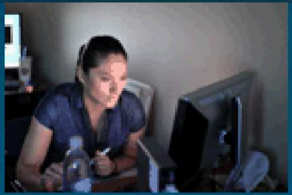
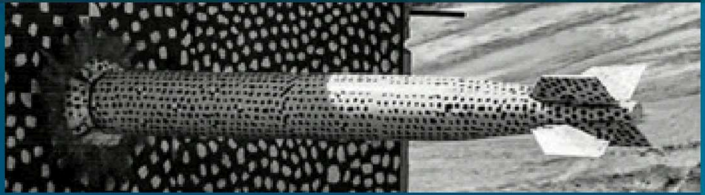
SAND2019-3644C

Corrosion and mechanical behavior of direct energy deposited high entropy alloy (CoCrFeMnNi)





Corrosion Conference & Expo 2019

Financial assistance from the Laboratory Directed Research & Development (LDRD) office is gratefully acknowledged

PRESENTED BY

Michael A. Melia

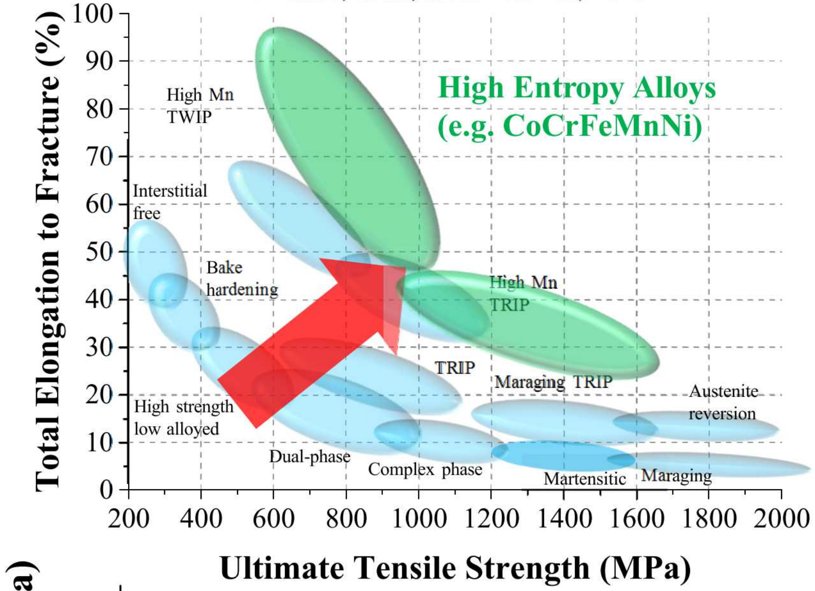
Co-authors: (SNL) Jay Carroll, Shaun R. Whetten, Michael Chandross, Nicolas Argibay, Eric Schindelholz, Andrew B. Kustas;

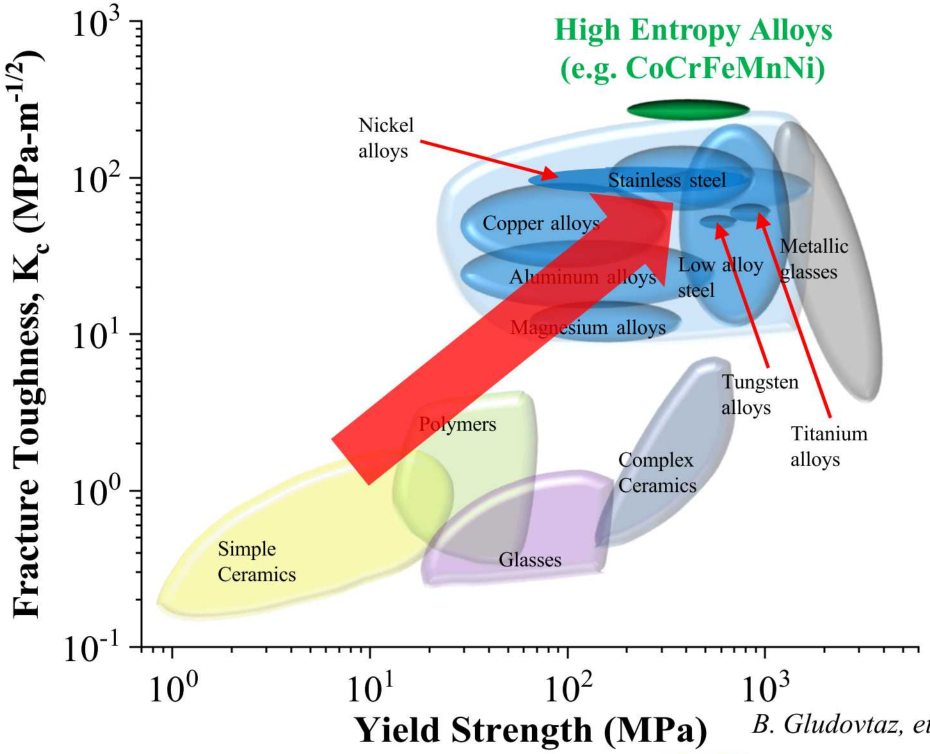
(OSU) Saba Navabzadeh Esmaeely, Jenifer Locke;

(AMES) Emma White, Iver Anderson

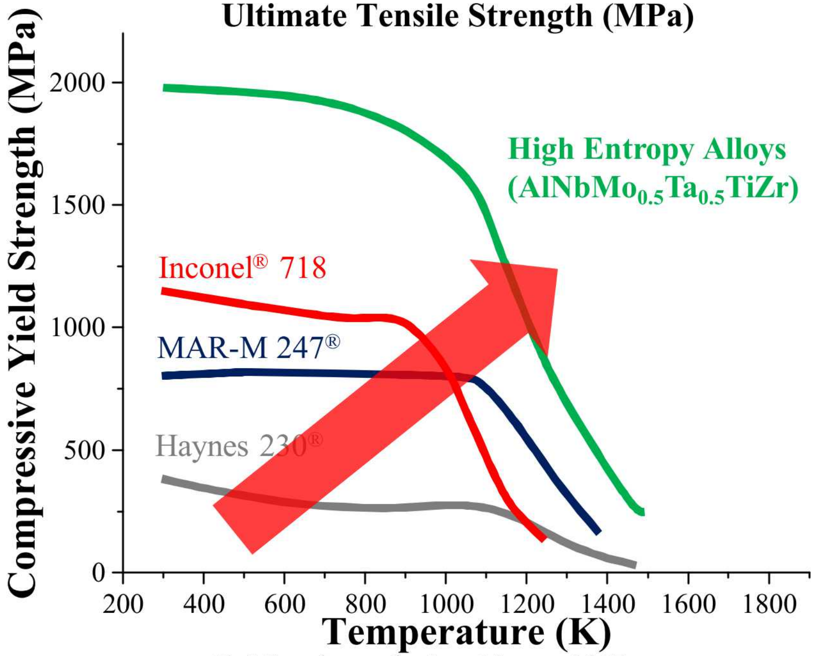
High Entropy Alloys (HEAs): Unusual mechanical properties

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

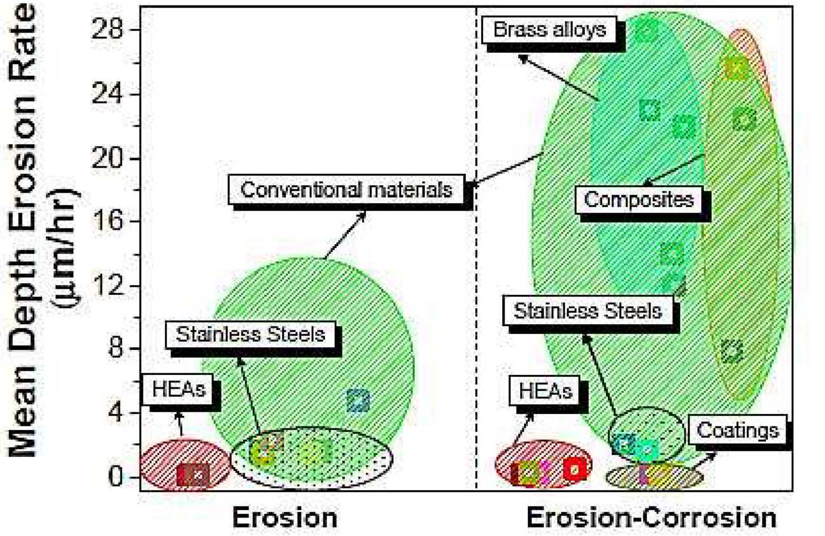




B. Gludovtaz, et al., Science., 2014



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



A. Ayyagari, et al., Metals, 2018

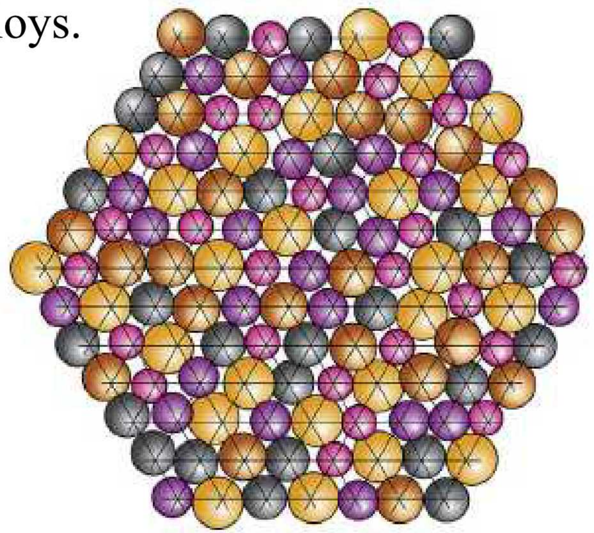
What makes HEAs unique?

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

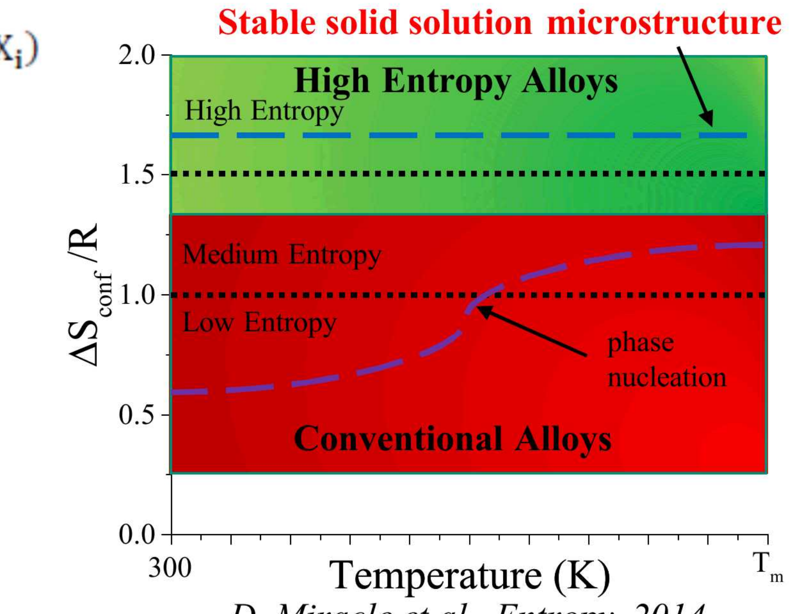
$$\Delta G^{SS} < \Delta G^{IM} \quad \rightarrow \quad \Delta S^{SS} > \frac{\Delta H^{IM} - \Delta H^{SS}}{T}$$



Disordered solid solution

D. Miracle et al., Acta Mat. (2017)

olution.



D. Miracle et al., Entropy, 2014

Thermodynamically stable and ***predictable*** solid solution microstructure, independent of processing route.

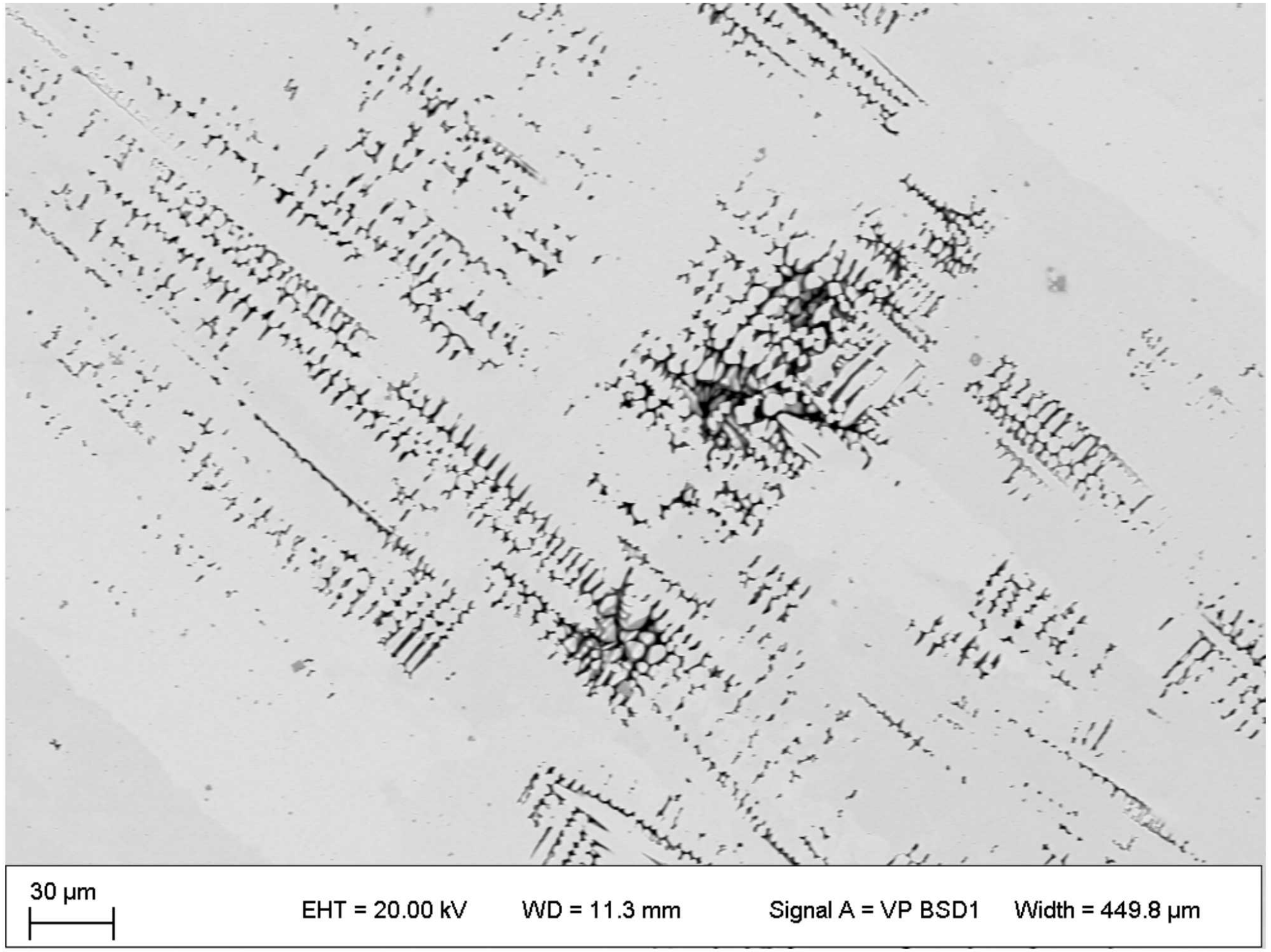
Beneficial for layer-by-layer melting/re-melting of AM…

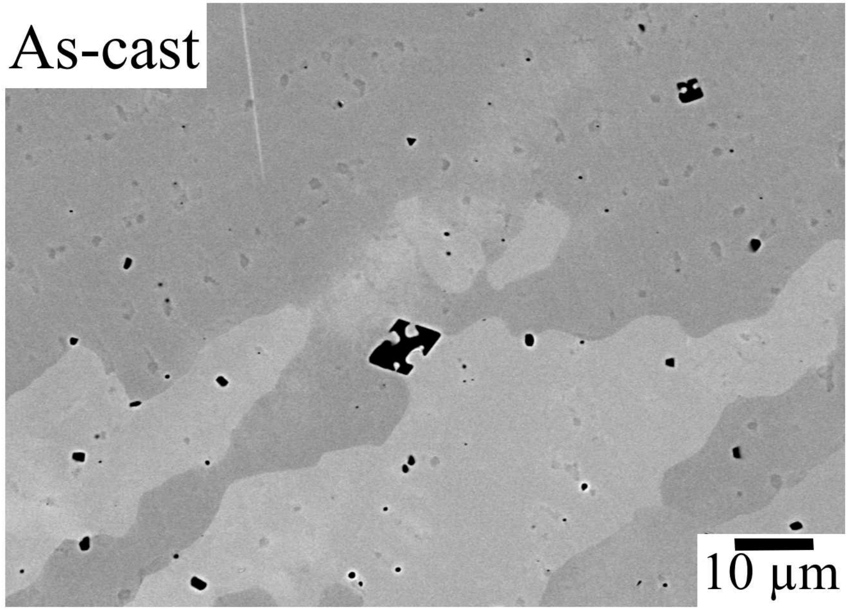
*Caveat – several HEAs are multiphase and contain intermetallics

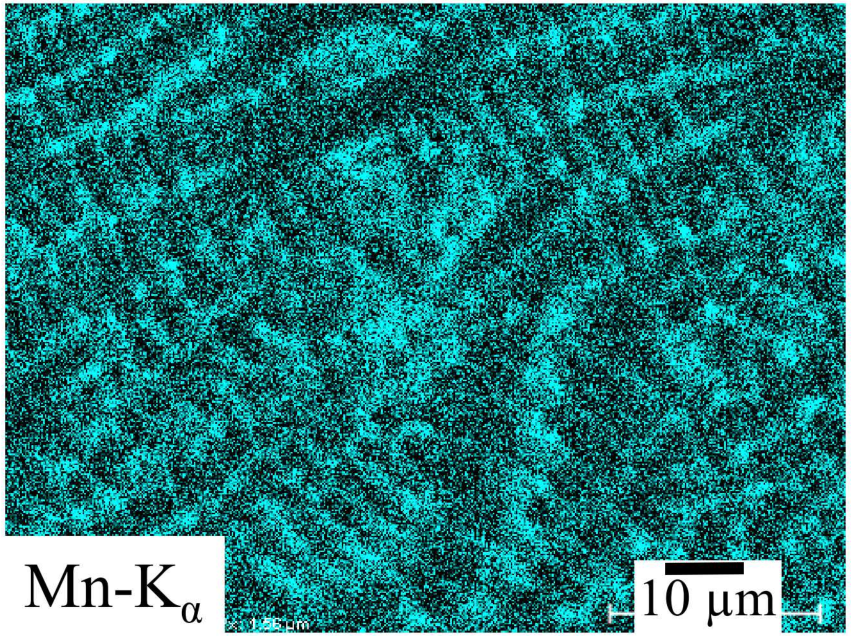
**Cannot ignore enthalpy!

This hypothesis remains controversial and highly-debated, and why the proposed work has high scientific impact potential.

Cast microstructure of CoCrFeMnNi HEA







Additive manufacturing of HEAs

Why AM? Faster cooling rates, smaller non-metalli MMA12 usion size, material waste, etc.

Show low porosity, single phase parts can be built with the LENS technique.
Metrics for success will be from:

- Fully dense part produced by LENS.
- Single phase (FCC) microstructure with limited chemical segregation.
- Similar or superior **mechanical** behavior to HEA literature.
- Similar or superior **corrosion** behavior to HEA literature.
    - Will hypothesis that 20 at% Cr leads to similar/identical corrosion behavior as 304L stainless steel hold?

Project end goals: Use *in situ* mixing capabilities of LENS technique 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?

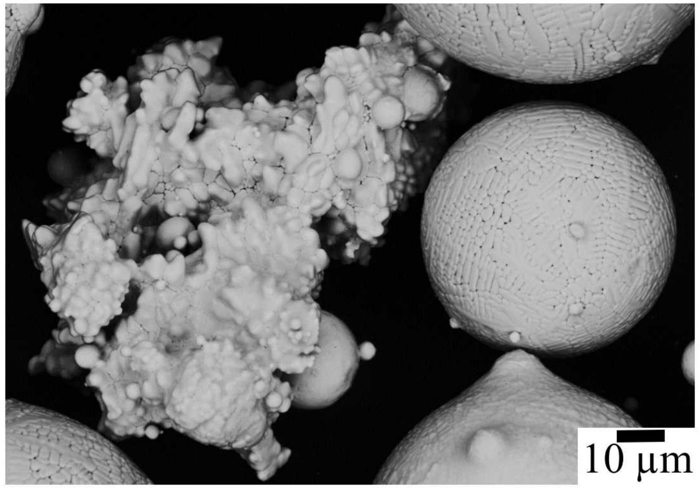
Slide 5

MMA12 Should I add a separate slide on this including literature?

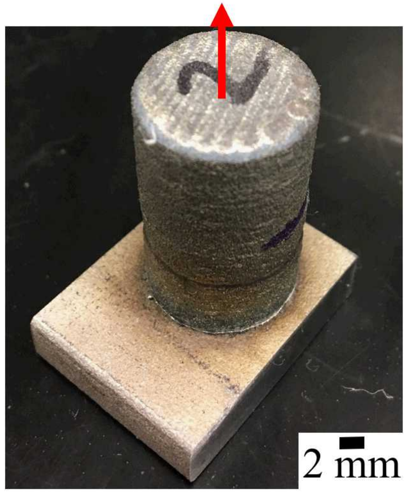
Melia, Michael Anthony, 3/19/2019

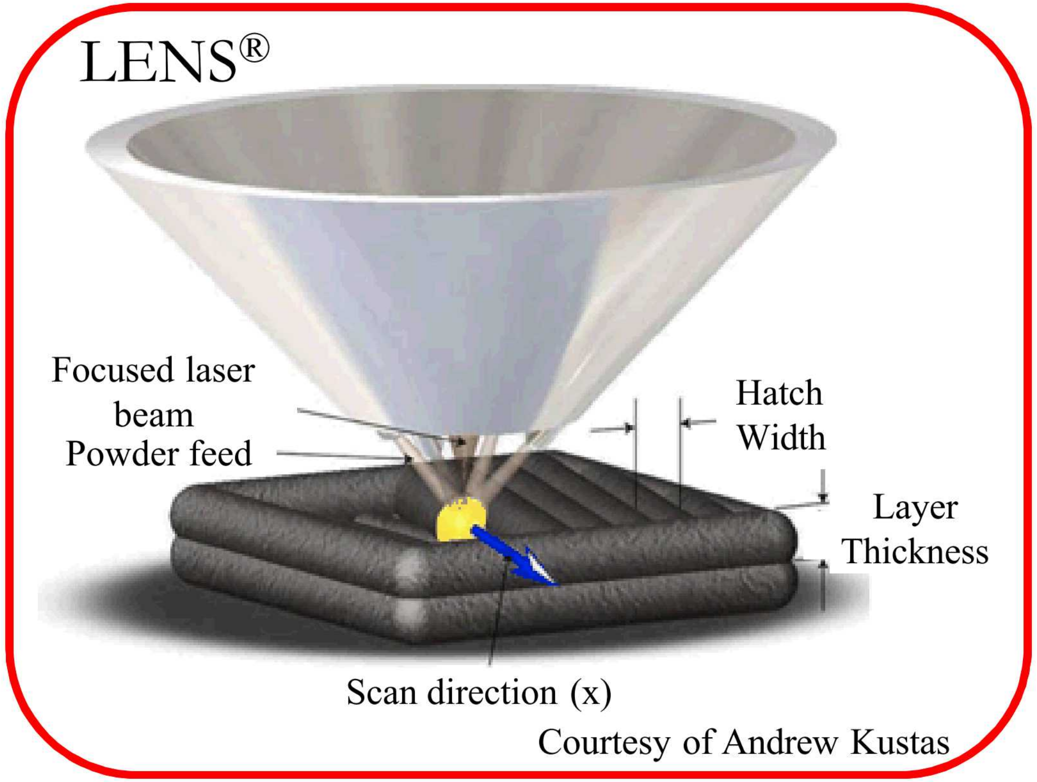
Powder and DED characteristics

Average powder diameter = 67 µm



Build direction





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

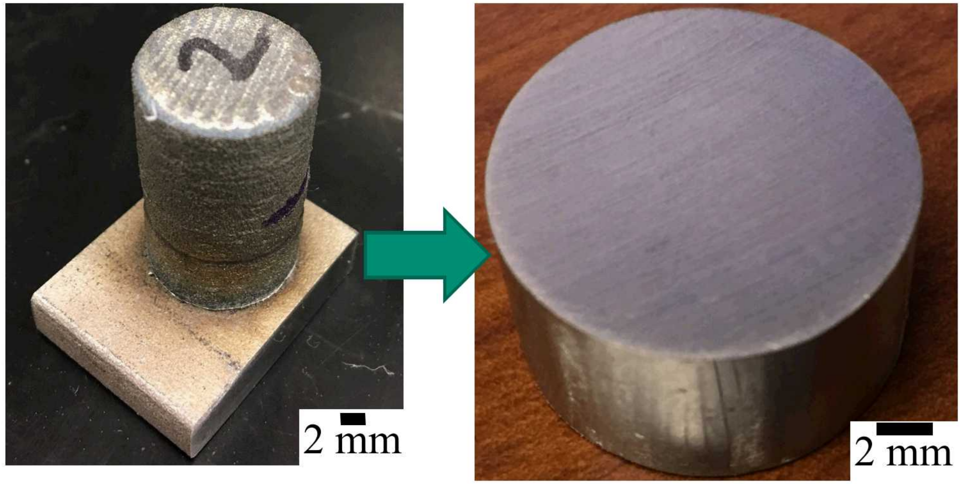
- Inert atmosphere maintained at <50ppm O_2 and <10ppm H_2O by a continuously flowing Ar gas.
- Laser power: 350 – 400 W.
- Build velocity: 400 – 600 mm/min.
- A 90 degree cross hatch build pattern was employed, first material deposited each layer was the perimeter of the build.

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.

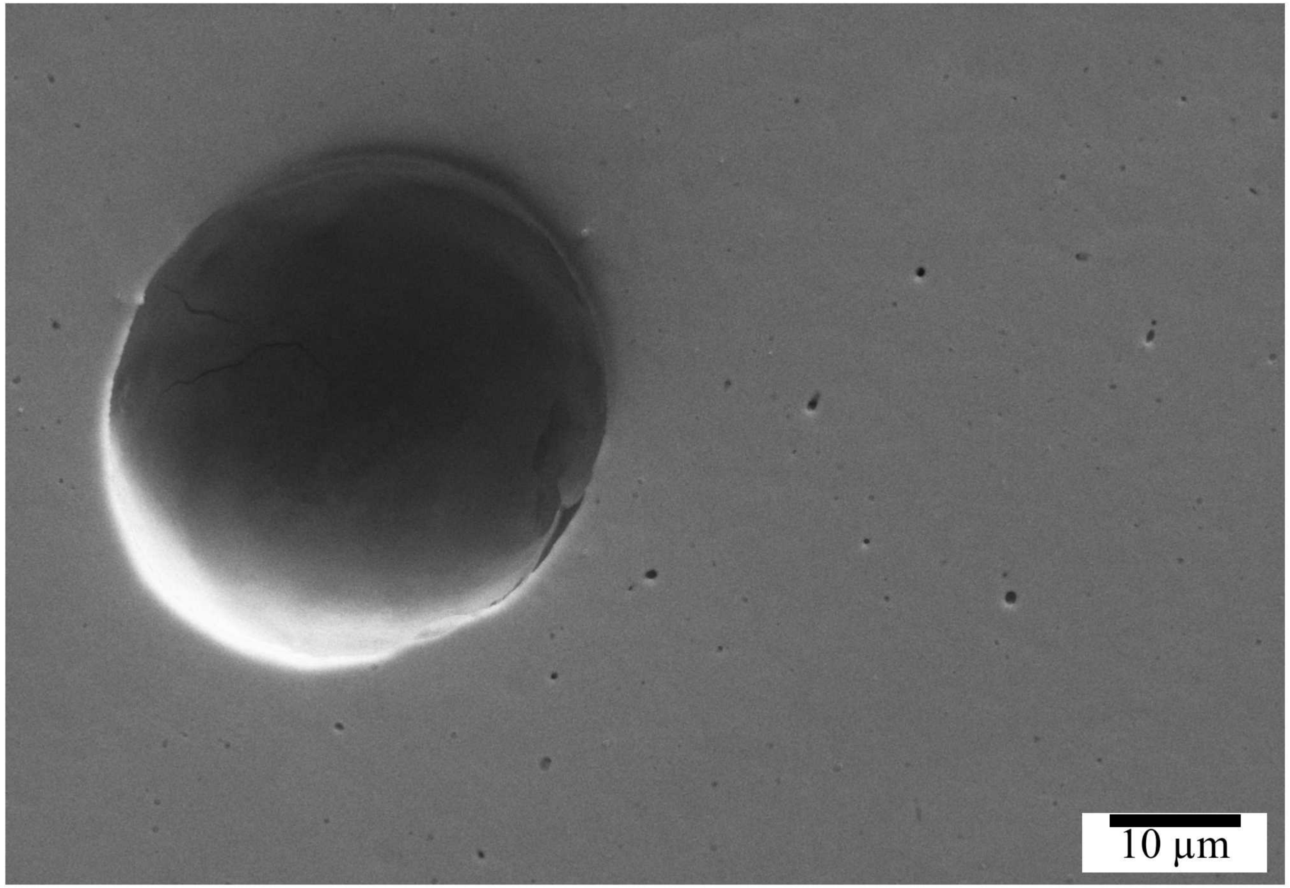
Density/porosity of DED HEA



Archimedes density measurement was performed to quantify porosity throughout as-built specimen.

Theoretical density = 8.04 g/cm^3
Archimedes density = 7.94 g/cm^3

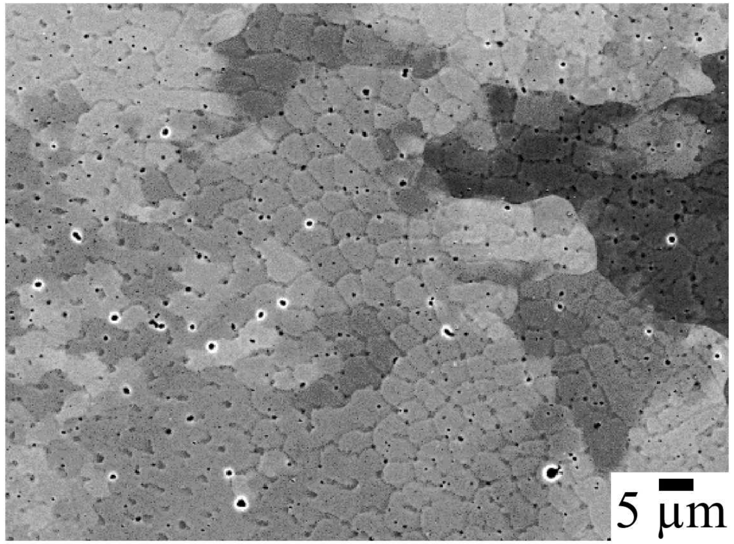
1.2 vol% porosity



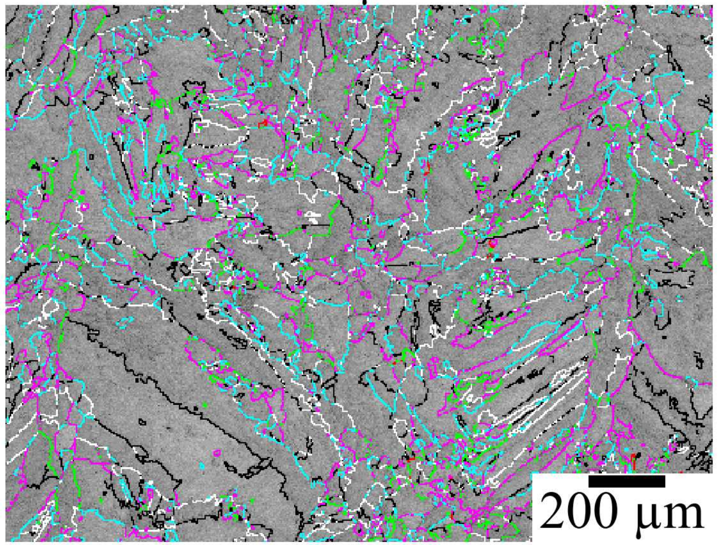
All observed porosity was in the form of gas porosity (10 to 40 µm in diameter).

Microstructure characterization

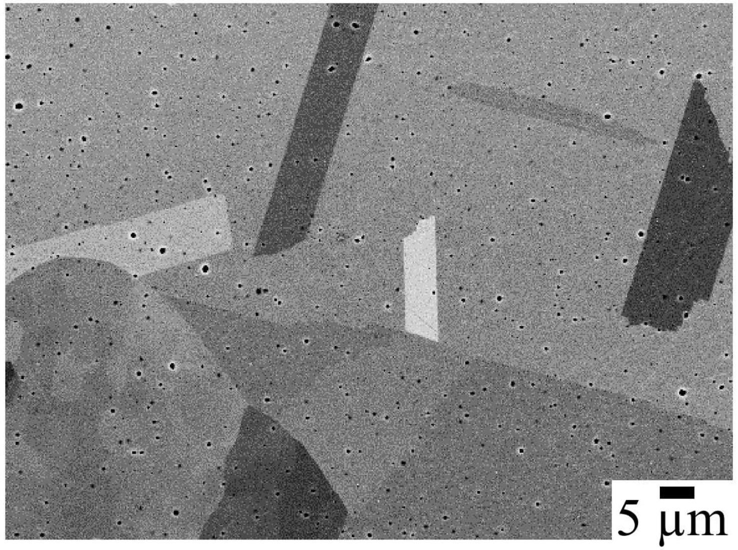
As-built



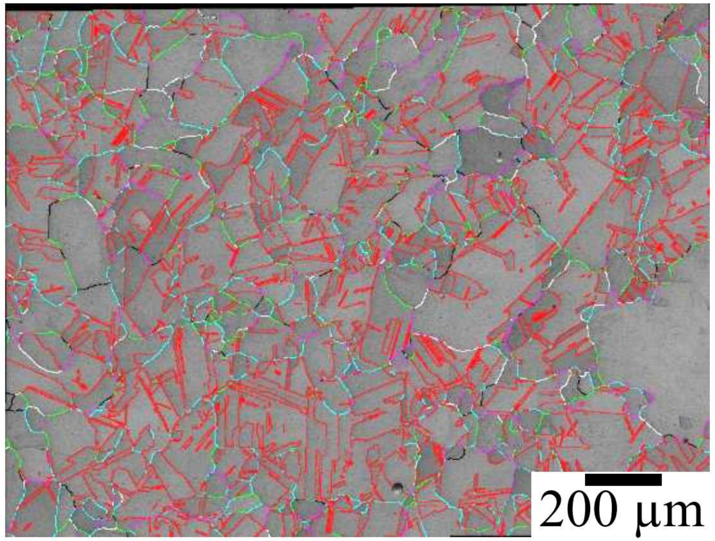
Grain size = 42.1 µm

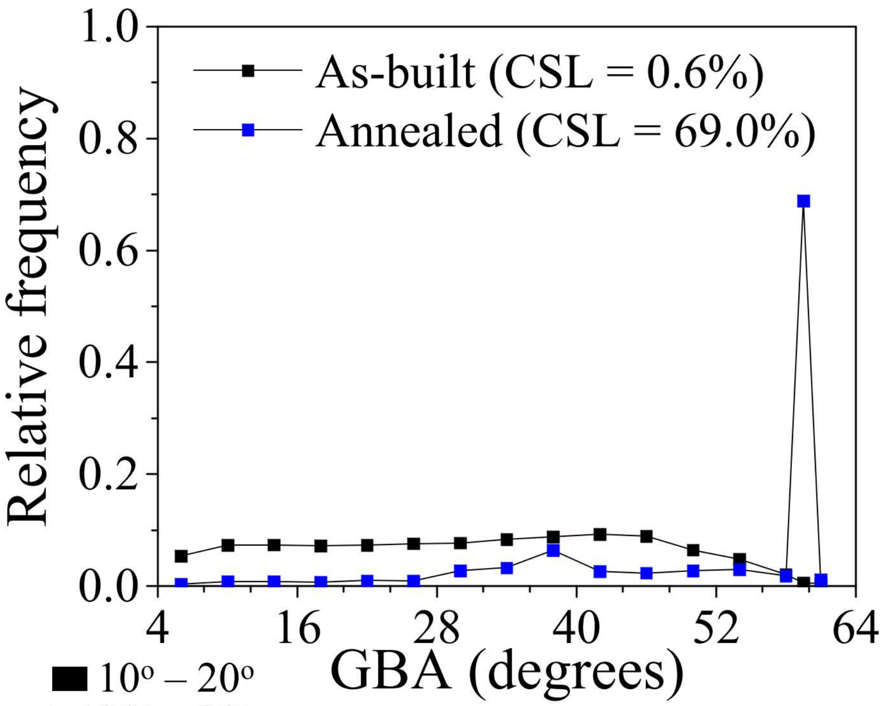


Annealed



Grain size without twins = 99.3 µm





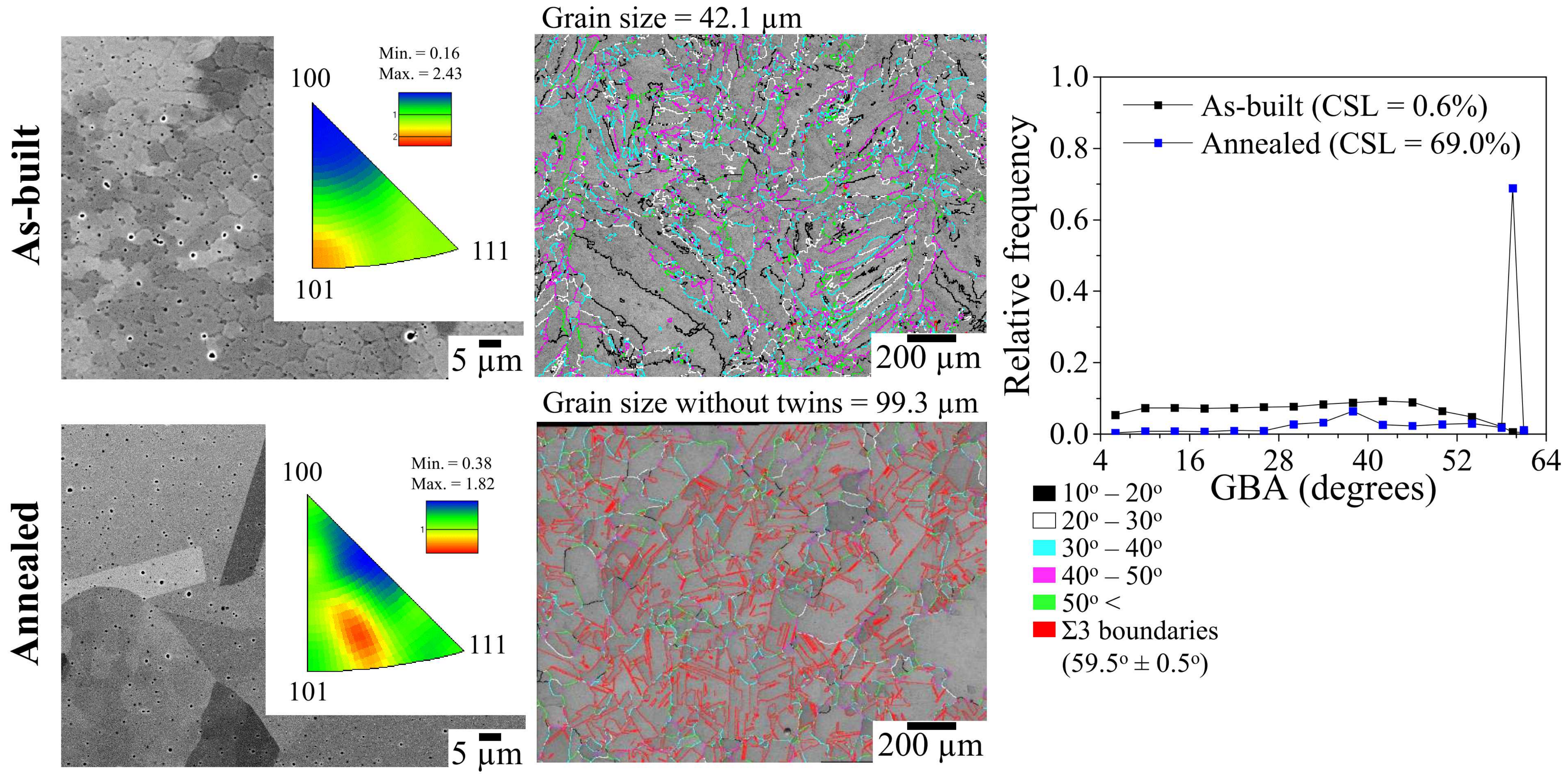
- 10° – 20°
- 20° – 30°
- 30° – 40°
- 40° – 50°
- 50° <
- Σ3 boundaries (59.5° ± 0.5°)

Slide 8

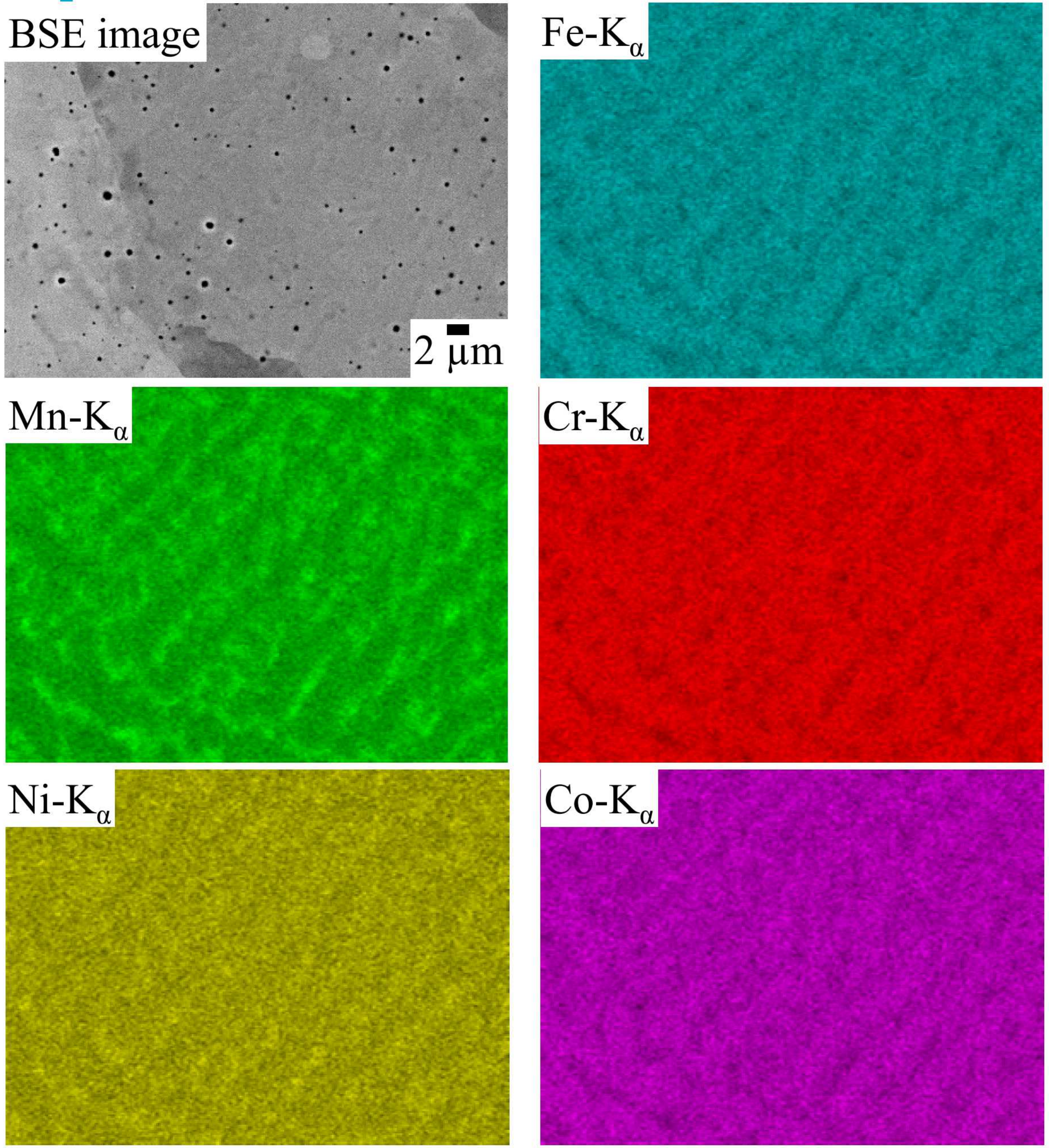
MMA3 Why do we care about GBC.

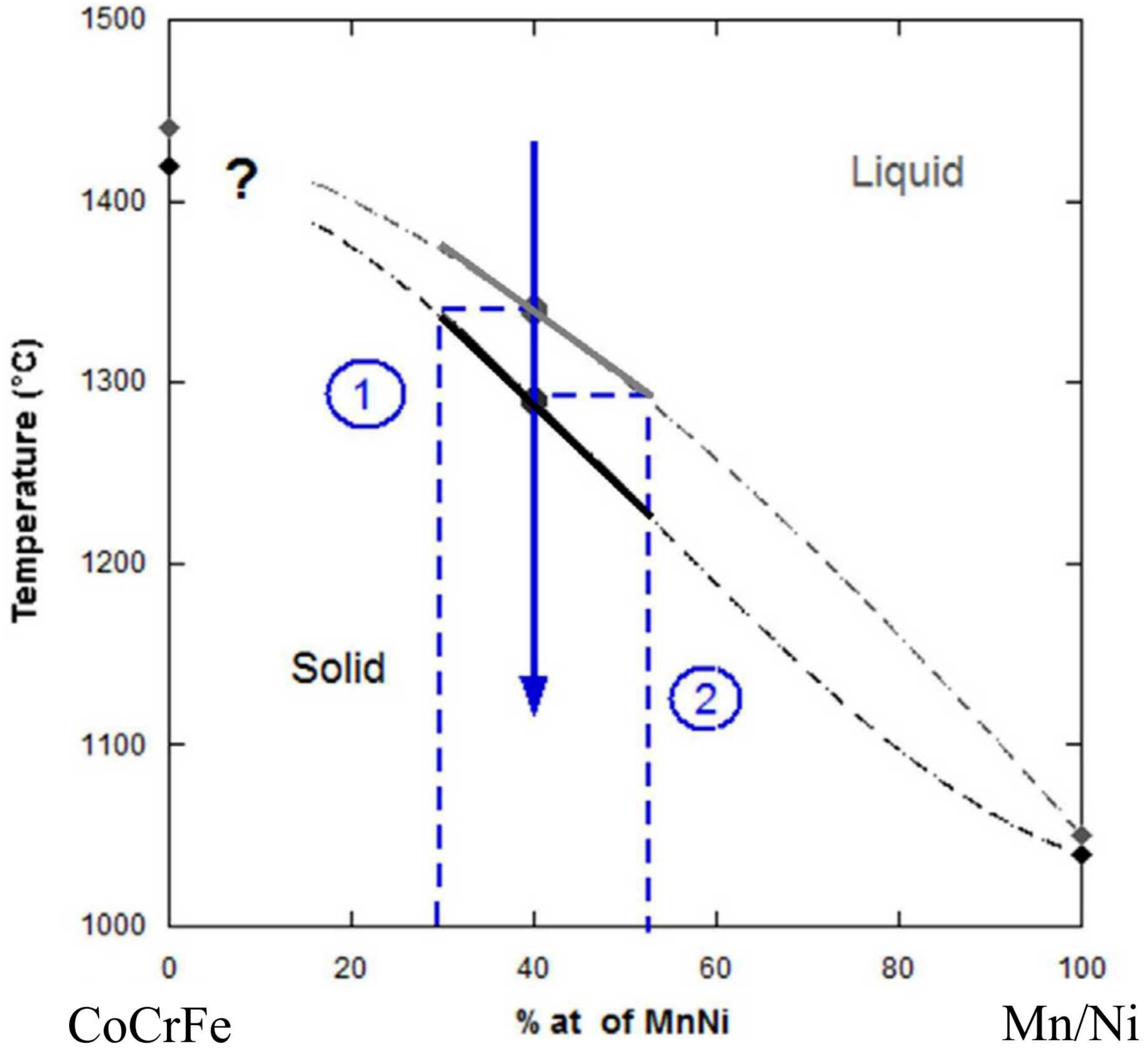
Melia, Michael Anthony, 3/13/2019

Microstructure characterization



Microstructure characterization of CoCrFeMnNi alloy



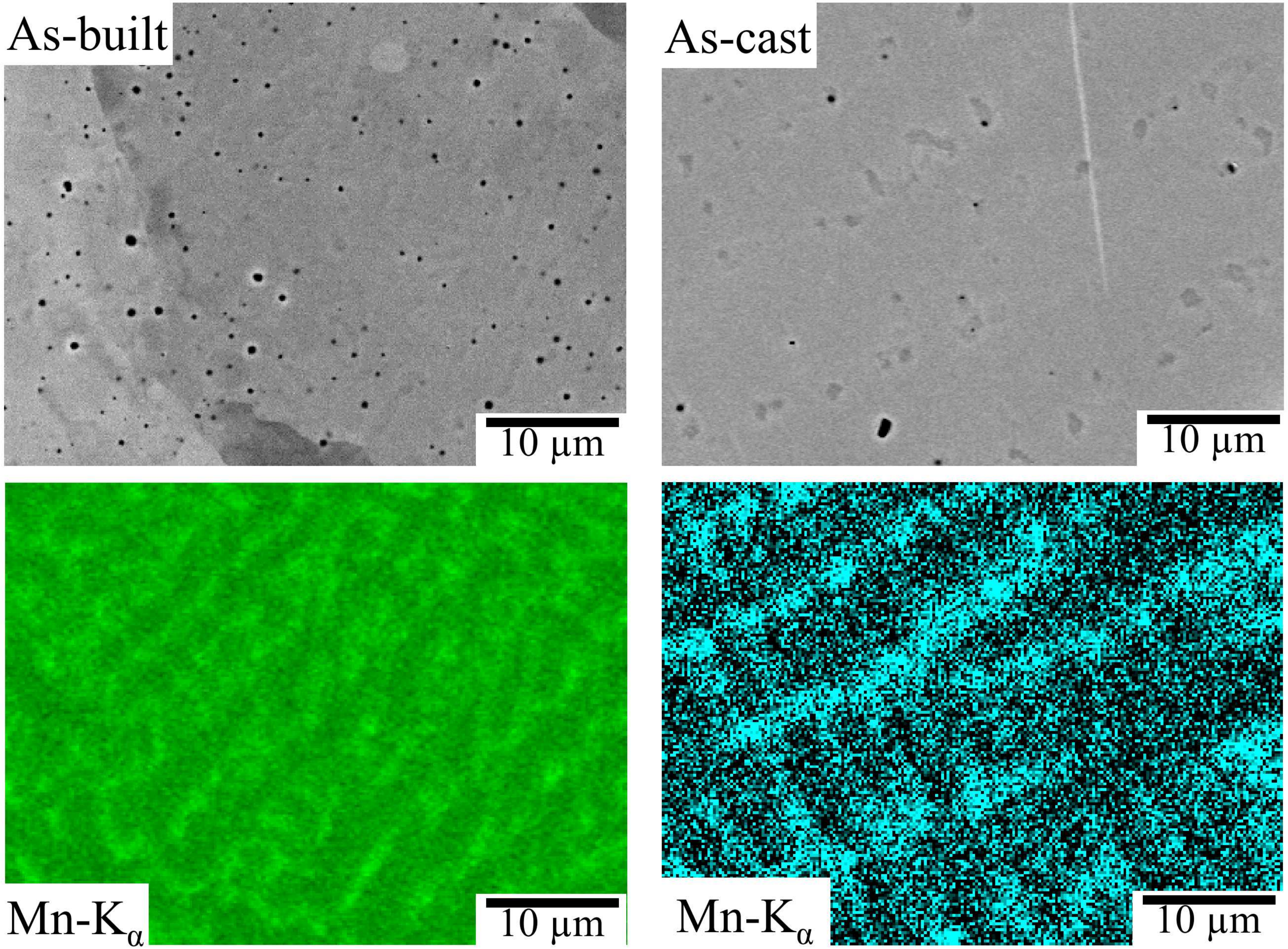


Mn/Ni enriched at interdendritic regions.

M. Laurent-Brocq, et al., Insights into the phase diagram of the CrMnFeCoNi high entropy alloy, Acta Materialia, 88 (2015) 355-365.

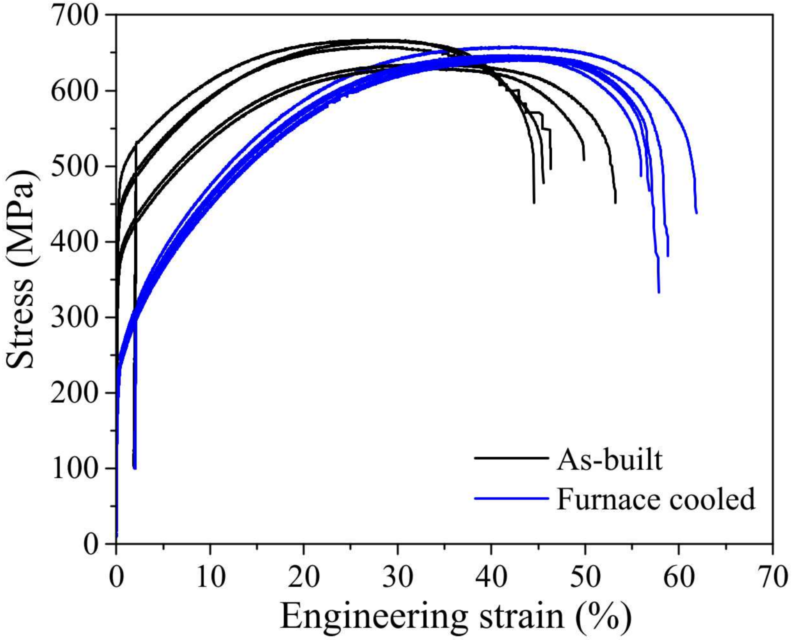
Microstructure characterization of CoCrFeMnNi alloy

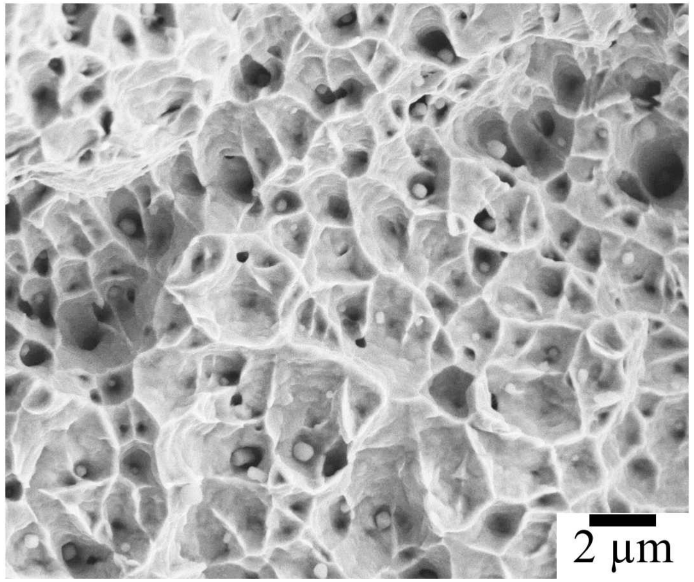
Interdenrite thickness: 0.5 – 1 µm



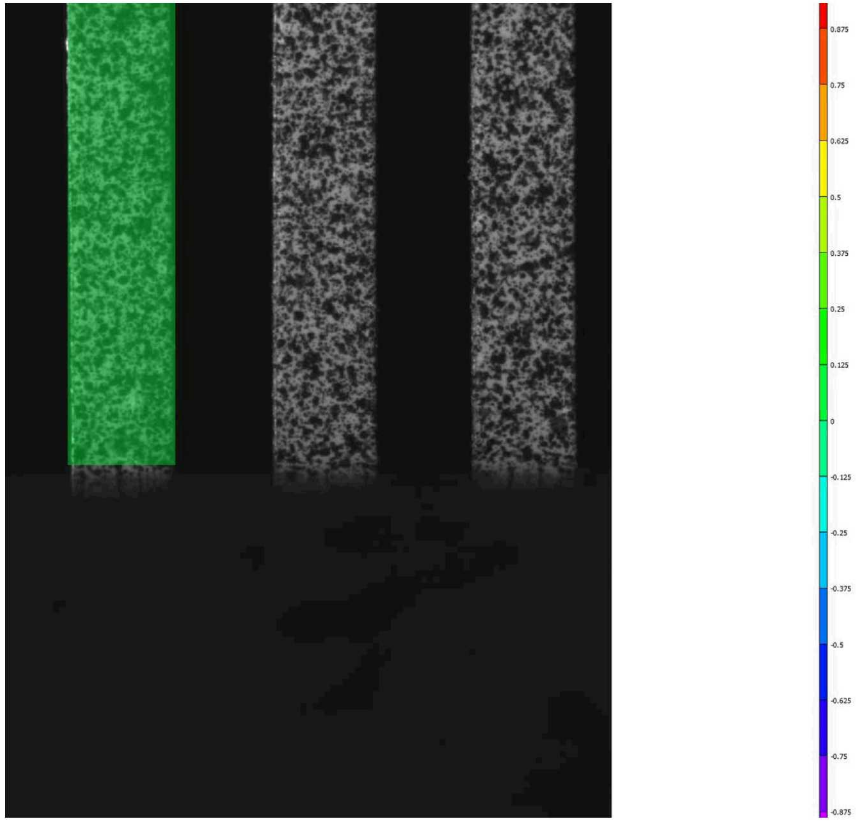
Interdenrite thickness: ~ 5 µm

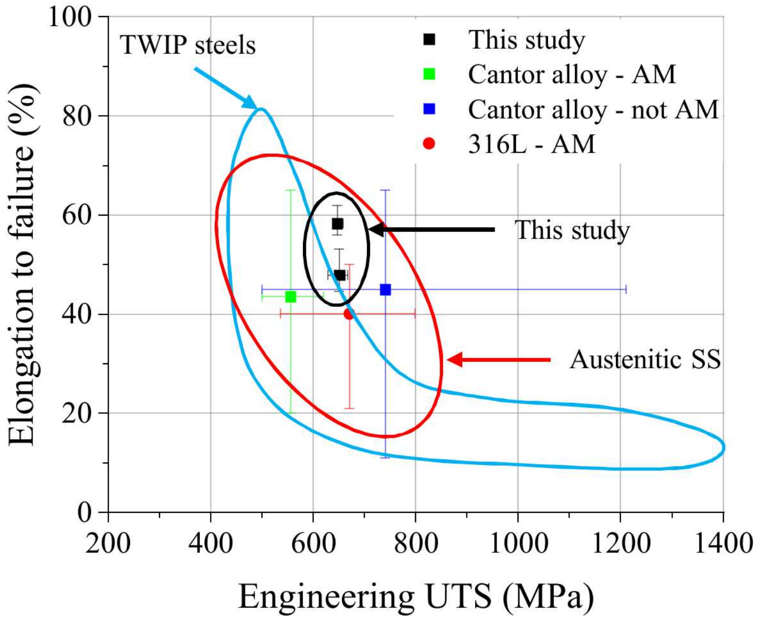
Mechanical properties of CoCrFeMnNi alloy





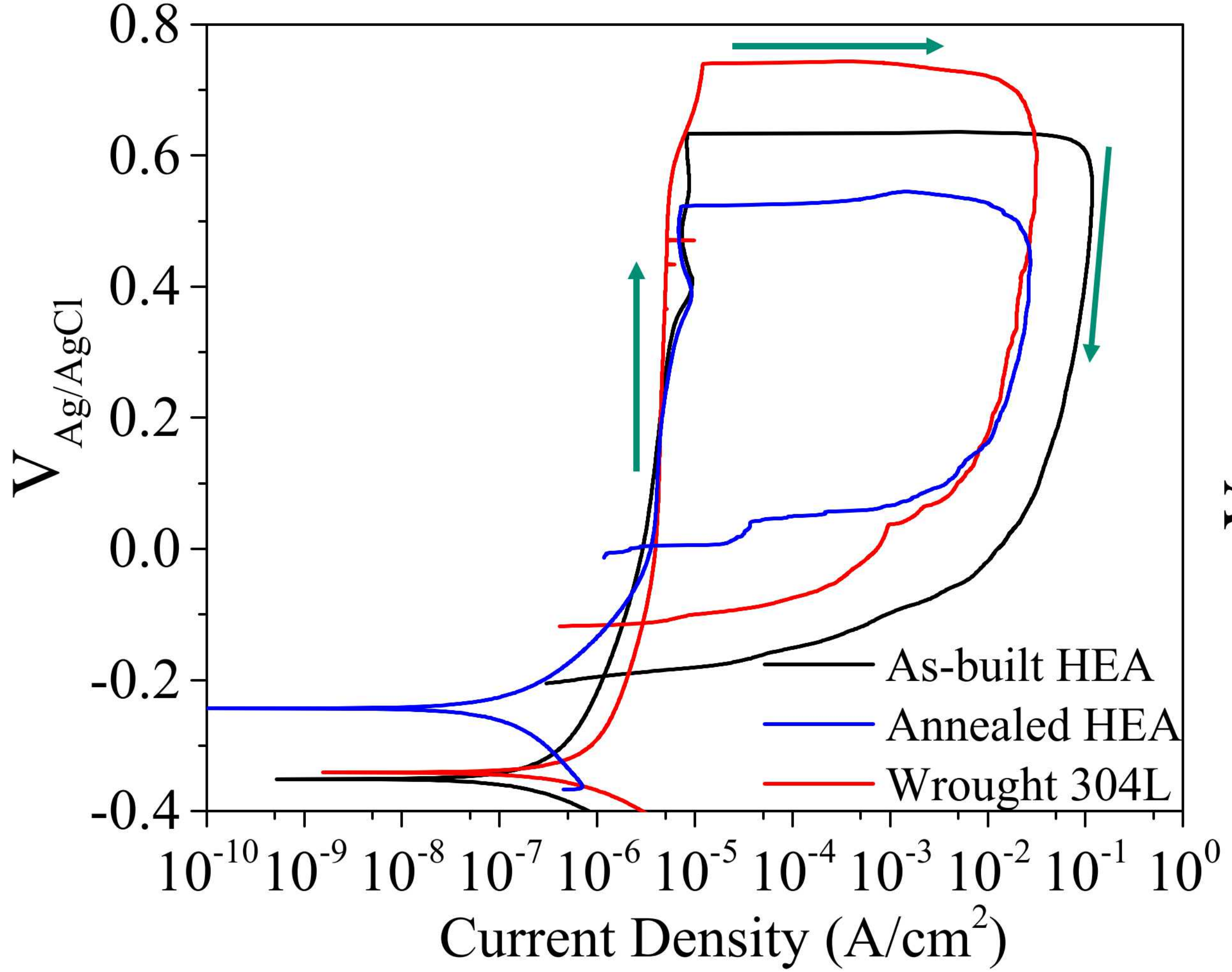
Digital image correlation (localization of strain).

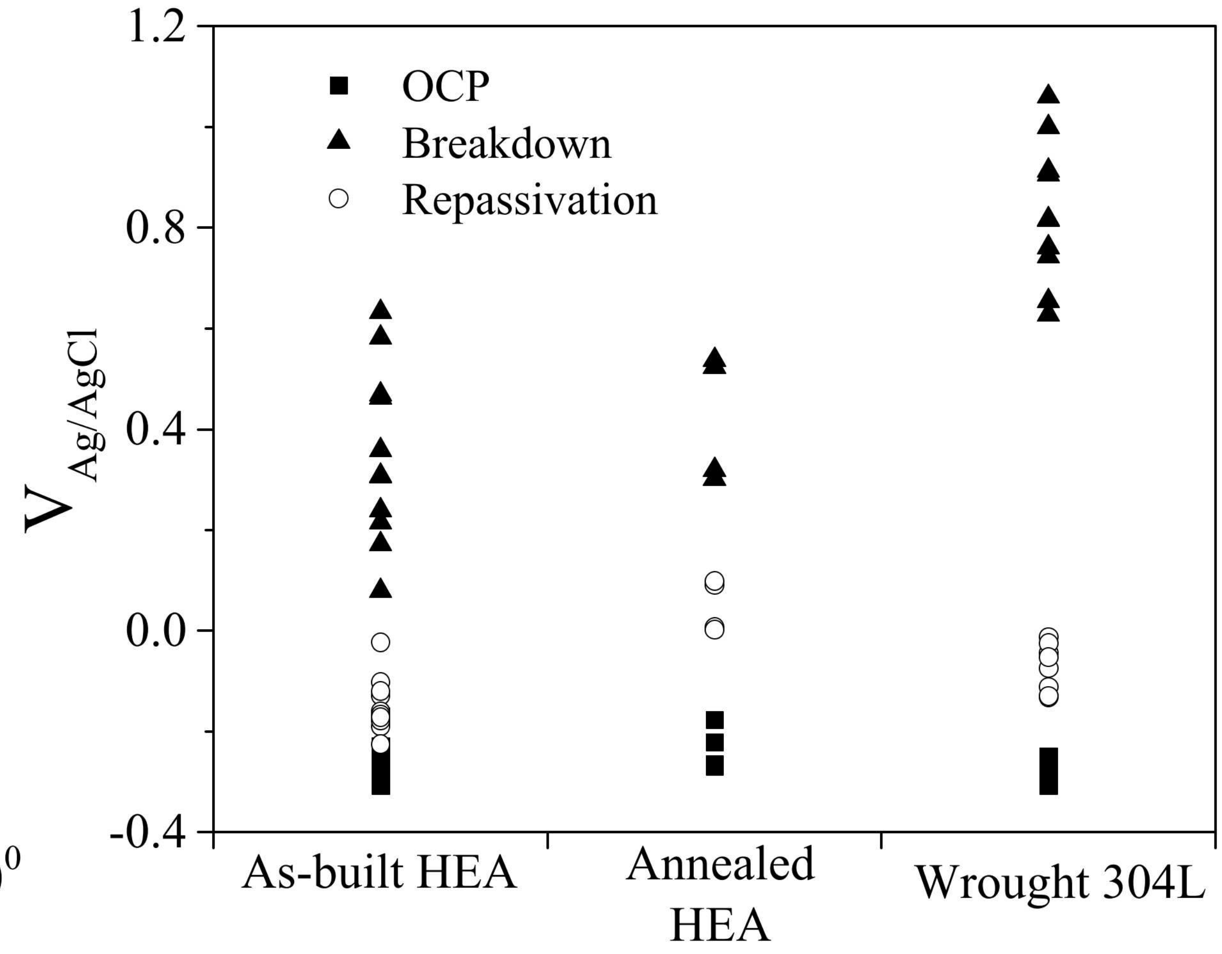




MMA7

Anodic polarization behavior of CoCrFeMnNi alloy





Cyclic polarization performed in quiescent 0.6 M NaCl (pH ~ 6).

Potential scan rate = 1 mV/sec.

Why would the breakdown potential of the HEA be different from 304?

Slide 13

MMA7 Suggest the 3 possible routes to why Rp and breakdown potential are different from AP vs annealed and HEA vs 304.

Melia, Michael Anthony, 3/13/2019

Anodic polarization behavior of CoCrFeMnNi alloy

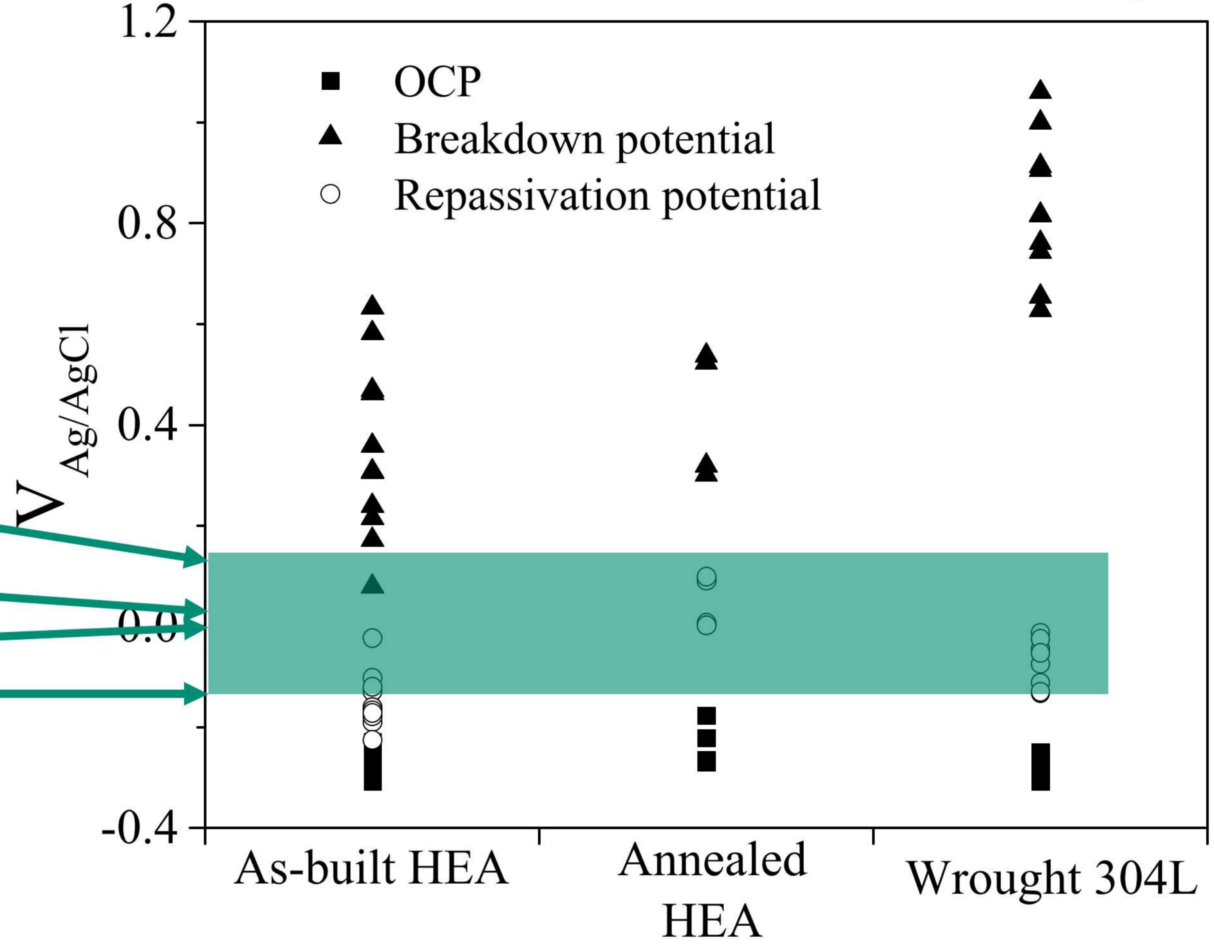
Breakdown potentials from corrosion studies in NaCl solutions.

Ayyagari et al. (0.05 V)

Ye et al. (0.018 V)

Szklarz et al. (0.0 V)

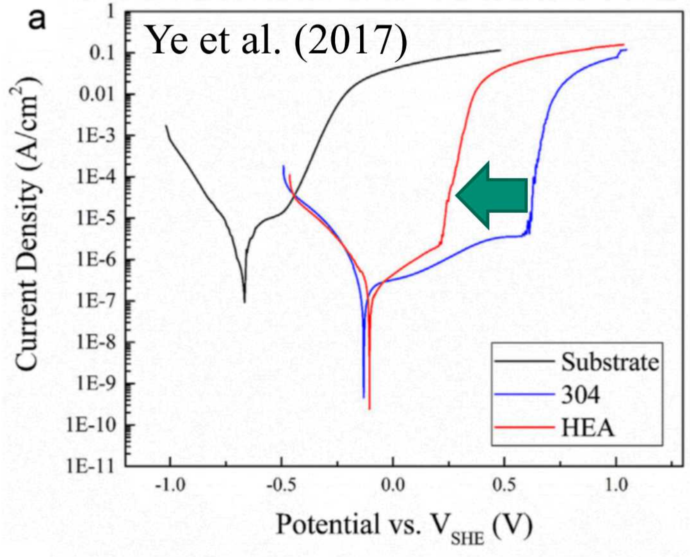
Rodriguez et al. (-0.28 V)



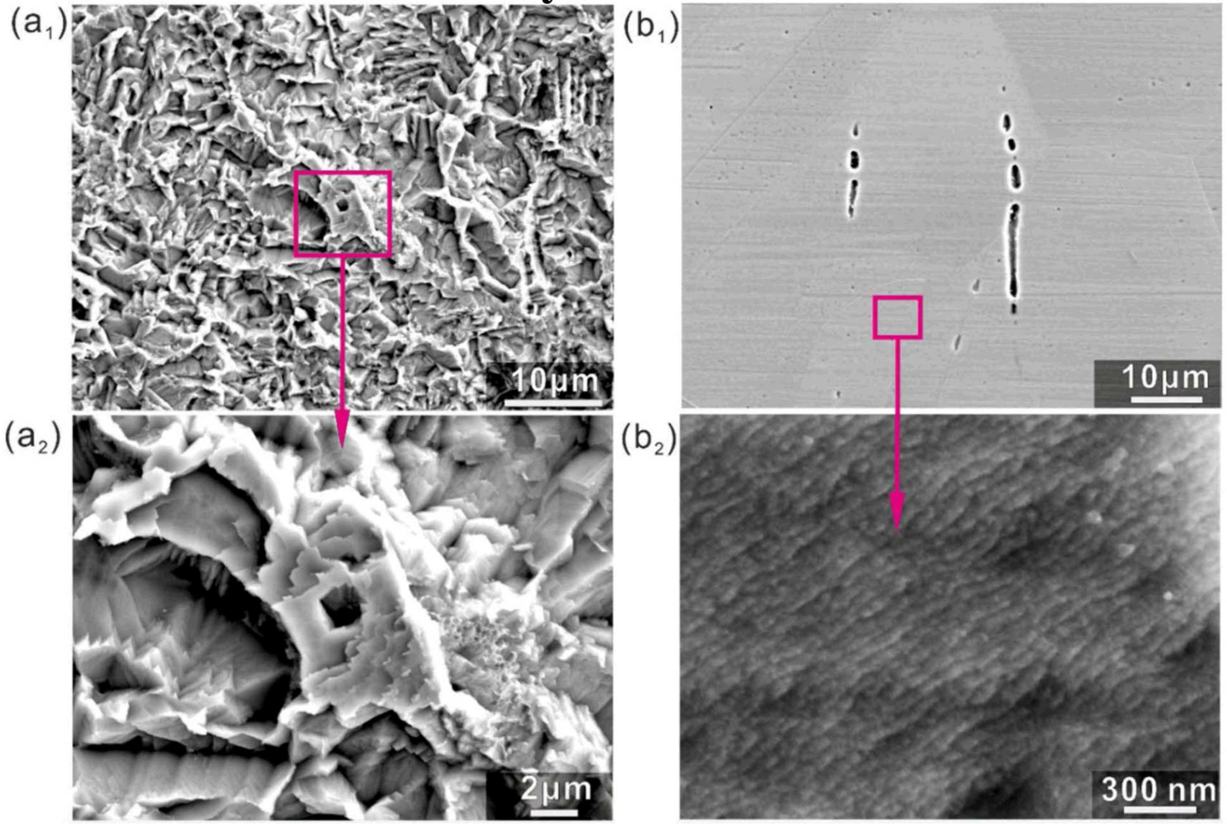
The breakdown potential for similar CoCrFeMnNi alloys in NaCl solutions were 100-200 mV lower than the as-built and annealed material in this study.

Possibly because of the refinement of nonmetallic inclusions common for AM material.

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



It has been common to see a ~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.**
- **Lack of bounded water**.

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

Pitting resistance equivalent number (PREn) = %Cr+3.3%Mo+30%N

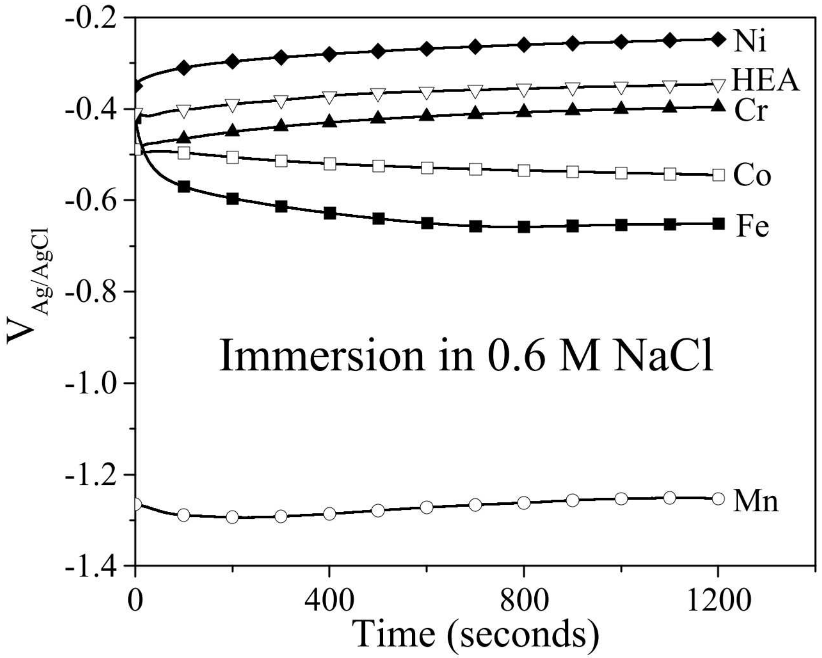
PRE_{MN} = %Cr+3.3%Mo+30%N-1.0%Mn (Rondelli et al. 1995)

Composition (wt%)	**Cr**	**Mn**	**Mo**	**N**	**PRE_{MN}**
304L	18.4	1.76	0.31	0.073	18.8
As-built	18.2	18.5	0.002	0.002	-0.2334

The PRE_{MN} may not make complete sense here, but there have been plenty of studies showing Mn has an adverse effect on local corrosion resistance of steels:

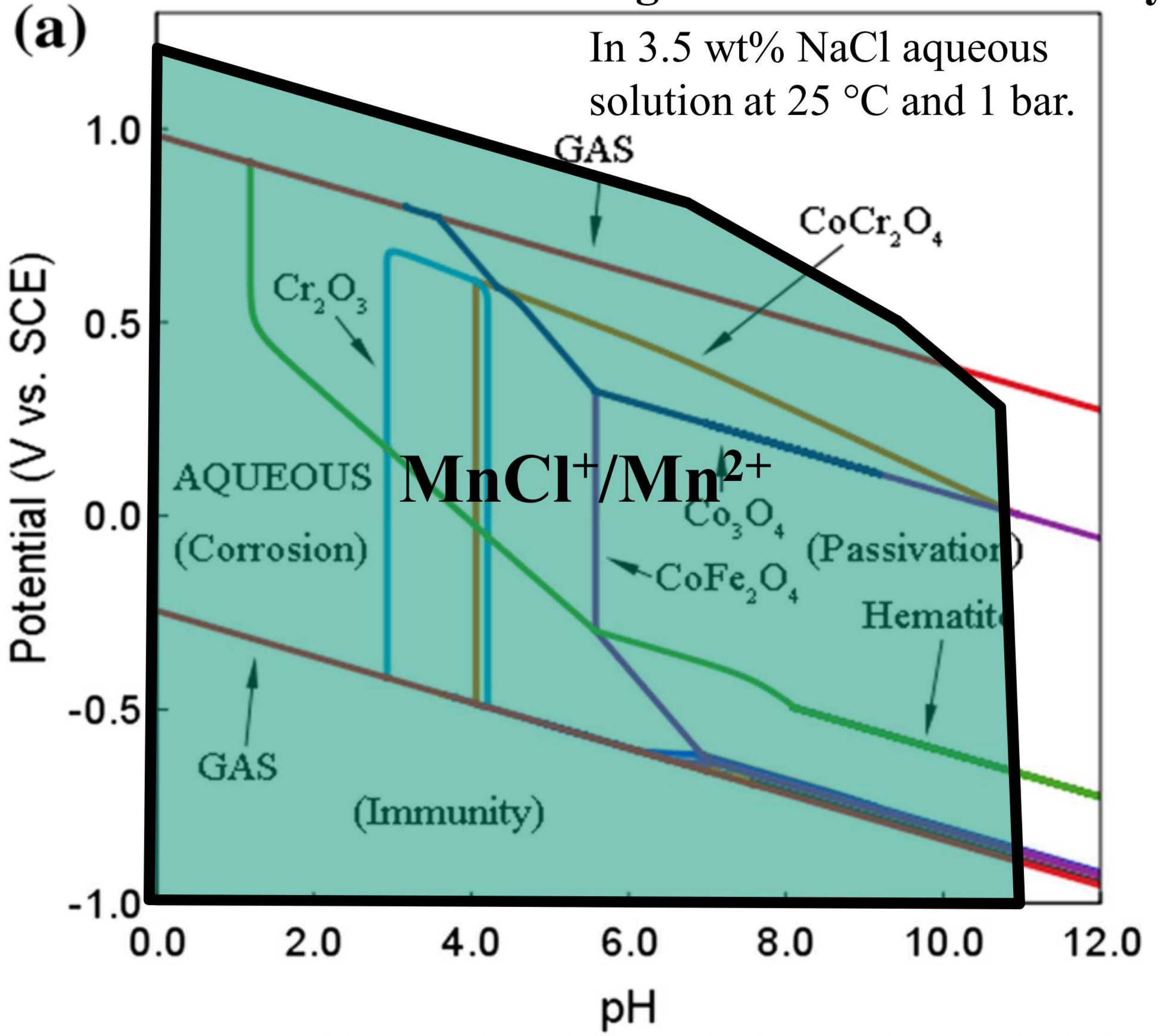
- Ahila et al. (1996)
- An et al. (2016)
- Kemp et al. (1995)
- Rondelli et al. (1995)
- Toor et al. (2008)
- Zhu et al. (1998)
- Zhang et al. (1999)
- Tjong et al. (1986)
- Moon et al. (2019)

What about the other alloying elements?



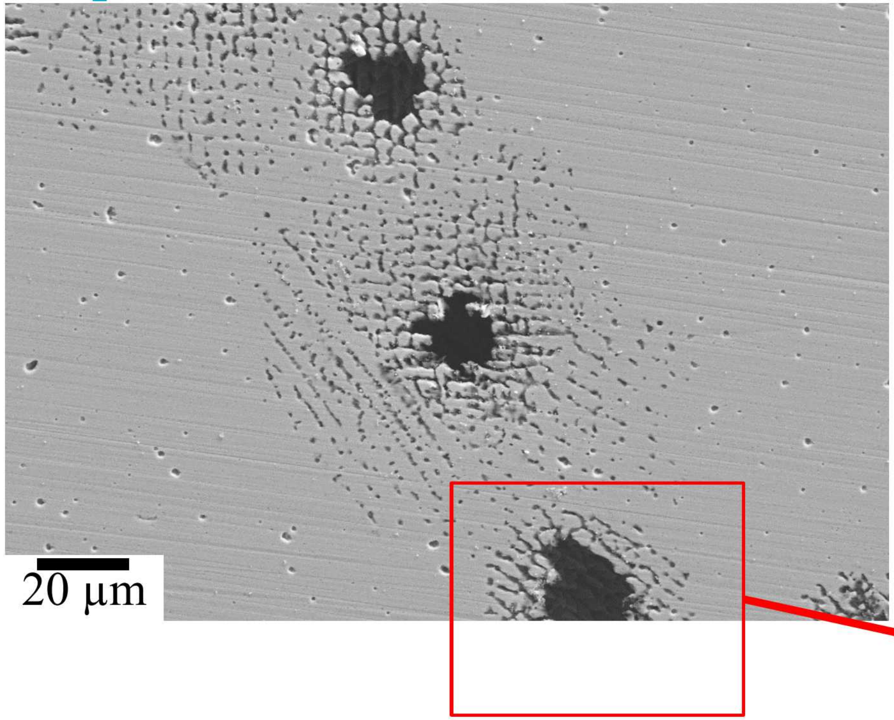
Passive behavior of CoCrFeMnNi alloy

Calculated Pourbaix diagram for CoCrFeNi alloy

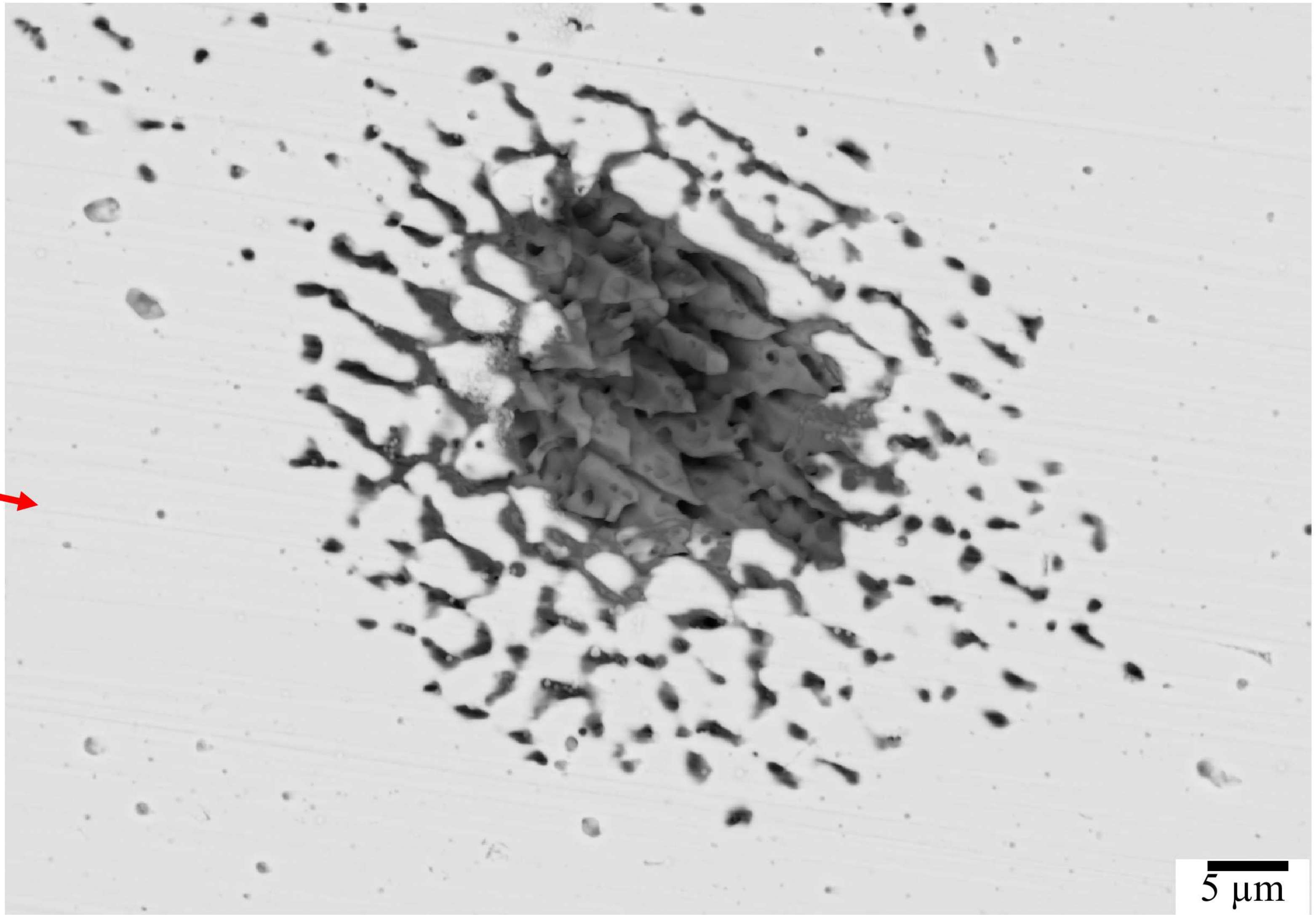


B. Zhang, Y. Zhang, S.M. Guo, A thermodynamic study of corrosion behaviors for CoCrFeNi-based high-entropy alloys, Journal of Materials Science, 53 (2018) 14729-14738.

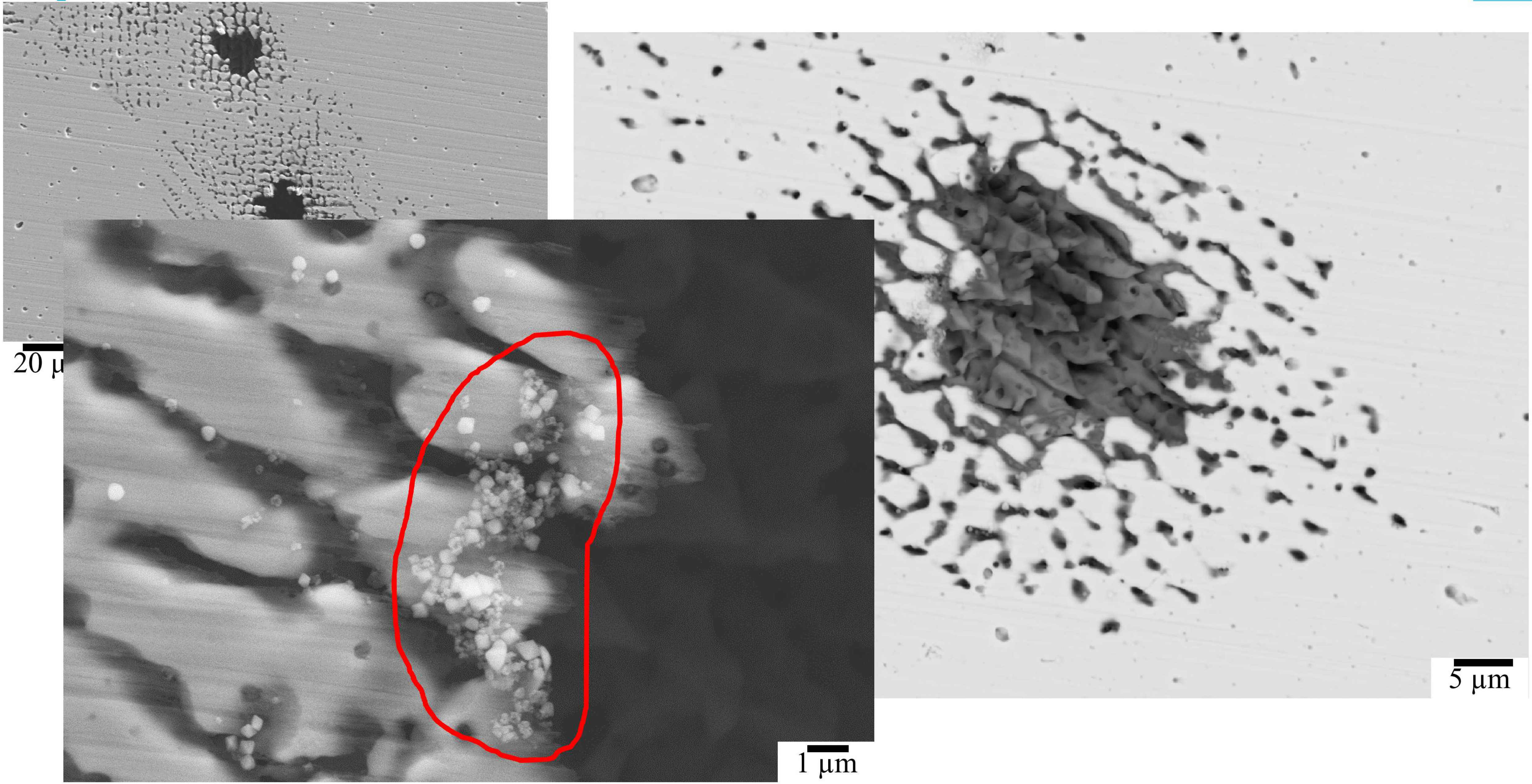
Pit morphology of CoCrFeMnNi alloy – **as-built**



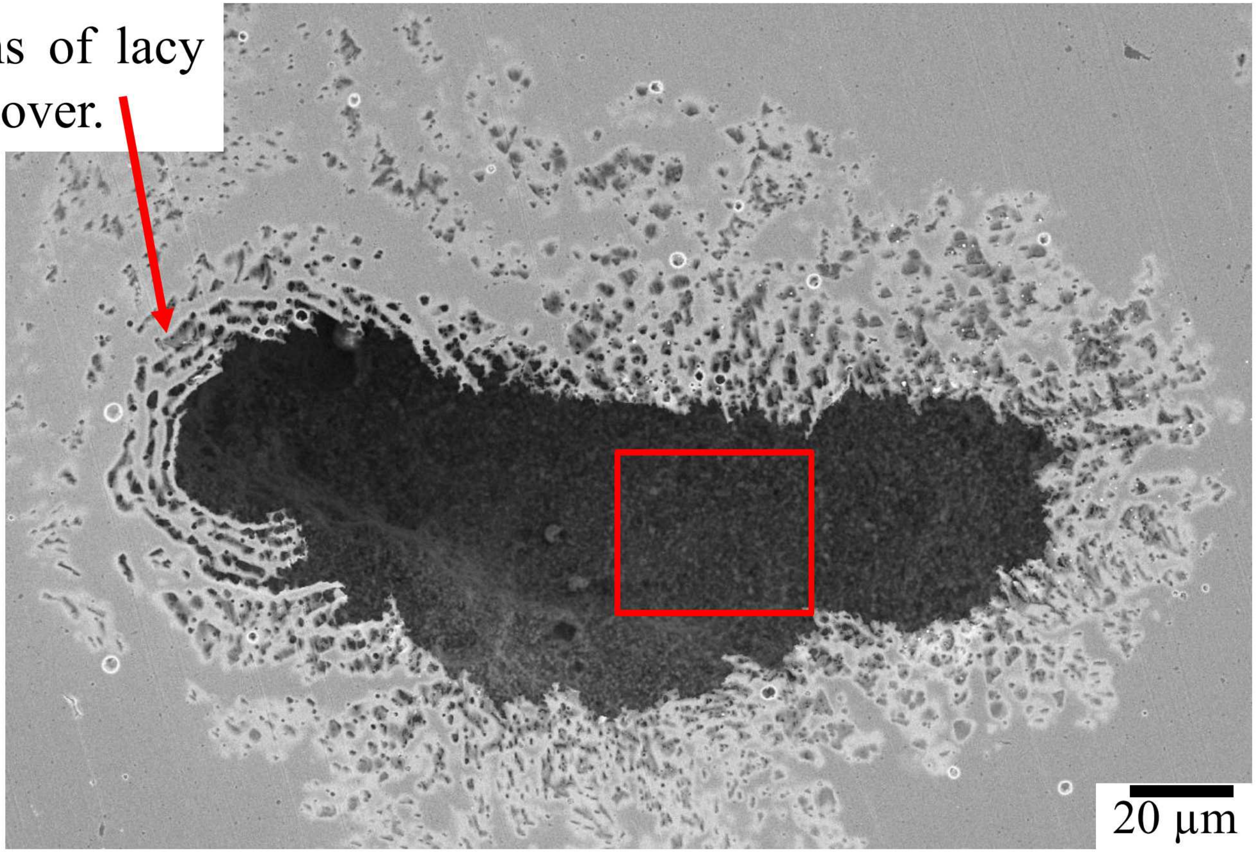
Interdendrite regions are preferentially corroding leading to a unique pit morphology with a porous pit cover (not traditionally lacy pit cover) along with a tortuous pit bottom, again associated with preferred interdendrite corrosion.

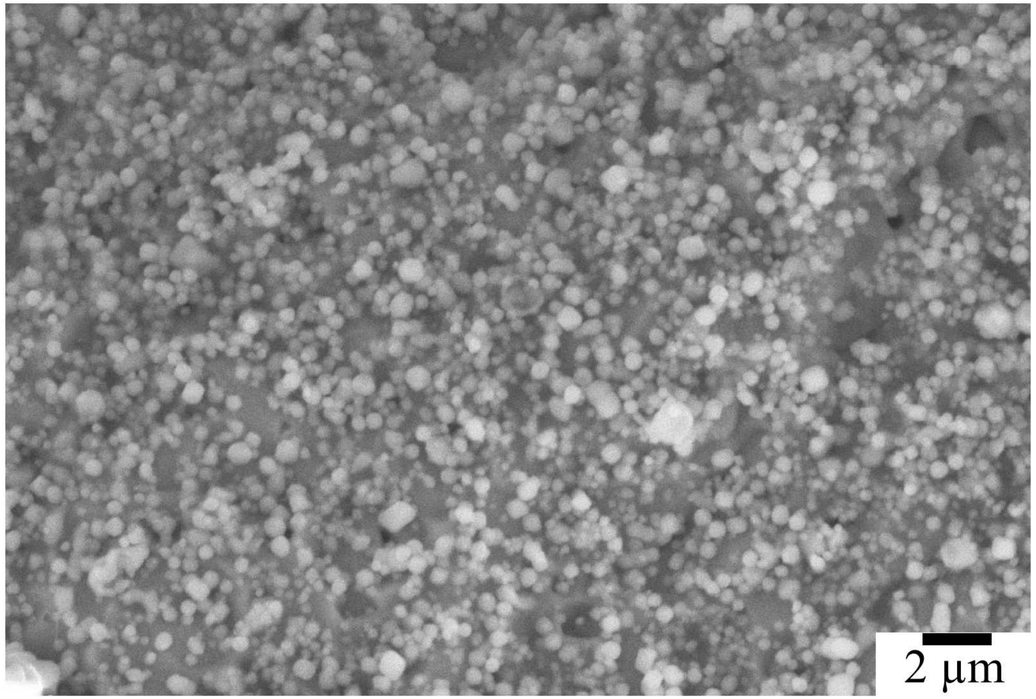


Pit morphology of CoCrFeMnNi alloy – **as-built**



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?**

Conclusions

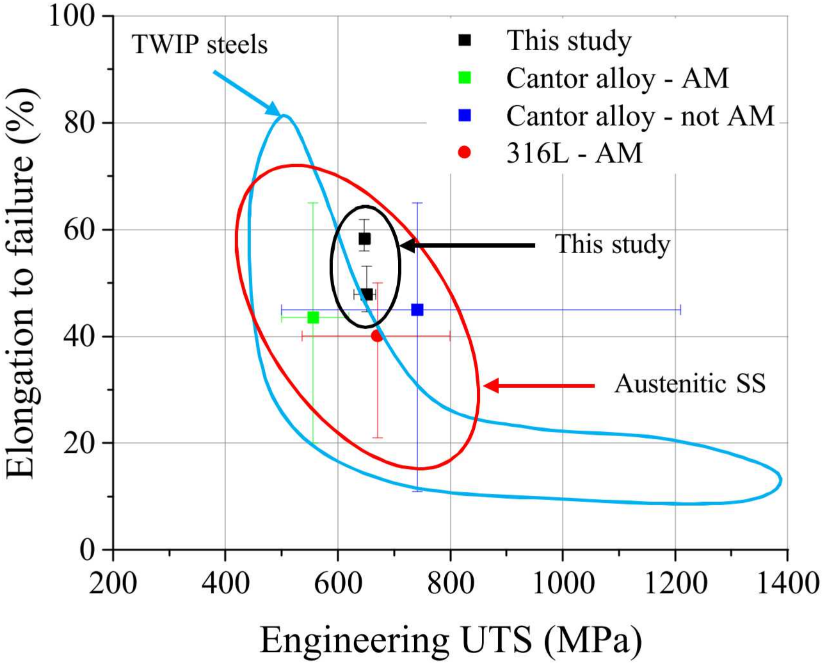
Successfully built a low porosity, single FCC phase HEA with the LENS technique.

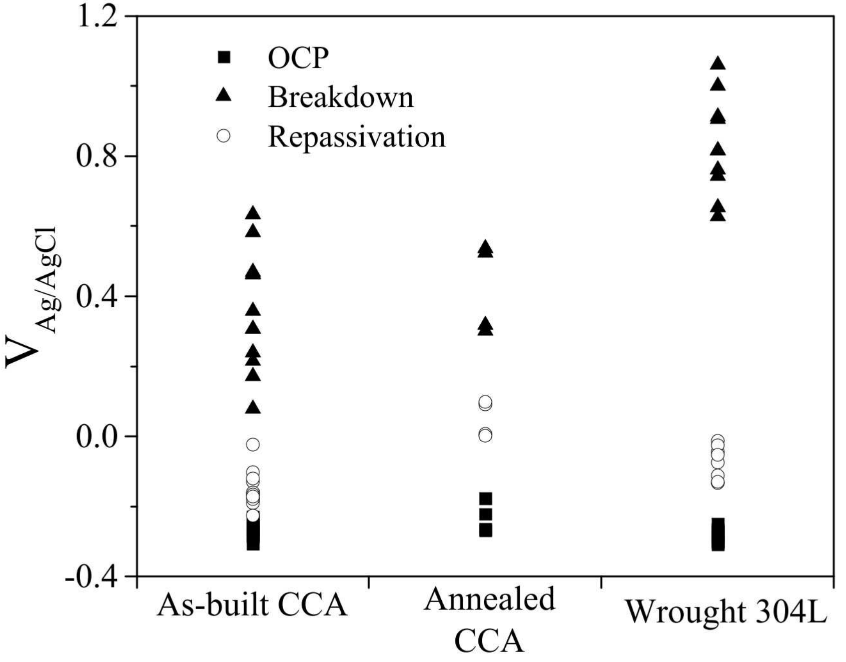
Chemical heterogeneity persists but is less severe than as-cast material. Post process heat treatments homogenized microstructure.

Mechanical properties were similar to previous work with minimal sample to sample scatter compared to other additive work.

Corrosion behavior showed a significant passive region in 0.6 M NaCl solutions, however it was not as large as 304L stainless.

- Likely culprit is abundance of Mn.
    - **Galvanic couple effects.**
    - **Less stable passive corrosion product.**
- Pit morphology and passivation studies should better define this.



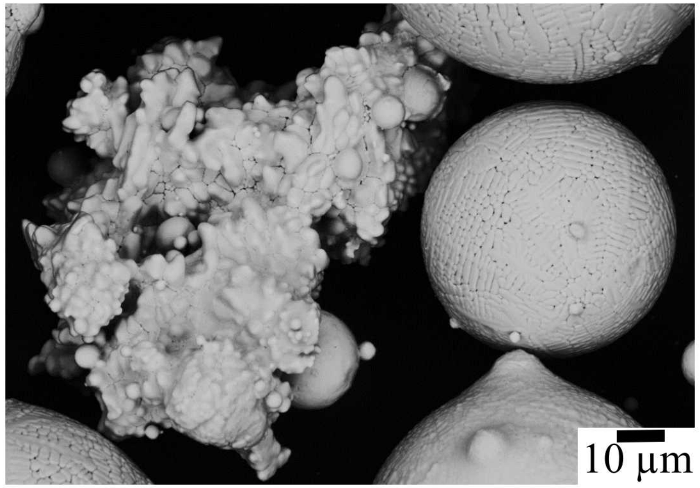


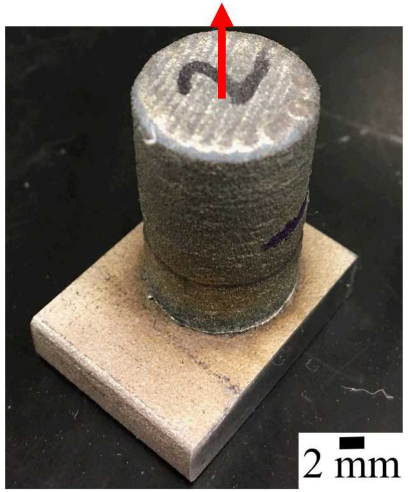
Questions?

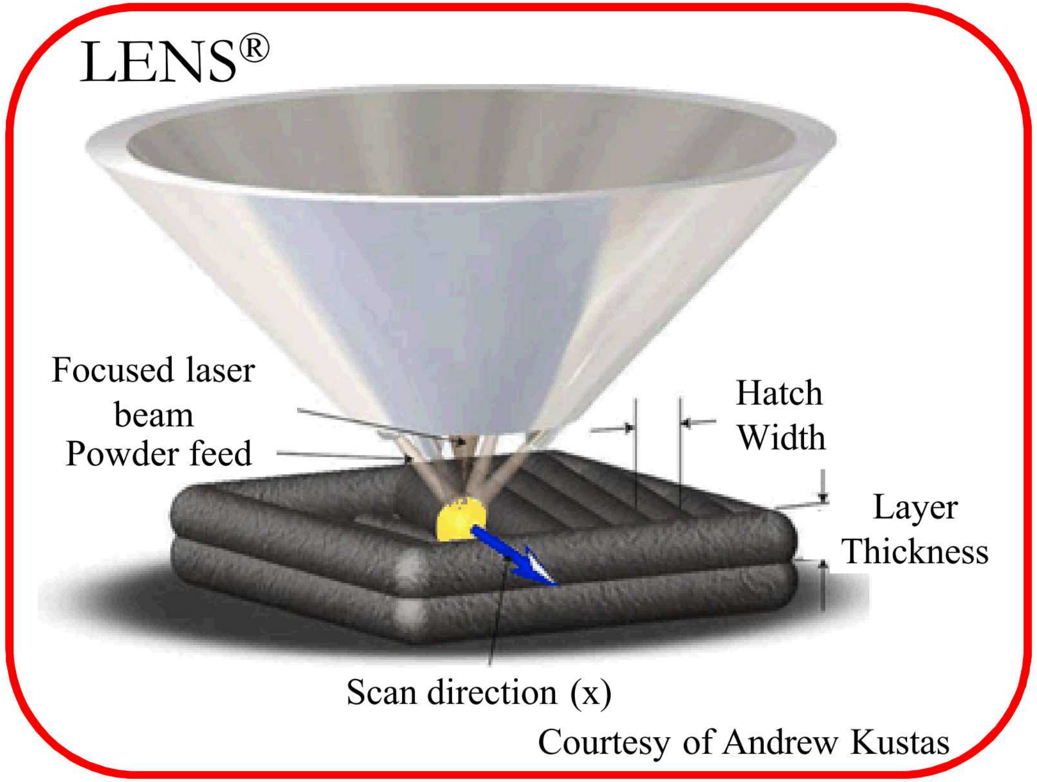
Extra slides

Powder and DED characteristics

Average powder diameter = 67 µm







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

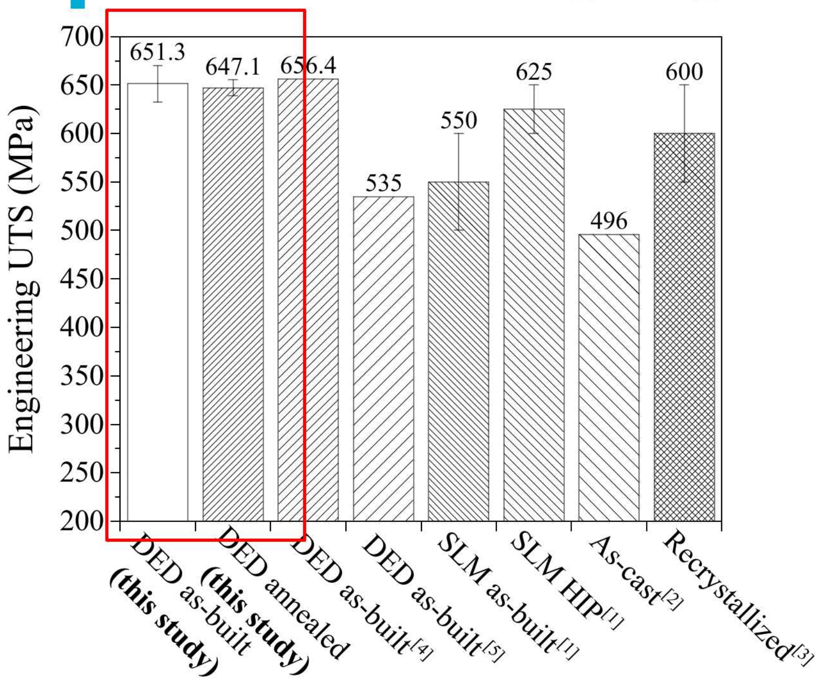
- Inert atmosphere maintained at <50ppm O_2 and <10ppm H_2O by a continuously flowing Ar gas.
- Laser power: 350 – 400 W.
- Build velocity: 400 – 600 mm/min.
- A 90 degree cross hatch build pattern was employed, first material deposited each layer was the perimeter of the build.

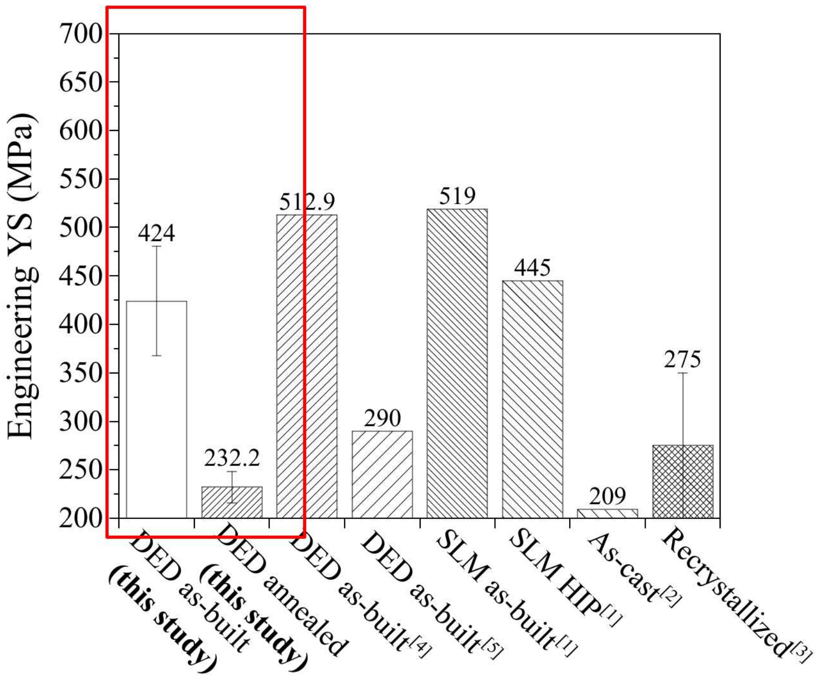
Composition (wt%)	**Al**	**C**	**Co**	**Cr**	**Fe**	**Mn**	**Ni**	**N**	**O**	**S**
Powder	0.003 ± 0.00045	0.005 ± 0.00075	20.91 ± 0.42	18.46 ± 0.37	20.14 ± 0.40	19.06 ± 0.38	21.34 ± 0.43	0.002 ± 0.00026	0.064 ± 0.0096	0.008 ± 0.0012
As-built	0.006 ± 0.00012	0.005 ± 0.00075	21.3 ± 0.43	18.2 ± 0.36	20.5	18.5 ± 0.37	21.5 ± 0.43	0.0021 ± 0.00032	0.055 ± 0.0083	0.005 ± 0.00075

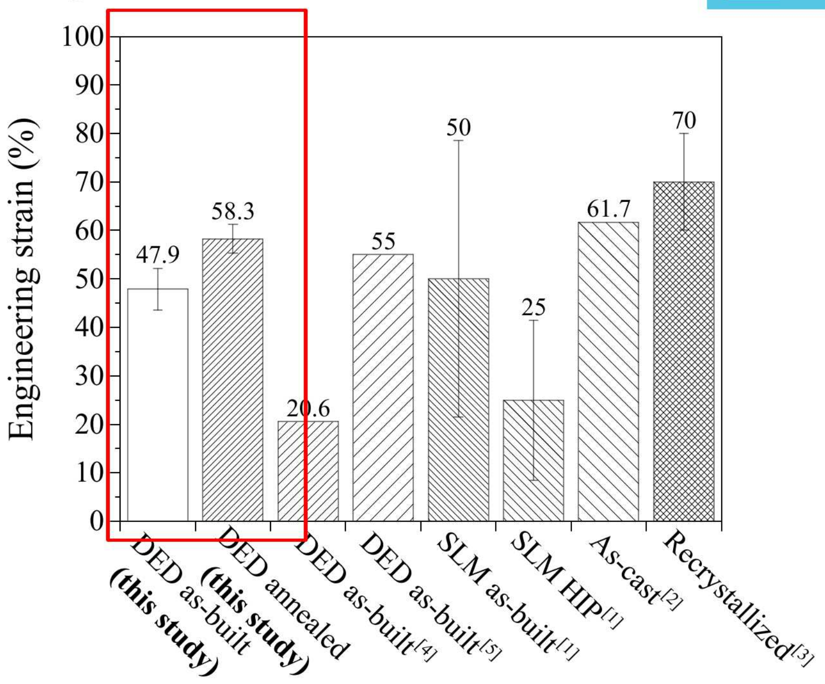
Powder from Ames Lab: Drs. Emma White and Iver Anderson

Chemical analysis by NSL Analytical.

Mechanical properties of CoCrFeMnNi alloy

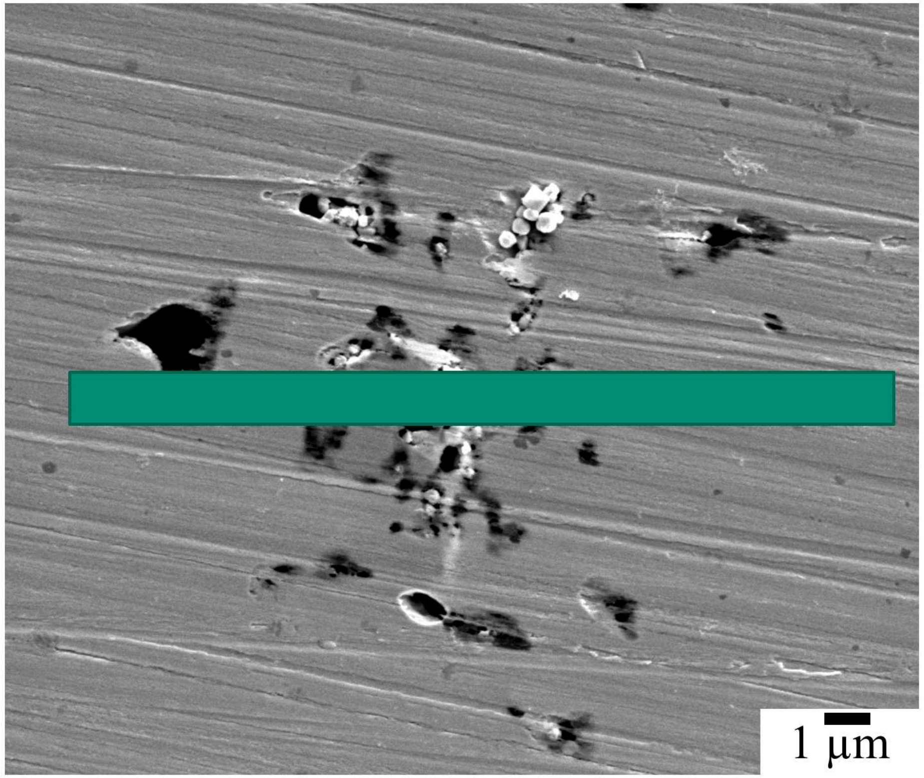


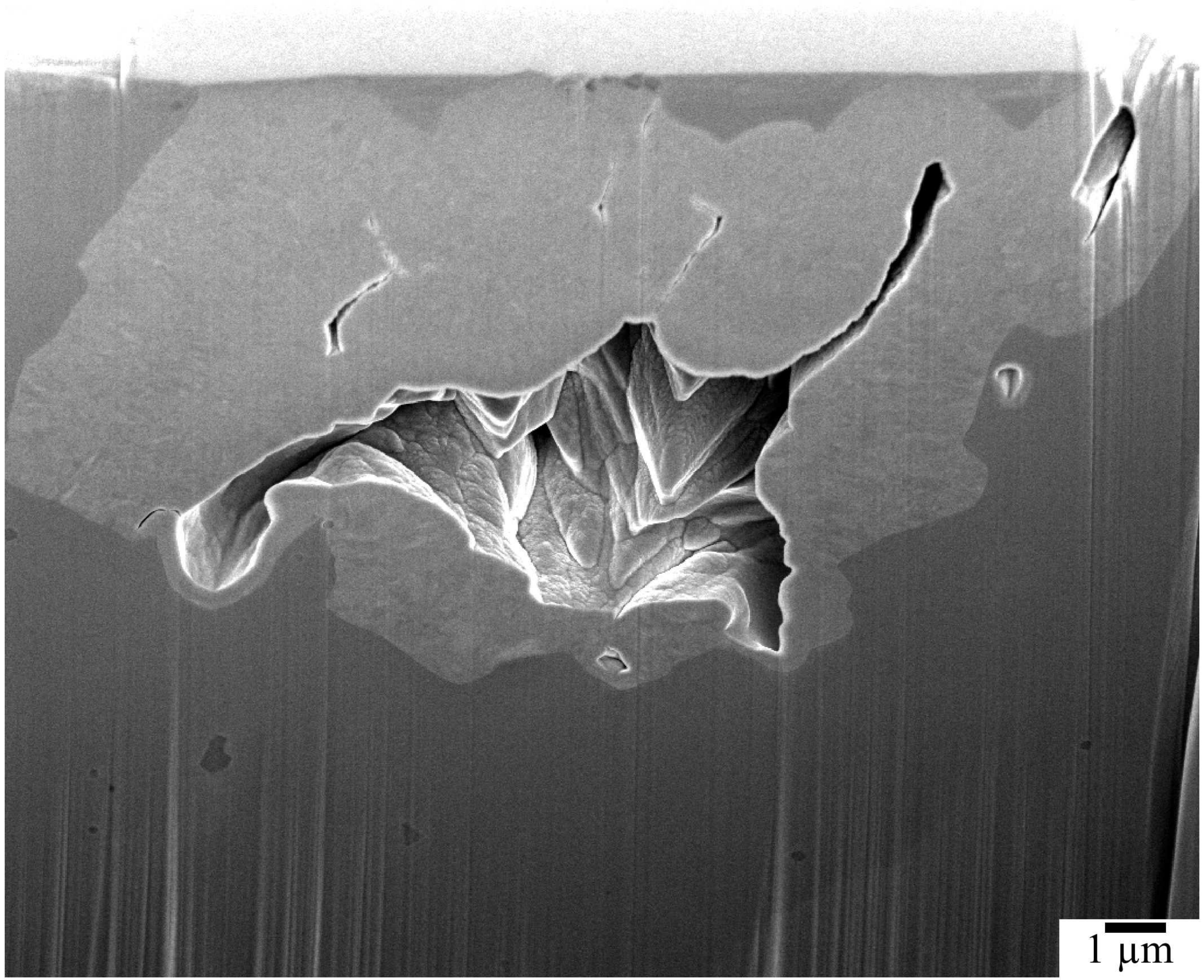




Include Tong and Wang data.

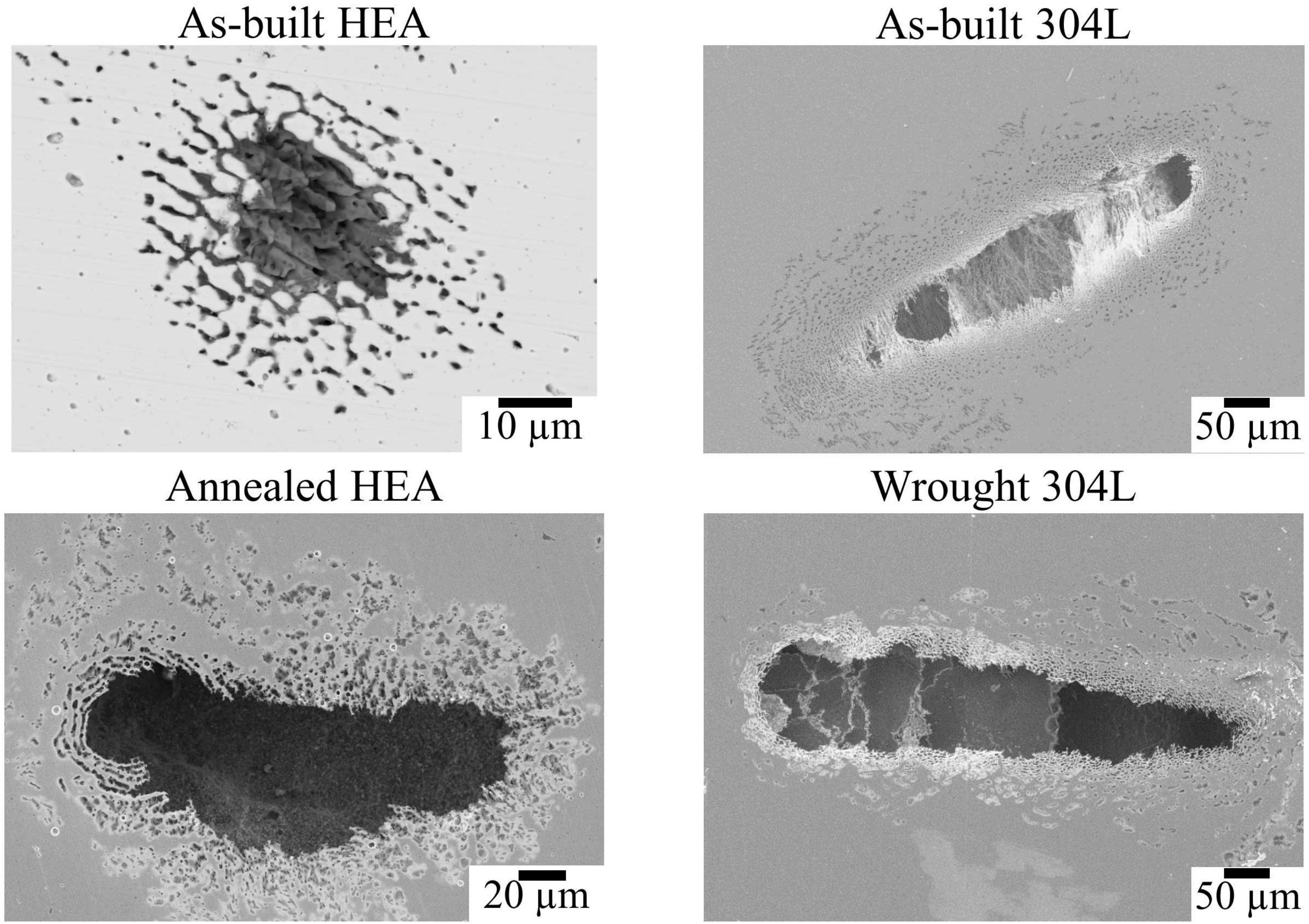
Pit morphology of CoCrFeMnNi alloy – **as-built**





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

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



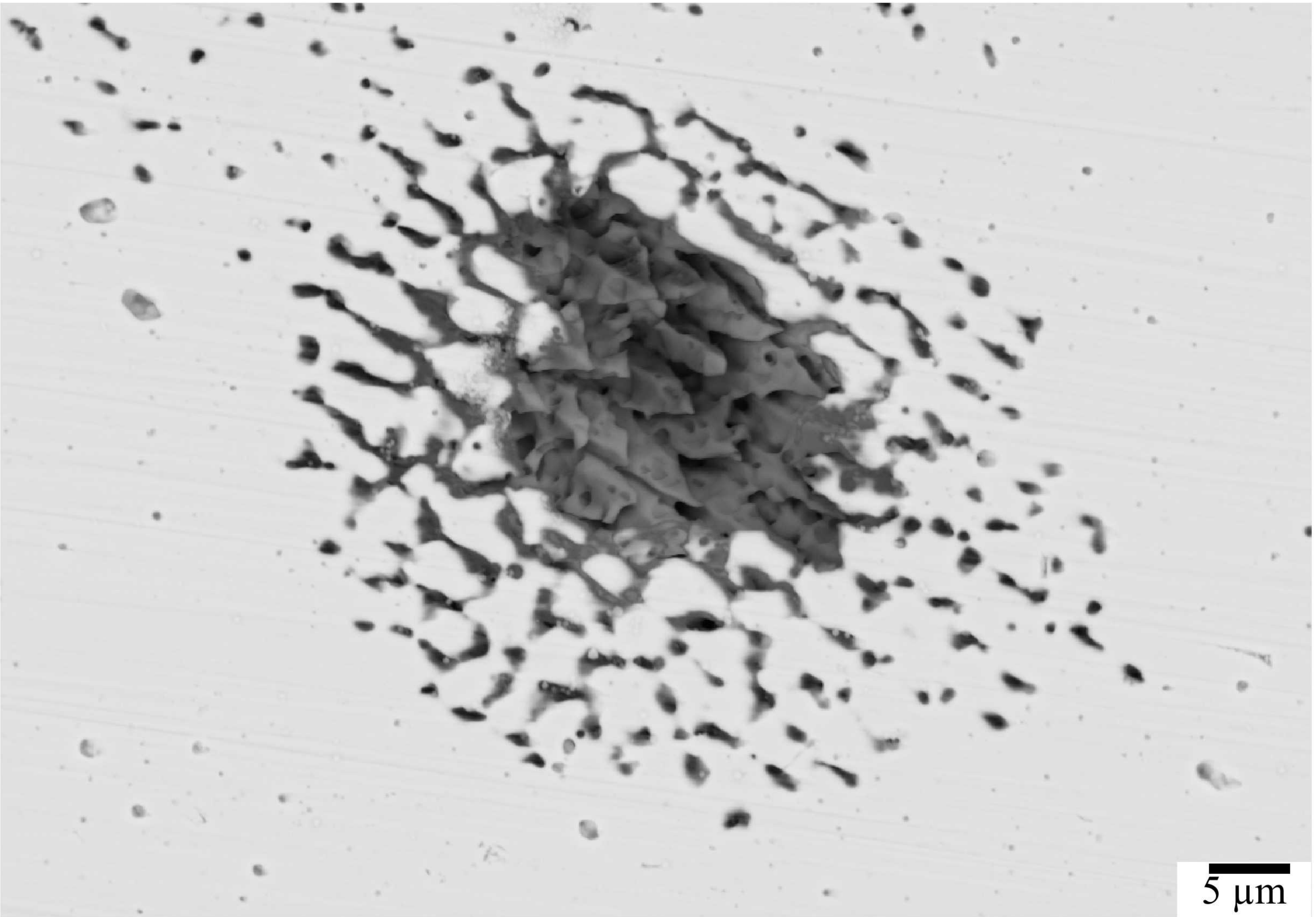
Annealed/wrought conditions show flat pit bottoms and lacy pit morphology.
Inter/intra dendrite regions will have some control of pit morphology/propagation for as-built material.

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?