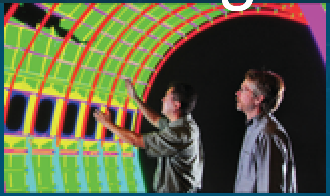
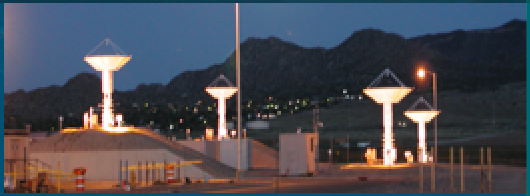
Sandia National Laboratories

SAND2021-5634C

Properties of Cold Sprayed and Controlled Atmosphere Plasma Sprayed High Entropy Alloy (CoCrFeMnNi) Coatings





PRESENTED BY

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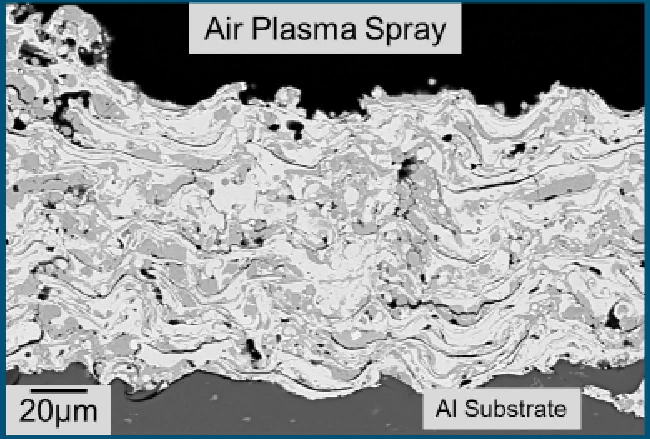
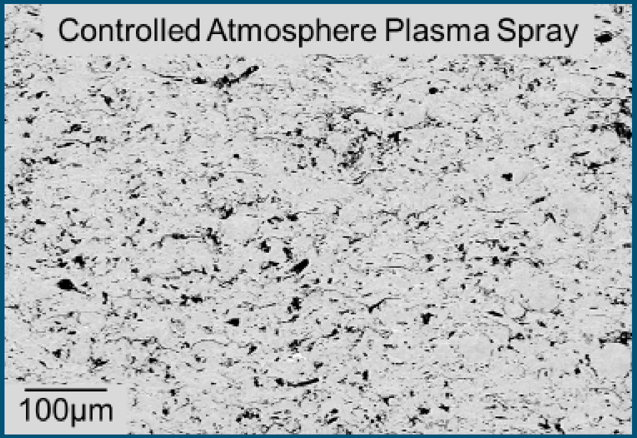
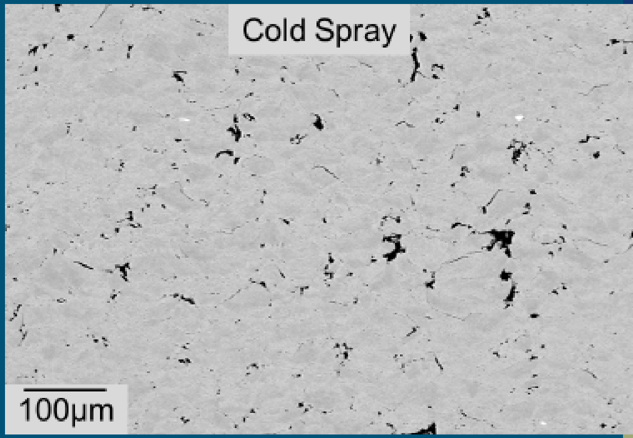
SAND#:

Outline of Talk

1. Overview of Thermal Spray processing
2. Background of High Entropy Alloys
3. Initial processing results – Air plasma spray
4. Characterization of Controlled Atmosphere Plasma Spray (CAPS) and Cold Spray coatings
5. Conclusions

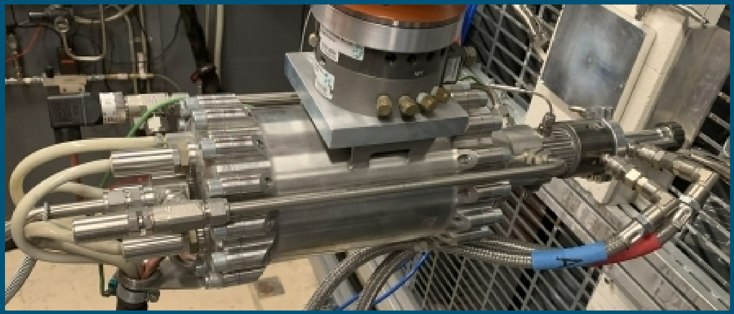






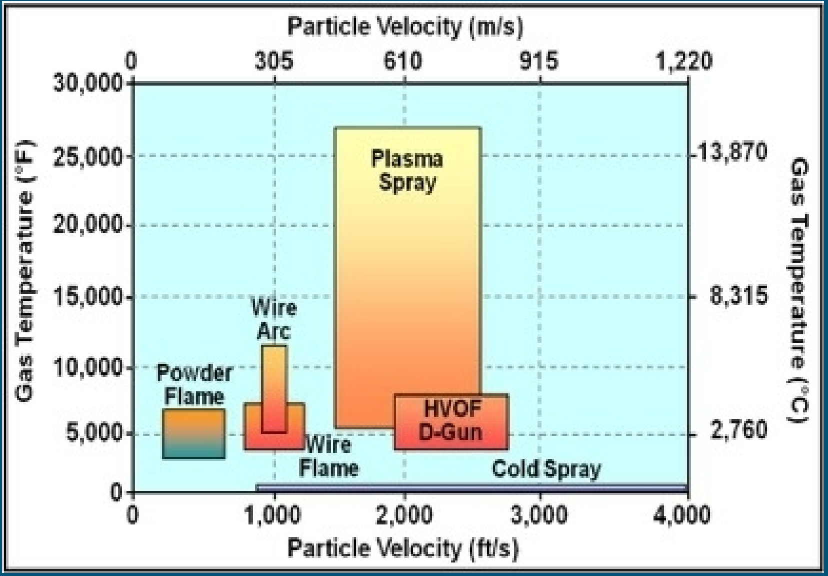
Thermal Spray Processing Conditions for High Entropy Alloy Film Deposition

Impact 5/11 Cold Spray System at Sandia



SG100 Torch used for CAPS at Sandia

Cold Spray and plasma spray deposition rely on fundamentally different mechanisms to form coatings which cover a wide area of process conditions (Temperature and Velocity)

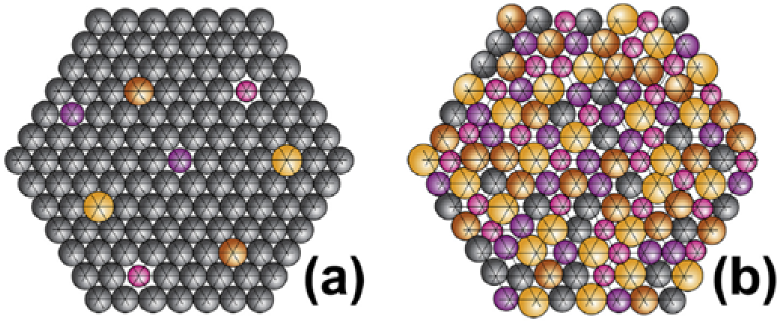


*Adapted from plots by R.C. McCune, Ford Motor Co. & A. Papyrin, Ktech Corp.

- Thermal Spray technologies encompass a wide range of particle processing temperatures and velocities
- Two of the largest differences are between plasma spray and cold spray
- Plasma spray relies on melting of particles and droplet quenching
- Cold Spray relies on high velocity – low temperature impacts to induce plastic deformation

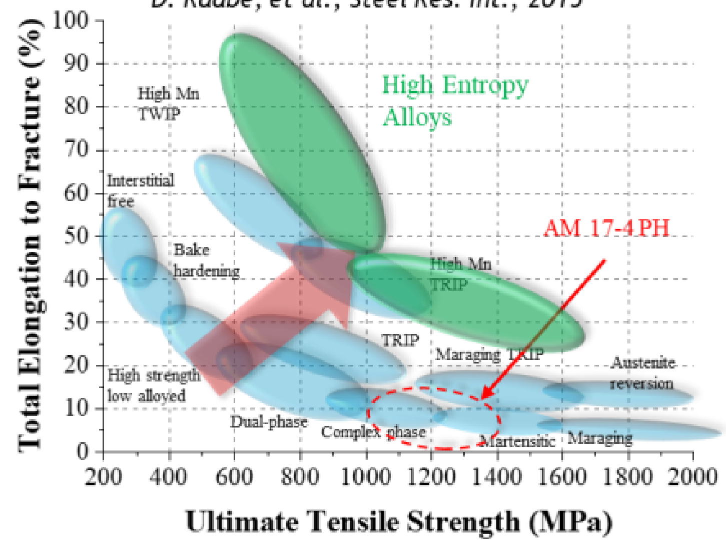
Background of High Entropy Alloys

Atomic representations of (a) conventional alloy and (b) HEA/RHEA



Miracle, et al. Acta, 2017

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

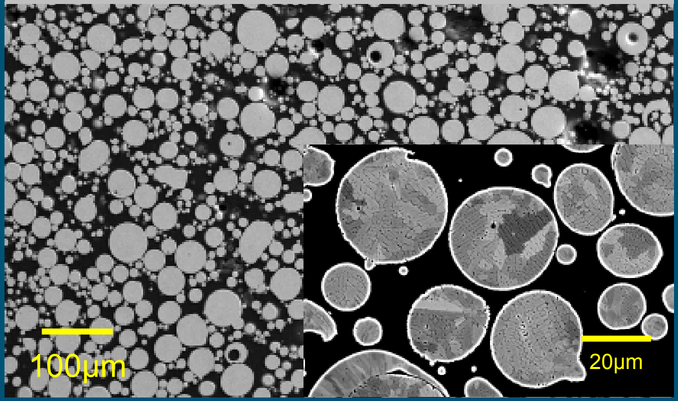


- High Entropy Alloys (HEAs) are loosely defined as alloys containing five or more constituents at roughly 5-35 at. % each
  - Alloys with four or more constituents interchangeably called HEAs or complex concentrated alloys (CCAs)
- The chemistry results in high configurational entropy which is theorized to stabilize single-phase solid solutions
  - HEAs can be multiphase
- CCAs/HEAs have properties exceeding most conventional alloys, plus resistance to phase precipitation

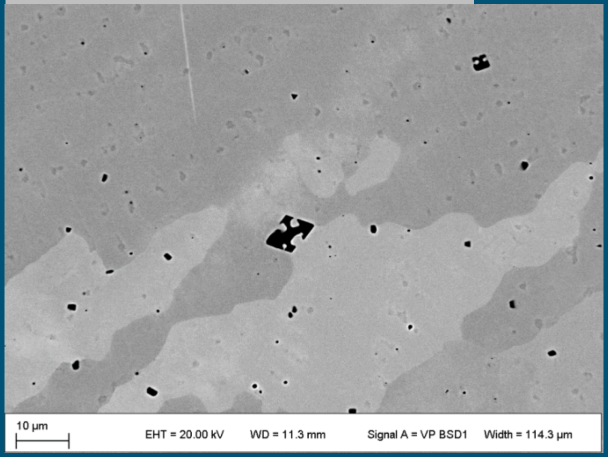
As-Received Powder Properties (Cantor Alloy – CoCrFeMnNi)

- Powder was high pressure gas atomized (hpga), AMES Laboratory: 45um powder
- Despite promising properties, there are challenges with conventional processing methods (i.e., casting): defects and insufficient mixing of constituents.
- Example below: CoCrFeMnNi HEA – microsegregation of Mn and Cr, microshrinkage porosity.

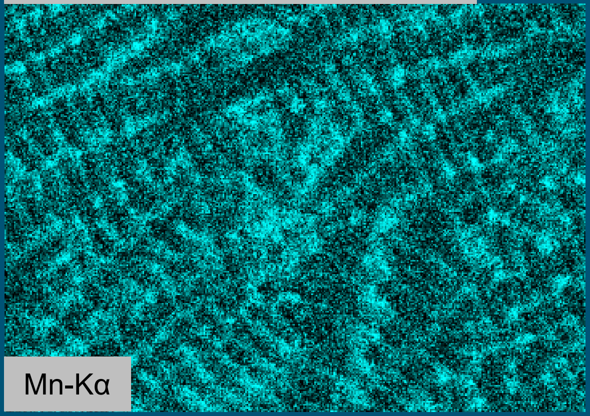
Channeling Contrast SEM of HEA Powder



Micro-shrinkage porosity:



Micro-segregation of Mn:



*Kustas, Andrew, et al. "Advanced Manufacturing of High Entropy Alloys." TMS, 2019.

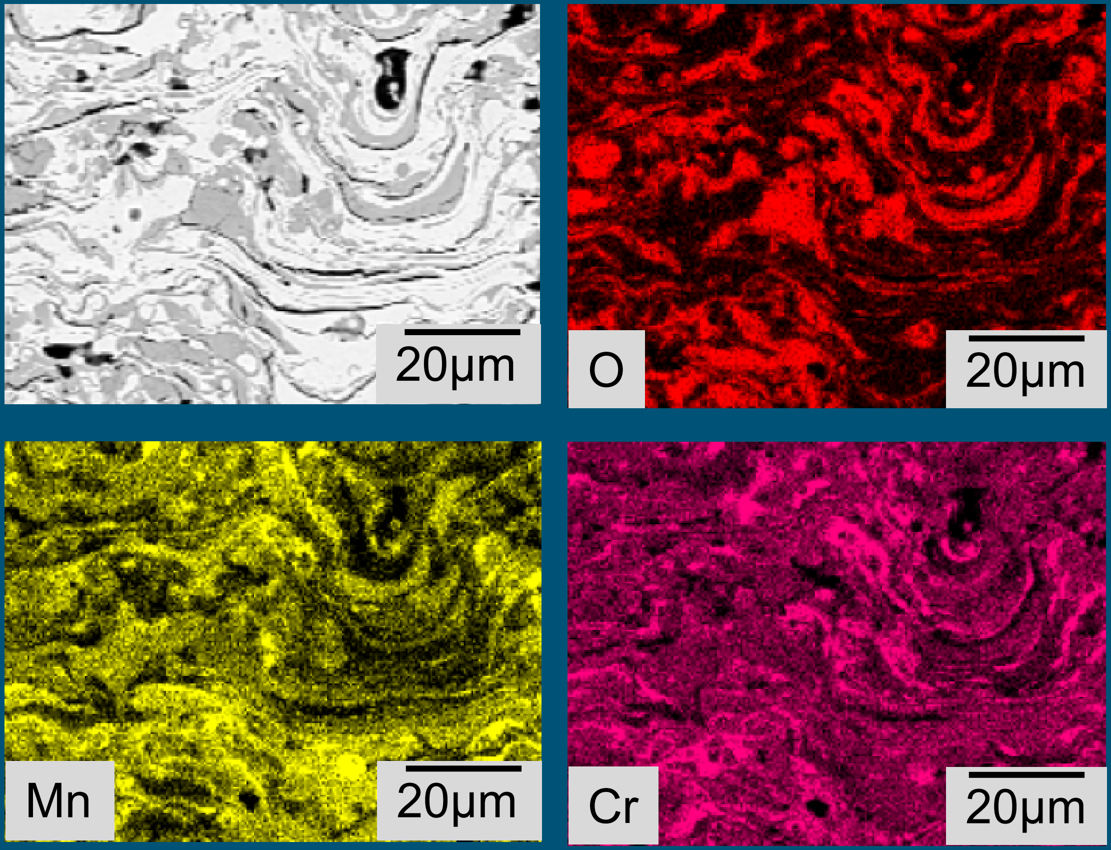
Composition (wt%)	Al	C	Co	Cr	Fe	Mn	Ni	N	O	S
HEA Powder	0.003 ± 0.00045	0.005 ± 0.00075	20.91 ± 0.42	18.46 ± 0.37	20.14 ± 0.40	19.06 ± 0.38	21.34 ± 0.43	0.002 ± 0.00026	0.064 ± 0.0096	0.008 ± 0.0012

RESULTS

Air Plasma Sprayed High Entropy Alloy

Samples sprayed using Triplex APS system using Argon processing gas

- Inhomogeneous distribution of alloying constituents with depleted and enriched regions throughout coating thickness
- Significant oxygen content interwoven within coating (processed in air)
- Chromium rich oxides present throughout the film
- Porosity = 6.0 ± 0.6%

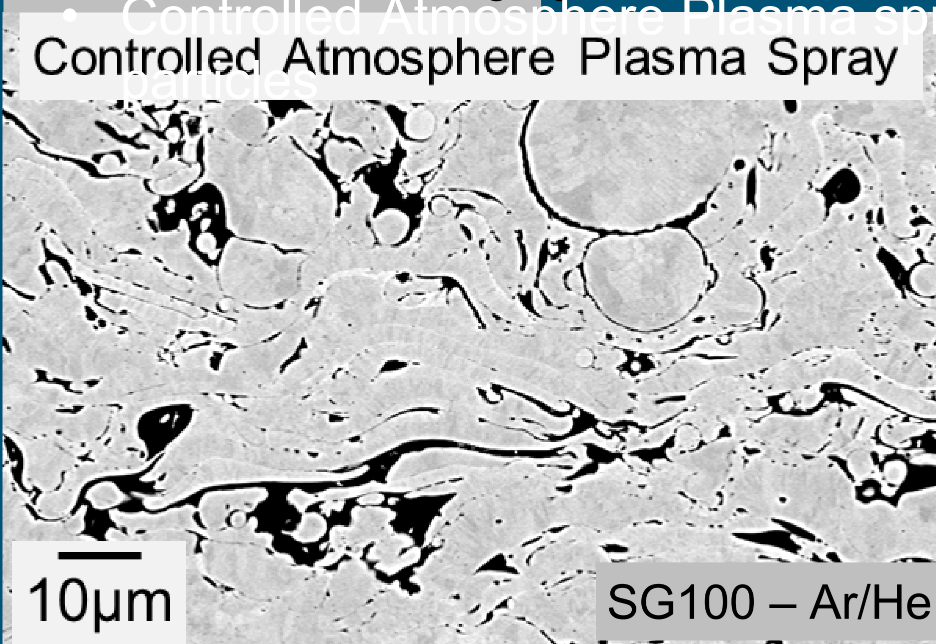


Can We Produce Coatings With Same Composition As Starting Powder?

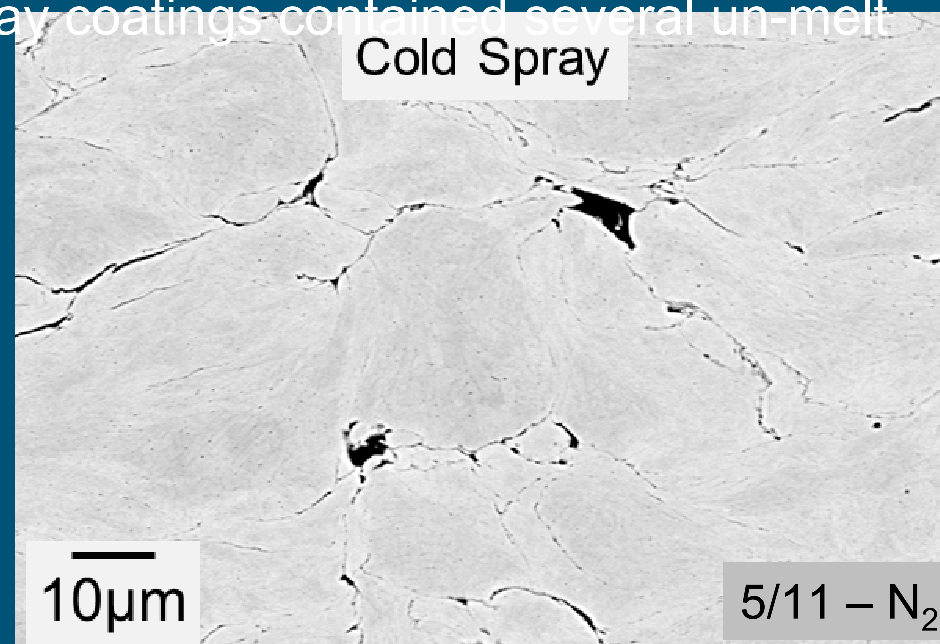
SEM/Image Analysis of Controlled Atmosphere Plasma Spray and Cold Spray HEA

- Significant microstructural differences observed in the CAPS vs Cold Spray films
- Image analysis using Python was used to determine area fraction of porosity
    - Averages and St. Dev determined using three images at two magnifications
- Porosity is significantly reduced when using Cold Spray processing
- Controlled Atmosphere Plasma spray coatings contained several un-melt particles

Backscatter SEM Imaging:



Density = 89.3 ± 1.2%



Density = 97.2 ± 0.4%

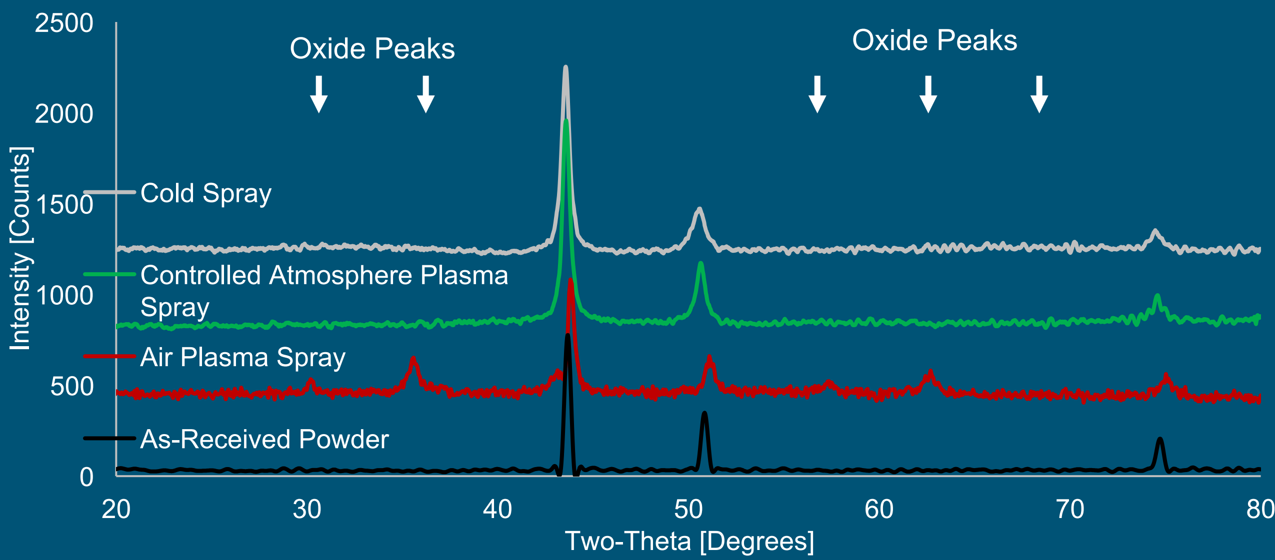
Phase and Composition Analysis of Sprayed High Entropy Alloy

- No evidence of change in concentration of oxygen, nitrogen, or hydrogen from spray processing
- XRD shows phase retention of as-received powder for CAPS and Cold Spray coatings
- APS films show oxide peaks: EDS (Mn and Fe

Composition determined by IGF – LECO ONG836

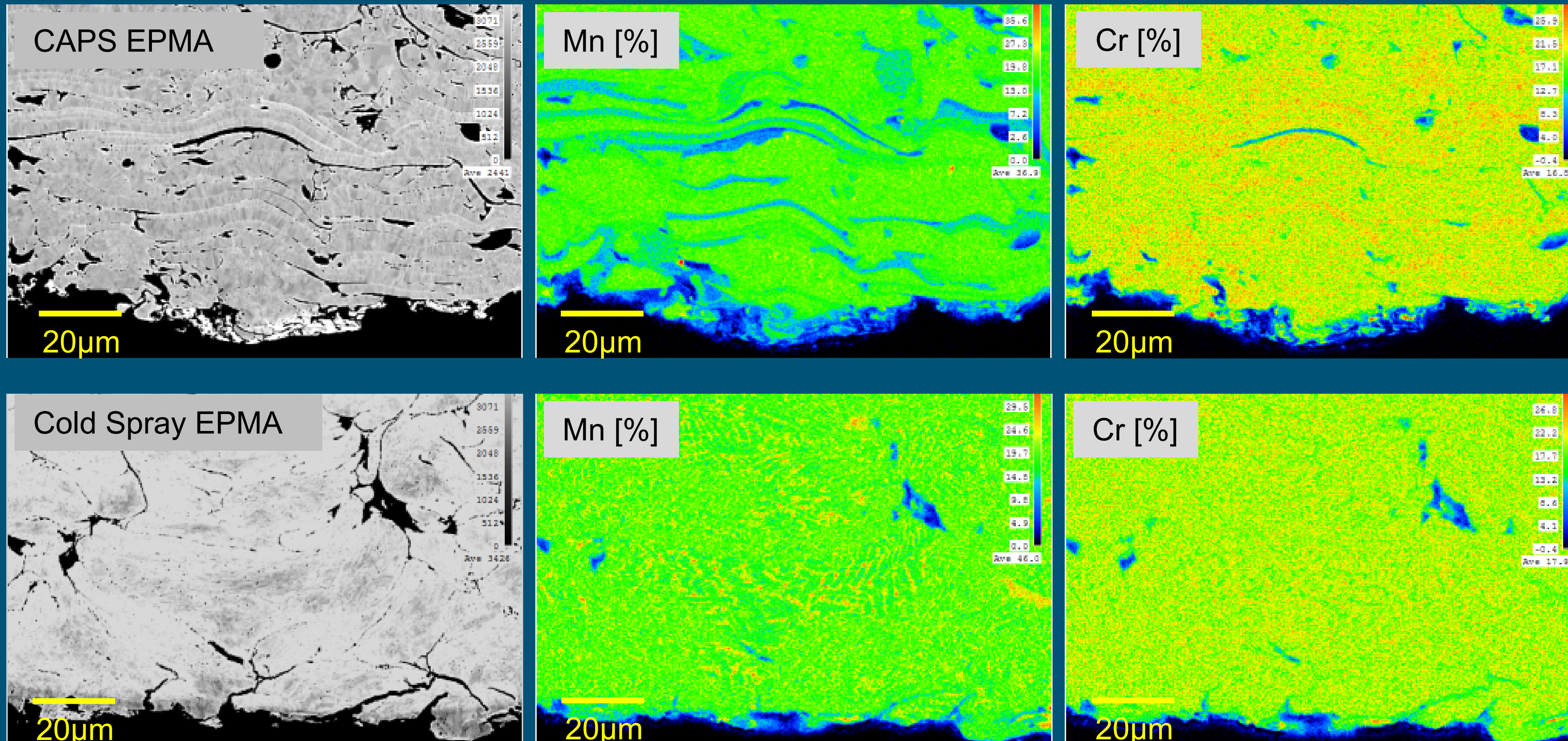
	Oxygen [wt%]	Nitrogen [wt%]	Hydrogen [ppm]
	Average	Average	Average
Powder	0.14±0.01	Not Quantifiable	16±1.1
Cold Spray	0.17±0.03	0.008±0.003	20±8.7
CAPS	0.16±0.03	0.003±0.003	17±4.7

XRD Spectral Results for Thermal Sprayed HEAs



Phase analysis conducted on a Bruker D2-Phaser using a Cu Kα source

Manganese Evaporation in Plasma Spray Processing of High Entropy Alloy

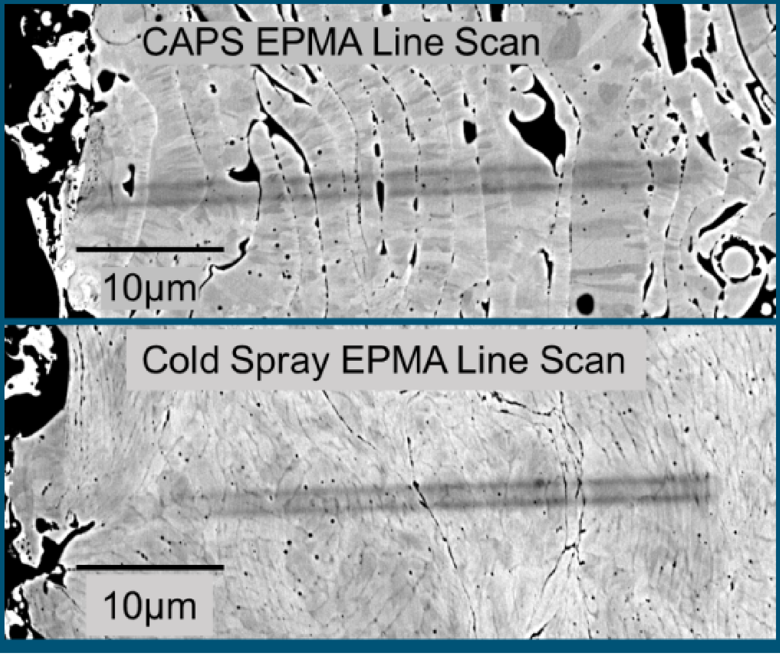


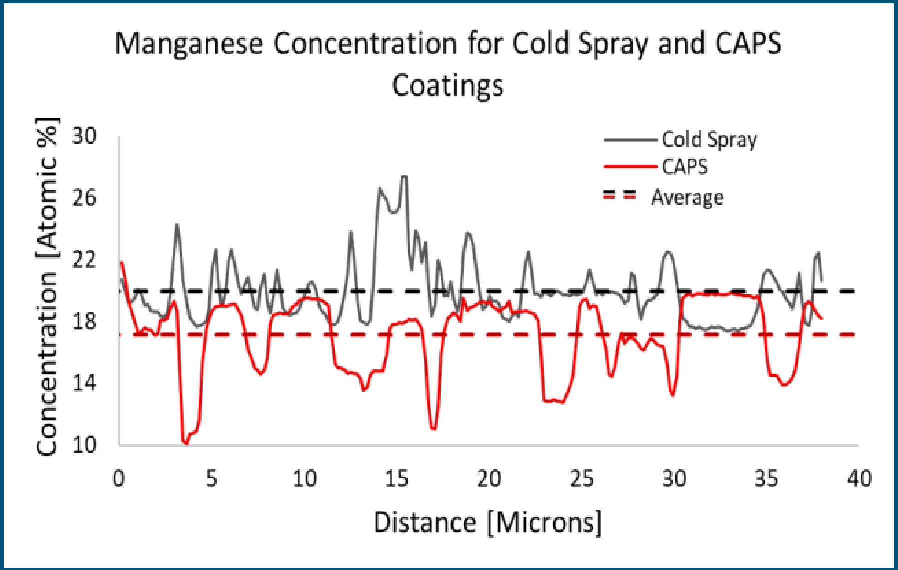
- Electron Probe Micro-Analyzer (EPMA) used to measure Mn composition
- Observable Mn depletion along splat boundaries
- Boiling Point of Mn is in range of expected in-flight particle temperatures (especially boundary layer)
- Large vapor pressure compared to other constituents indicates faster evaporation rate
  - Manganese vapor pressure at 1280-1349°C is ~10^{-3} - 10^{-4} *

*Mackowiak, J., Physical chemistry for metallurgists, Allen &

Manganese Evaporation in Plasma Spray Processing of High Entropy Alloy – EPMA Line Scans

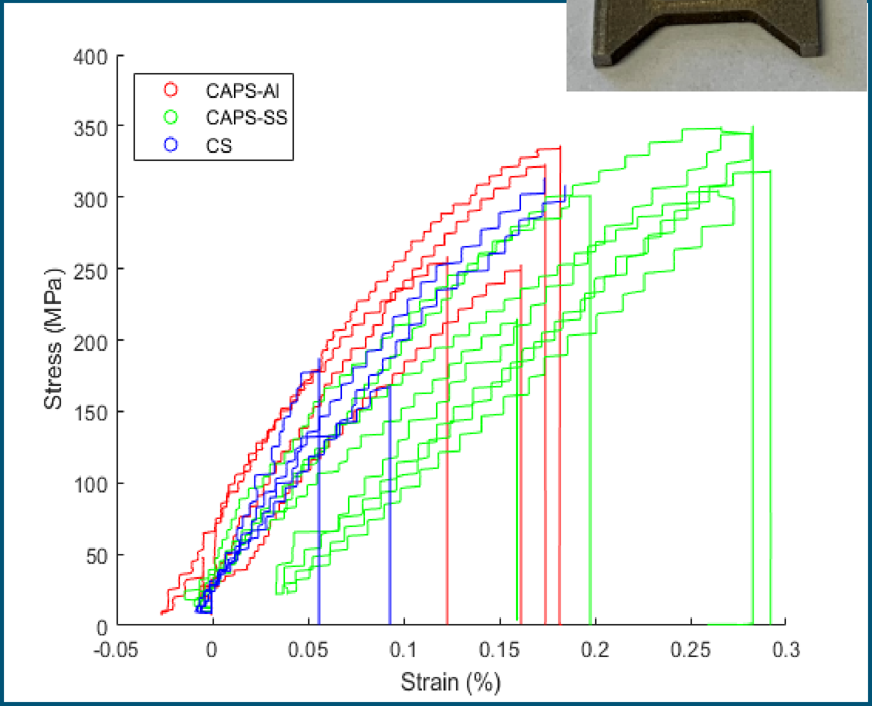
- Manganese depletion observed along boundaries in Plasma Sprayed samples (Right)
  - Due to differences in vapor pressure of the individual constituents
- Low temperature of kinetic processing prevents manganese evaporation
- Cold Spray Mn composition is 19.86% compared to the average CAPS composition of 17.74%
  - Powder Mn composition is 19.06%
- Dips in CAPS Mn reach 10%, indicating significant localized depletion of Mn
- Manganese depletion could result in differences in inter-splat bonding, corrosion, and mechanical properties
  - Changes in diffusion
  - Increase in pure chromium oxides
  - Reduced twinning

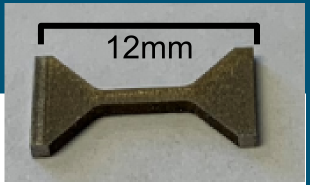




Mechanical Properties of Thermal Sprayed HEA

- Mechanical properties were measured using micro-tensile bars of coating which was electrical discharge machined to size
- CAPS HEA coatings were sprayed on aluminum (Al) and 316 steel substrates (SS)
  - Coatings on aluminum delaminated, but were thick enough to cut tensile bars
- Cold Spray coatings on aluminum substrates
- Large deviation in measured mechanical properties indicates no statistical evidence of differences between the processes
- Vickers hardness data shows significant work hardening of the Cold Spray coatings





Vickers Hardness Data:

	Powder (10 values)	CAPS (25 values)	CS (25 values)
Average	163	196	351
St Dev	19	18	32

Tensile Bar Summary:

	Cold Spray	CAPS - SS	CAPS - Al
UTS [Mpa]	245 ± 78	297 ± 58	293 ± 43
Ductility [%]	0.13 ± .06	0.23 ± 0.06	0.16 ± 0.03
Modulus [Gpa]	180 ± 58	116 ± 15	160 ± 20

Summary of Thermal Spray Processing of Cantor HEA

- Severe oxidation was present in the APS coating, with no oxidation observed for CAPS and Cold Spray coatings
- The density of Cold Spray was considerably higher than CAPS (~8%)
- No compositional or phase changes occurred in Cold Spray coatings
- Reduction of Mn composition in CAPS coatings which was attributed to evaporation due to the low vapor pressure of Mn compared to the other constituents
- Plastic deformation during Cold Spray processing resulted in significant cold working which increased hardness by ~200%, while only a slightly higher hardness was observed for the CAPS coating relative to the feedstock powder
- Coatings from both CAPS and Cold Spray exhibit very low ductility before brittle fracture during tensile testing, with lower UTS and YS compared to bulk values