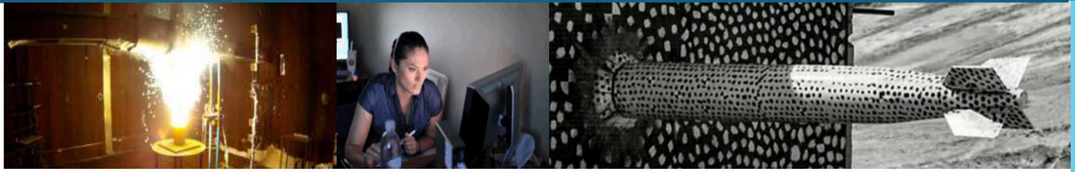
SAND2020-2107C

Additive Manufacturing of Bulk Refractory High Entropy Alloys with Tailored Mechanical Properties



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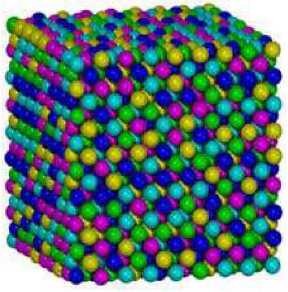
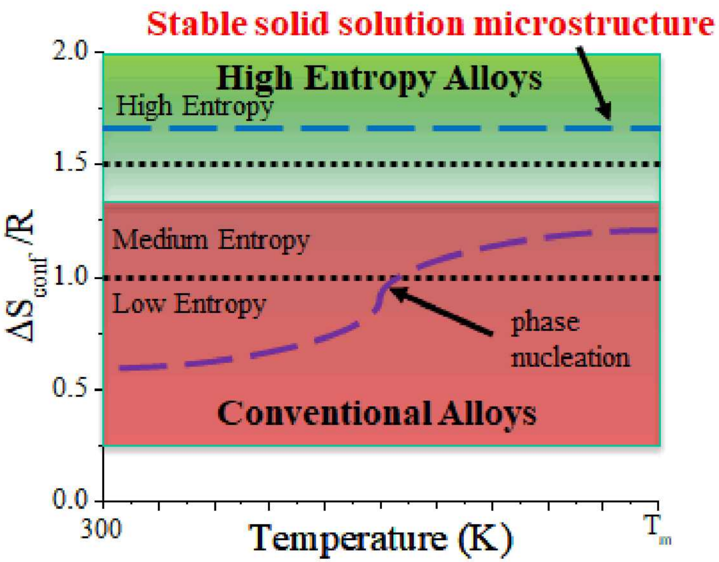
Outline

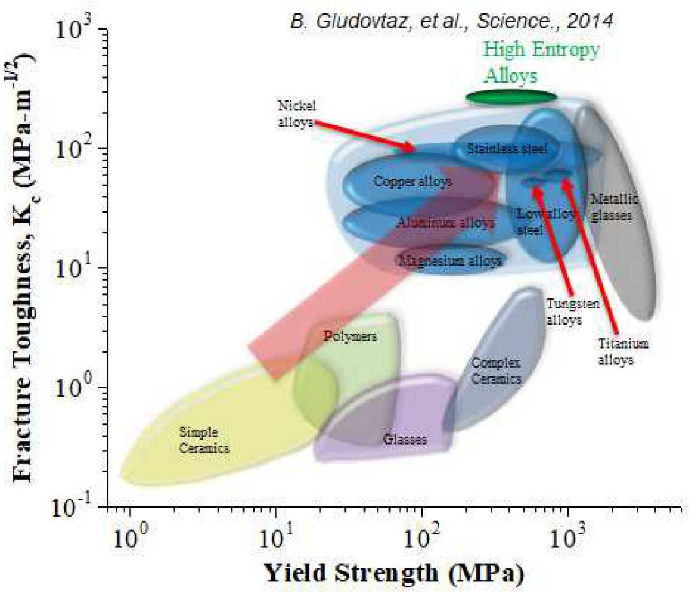
- Introduction/Motivation
  - High Entropy Alloys
  - Refractory Metals
  - Objective
- High-throughput Alloy Screening
- Nb-Cantor Graded Screening
- Ta-Cantor Graded Screening
- Ti64-Cantor Graded Screening
- Summary Conclusions

Introduction – High Entropy Alloys (HEA)





D. Miracle et al., Entropy, 2014


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

Benefits:

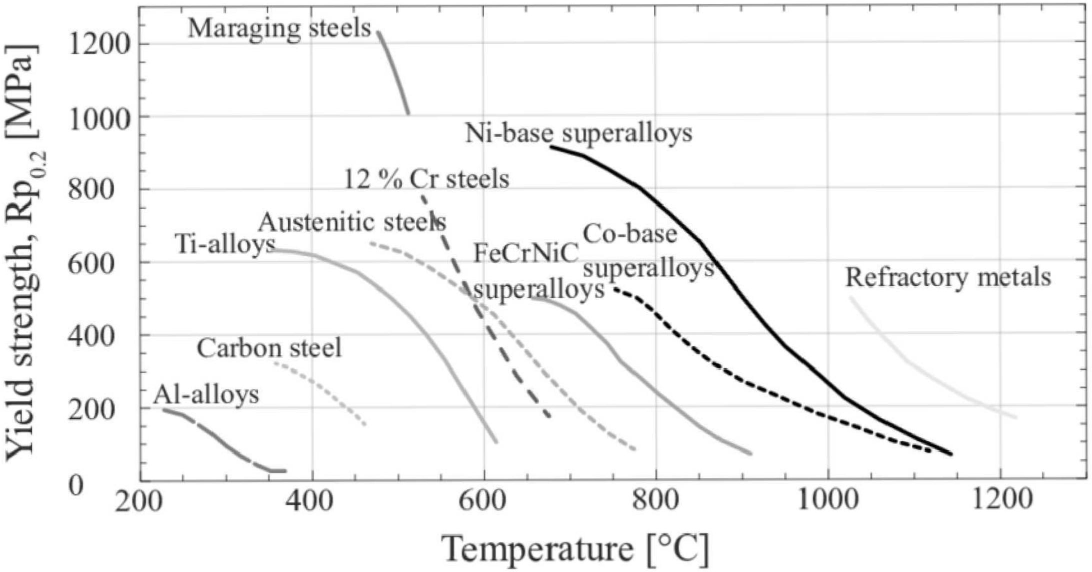
- Exceptional properties exceeding most conventional alloys, suggesting improved resistance to failures AM defects
- Improved high temperature properties compared to the individual elemental constituents

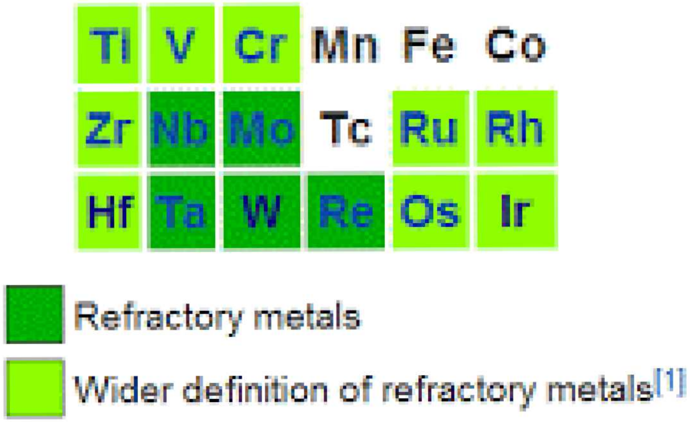
Challenges:

- All composition ranges may not promote solid solution
- Increasing elemental composition increases the achievable phase complexity requiring significant experimental efforts

Additive manufacturing provides a means to rapidly explore the composition/phase space of new HEA's.

Introduction - Refractory Metals





Ti	V	Cr	Mn	Fe	Co
Zr	Nb	Mo	Tc	Ru	Rh
Hf	Ta	W	Re	Os	Ir

- 🟩 Refractory metals
- 🟩 Wider definition of refractory metals[1]

https://sites.google.com/site/concentrationofminerals/industrial-classification-of-metals/refractory-metals

Benefits:

- ➢Exceptional mechanical properties at high service temperatures
- ➢Withstand radiation bombardment without rapid degradation
- ➢Resistance to corrosion

Challenges:

- ➢Scarcity
- ➢High costs
- ➢High temperature oxidation
- ➢Ranging mechanical properties

Objective

Explore the phase space of Rf_xCoCrFeMnNi high entropy alloys utilizing a high-throughput additive manufacturing approach to establish microstructural/mechanical property relationships.

Why graded HEAs with Rfs?

Metallurgical/Science Impact:

Why Rf? – sufficiently different atomic characteristics (electronegativity, size, valence, etc.) – for phase stability analysis

Connecting process-structure properties, etc.

Engineering impact:

High temperature facing materials

Brittle to ductile interfaces

Tailored properties to meet site specific performance

Refractory metals chosen for this study:

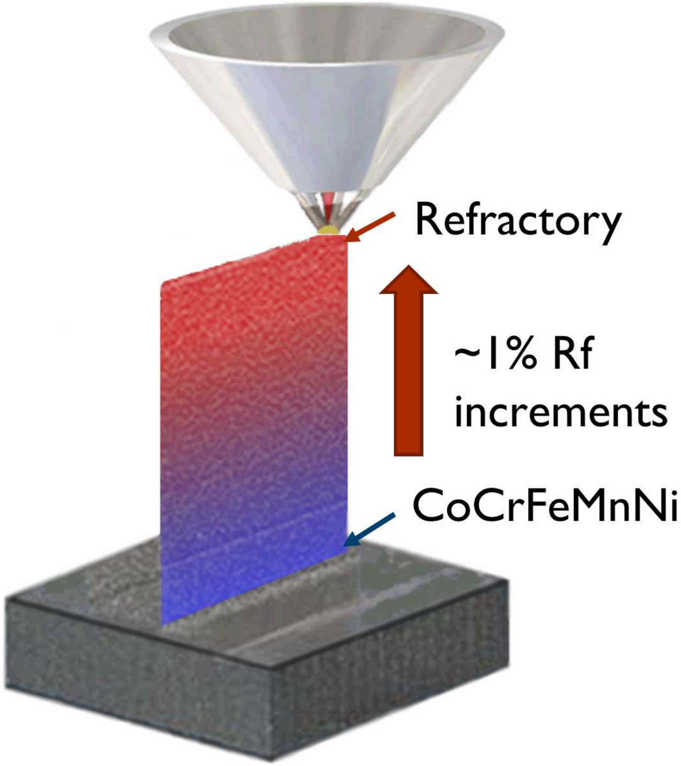
Nb – Lightest of Rf metals with low strength high ductility (strength improved by alloying.

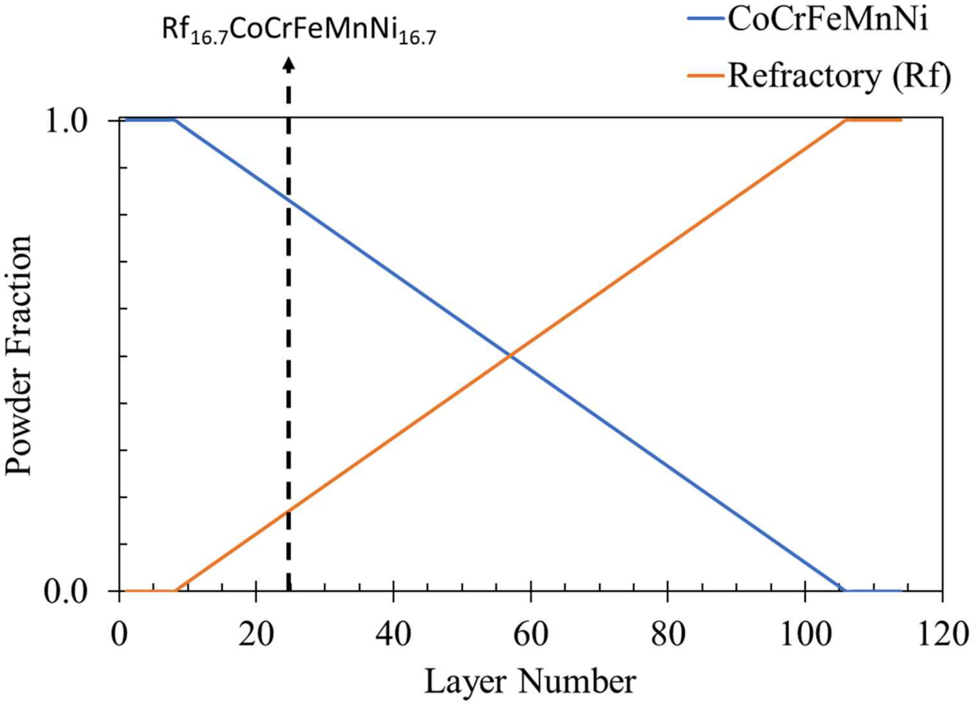
Ta – Good room temperature ductility and low ductile to brittle transition temperature.

Ti-6Al-4V – Non-traditional defined Rf metal due to low creep resistance.

High-throughput Alloy Screening

$$Rf_x CoCrFeMnNi_{(1-x)/5}$$

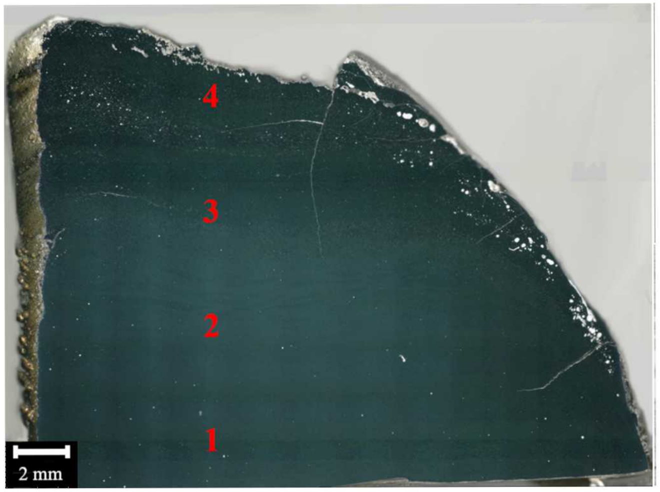


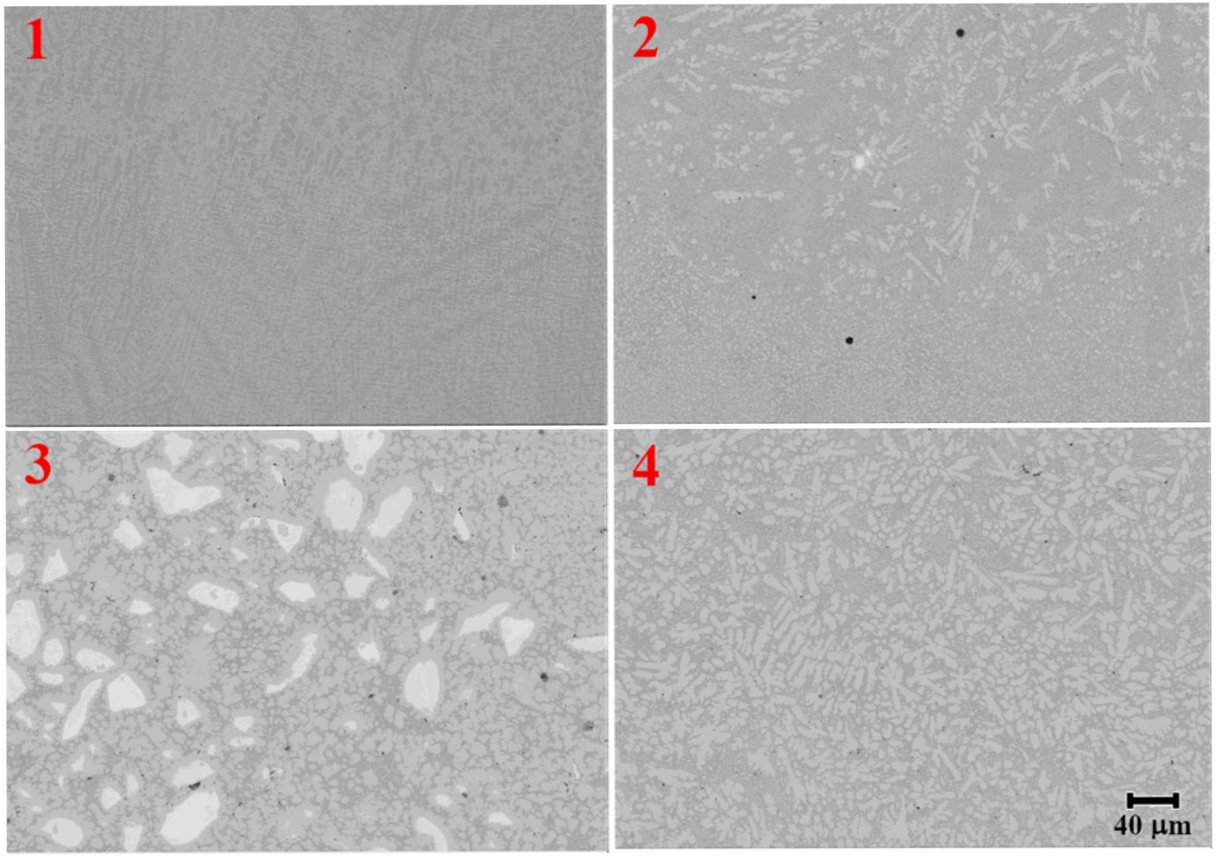


Rapid Microstructure/Mechanical Analysis:

- Single pass thin wall structures fabricated from equiatomic CoCrFeMnNi with incrementally increasing Rf content
- SEM-EDS performed across entire height to assess the elemental distribution
- Micro-hardness measurements taken across the entire height

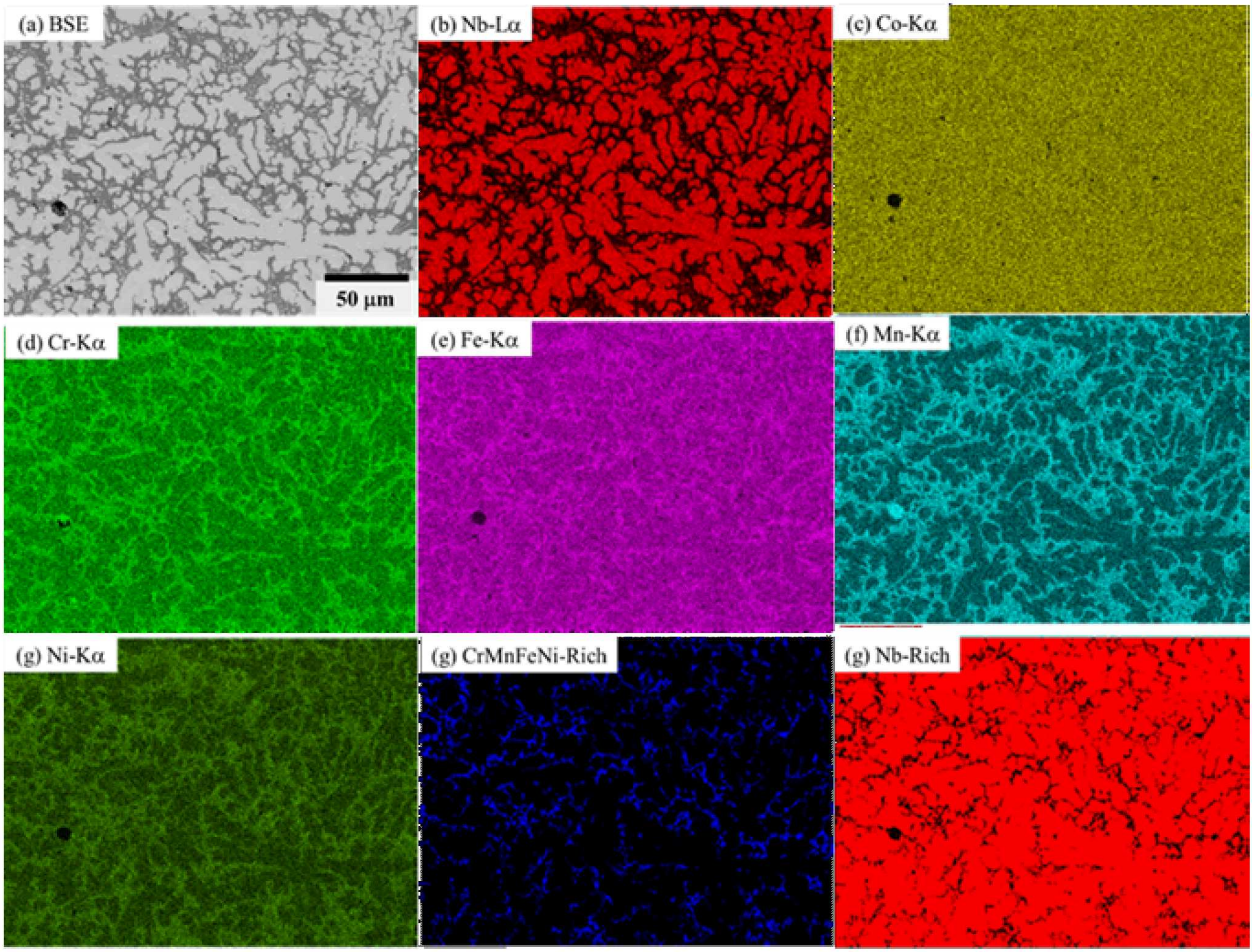
Nb$_x$CoCrFeMnNi - Microstructure





1:Typical Cantor coarse grain AM microstructure (FCC)
2:Two phases present – fine Nb-rich particulate/lamellar + Nb-rich coarse dendritic structure
3:Three phases Insufficiently fused Nb particles with intermetallic phases
4:Two phases Complete fusion of Nb with coarse Nb-rich phases and fine lamellar interdendritic structure

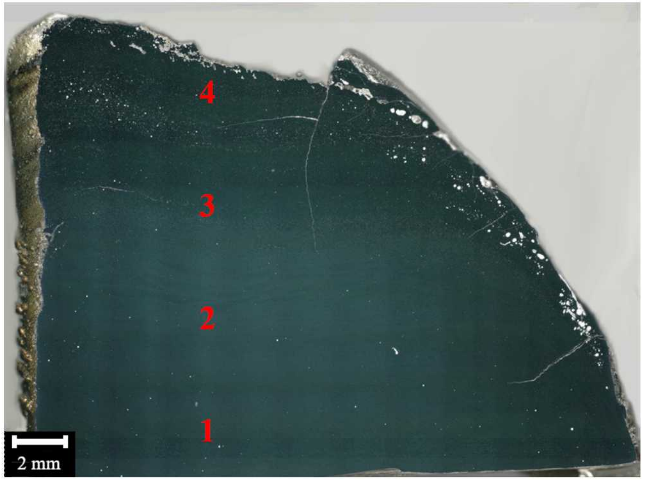
$Nb_{17}CoCrFeMnNi_{17}$ – SEM-EDS

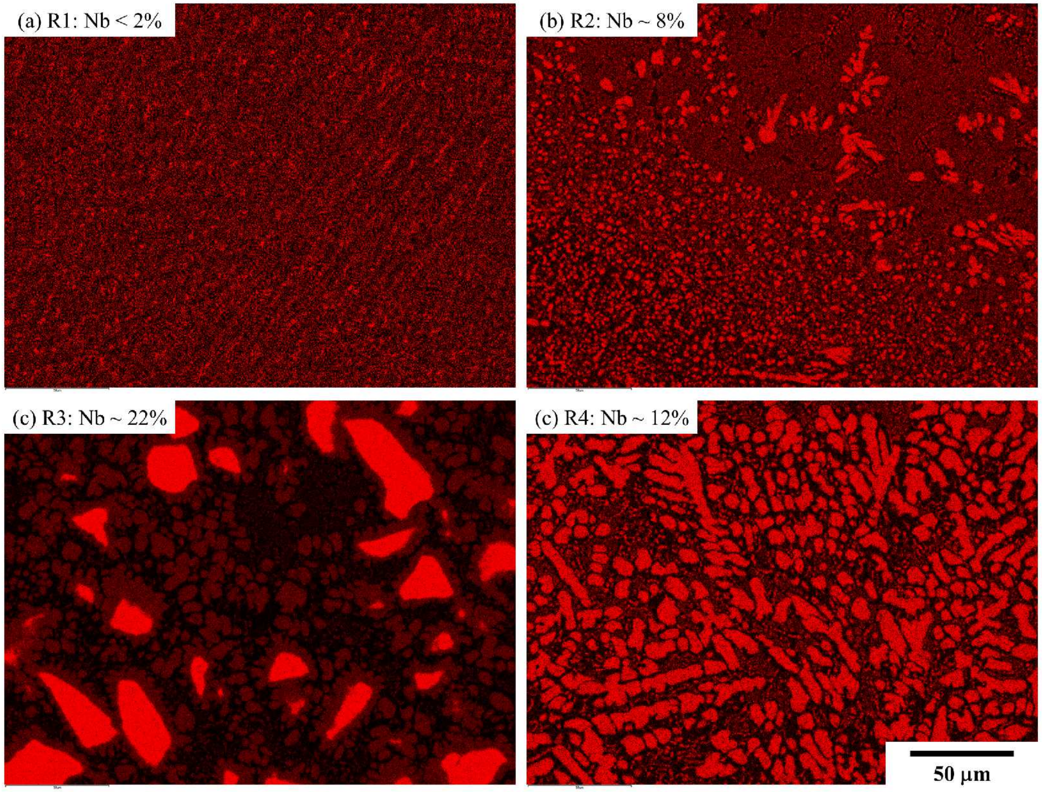


- Light Phase: Nb
- Dark Phase: Cr-Fe-Mn-Ni
- Even: Co

Segregation of Nb occurs early and solid solution never formed

Nb$_{17}$CoCrFeMnNi$_{17}$ – SEM-EDS




(a) R1: Nb < 2%

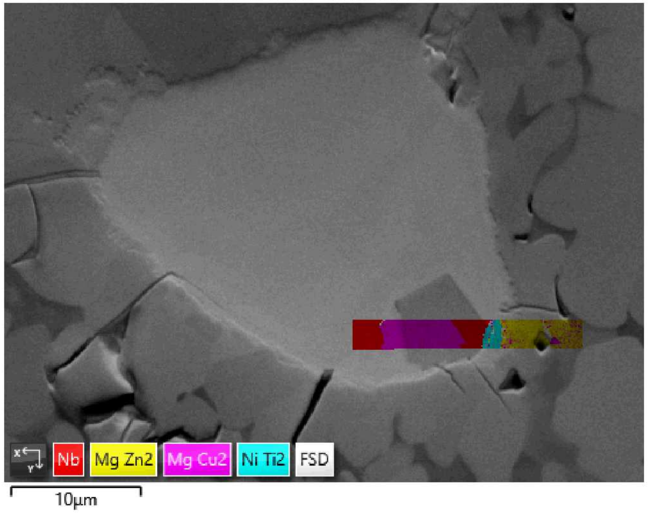
(b) R2: Nb ~ 8%

(c) R3: Nb ~ 22%

(c) R4: Nb ~ 12%

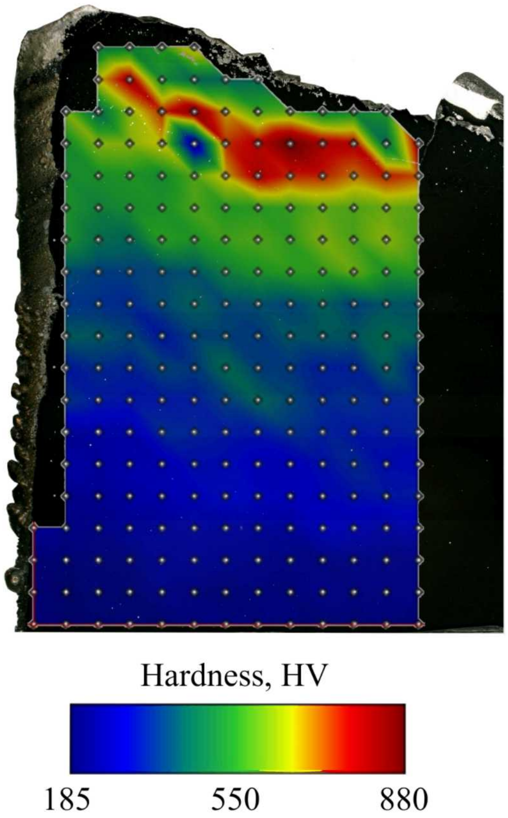
Insufficiently melted Nb particle from R3

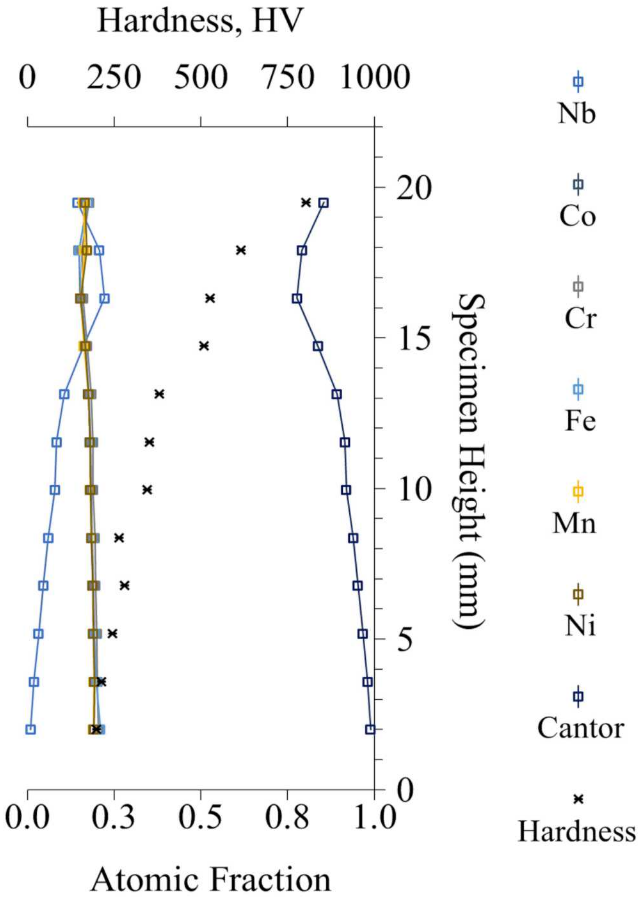
EBSD Layered Image 31

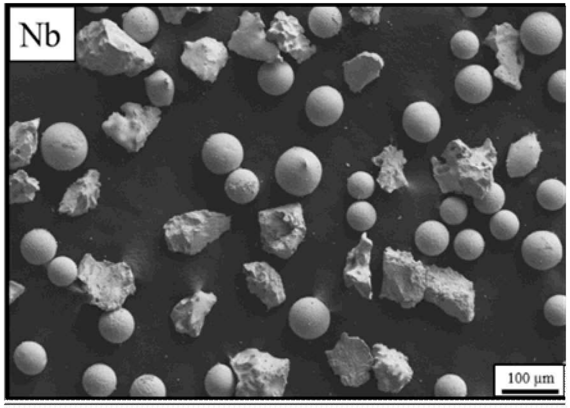


- Intermetallic phases formed around unmelted Nb particles
- Complete fusion occurred after Nb content failed to increase near top

$Nb_xCoCrFeMnNi$ – Hardness Map



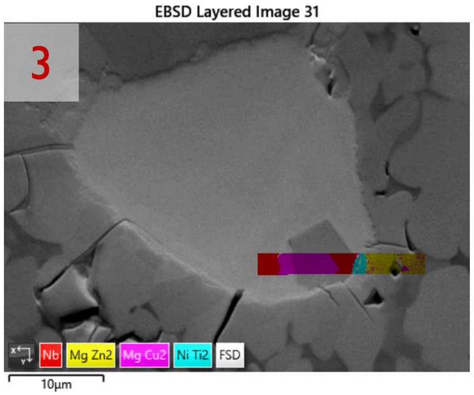


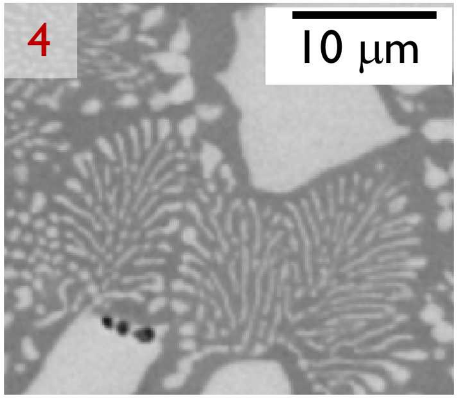


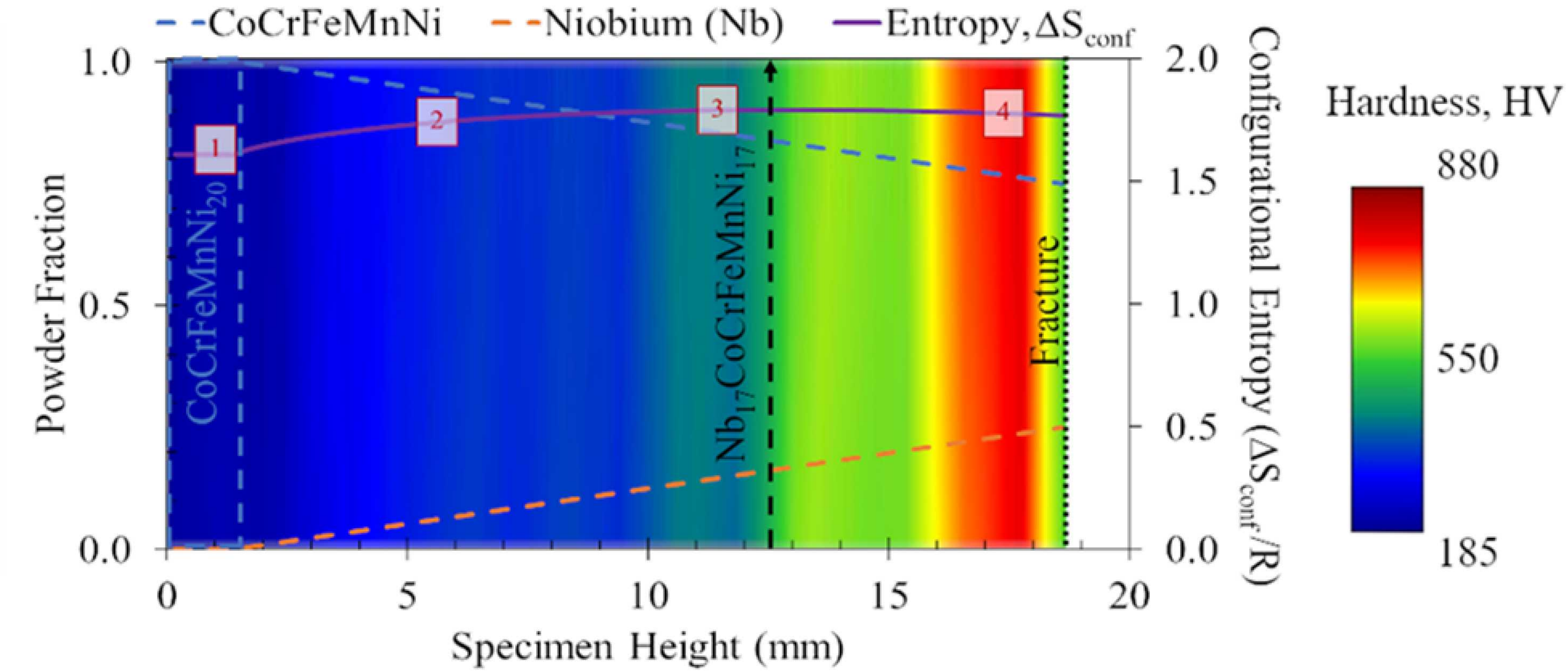
Powder Element	Avalanche Energy (mJ/kg)	Avalanche Angle (°)	Break Energy (mJ/kg)
Nb	20.99 (9.1)	52.9 (5.9)	67.58 (5.5)

- >30% Nb not achieved due to poor flowability of Nb powder
- **Hardness increased to over 800 HV near equiatomic regime indicating impressive strengths of Nb-HEA can be achieved**

$Nb_xCoCrFeMnNi$

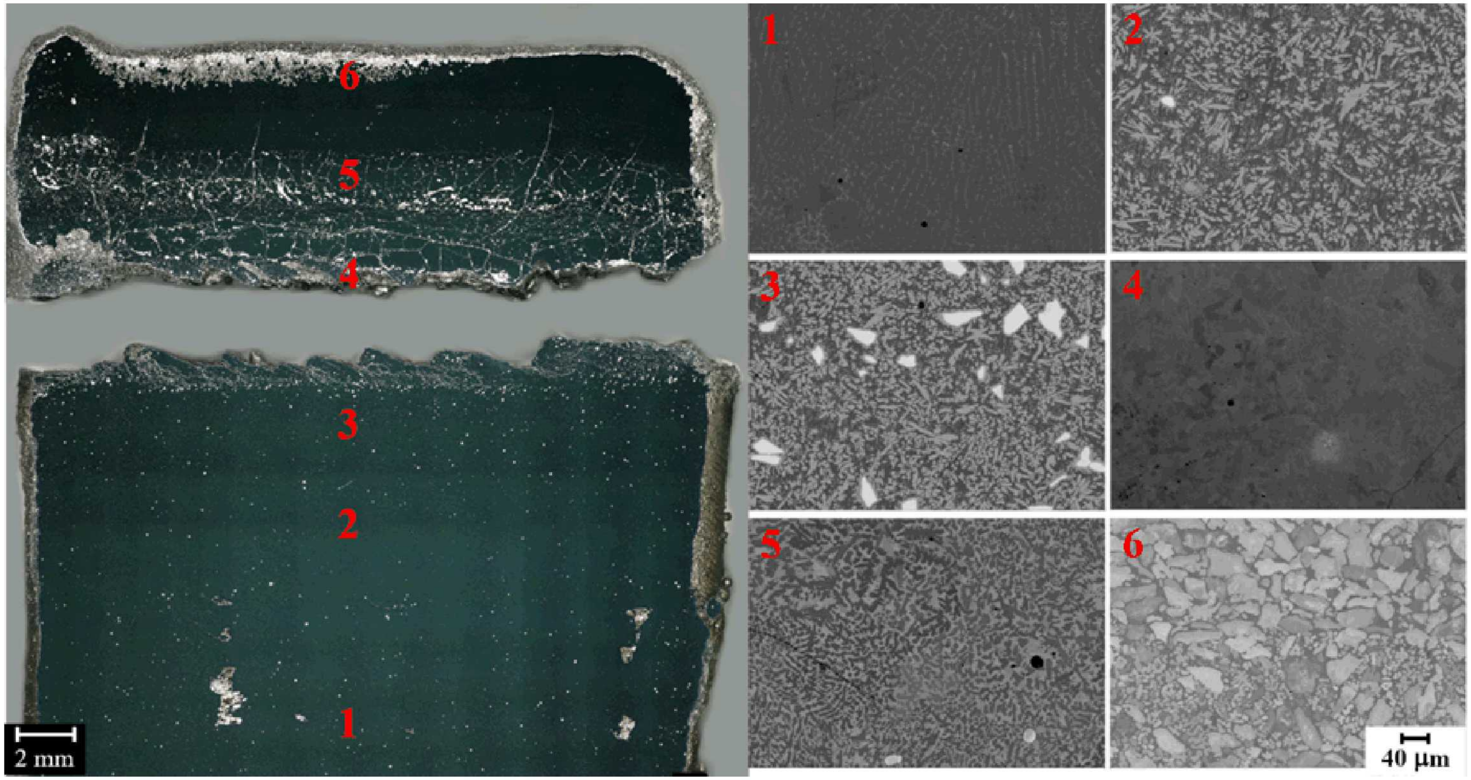






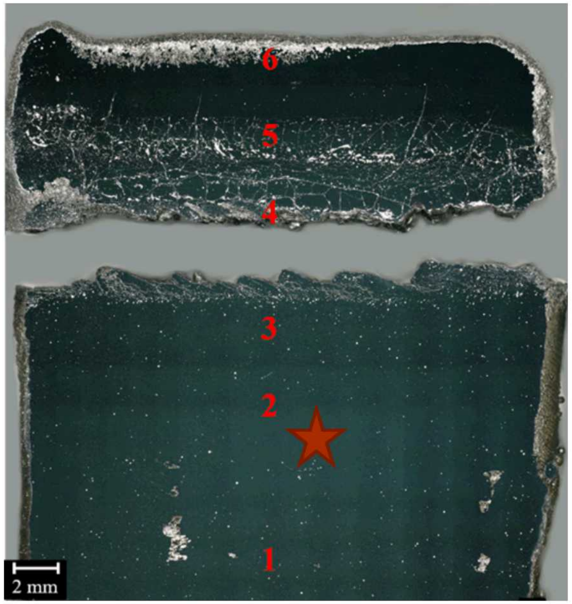
- Intermetallic phases formed near the equiatomic regime
- Maximum hardness occurred after equiatomic regime at high configurational entropy

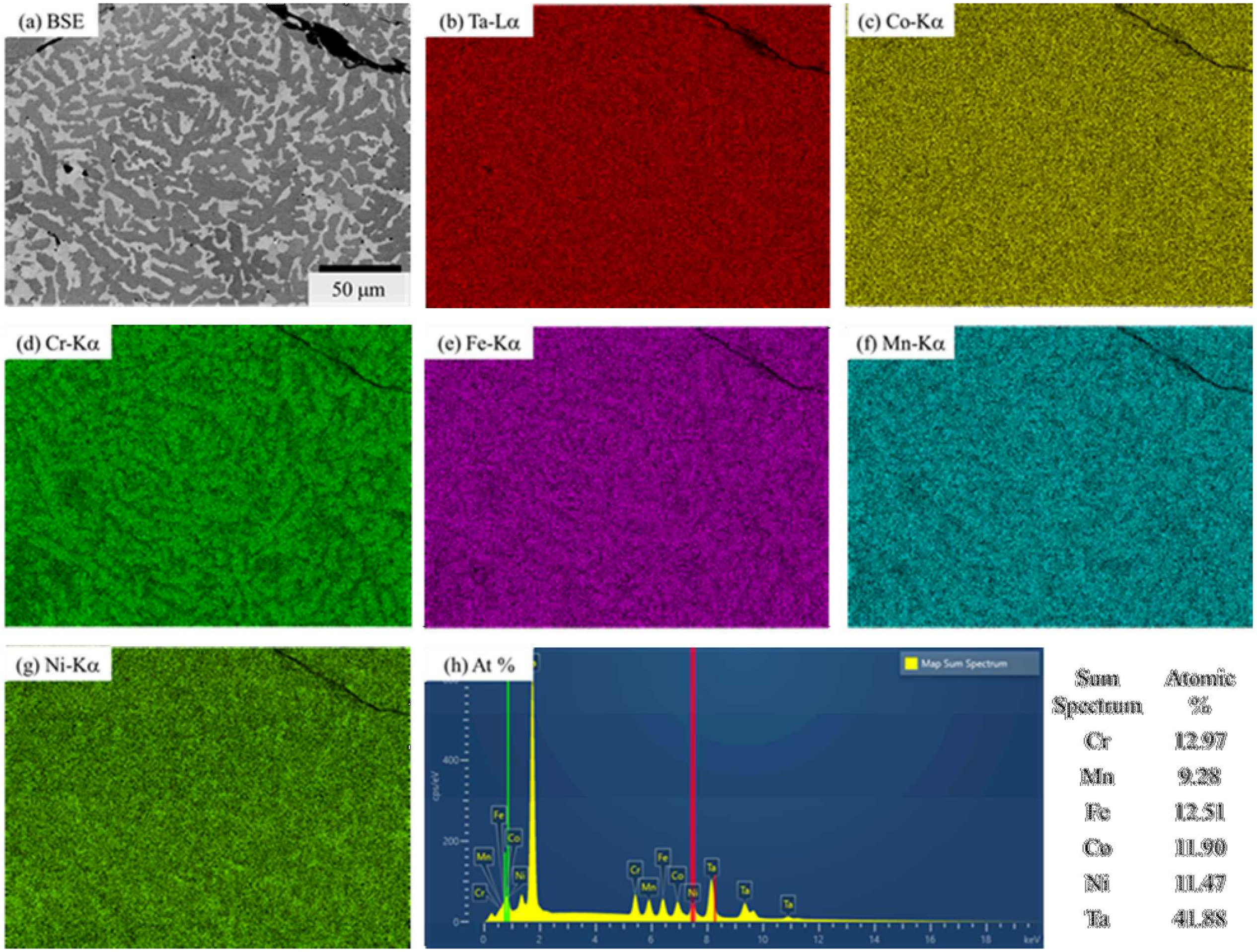
$Ta_xCoCrFeMnNi$



1: Single phase – Typical Cantor microstructure
2: Two phases present – transitions from fine particulate to lamellar
3: Three phases – Insufficiently fused Ta particles with intermetallic phase, fracture occurs
4: Single phase – Complete fusion of Ta with apparent single phase region
5: Reappearance of two-phase – dendritic/lamellar
6: Mix of coarse Ta-rich regions with fine two-phase lamellar microstructure

Ta$_{17}$CoCrFeMnNi$_{17}$





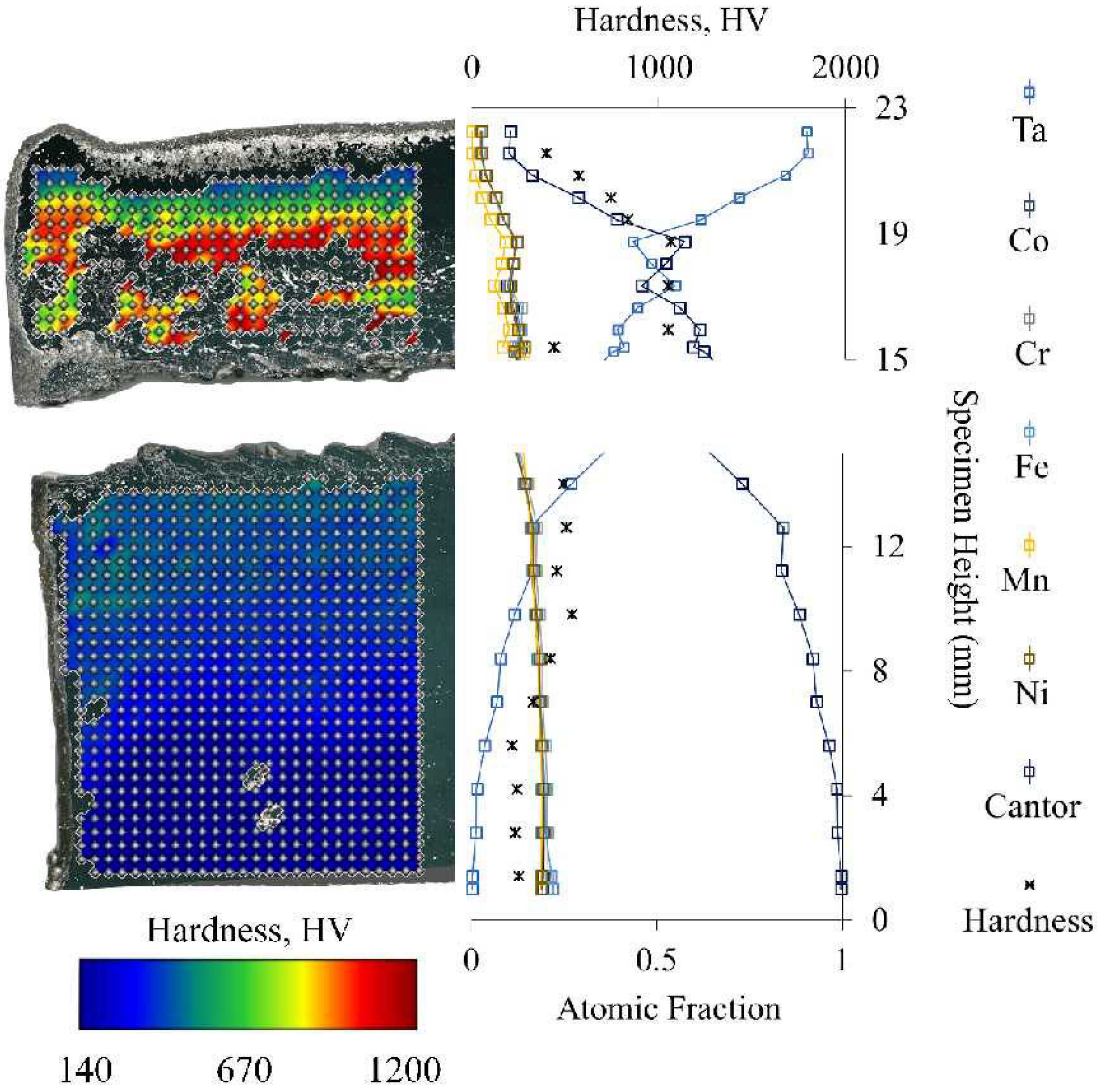
Sum Spectrum	Atomic %
Cr	12.97
Mn	9.28
Fe	12.51
Co	11.90
Ni	11.47
Ta	41.88

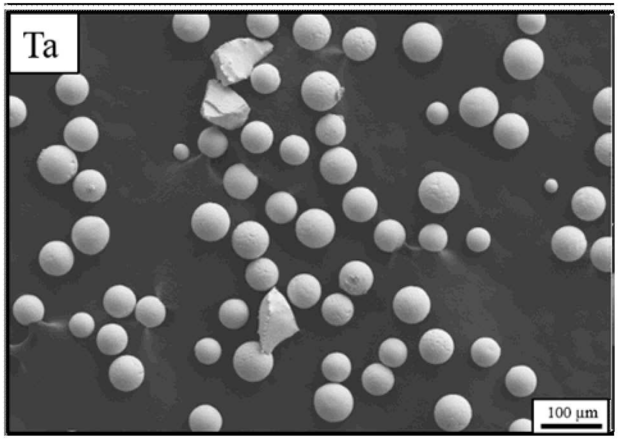
- Light Phase: Ta-Ni
- Dark Phase: Cr-Mn-Fe
- Even: Co

Ta segregated through most regions, solid solution not formed at equiatomic regime

Single phase appears to have been achieved in region directly after fracture

$Ta_xCoCrFeMnNi$ – Hardness Map

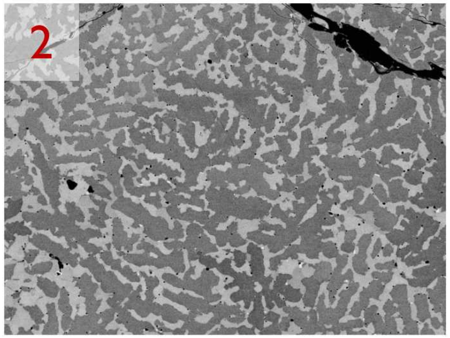


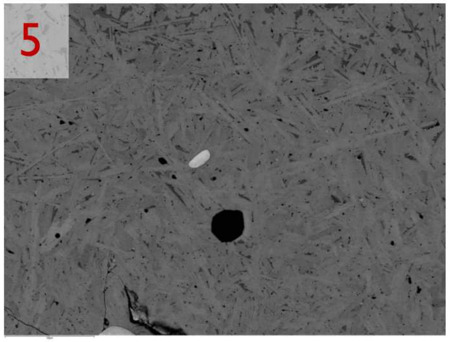


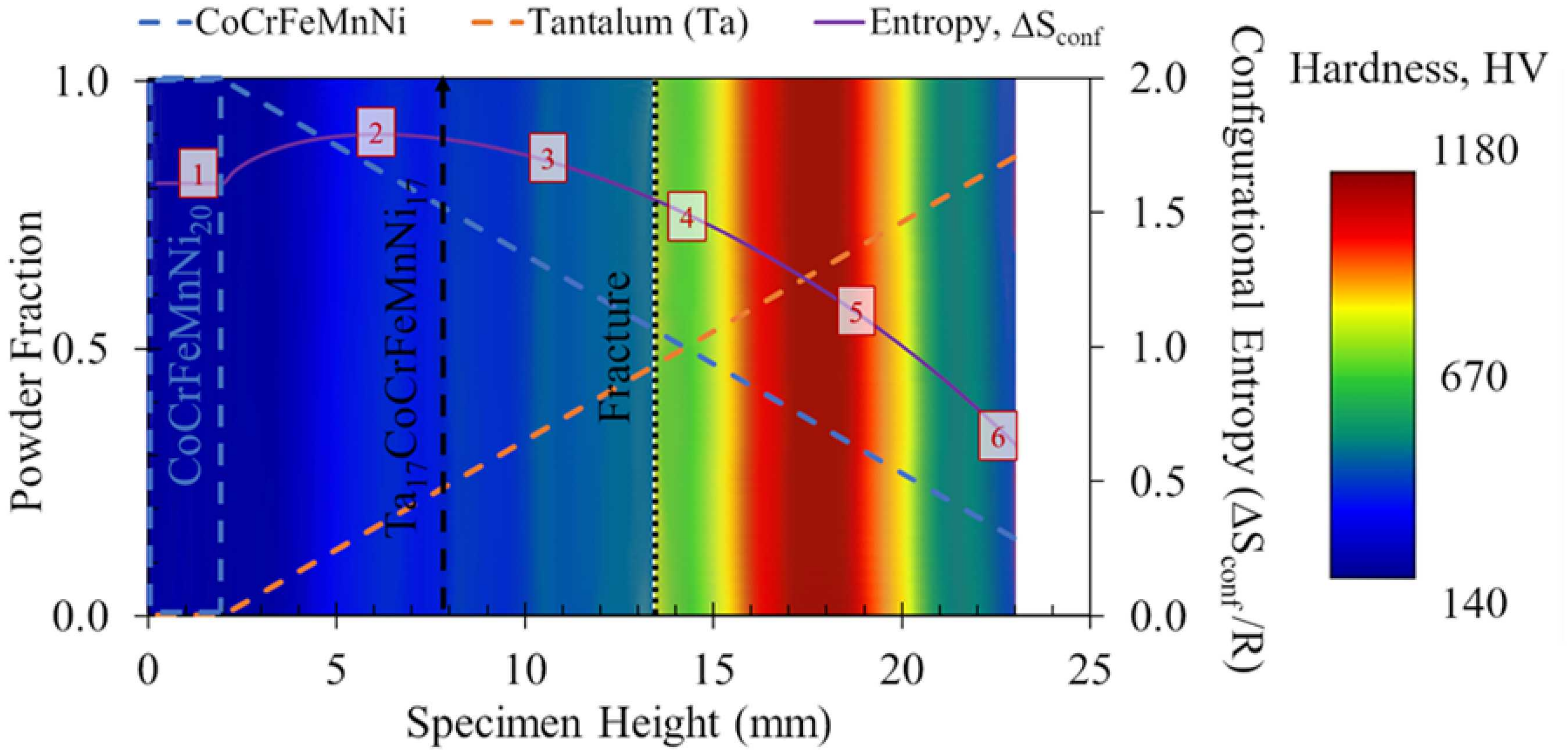
Powder Element	Avalanche Energy (mJ/kg)	Avalanche Angle (°)	Break Energy (mJ/kg)
Ta	7.69 (42.9)	42.9 (2.5)	24.18 (3.7)

- Ta-HEA did not reach pure Ta again related to flowability
- **Hardness increased to 1200 HV near 50|50 Ta-Cantor region but was very brittle in this regime**

$Ta_xCoCrFeMnNi$

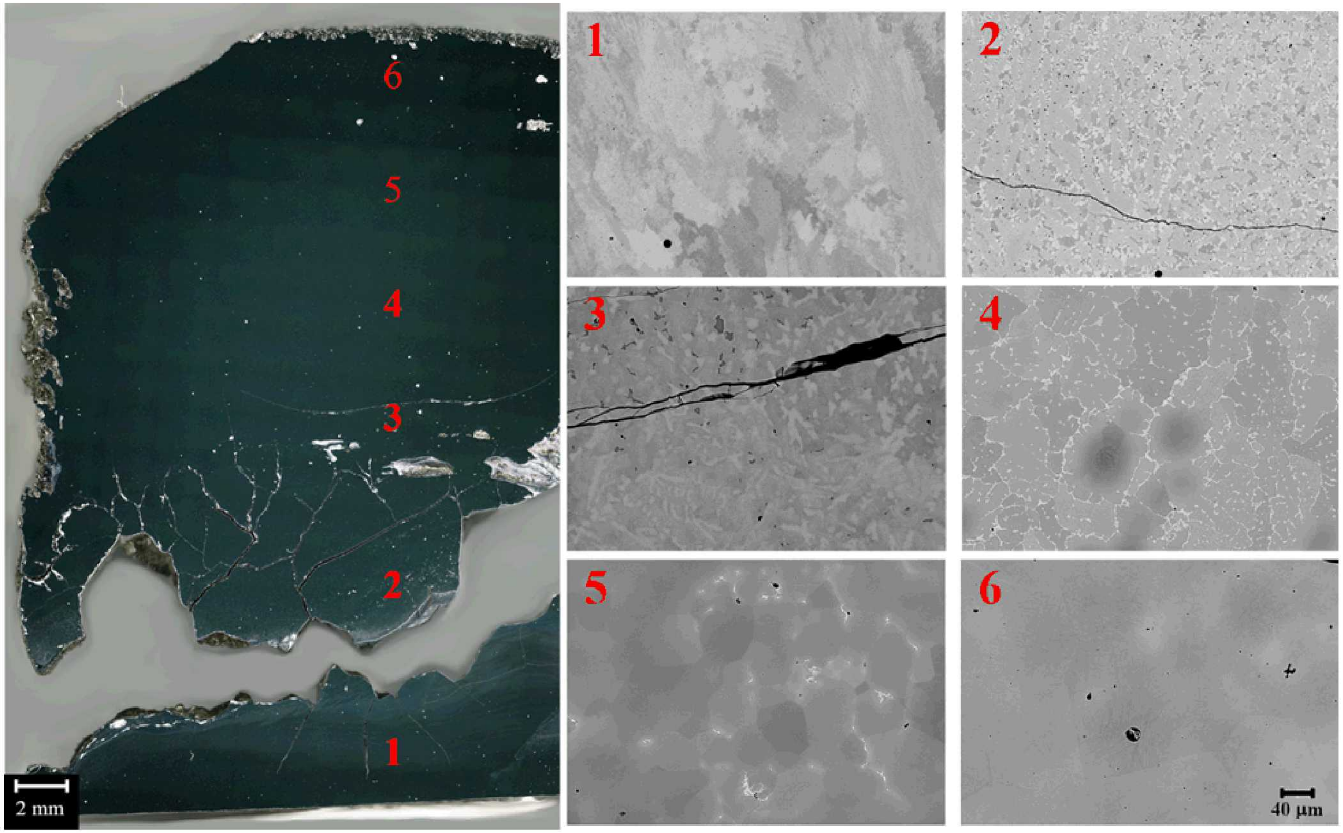






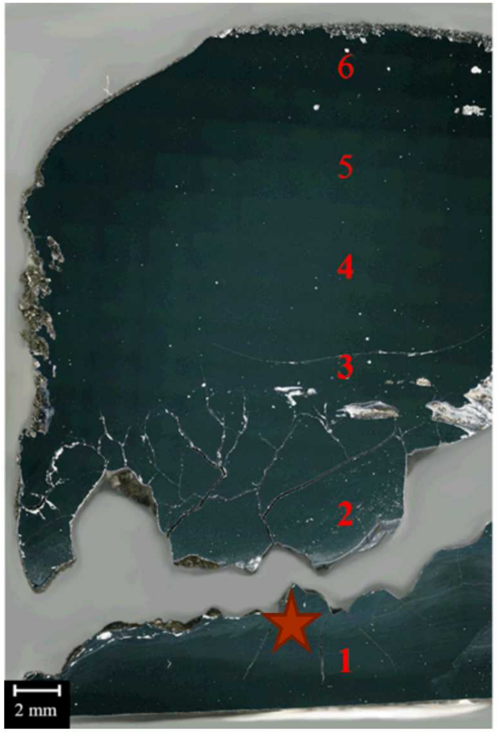
- ➢ Intermetallic phases formed near the equiatomic regime
- ➢ Maximum hardness occurred at the 50|50 Ta-Cantor region at relatively low configuration entropy

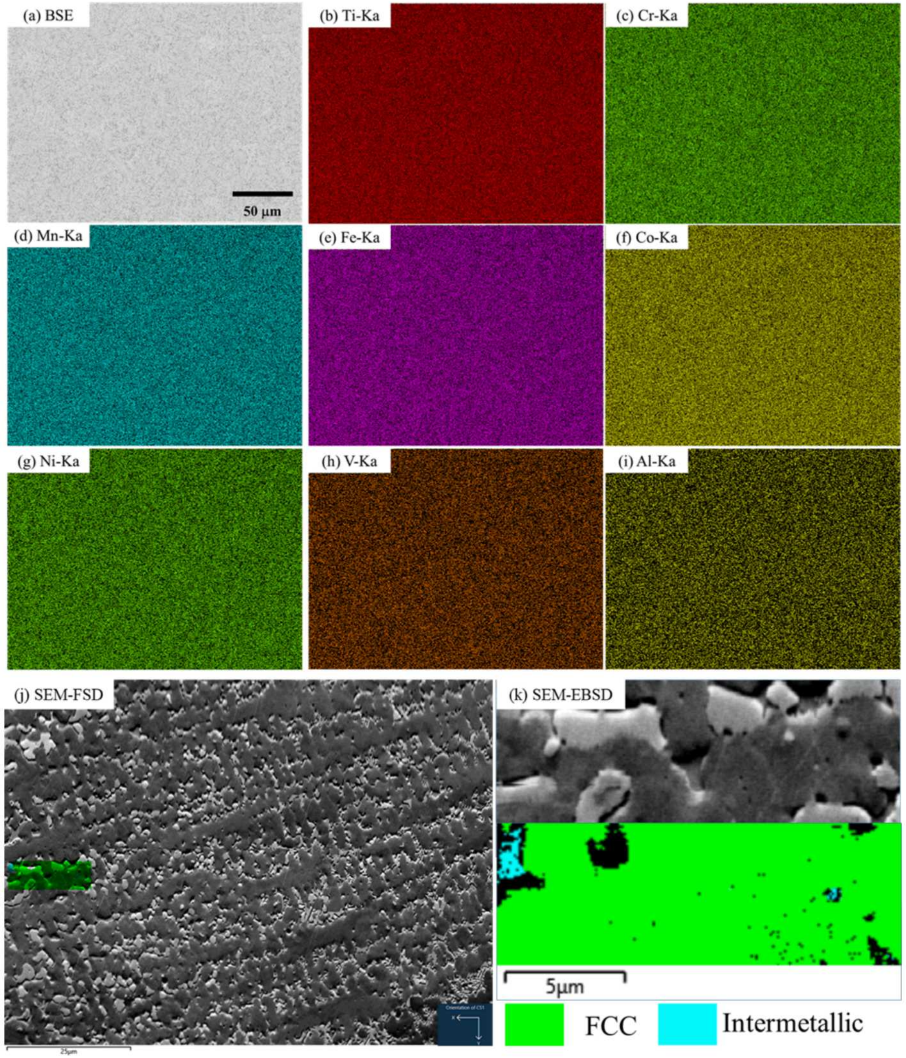
Ti64xCoCrFeMnNi



1: Single phase – Typical Cantor microstructure
2: Three phases present – Cracking begins to occur (refined multiphase structure)
3: Two-phases – Lamellar structure appears
4: Two phases – Large grains with intergranular second phase
5: Two phases – Intergranular second phase diminishes to mostly large equiaxed grains
6: Single phase – Typical α/α' AM microstructure

Ta$_{17}$CoCrFeMnNi$_{17}$

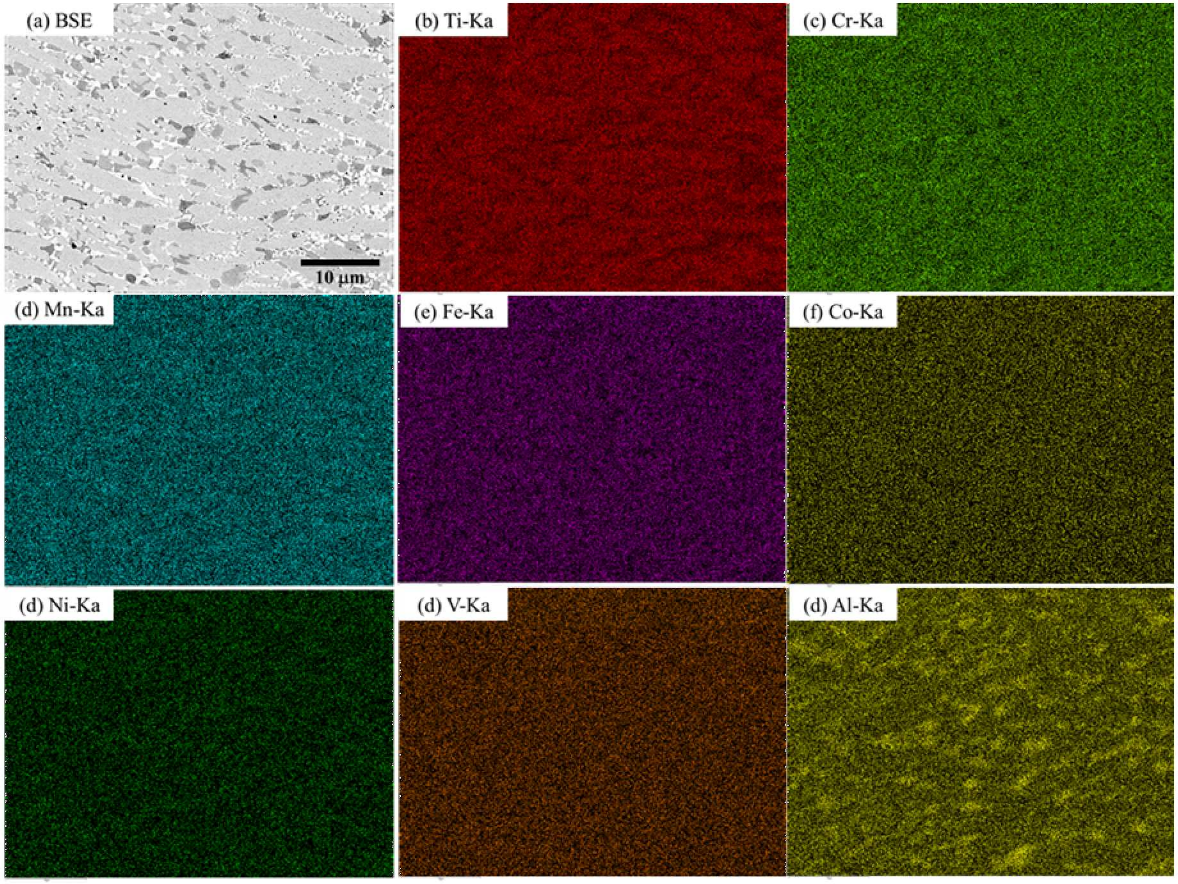




Solid solution appears to form at equiatomic region

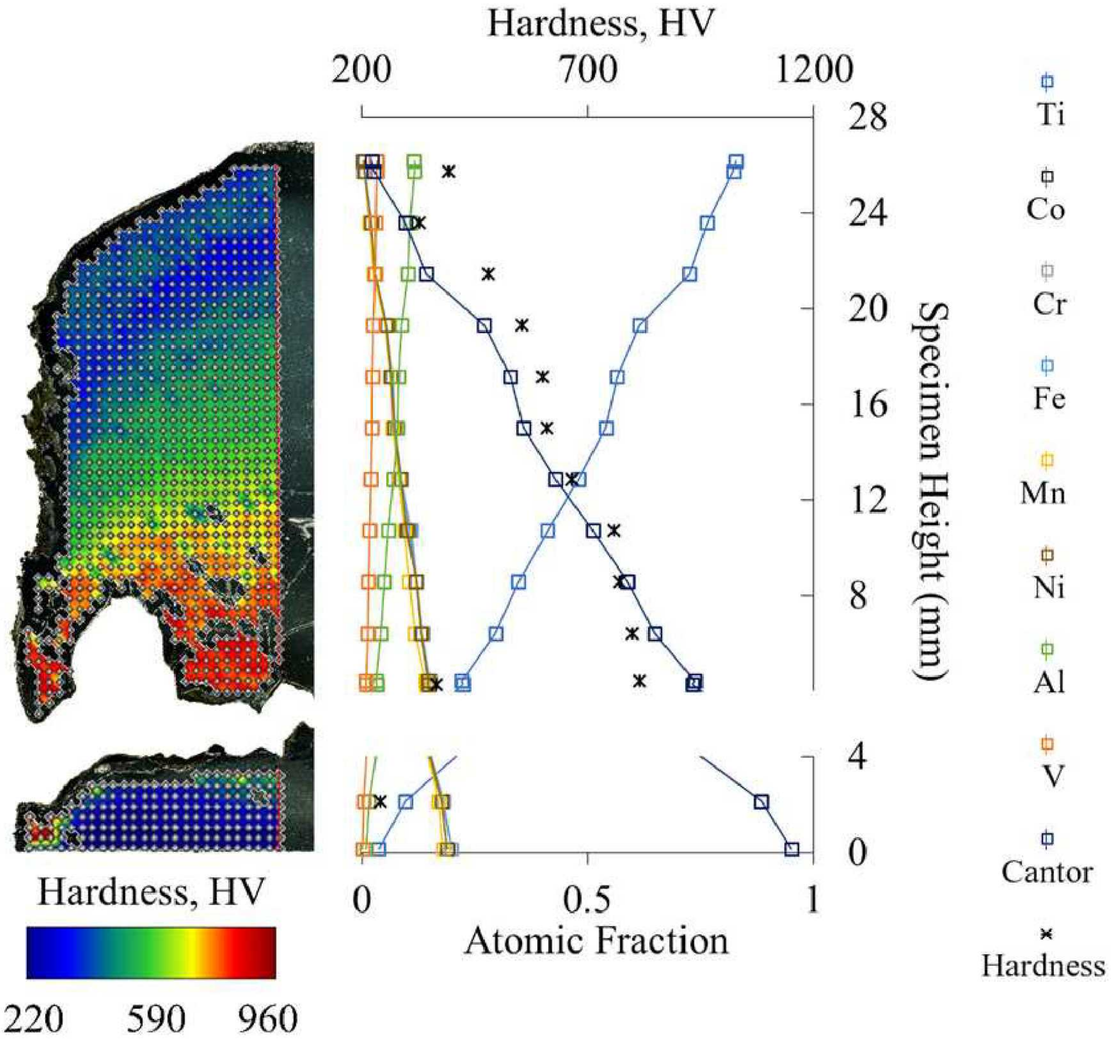
Higher resolution EBSD reveals interdendritic intermetallic phase is present

Ti64$_{22}$CoCrFeMnNi$_{15}$



- Bright Phase: Cr-Mn
- Light Phase: Ti64-Cr-Mn-Fe
- Dark Phase: Ni-Al
- Even: Co-V

Ti64$_x$CoCrFeMnNi

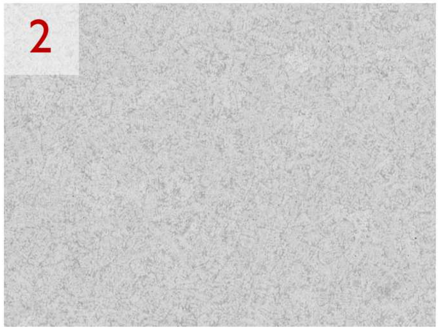


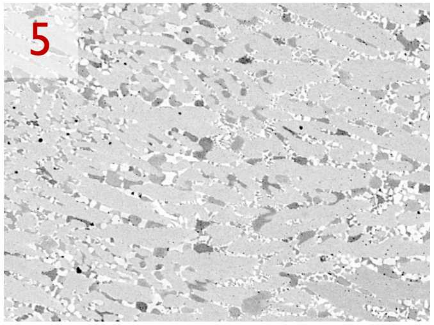
Ti64 powder image coming soon…

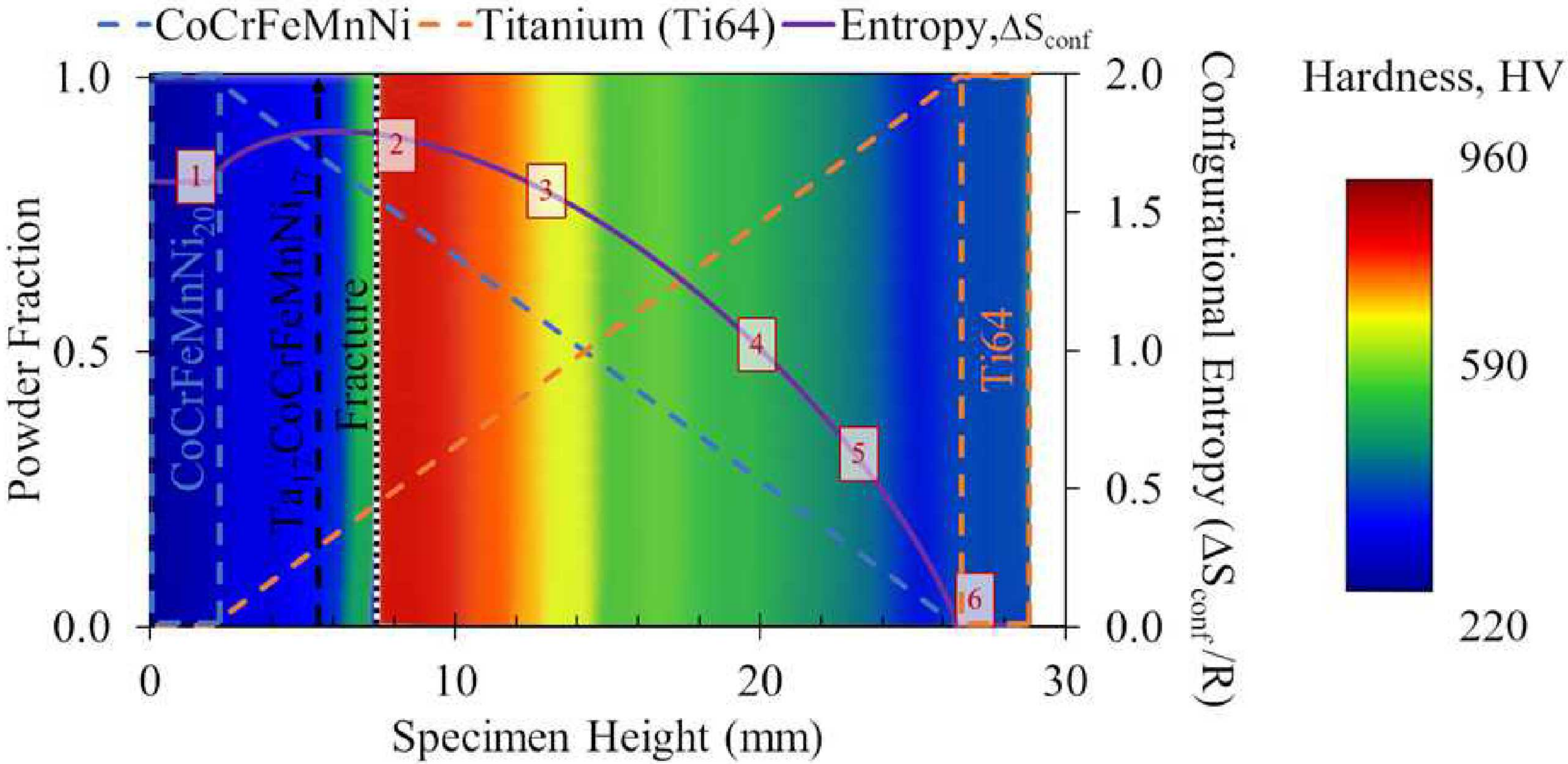
Powder Element	Avalanche Energy (mJ/kg)	Avalanche Angle (°)	Break Energy (mJ/kg)
Ti-6Al-4V	6.81 (2.1)	26.6 (0.9)	13.93 (1.5)

- Ti64-HEA did reach purity
- **Hardness reached up to 960 HV at near equiatomic regime**

$Ti64_xCoCrFeMnNi$







- ➢ Intermetallic phases were not observed at any composition
- ➢ Maximum hardness occurred near the equiatomic region at the higher end of the configurational entropy

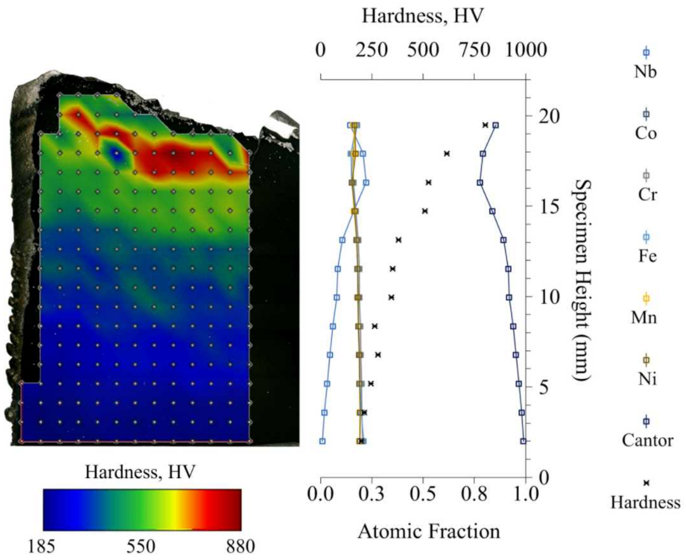
You have crazy chemistry…. so what??

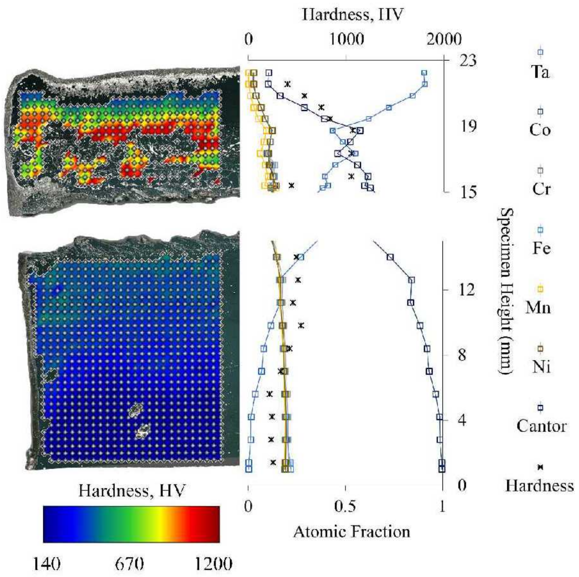
What did we do?

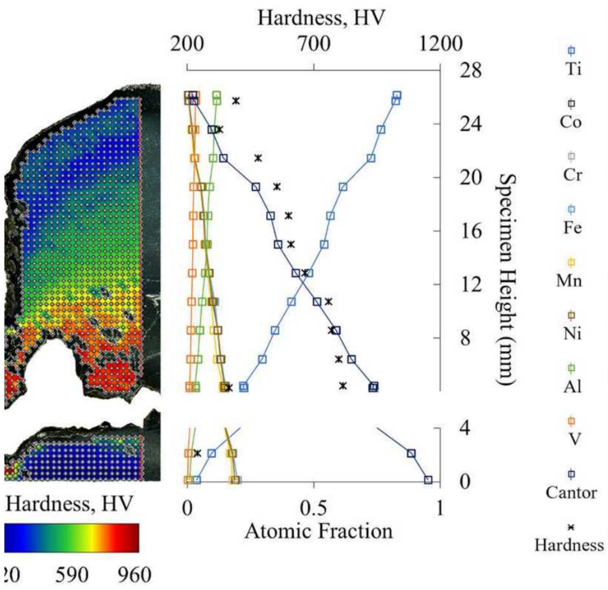
Showed that AM can provide opportunity for site-specific property control

Achieve unusual mechanical property combinations that cannot be achieved with base metals alone

Screen through large portions of phase space within single specimens







Summary & Conclusions

- Rapid high-throughput microstructural/mechanical evaluation through the large composition range was achieved for the RfxCoCrFeMnNi alloys
- Regions that promote high strengths were identified and the accompanying microstructure analyzed
- The high-throughput analysis indicate that both microstructure and configurational entropy contribute to the regions with exceptionally high strengths
- Highly brittle regions incapable of fabrication utilizing the process conditions investigated were identified and correlated to presence of intermetallic phases

Thank you for your attention

Questions?