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Cold Sprayed HEA Coatings

Microstructure and Tribological Behaviour of Cold Spray $AlCoCrFeNi_{2.1}$ Eutectic High-Entropy Alloy

Cristian V. Cojocaru, Maniya Aghasibeig, Eric Irissou

NRC AST, Boucherville, Québec, Canada

32nd Cold Spray Club, June 2025, Gallipoli, Italy

MATERIALS AND PROCESSES

Areas of expertise

- Polymers and bioproducts
- Advanced polymer composites
- Simulation and numerical modeling
- Powder forming
- Materials for energy technologies
- Thermal spray

Objectives

- **Develop novel materials & processes**
- **Provide expert services to Canadian industry across many sectors: e.g. automotive, aerospace, defense, medical devices, energy**
- **Support innovation and competitiveness**

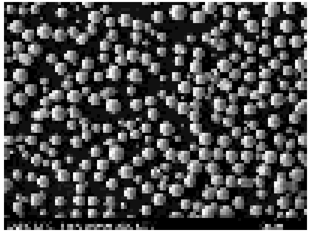
NRC-Thermal Spray Facility and Equipment

- 5 dedicated robotic spray booths
- 21 commercial spray systems (Plasma, Wire-arc, cold spray, HVOF, Flame)
- Comprehensive process diagnostics, monitoring and numerical simulation capabilities (Industry 4.0)
- Comprehensive thermal spray coating testing and characterization capabilities
- Thermal cycle laser rig and thermal cycle water vapor rig for thermal and environmental barrier coatings

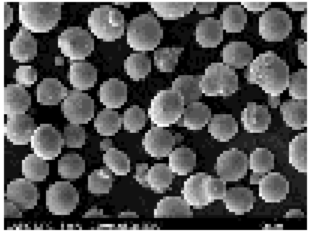
NRC R&D on Cold Spray of MCrAlYs

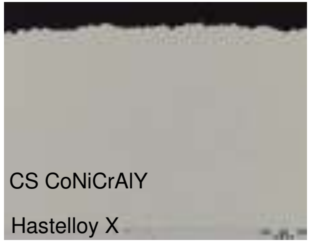
- Feedstock: MCrAlX (M=Co, Ni and X= Y, HfSi)
- High-pressure CS: N_2 used as propelling gas
- Effect of powder granulometry, gas temperature / pressure / standoff distance (SOD) / gun traverse speed
- Very well adhered and dense cold-sprayed coatings
- Roughness: 6 to 12um, tunable with powder granulometry
- Porosity: 1 to 2.5% depending on feedstock PSD
- Bond strength: > 70 ± 5 MPa

‘Fine’: -22/ +5 µm



‘Coarse’: -45/+20 µm





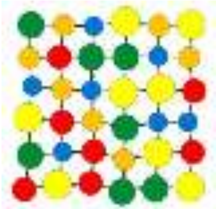
Emerging materials: High Entropy Alloys (HEA)

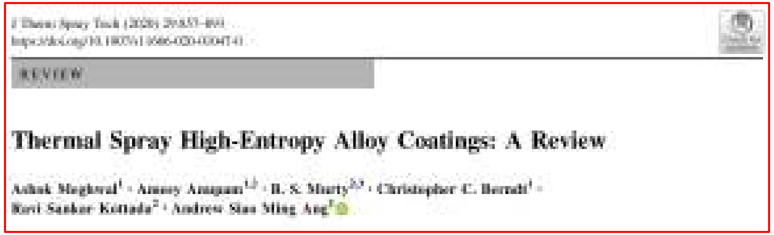
HEAs: solid solution alloys of five or more elements in equi- or near-equi-atomic ratios *(Yeh and Cantor 2004)*

*More broadly: alloys containing **n** major elements, where **n** is between **5** and **13**, and the molar ratio of each element is from **5** to **35 at%.***

Reasons for HEA special properties

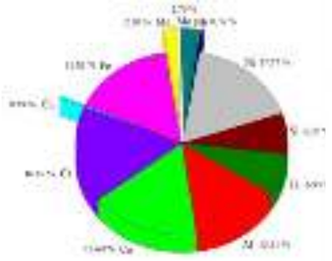
- High mixing entropy
- Sluggish diffusion
- Lattice distortion
- Cocktail effect



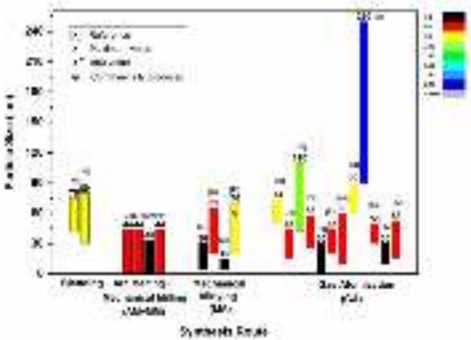

REVIEW

Thermal Spray High-Entropy Alloy Coatings: A Review

Ashok Meghwal · Ameey Anupam · B. S. Murty · Christopher C. Berndt · Ravi Sankar Kottada · Andrew Siao Ming Ang



Elements occurrence in HEA used as a feedstock for different TS processes



Synthesis routes reported to construct HEA feedstocks for TS:
(1) blending, (2) arc melting followed by mechanical milling, (3) mechanical alloying, and (4) gas atomization.

J Therm Spray Tech (2022) 31:1129–1142
https://doi.org/10.1007/s11666-022-01361-9

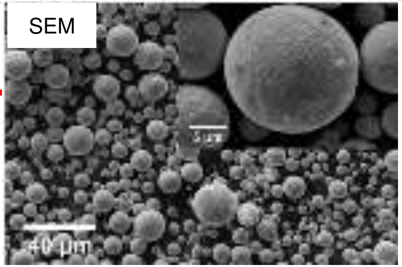
PEER REVIEWED

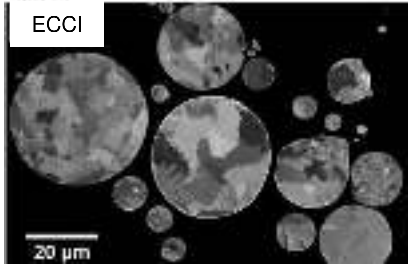
Cold Spray and Laser-Assisted Cold Spray of CrMnCoFeNi High Entropy Alloy Using Nitrogen as the Propelling Gas

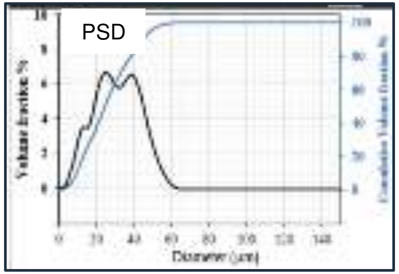
Roghayeh Nikbakht[1] · Cristian V. Cojocaru[2] · Maniya Aghasibeig[2] · Éric Irissou[2] · Taek-Soo Kim[3] · Hyoung Seop Kim[4] · Bertrand Jodoin[1]

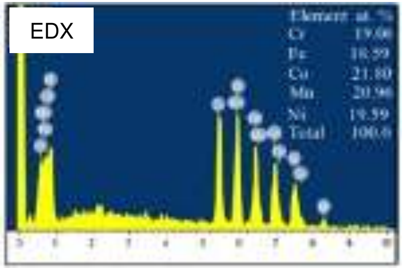
CrMnCoFeNi: Cantor alloy

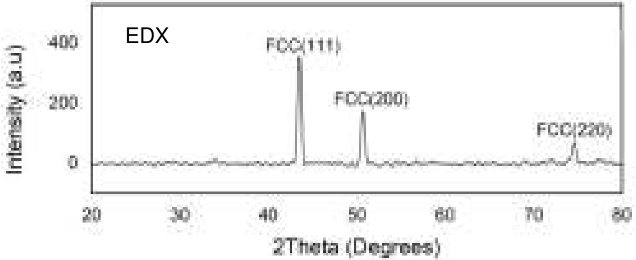
- single-phase solid solution
- powder: spherical morphology
- dendritic grain distribution
- PSD: +9.5/-45um,D50=25um
- FCC crystal structure











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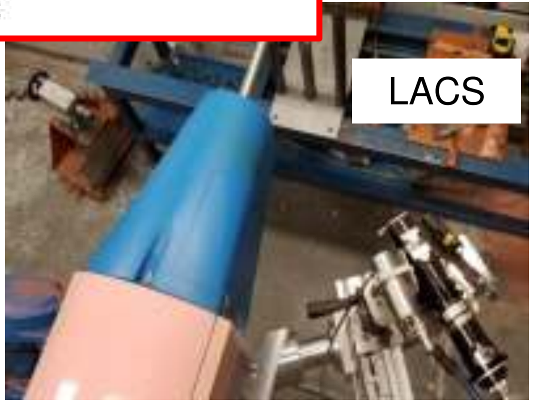
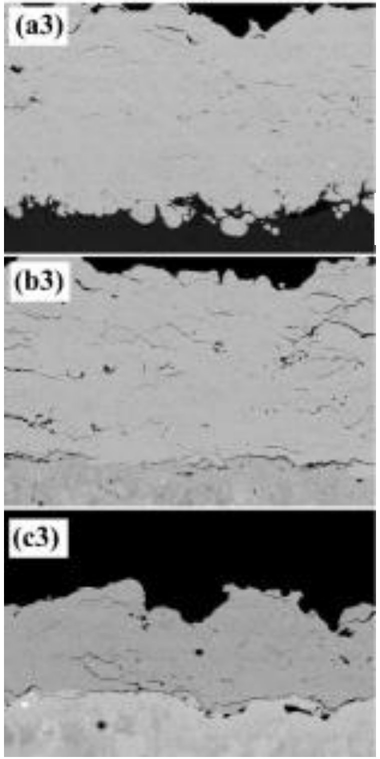


Substrates	Al6061	Mild steel	Hastelloy X
R_a (µm)	4.68±0.16	3.70±0.19	2.72±0.22
Hardness (HV) at 300gf	104±1.9	204±2.36	236±0.85



HEA CrMnCoFeNi coatings on different substrates

Al6061

steel

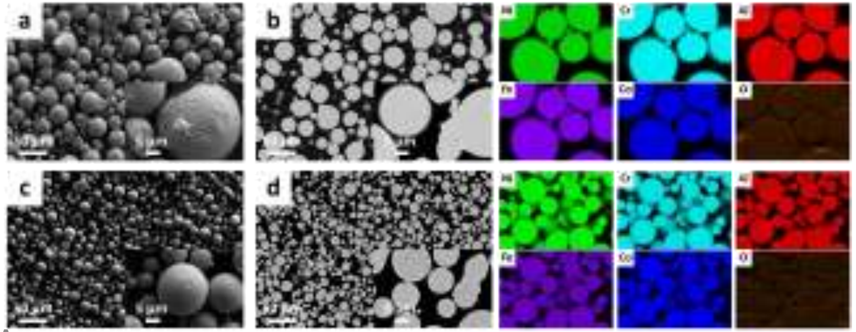
Hastalloy X

HEAs vs. MCrAlYs
HEA Chemistries Explored

Alloy	Co	Ni	Cr	Al	Y	Fe
CoNiCrAlY (wt.%)	38	32	21	8.5	0.5	-
NiCoCrAlY (wt.%)	21-22	46.5-49.5	18	11-13	0.5	-
AlCoCrFeNi (at.%)	20	20	20	20	-	20
AlCoCrFeNi (wt.%)	23.5	23	20.5	10.5-11		22
$AlCoCrFeNi_{2.1}$ (at.%)	17	35	16	16		16
$AlCoCrFeNi_{2.1}$ (wt.%)	19	39.5	16	8.5		17

(a) and (b) 3D and cross-section SEM of **AlCoCrFeNi equiatomic** powder (+15/-53um).

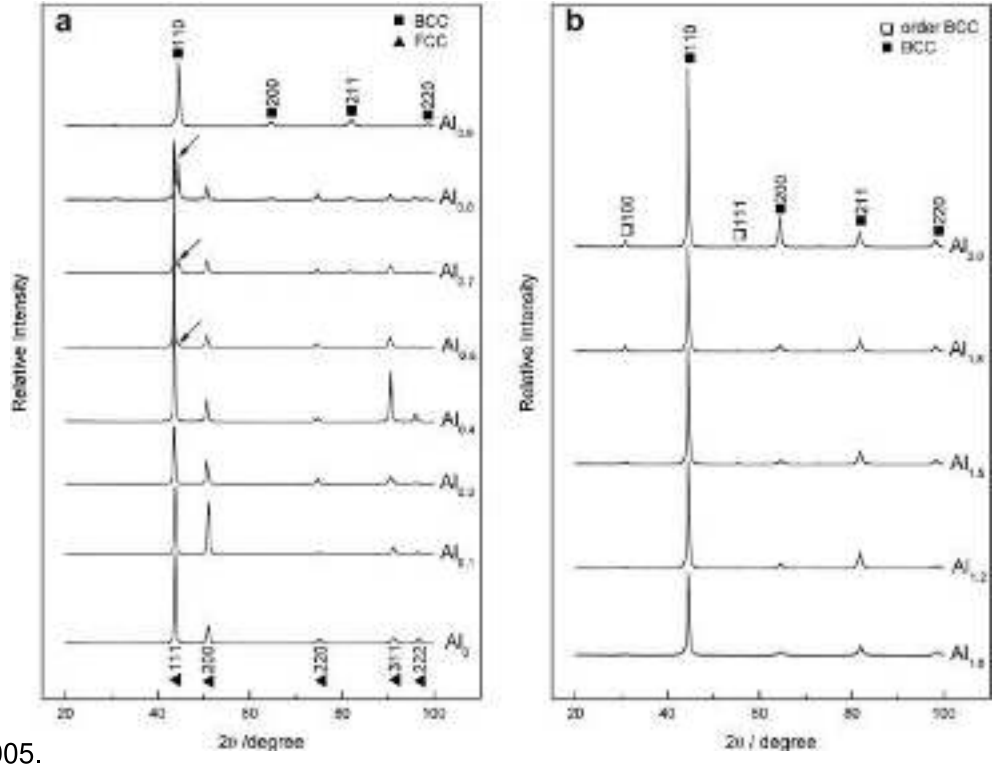
(c) and (d) 3D and cross-section SEM of **$AlCoCrFeNi_{2.1}$** eutectic powder (+5/-25um).



EDX mapping of both equiatomic and eutectic HEA compositions

The AlCoCrFeNi$_{2.1}$ System

- Al is the BCC stabilizer; addition of Al promotes the formation of NiAl BCC/B2
- Ni is the FCC stabilizer, with ~2.1 mole ratio of Ni, we achieve the eutectic composition



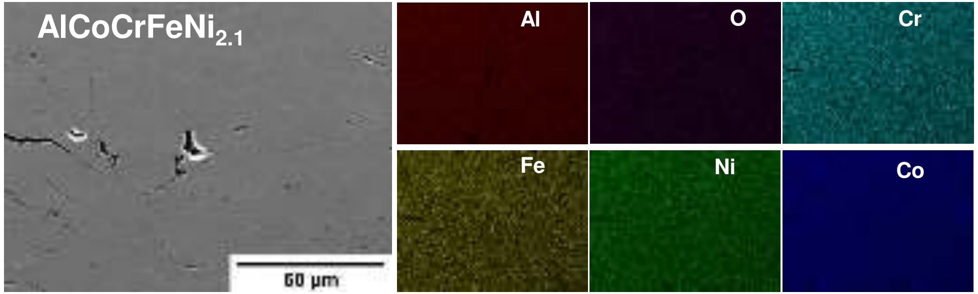
Increasing Al content

Wang et al. (2012) Intermetallics 44–51. https://doi.org/10.1016/J.INTERMET.2012.03.005.


Surface & Coatings Technology

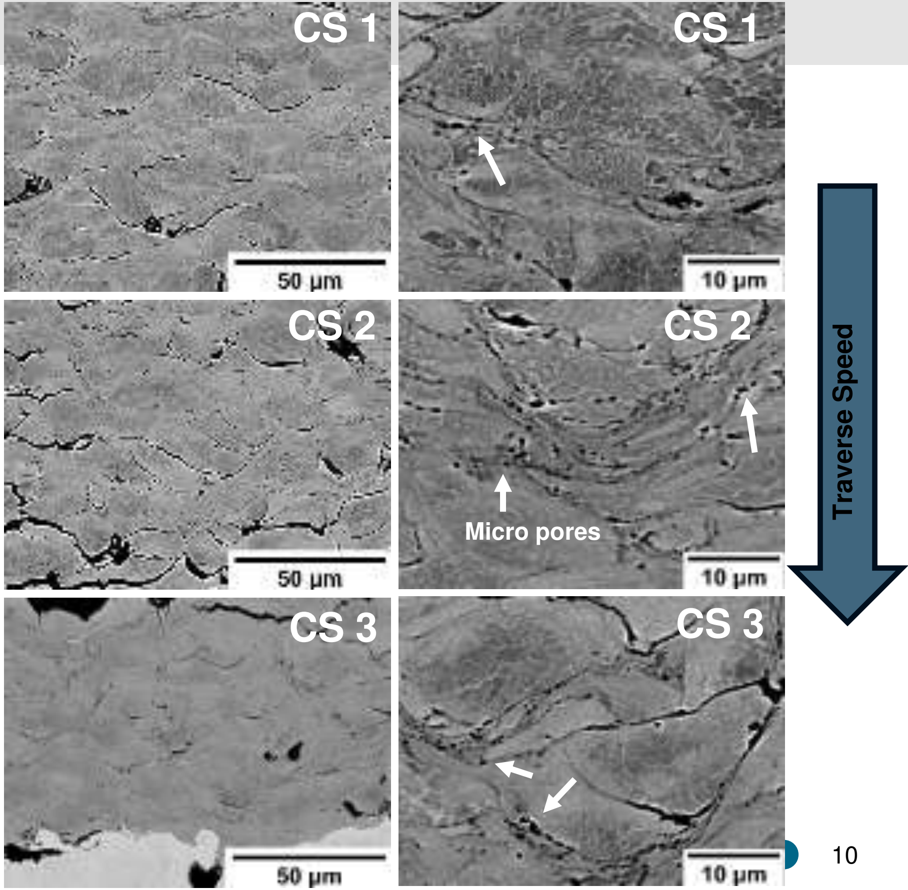
Deposition, microstructure and hardness of $AlCoCrFeNi_{2.1}$ eutectic high entropy alloy coatings by cold spray, HVOF, and plasma spray

Jingjie Wei[a], Cristian Cojocaru[b], Maniya Aghasibeig[b], Chenwei Shao[a], Zehua Li[a], Jiahui Zhang[a], Eric Irissou[b], Yu Zou[a,*]



EDS cross-section mapping

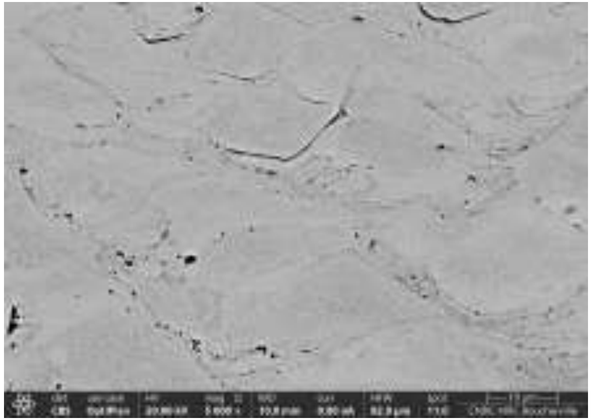
SEM BSE of coating cross-section



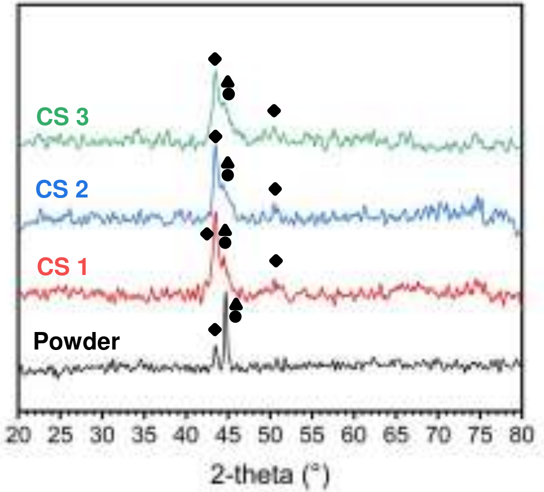
- No signs of elemental segregation or microstructure changes
- Higher traverse speed increases micropores at particle interfaces, potentially leading to weaker bonding

$AlCoCrFeNi_{2.1}$ Coatings: Phase Transformations

Cold Spray Giken PCs100

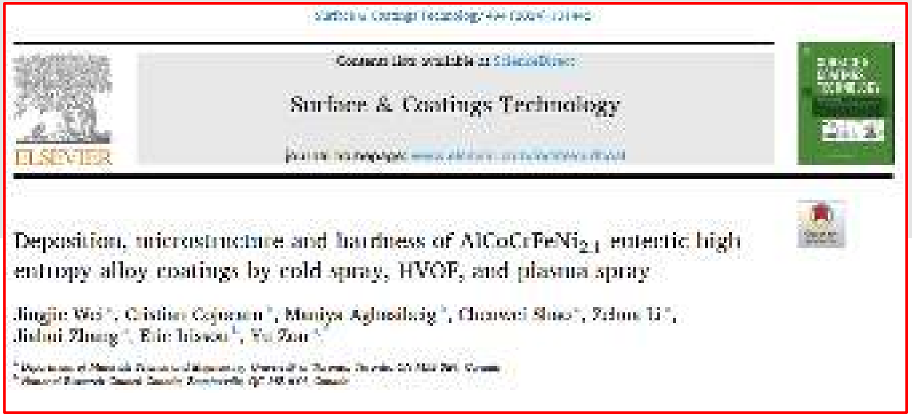


Pgas:7.5MPa; 950°C; SOD 50mm; vgun;200mm/s



- Cold spray (high strain/strain rate) favours preservation of FCC CoCrFeNi rich phase
- Peak broadening + low signal-to-noise ratio indicate high residual strain and dislocation density

Cold Spray: Preservation of Microstructure


Contents lists available at ScienceDirect

Surface & Coatings Technology

ELSEVIER

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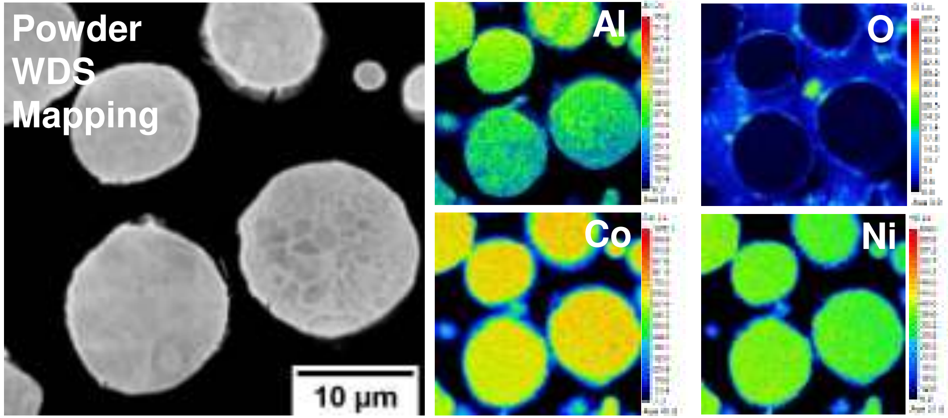
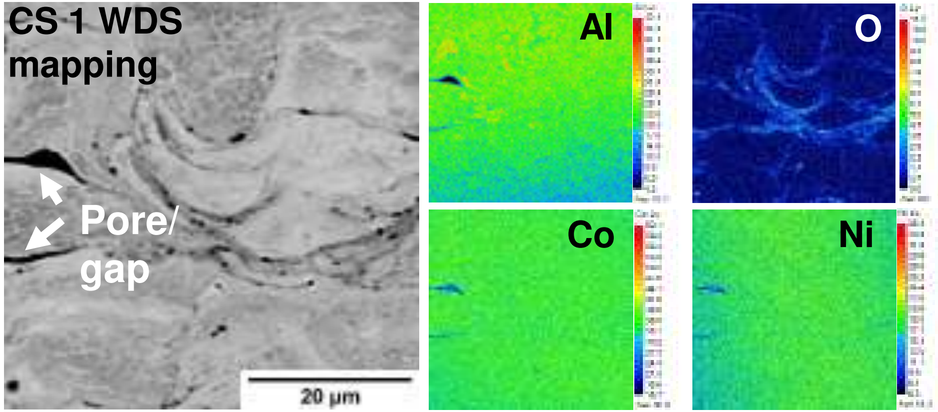
WDS: Wavelength Dispersive Spectroscopy

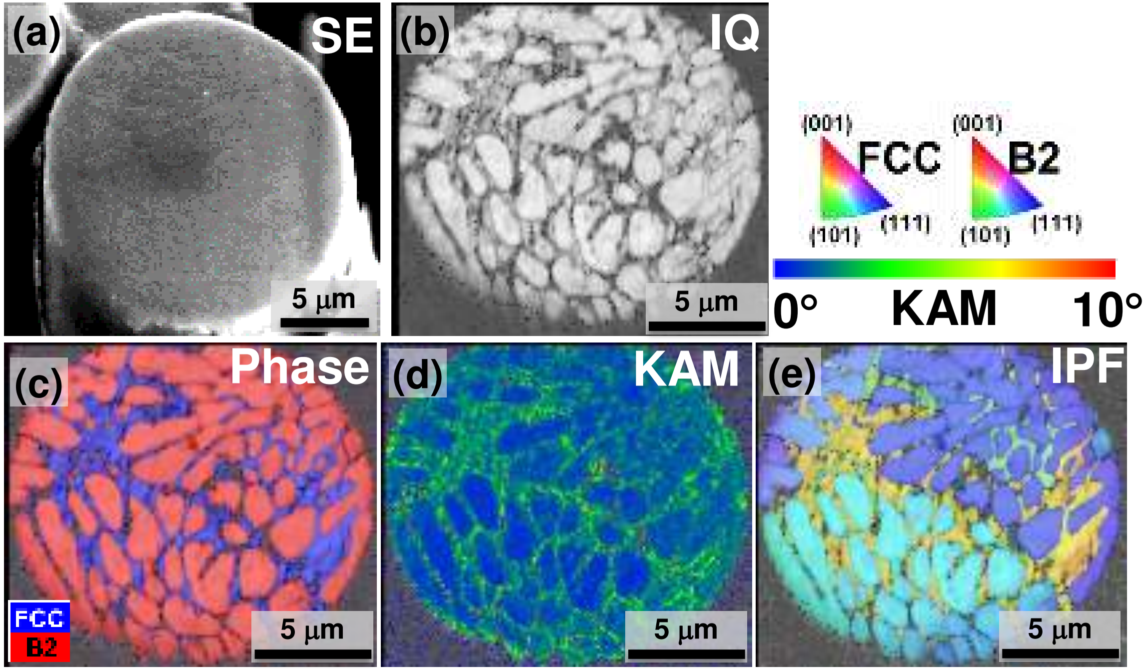




- Comparison with feedstock powder indicate successful preservation of microstructure
- Thin layer of oxide at particle interfaces
- No signs of significant elemental segregation/diffusion in lamellar microstructure

AlCoCrFeNi2.1 Eutectic High Entropy Alloy Powder Features via EBSD Analysis

- Mostly spherical particles with a size range of ~5 - 30 μm.
- FCC + B2 dual-phase powders with eutectic B2 embedded in FCC matrix.
- Average volume fraction of phases:
  - FCC = 35%
  - B2 = 65%
- Each powder exhibits similar orientation profile for B2 phases, whereas FCC orientation changes.

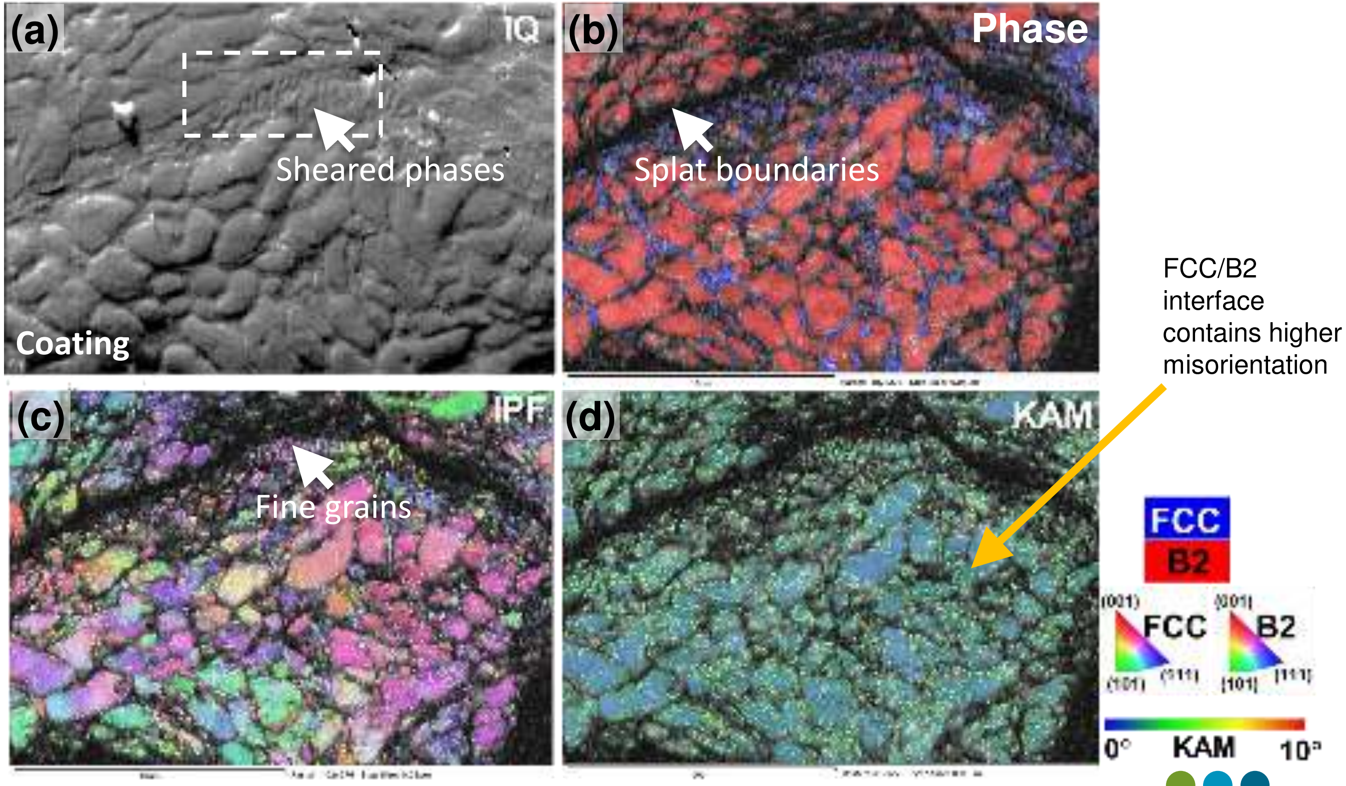


Collaboration with Prof. Yu Zou, Dept. of Mat. Science, Univ. of Toronto

Dash *et al.*, 2025 [Manuscript under preparation].

Deformation features of the cold sprayed EHEA coating via EBSD Analysis

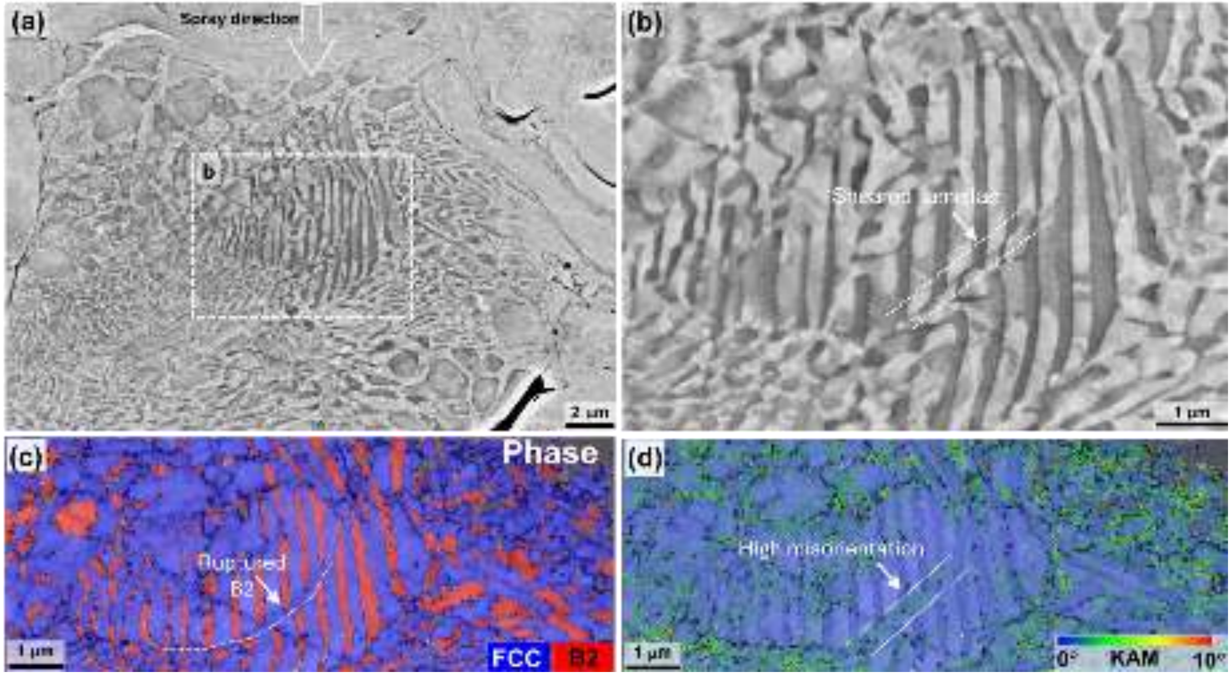
- Closer to the particle boundary higher FCC content is observed.
- FCC inter-dendritic regions are dynamically recrystallized.
- B2 grains prevail with less deformation and not much lattice rotations
- Further, HR-TKD and TEM analysis will be performed to understand inter-particle boundary deformation mechanisms.



Dash *et al.*, 2025 [Manuscript under preparation].

Deformation features of the cold sprayed EHEA coating

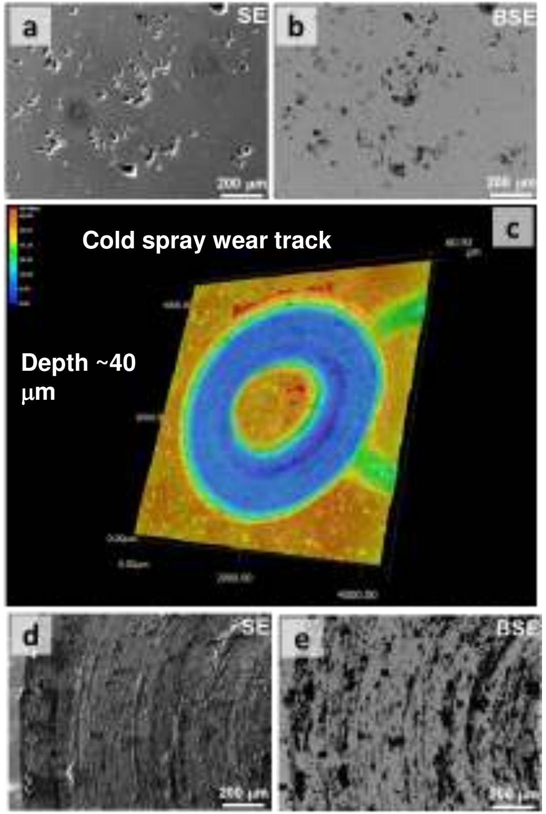
- To study why the lamellar eutectic structure is prone to cracking, internal eutectic structure are analyzed in the coating.
- Cracking initiates from shearing of the thin FCC and B2 lamellae.
- Network FCC and dendritic B2 have higher volume to accommodate sever plastic deformation.
- Lamellar FCC and B2 show shear at ballistic (~10^9 s^{-1}) impact strain rates and tend fracture early.



- More misorientation can be observed within the sheared region owing to severe strain localization.

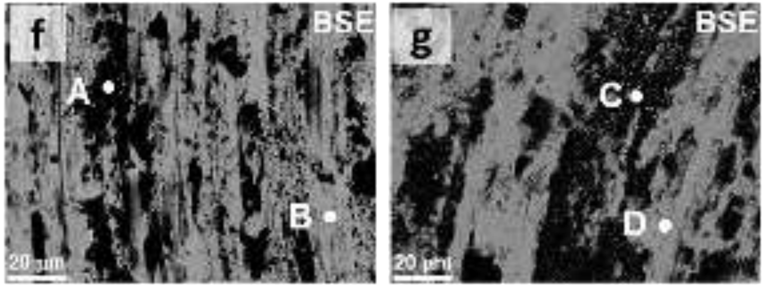
Dash *et al.*, 2025 [Manuscript under preparation].

Cold Spray $AlCoCrFeNi_{2.1}$
Wear behavior



Al_2O_3 balls (1/4 in. in diam.) under a load of 10 N for 30 min.at 100 RPM and with 1 mm track radius.

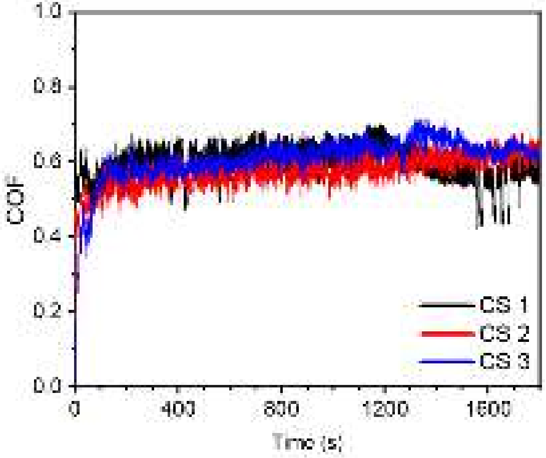
- Initial (polished) surface before wear tests shows pores; this could increase the CoF and provide higher resistance to wear.
- Tracks show debris accumulation → the cause of peaks in CoF plot.
- Dark oxide mostly (Fe,Ni)O patches in BSE limit further wear.



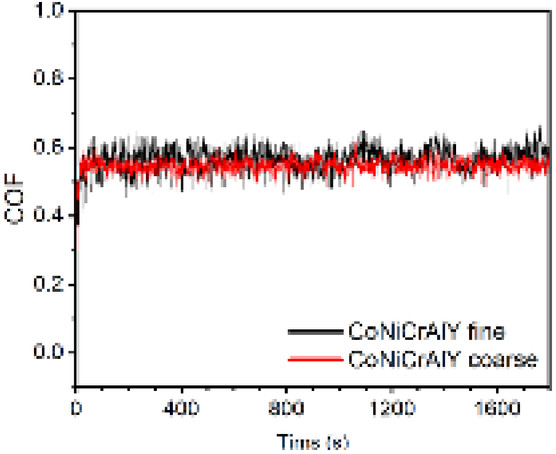
Points	Al (wt.%)	Co (wt.%)	Cr (wt.%)	Fe (wt.%)	Ni (wt.%)	O (wt.%)
A	10.6	13.9	18.7	23.5	19.5	13.8
B	9.1	18.2	17.2	17.3	35.9	2.4
C	18.2	10.9	9.5	15.1	21.7	24.5
D	13.1	12.5	13.5	17.7	42.9	0.3

Wear Performance: Cold Spray EHEA vs. CoNiCrAlY

Cold Spray
$AlCoCrFeNi_{2.1}$



Cold Spray
CoNiCrAlY



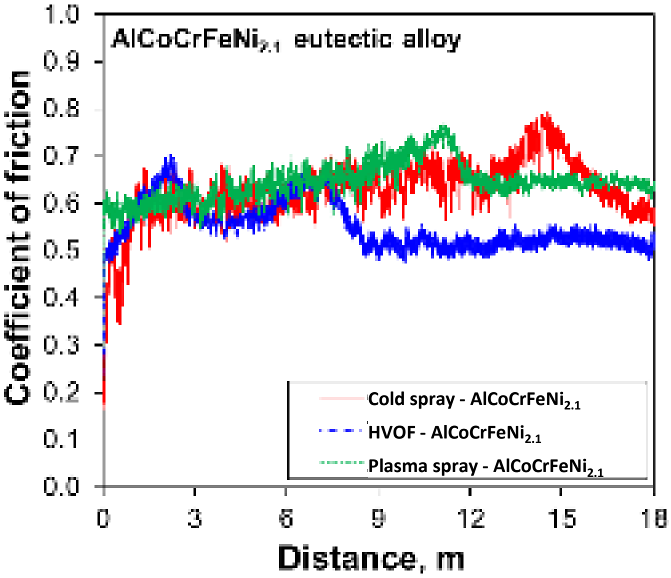
material	Pgas [MPa]	Tgas [°C]	SOD [mm]	Vgun [mm/s]
CoNiCrAlY fine	7.5	950	50	100
CoNiCrAlY coarse	7.5	950	50	100

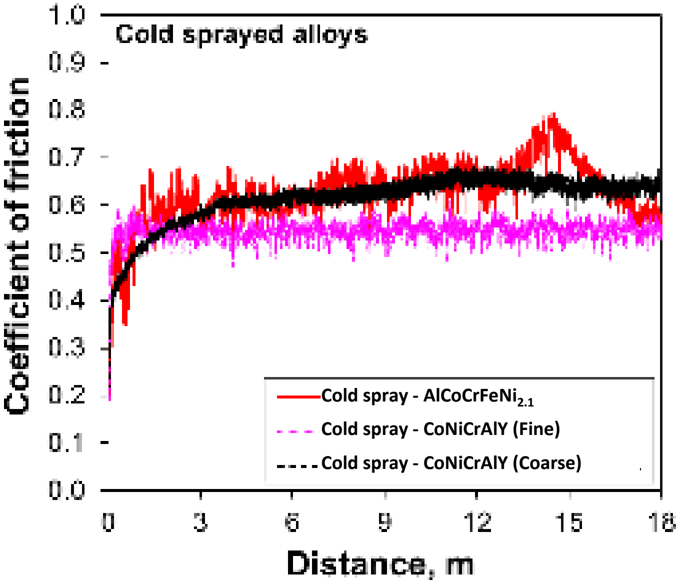
Pin-on-disk wear test:
Room Temperature
10N, 1mm radius, 100 RPM, 30 mins

- Cold sprayed EHEA and CoNiCrAlY coatings show similar COF
- Analysis of wear rates is necessary to draw conclusions

Coefficient of friction

- Cold and plasma sprayed EHEA and CoNiCrAlY coatings show similar CoF.
- HVOF coating show slightly lower CoF.

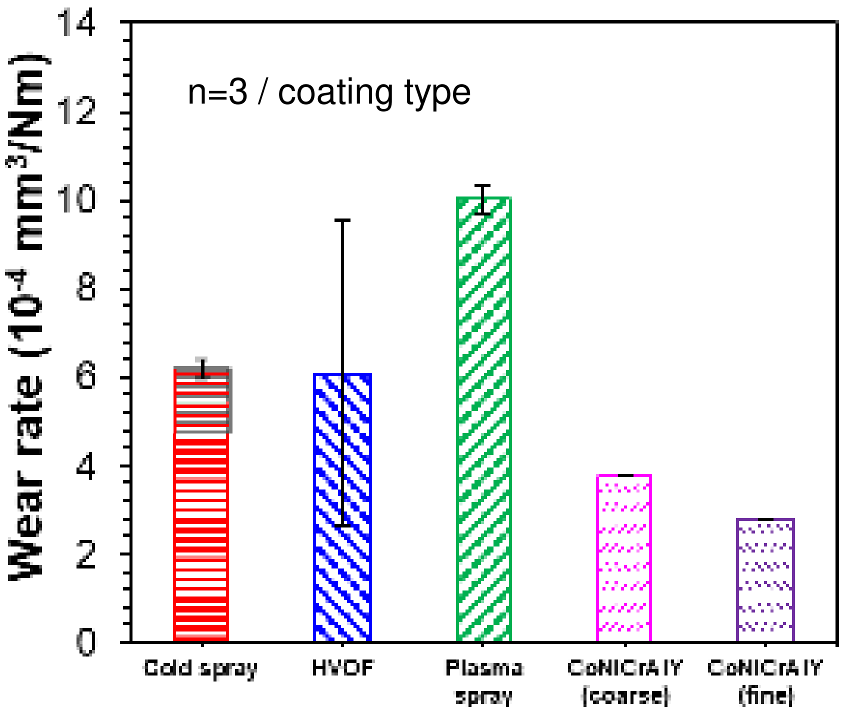




- All EHEA coatings show transition in the CoF at different stages:
  - Effect of the presence of oxides and their distribution.
  - In a first step, agglomeration of worn oxide particles increase CoF.
  - Accumulation of oxides agglomerates lead to formation of an oxide layer → decrease CoF.

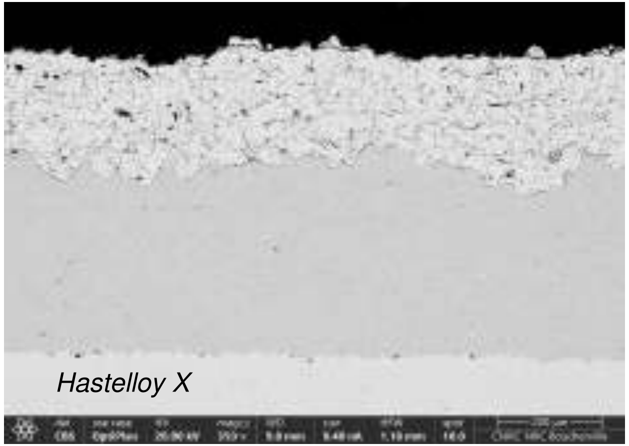
Wear rate: a comparison CS vs. HVOF vs. APS

- ❑ CS and APS coatings show stable wear rates compared with HVOF coating.
- ❑ HVOFs with lower average rate of wear could arise from the interplay of:
  - Formation of oxide layer lubrication at different time intervals
  - Accumulation of lubricating oxides leading to low wear rate
- ❑ CoNiCrAlYs with Yttrium doping has higher chances of forming tribo-oxide layer → Lower wear rate.



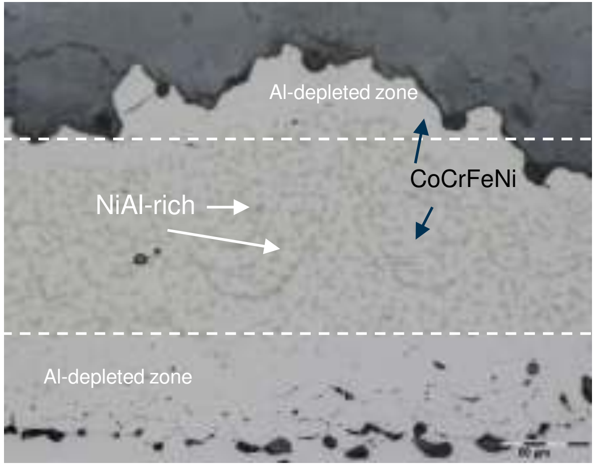
Cold Spray $AlCoCrFeNi_{2.1}$ as Bond Coat

As-sprayed TBC



Bond Coat: Cold sprayed $AlCoCrFeNi_{2.1}$

Top Coat: APS 8wt% YSZ



Furnace cycling testing: sample after 125 cycles @ 1150°C in air

Summary & Future Work

- Successful deposition of dense $AlCoCrFeNi_{2.1}$ EHEA coatings by cold spray
- Cold spray produces EHEA coatings with high hardness and minimal oxidation
- Microstructure is preserved yet phase transformation occurs due to rearrangement of the metastable BCC/B2 structure
- EHEA coatings show transition in the coefficient of friction (CoF) at different stages
- The accumulation of oxides agglomerates during wear tests lead to formation of an oxide layer and decrease CoF
- Continue wear behaviour study using both room temperature and high temperature (1000°C) setup
- Effects of annealing/high temperature testing on microstructure of deposited coatings
- Observe the development of oxide layer (i.e. thermally grown oxides in TBCs)

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Thank you!

Dr. Cristian V. Cojocaru
Senior Research Officer
Thermal Spray / AST
Tel: 450-645-4168
cristian.cojocaru@cnrc-nrc.gc.ca
www.nrc-cnrc.gc.ca