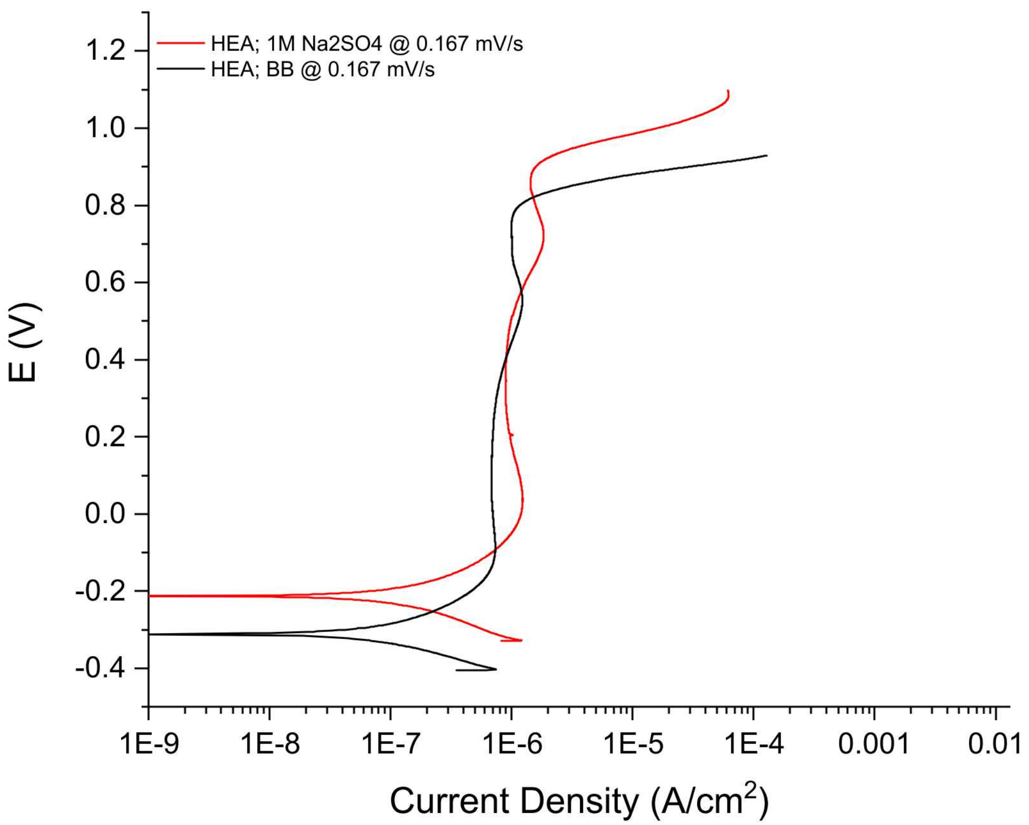




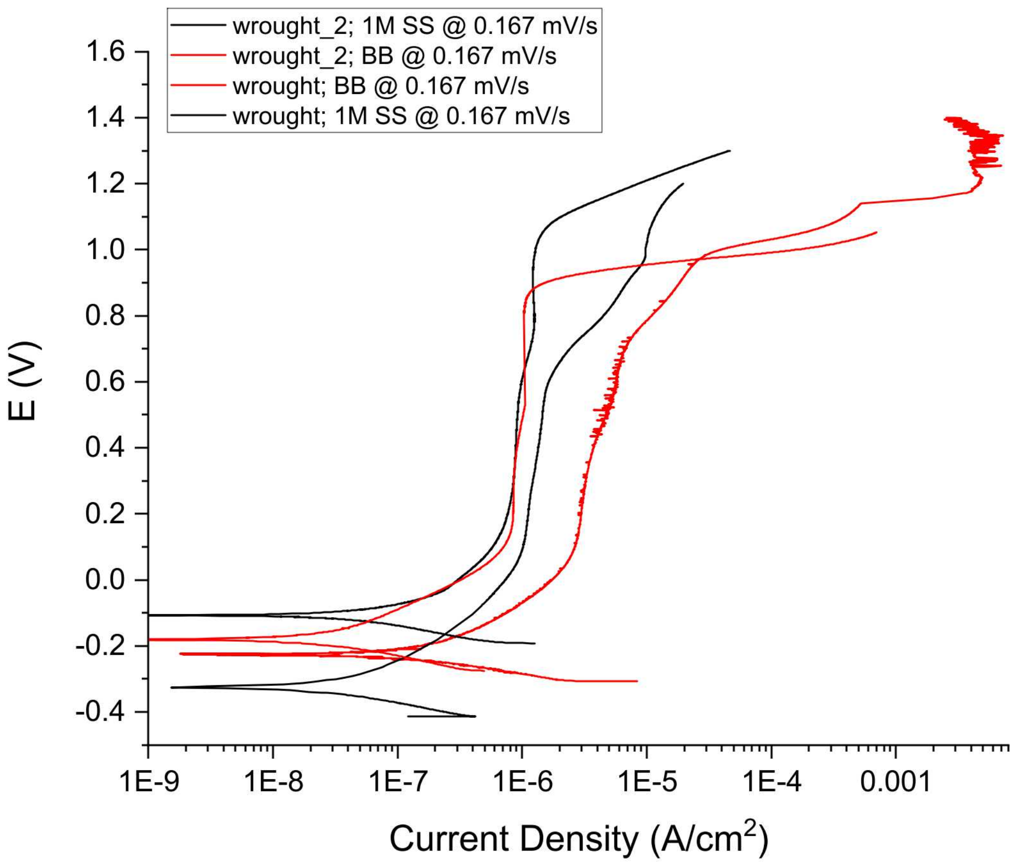
HEA LENS – Borate Buffer







HEA; 1M Na2SO4 @ 0.167 mV/s
HEA; BB @ 0.167 mV/s
E (V)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
1E-9
1E-8
1E-7
1E-6
1E-5
1E-4
0.001
0.01
Current Density (A/cm2)



wrought_2; 1M SS @ 0.167 mV/s
wrought_2; BB @ 0.167 mV/s
wrought; BB @ 0.167 mV/s
wrought; 1M SS @ 0.167 mV/s
E (V)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
1E-9
1E-8
1E-7
1E-6
1E-5
1E-4
0.001
Current Density (A/cm2)