



Advanced Manufacturing of High Entropy Alloys



TMS2019

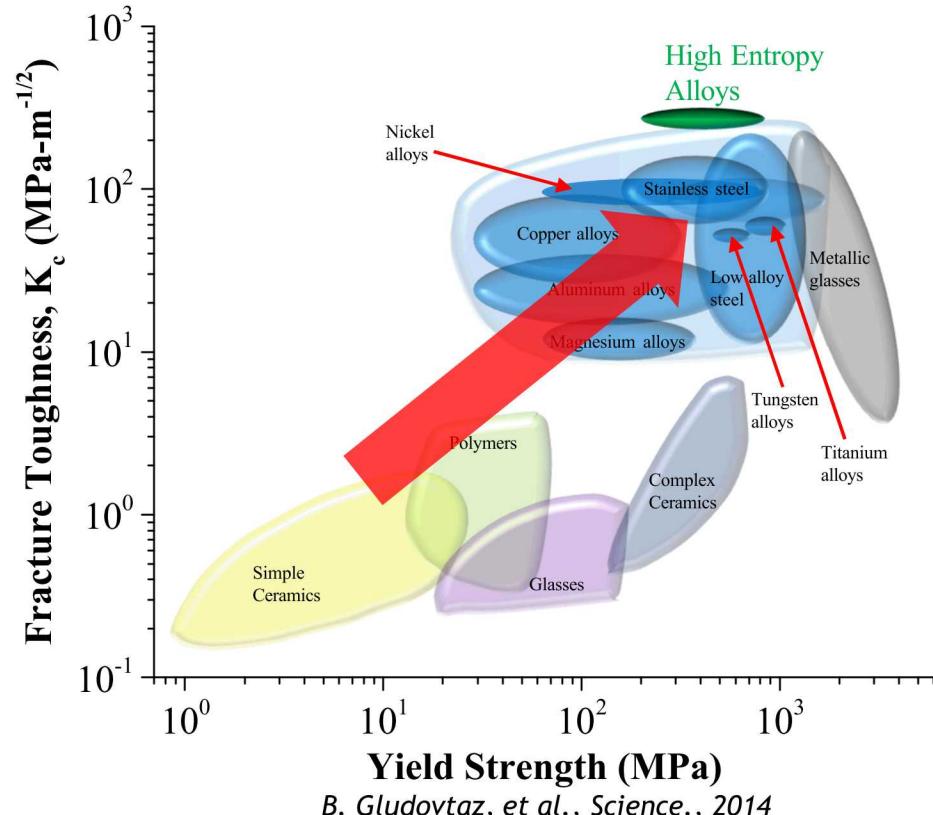
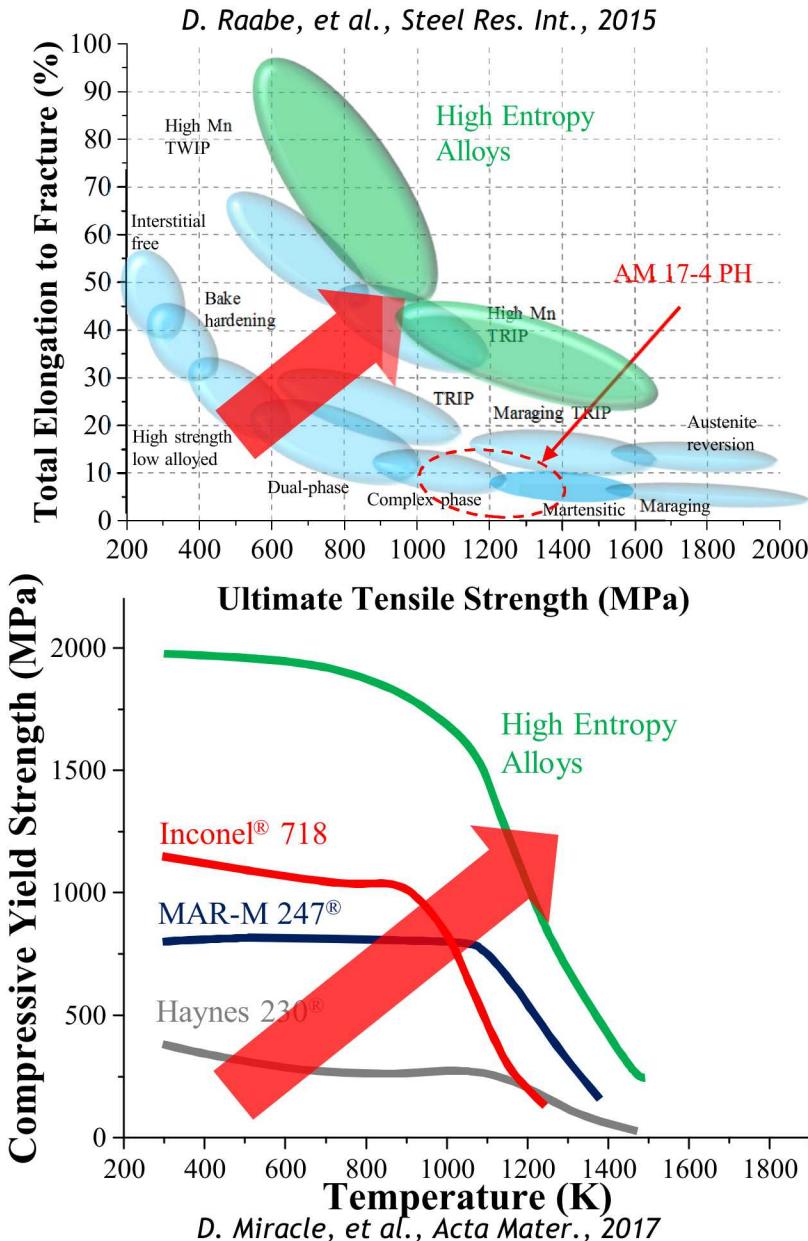
03.12.19

PRESENTED BY

Presenter: Andrew Kustas

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High Entropy Alloys: unusual mechanical properties



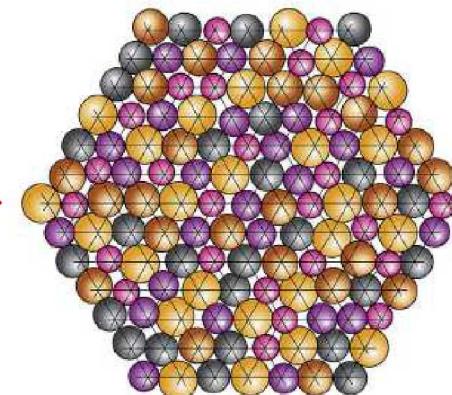
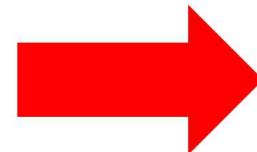
What makes HEAs so unique?

High Entropy Alloys: primarily solid solution alloys that contain 5+ alloying constituents, where microstructures have high configurational entropy ($\geq 1.4R$).*

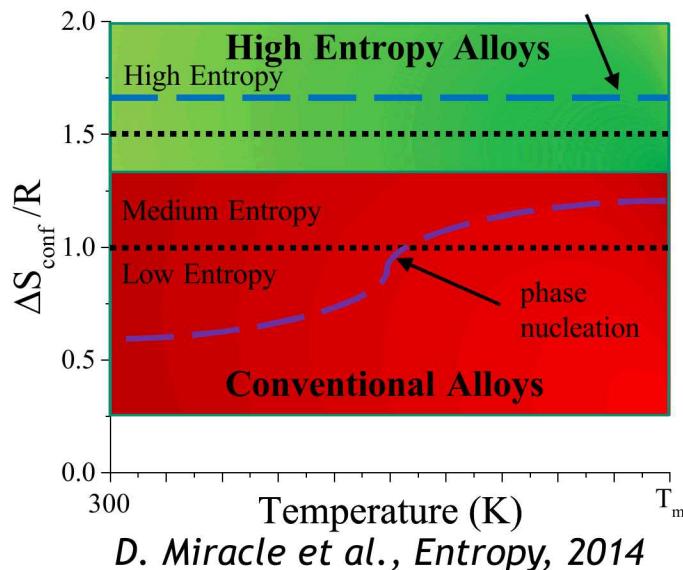
High configurational entropy is believed to thermodynamically suppresses phase separation, a primary route for degradation of mechanical properties.**

Competition between Gibbs energy for solid solution and intermetallic formation

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



Disordered solid solution
D. Miracle et al., Acta Mat., 2017

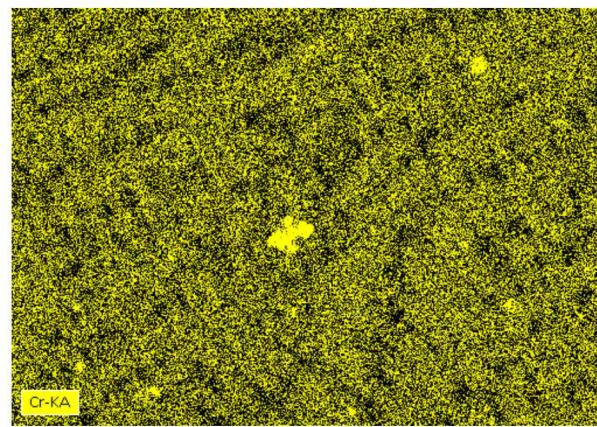
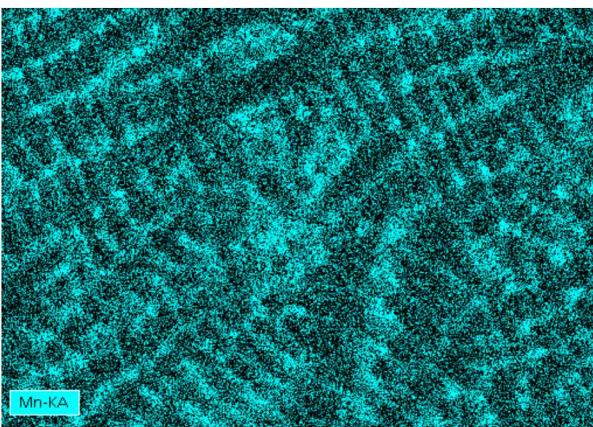
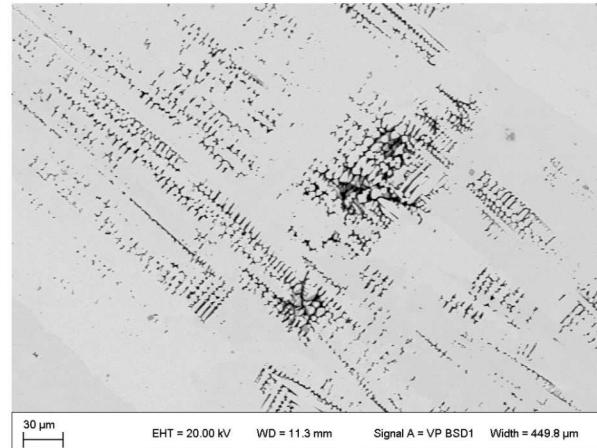
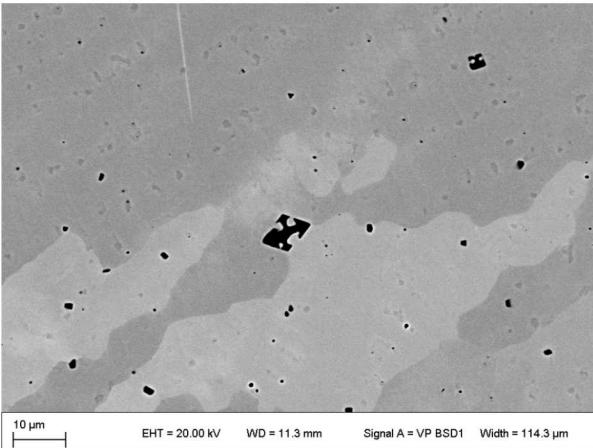


*Caveat – several HEAs are multiphase and contain intermetallics

**Cannot ignore enthalpy!

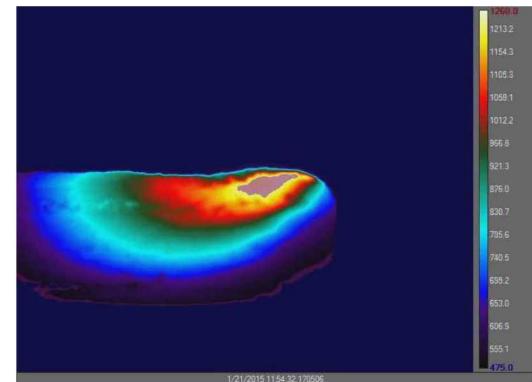
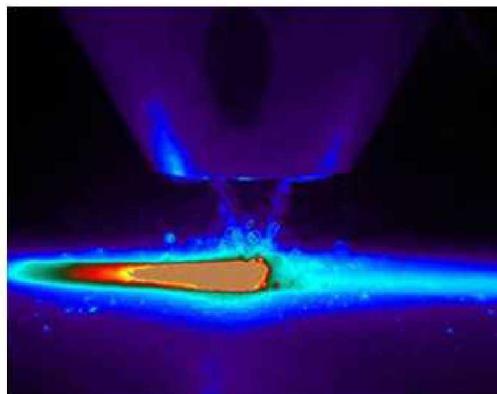
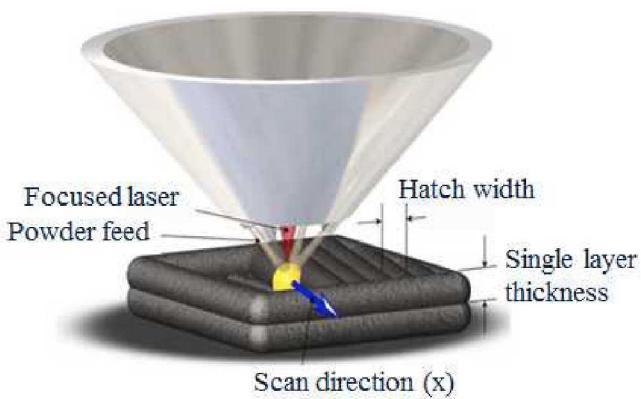
Practical challenges with conventional processing

- Despite promising properties, there are challenges with conventional processing (i.e., casting): defects and insufficient mixing of constituents.
- Example alloy: CoCrFeMnNi HEA – microsegregation of Mn and Cr, microshrinkage porosity.

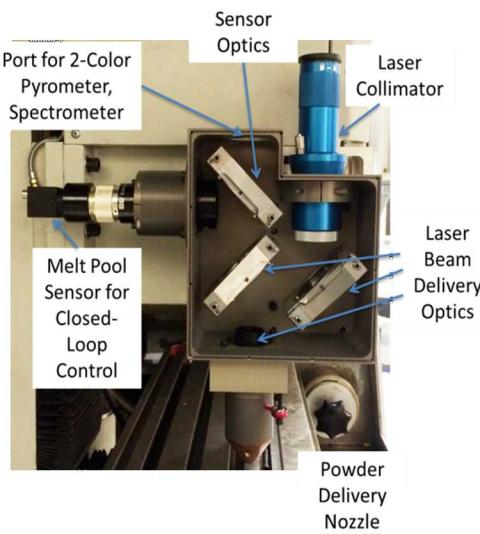
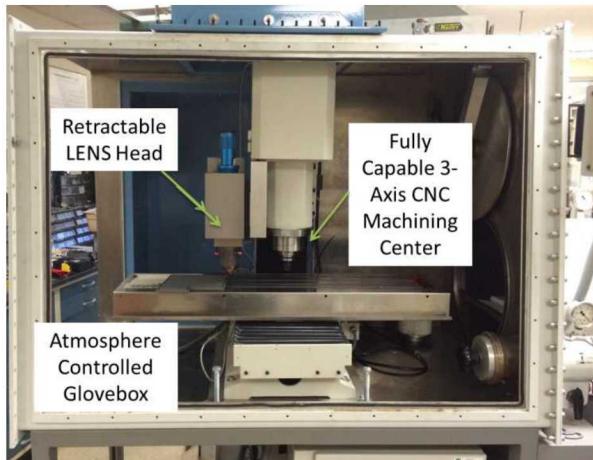


Our focus: explore advanced manufacturing routes of metal additive manufacturing, severe plastic deformation and thermal spray on the CoCrFeMnNi HEA exemplar.

Additive Manufacturing: Laser Engineered Net Shaping

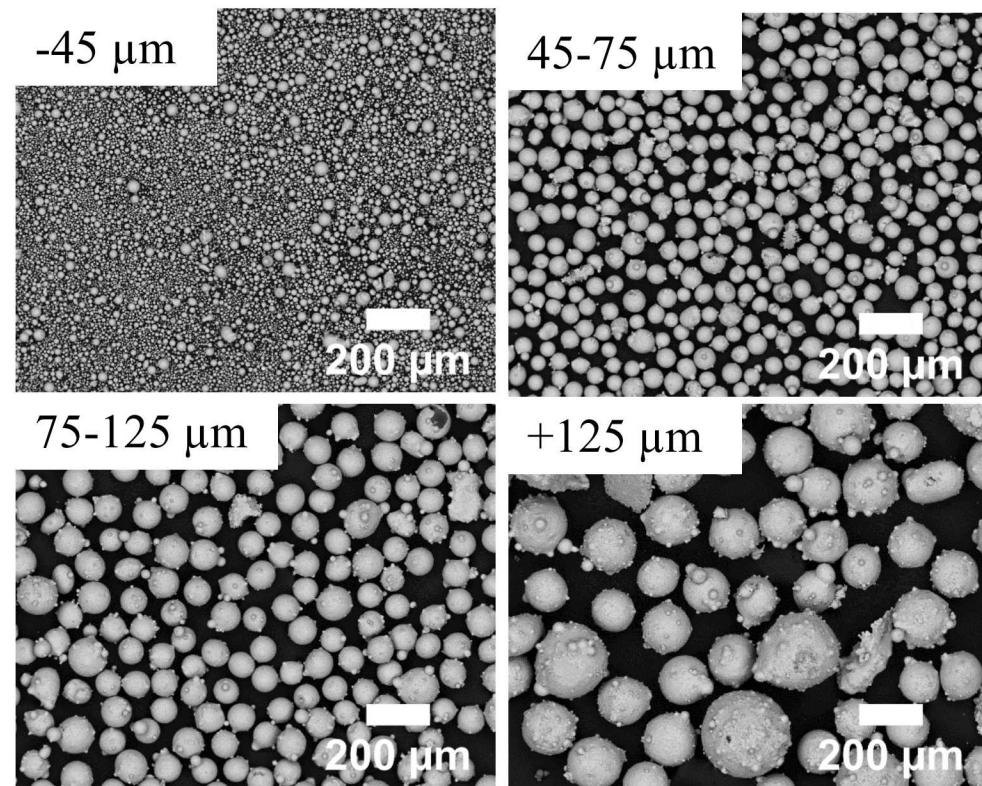


thermal history during bi-directional metal deposition



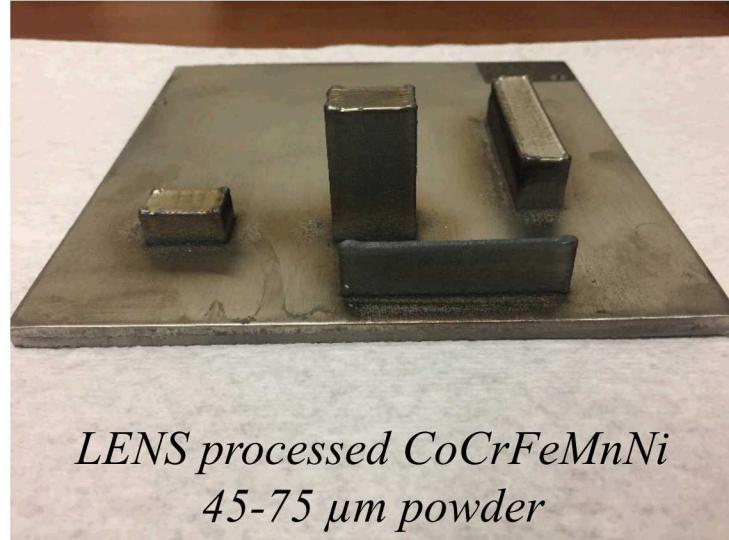
- Open architecture Laser Engineered Net Shaping (LENS) apparatus for multi-material and custom alloy printing.
- 2-color pyrometer and FLIR cameras for in situ melt pool geometry and temperature measurements.
- High temperature induction coil for in situ annealing.
- Hybrid AM and subtractive processing.
- Controlled powder feed rate with up to 5 independent powder chemistries – enable in situ alloy design studies.

CoCrFeMnNi powder feedstock

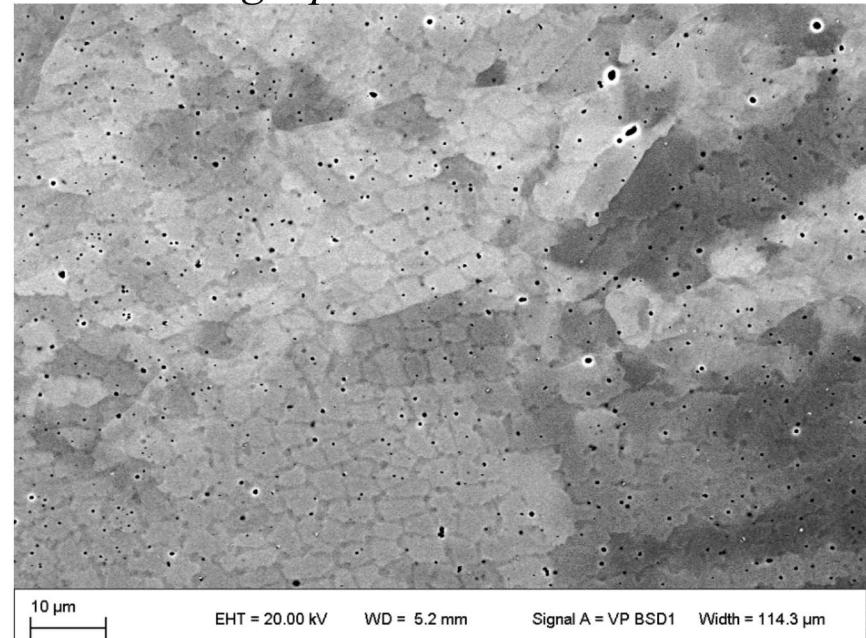
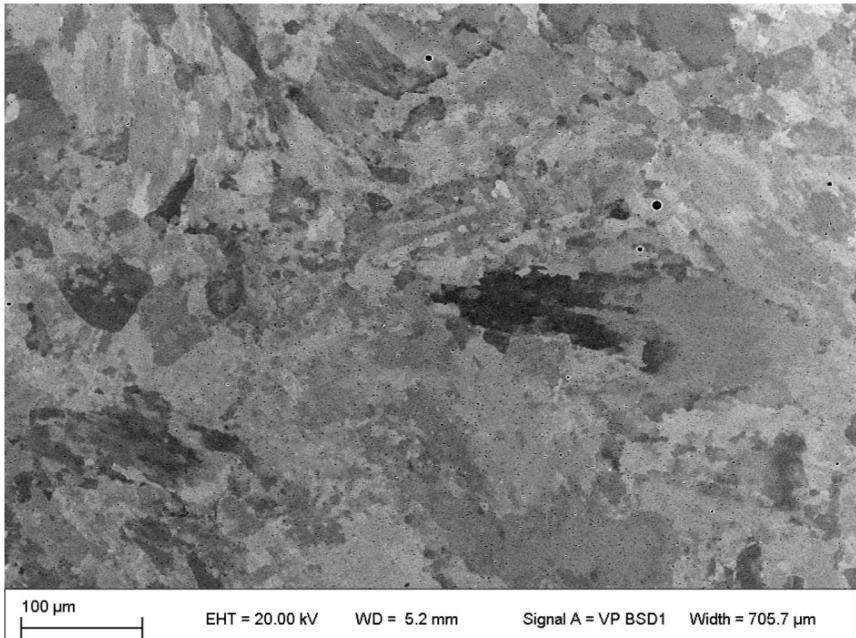


Pre-alloyed CoCrFeMnNi powder

Co	21.40%
Cr	18.38%
Fe	19.87%
Mn	19.23%
Ni	21.09%

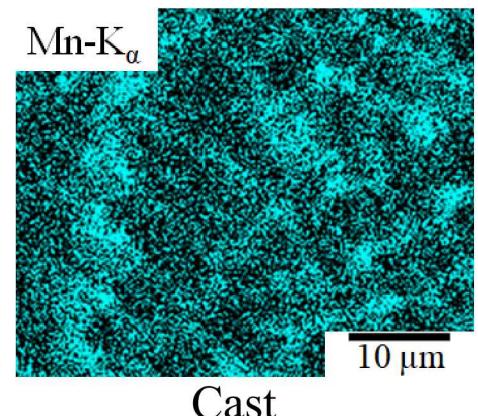
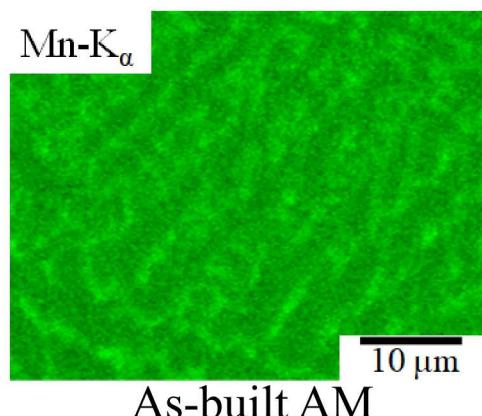


LENS processed CoCrFeMnNi HEA

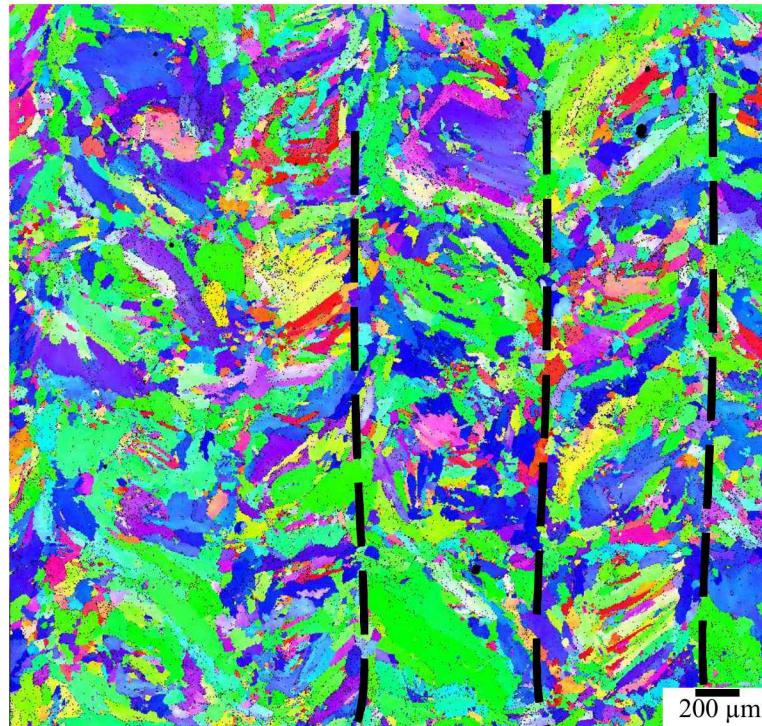
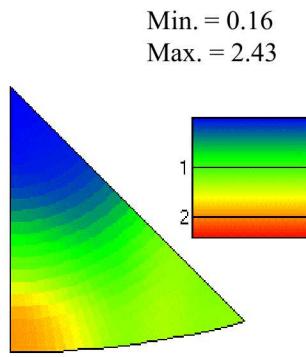
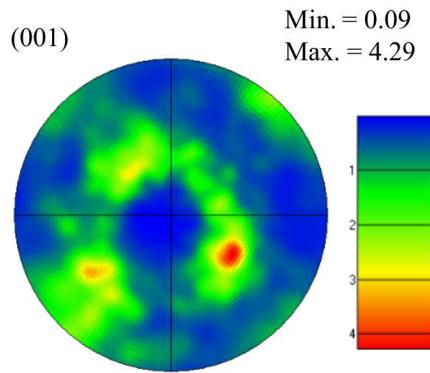


Predominately a fine cellular solidification substructure, more homogeneous solid solution.

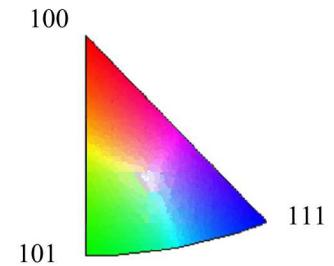
Small voids and oxides.



Grain structure results



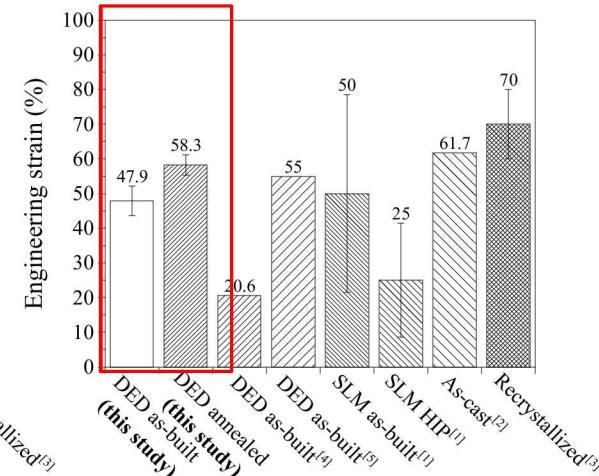
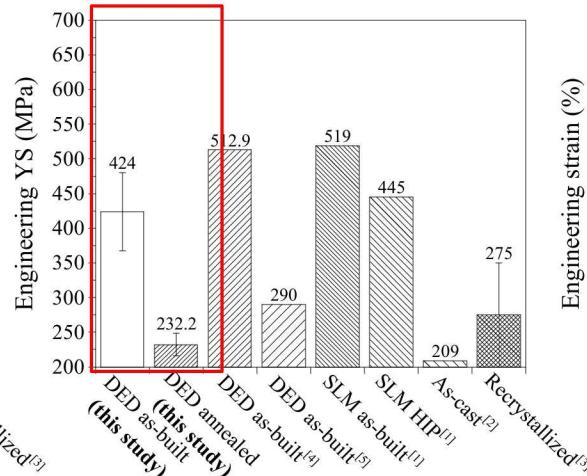
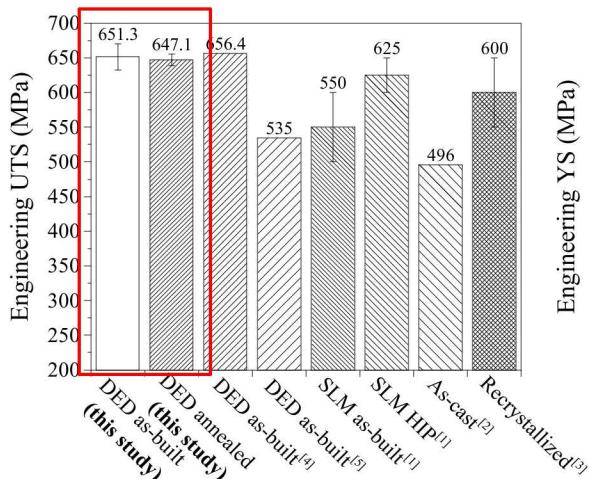
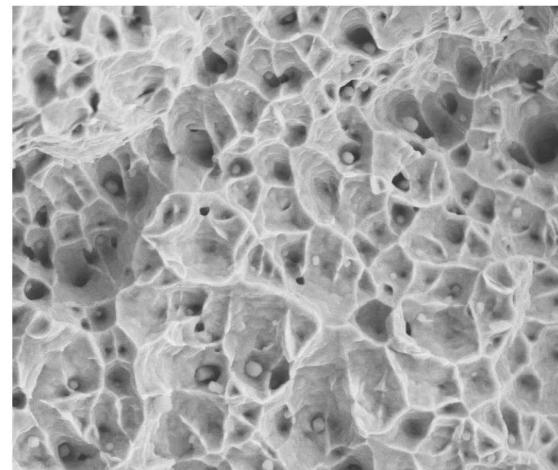
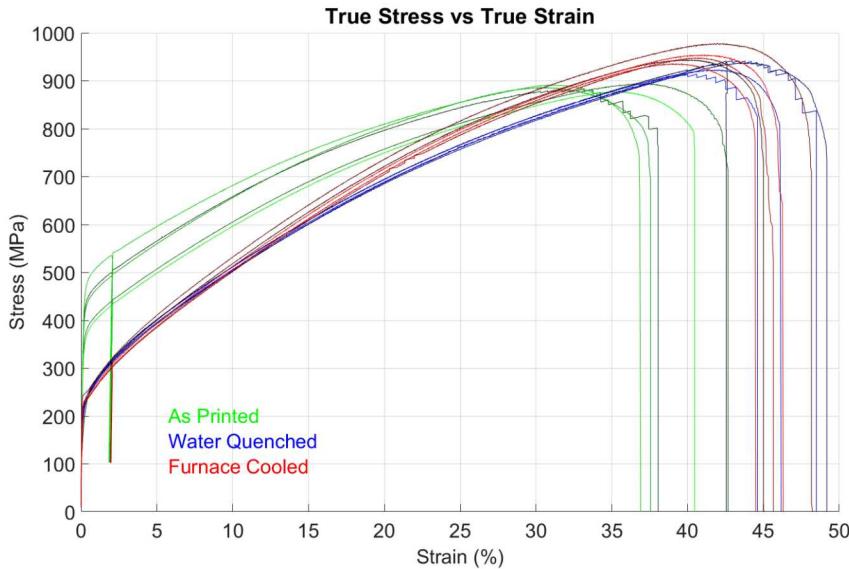
All pole figures are parallel to build direction



Typical coarse grain AM structure observed.

Relatively weak crystallographic texture with a slight $<110>$ preferred orientation along the build axis.

High strength and high ductility mechanical properties



Evidence of retaining high strength and high ductility for AM processed CoCrFeMnNi

[1] R. Li, et al., *Journal of Alloys and Compounds*, 746 (2018) 125-134.

[2] J.Y. He, et al., *Acta Materialia*, 62 (2014) 105-113.

[3] B. Gludovatz, et al., *JOM*, 67 (2015) 2262-2270.

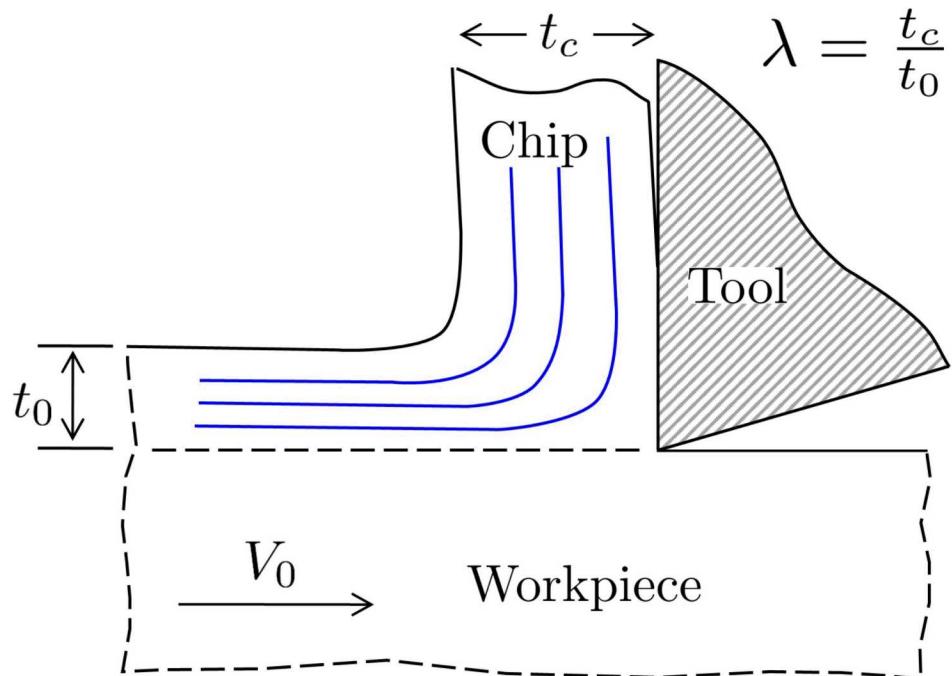
[4] G. Bi, et al., *SPIE/COS Photonics Asia, SPIE*, 2018, pp. 10.

[5] S. Xiang, et al., *Journal of Alloys and Compounds*, 773 (2019) 387-392.

Another look at properties of AM-processed HEAs via Severe Plastic Deformation



Free cutting (i.e., peeling)



Imposes large shear strains ($\gg 1$) in a narrow deformation zone at high strain rates (10^3 - 10^5 s $^{-1}$) and high homologous temperatures (0.5-0.8 T_m).

Deformation conditions:

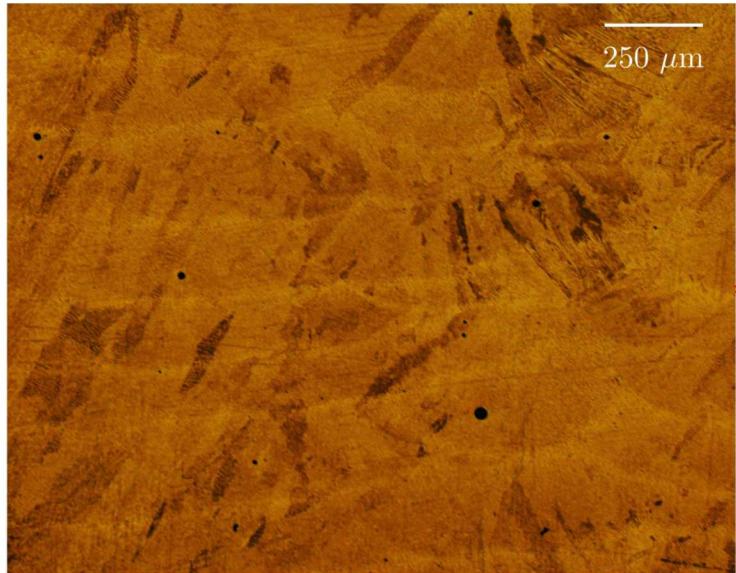
Initial depth of cut (t_o) = 125 micron

Cutting speed (V_o) = 0.25-2.5 m/s;

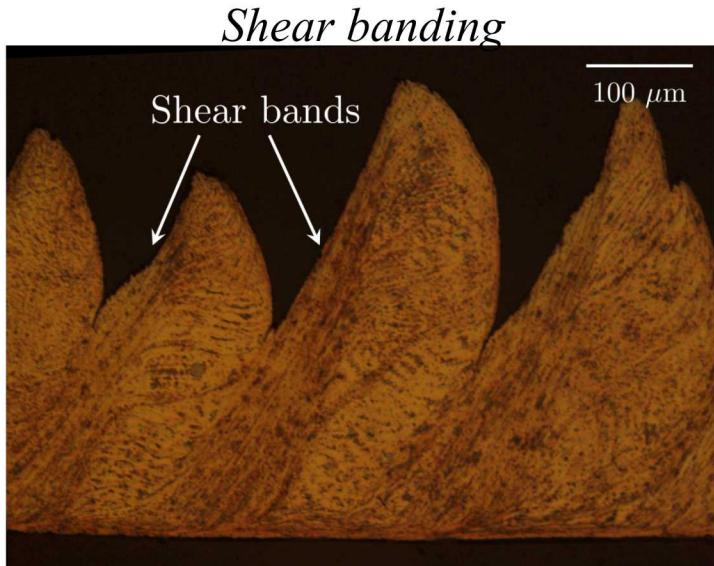
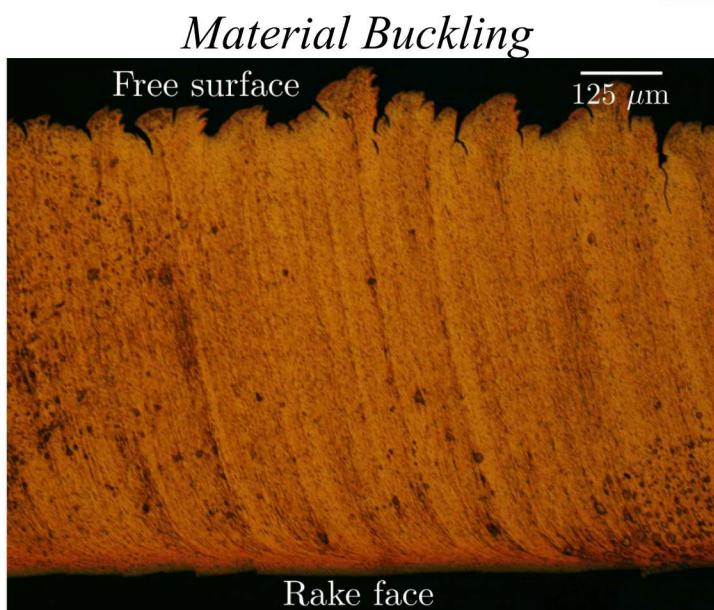
Strain rates = 10^3 - 10^4 s $^{-1}$

Unique deformation modes observed

Initial (as-built) CoCrFeMnNi microstructure – distinct AM layers

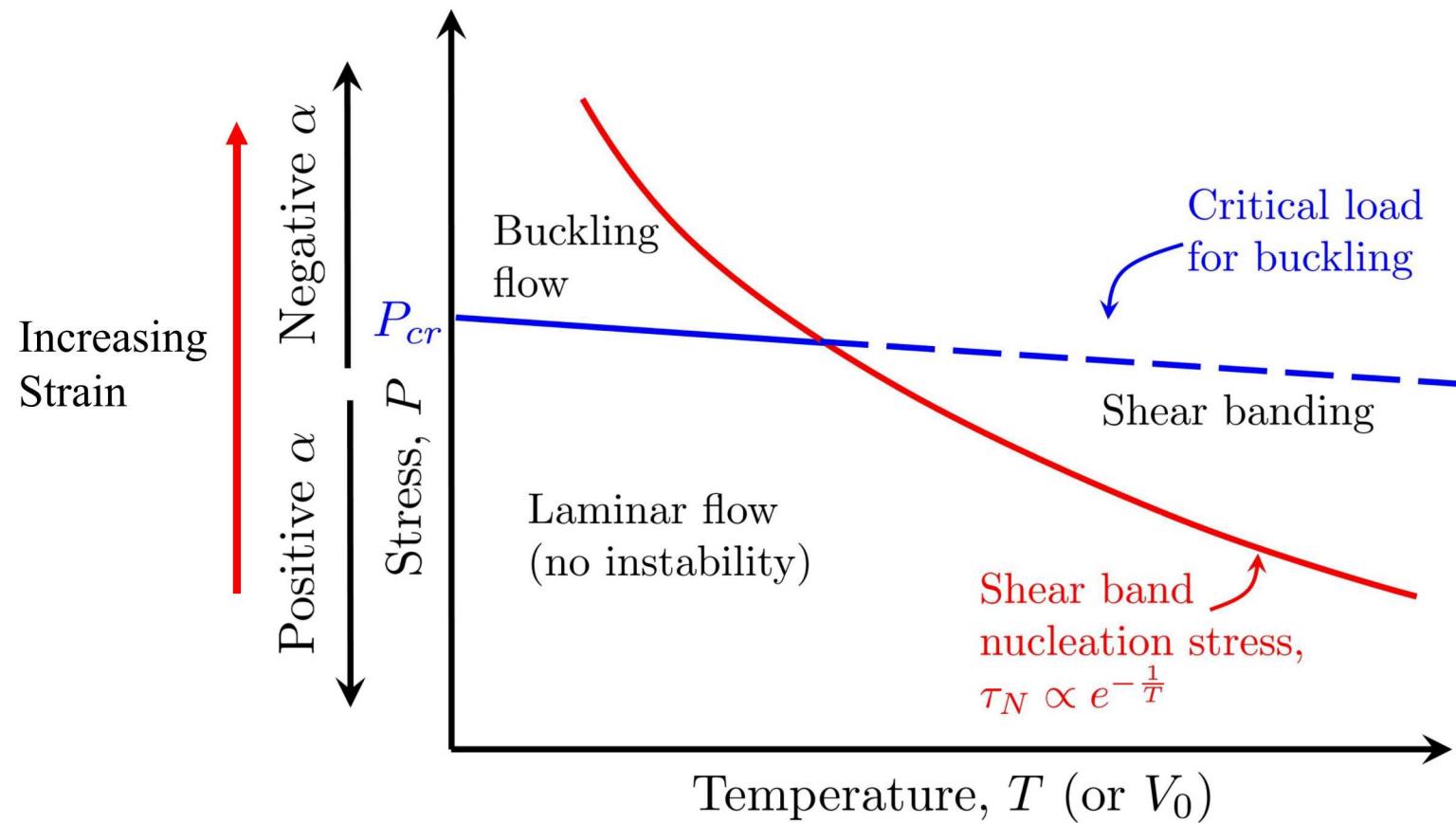


Low strain rate
High strain rate



*Two unusual flow behaviors in a single alloy:
indicative of unique work hardening properties
for HEAs.*

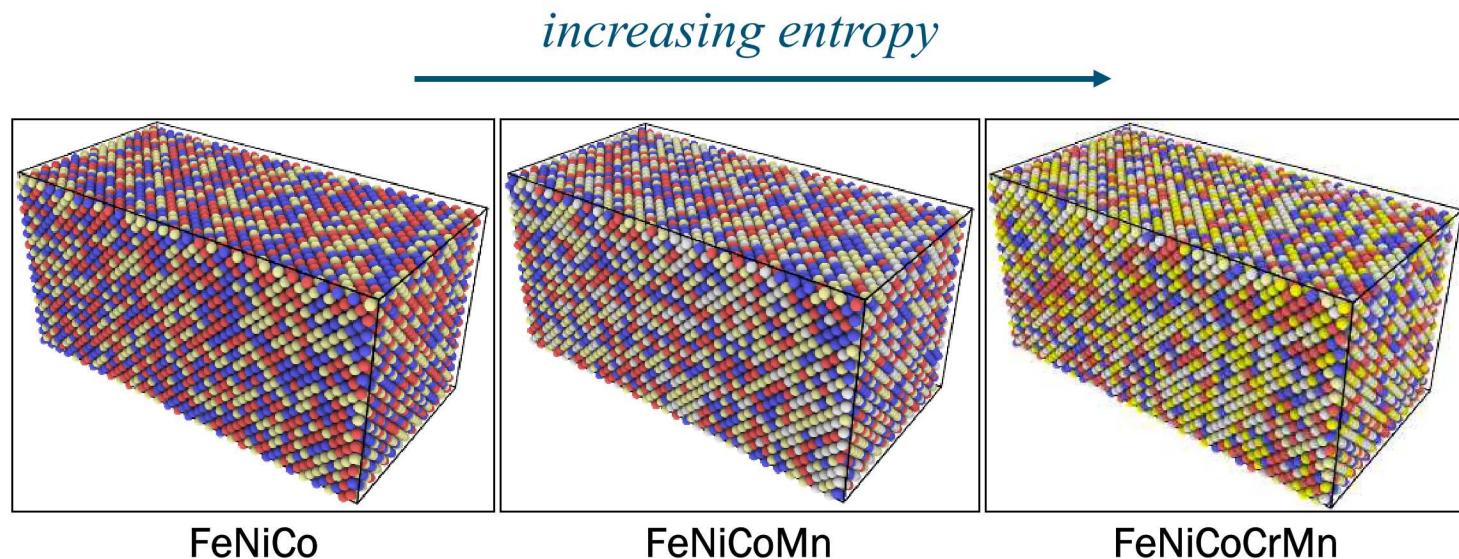
Defining predictive deformation mode maps



Establishing materials-based model to predict flow transitions from buckling/folding to shear banding.

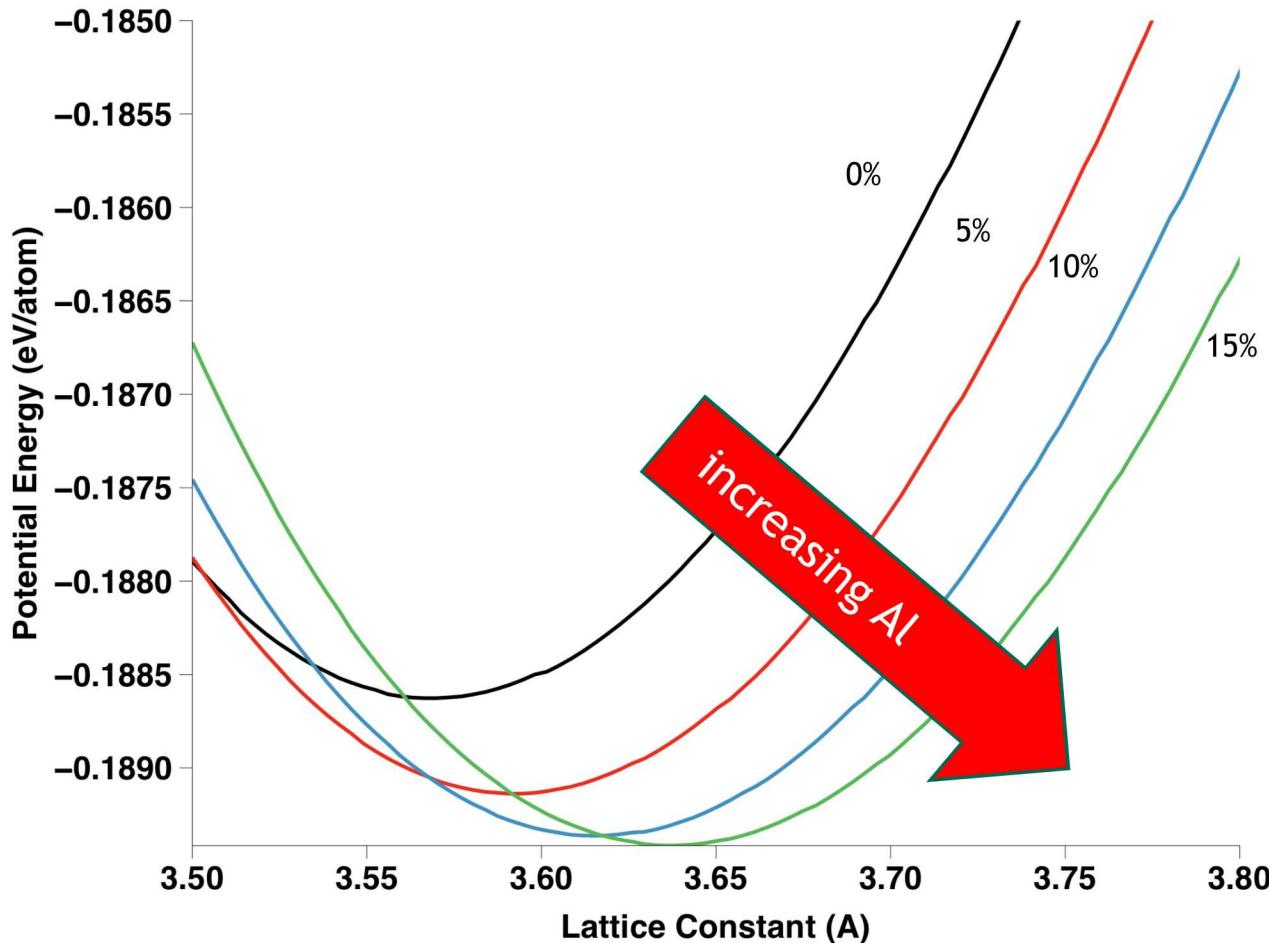
New Simulation Tools for Alloy Design and Optimization

- Molecular Dynamics (MD) effort to enable parametric **alloy optimization**
- These tools can also enable new insights about the stability of HEAs.



Atomistic (MD) simulations snapshots from investigations of HE alloy stability

New Simulation Tools for Alloy Design and Optimization

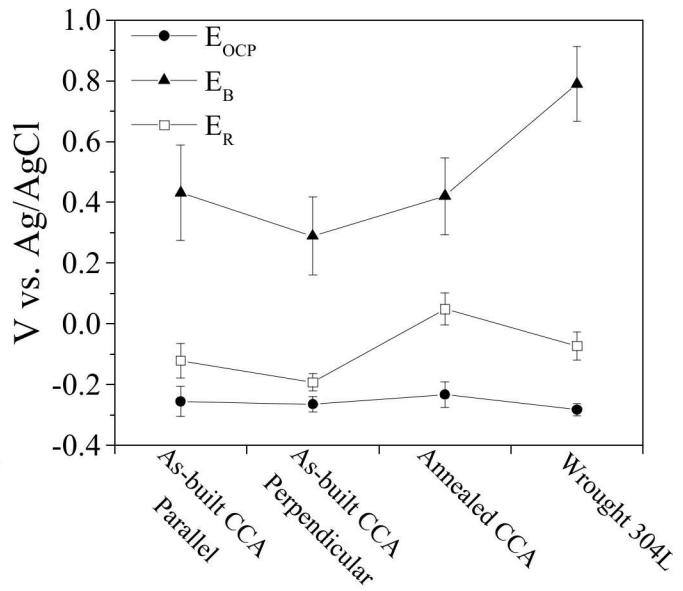
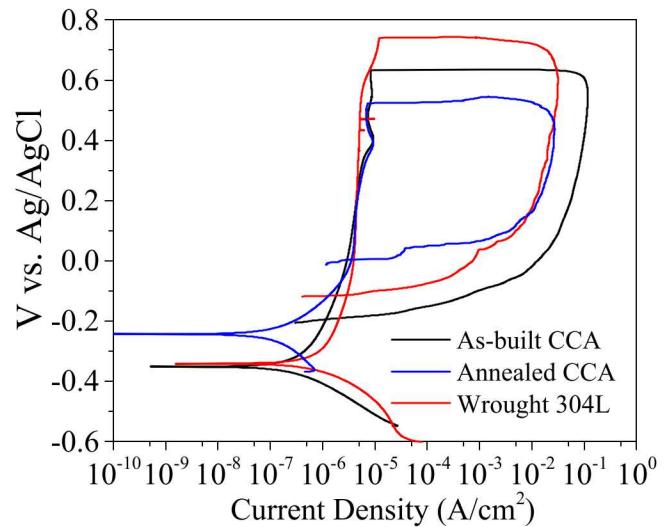


Atomistic (MD) simulations will enable new thermodynamic predictions of stable HEAs

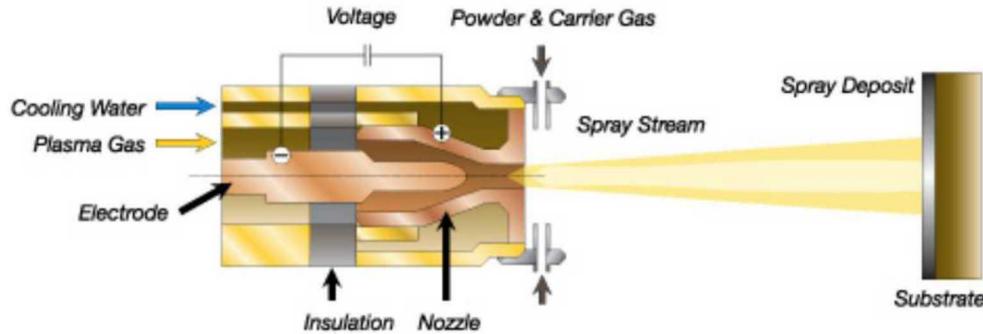
Summary

1. AM was successfully utilized with pre-alloyed CoCrFeMnNi powders to produce bulk geometries.
2. Microstructures of the AM material were significantly refined relative to conventionally processed HEA with more homogeneous composition.
3. Preliminary mechanical properties of HEAs were relatively insensitive to AM solidification – a promising outcome for structural applications.
4. Molecular dynamics was demonstrated as a novel approach to evaluate alloy optimization and rapidly sweep through the HEA composition space.

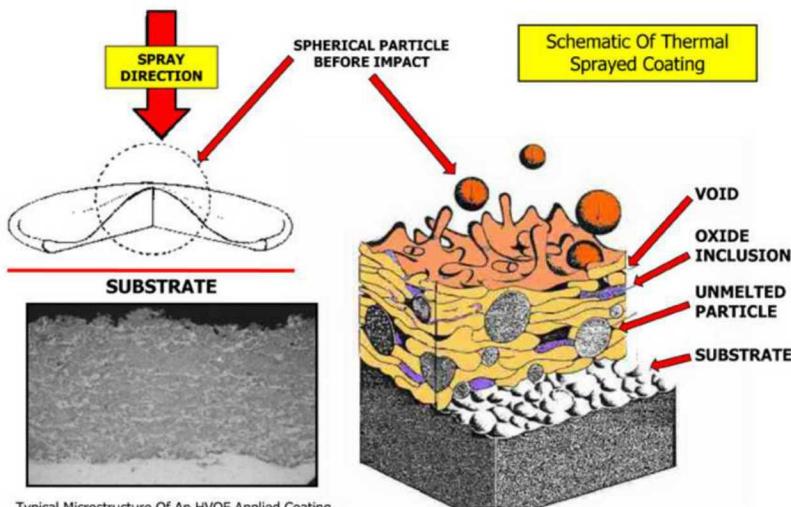
Corrosion Properties



Additive Manufacturing: Plasma Spray

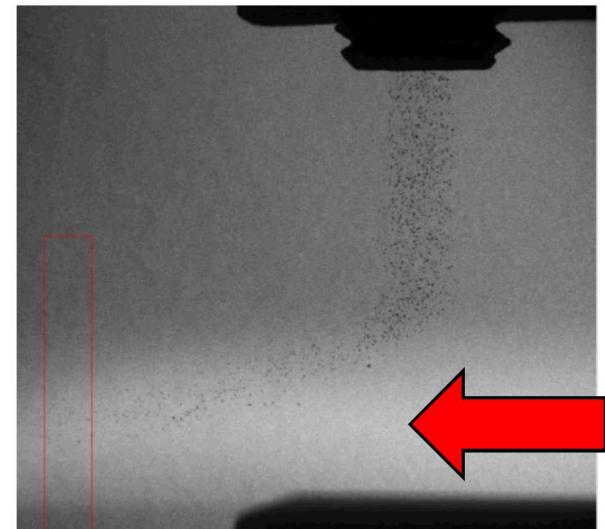


Schematic of defect laden microstructure



Typical Microstructure Of An HVOF Applied Coating.

Herman H 1988 Plasma-sprayed coatings. Sci. Am. 259, 112–7



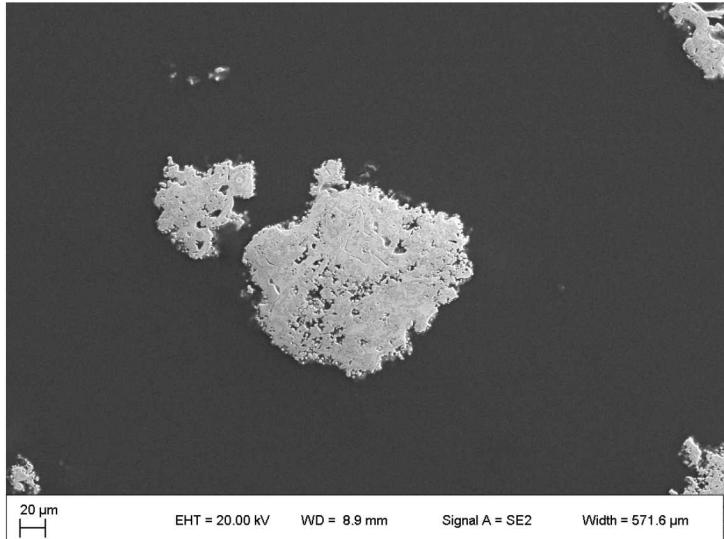
Powder imaging within plume

- Coating process whereby powder or wire feedstock is melted and accelerated towards a substrate to produce a lamellar, defect laden, thick film deposit (non-structural).
- Capable of depositing all classes of materials to thicknesses ranging from $\sim 20\mu\text{m}$ to several millimeters.
- The high energy density of plasma torches achieves high temperatures ($> 10,000\text{ }^{\circ}\text{C}$) from quenching/rapid solidification onto substrate.

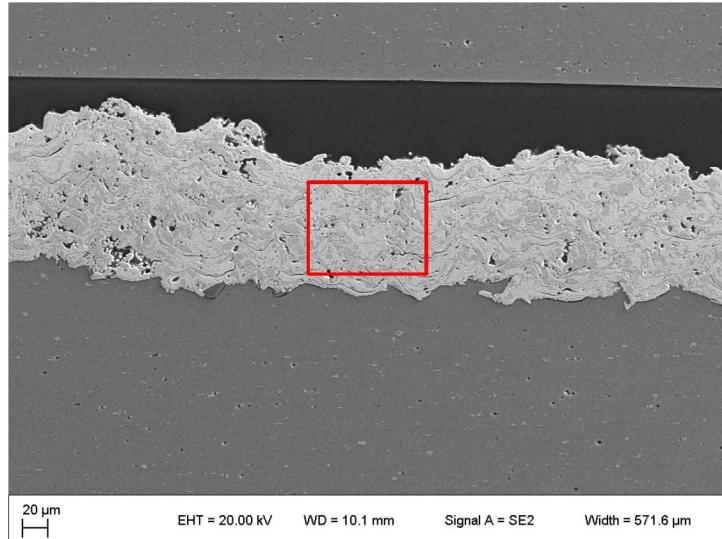
Explored air plasma spray with CoCrFeMnNi powder feedstock.

Defect-laden microstructure

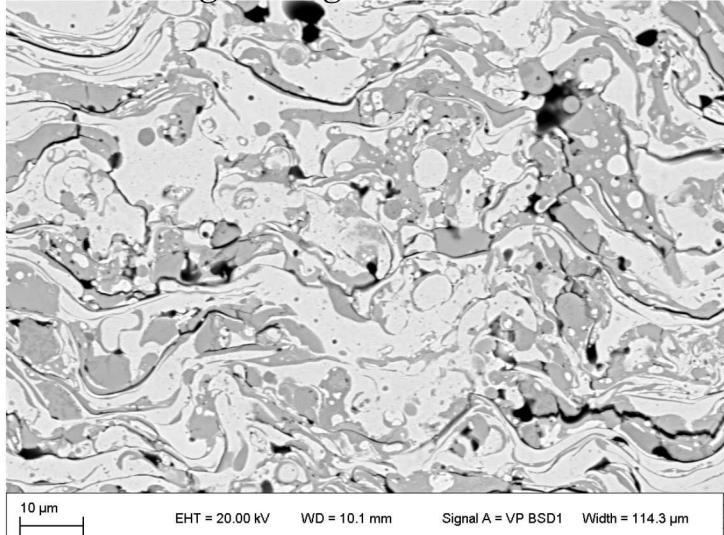
CoCrFeMnNi splat – plan view



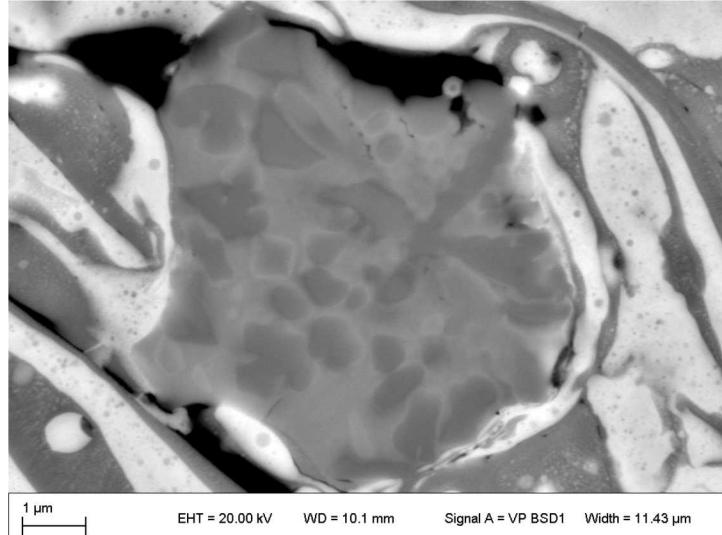
CoCrFeMnNi splat – cross-section



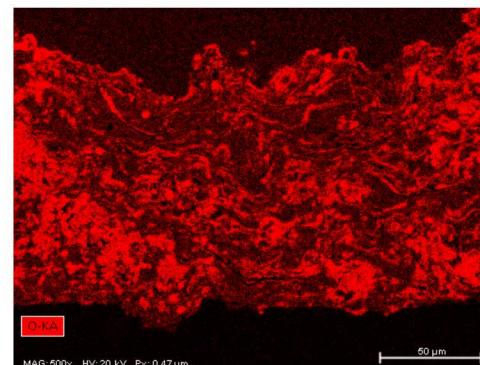
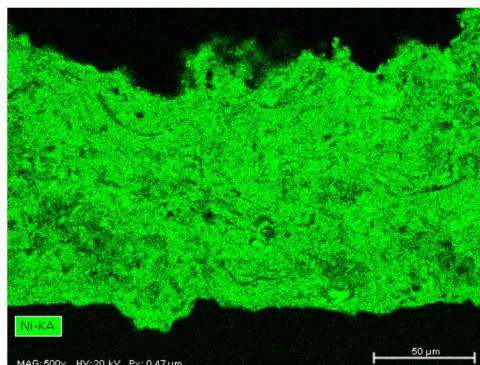
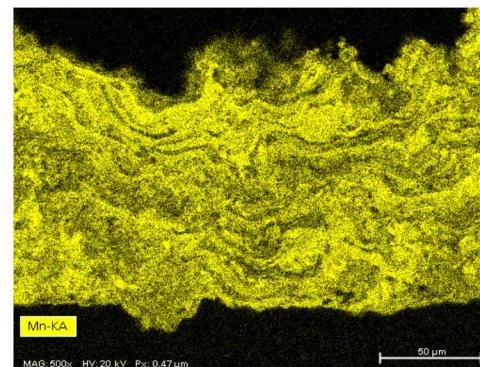
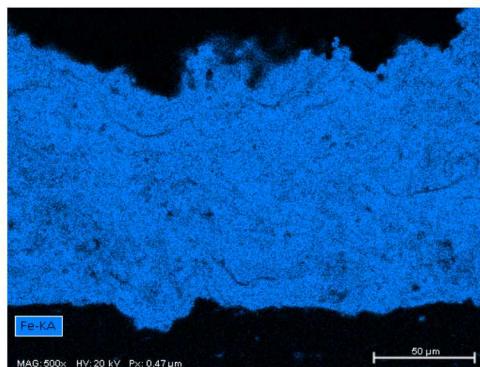
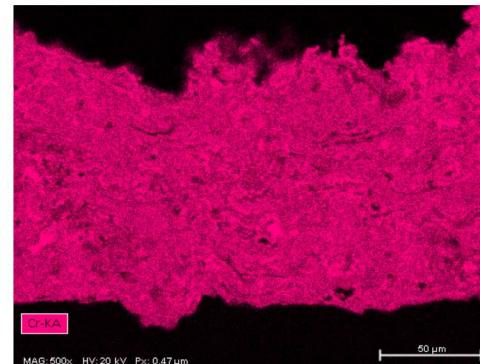
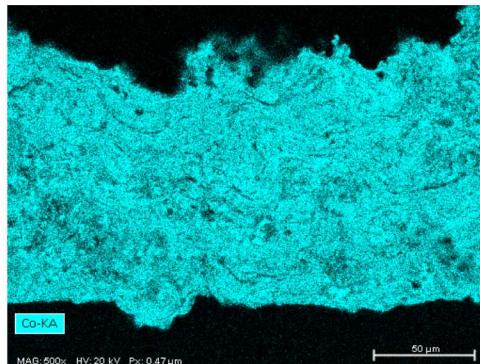
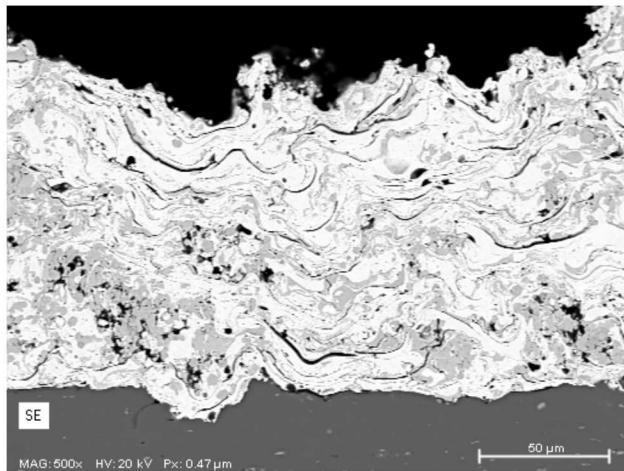
Higher mag. cross-section



Micron-size oxide inclusions



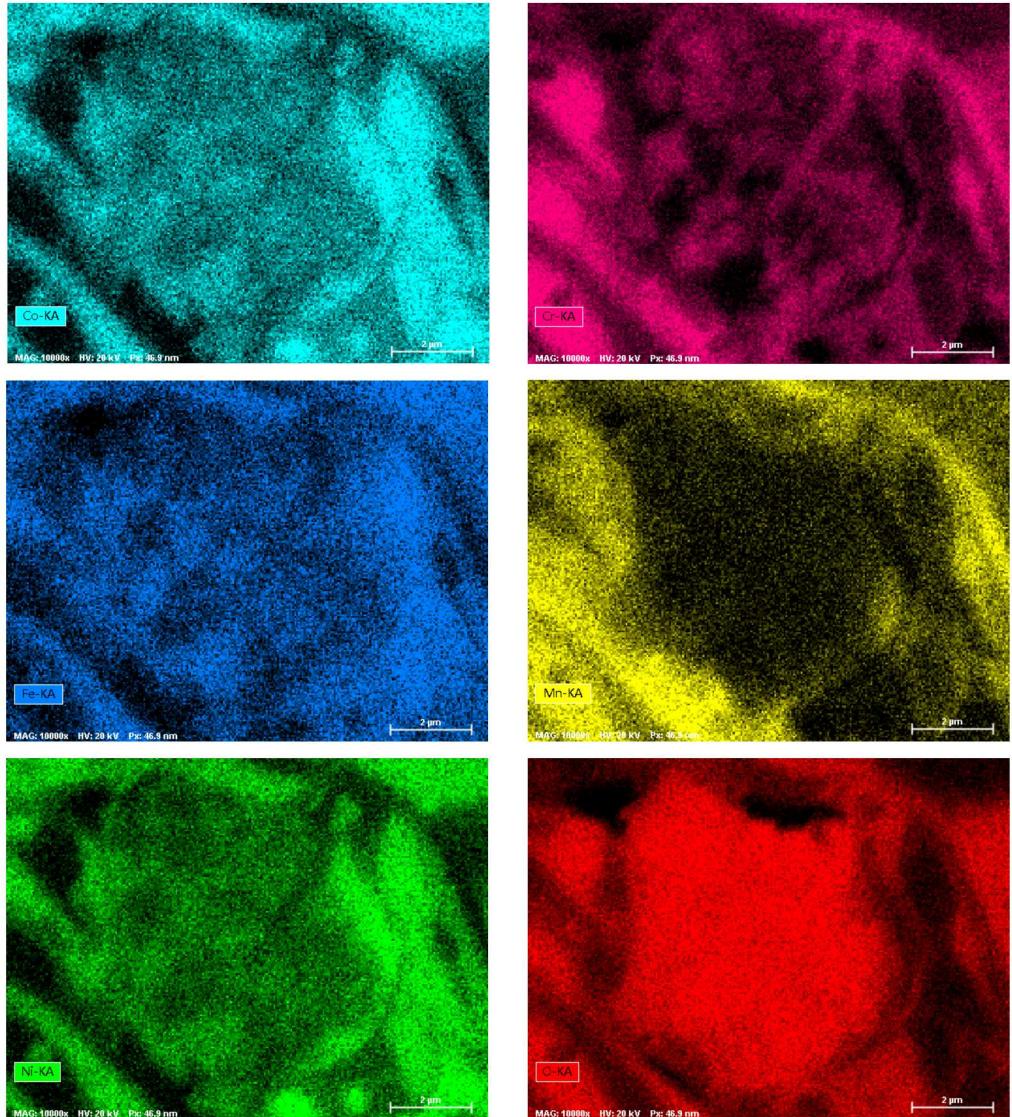
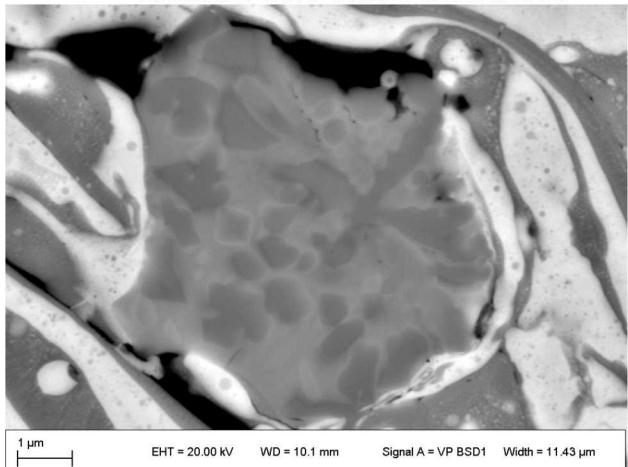
Mixed metallic and oxide HEA phases



- Inhomogeneous distribution of alloying constituents with depleted and enriched regions throughout coating thickness.
- Significant oxygen content interwoven within coating (processed in air).
- Depleted regions, notably Co, Mn, and Ni, corresponded with oxygen enrichment.

Mixed metallic and oxide HEA phases

Micron-size oxide inclusions



- Complex nanoscale multiphase oxide inclusions dispersed throughout coating.
- Some inclusions appeared to be mostly depleted in Mn.
- Analysis suggests oxides include those of Cr,