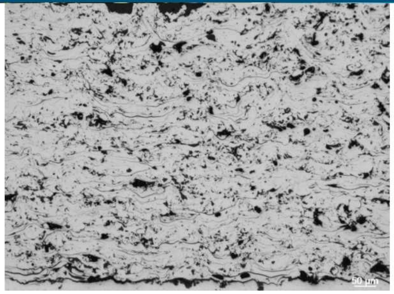
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2018-4194C

Multi-layer Metallization of Polymer Materials via Thermal Spray



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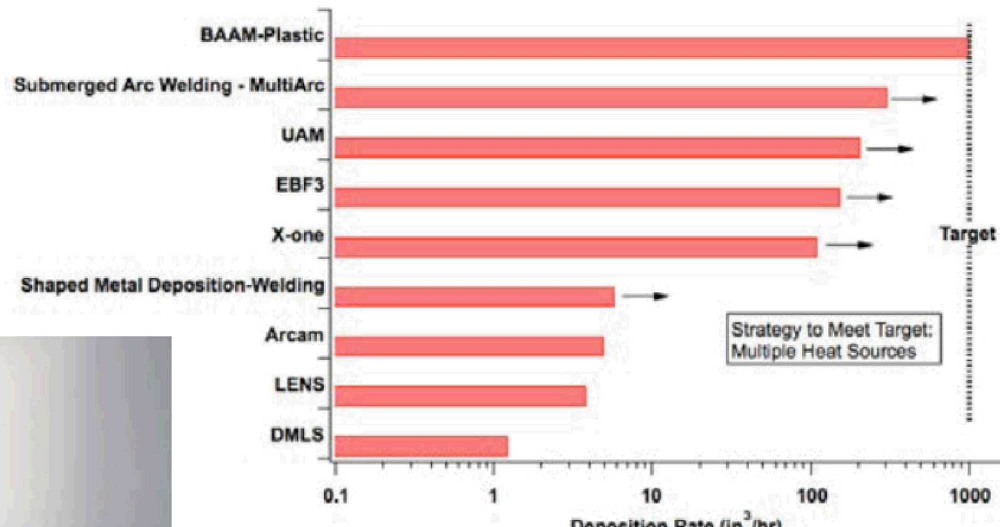
Outline

- Introduction and motivation – Can plastic parts be metallized effectively and cheaply?
  - 3D printed Big Area Additive Manufacturing (BAAM)
  - Thermal Spray Metallization techniques – Twin Wire Arc (TWA)
- Prospective Materials
  - Top coat layers
  - Bond coat layers
- Residual Stresses for adhesion
  - In-situ substrate curvature measurements
  - Stress profile calculations
- Indentation
  - Vickers hardness of layers
  - Brinell/Taber-like method of indentation

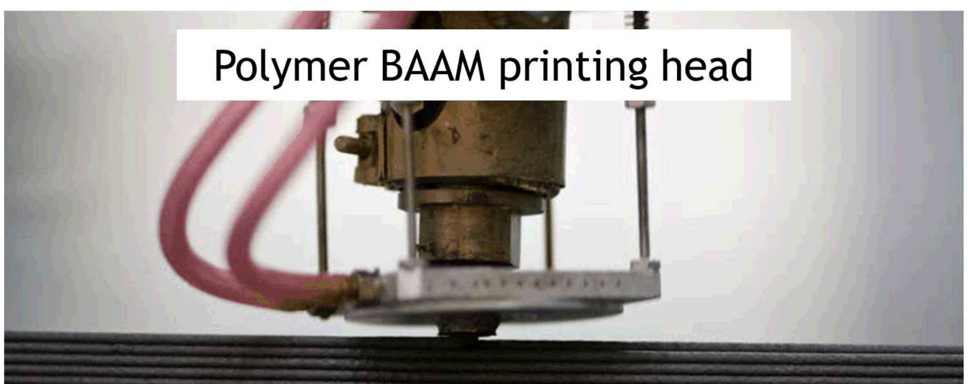
3D printed Polymer BAAM

Manufacturing Demonstration Facility (MDF) High Bay at the Hardin Valley Campus

"Big Area Additive Manufacturing (BAAM) focuses on systems that are greater than 200 ft^3 but less than 1000 ft^3 in build volume with production rates from 10 to 100 lb/hr"



BAAM Plastic at a volumetric printing rate of ~1000 in^3/hr



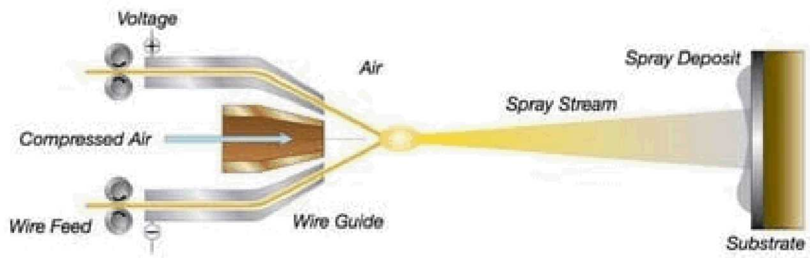
Polymer BAAM printing head

From ORNL's MDF Strategic plan 2016-2021

Thermal Spray Metallization

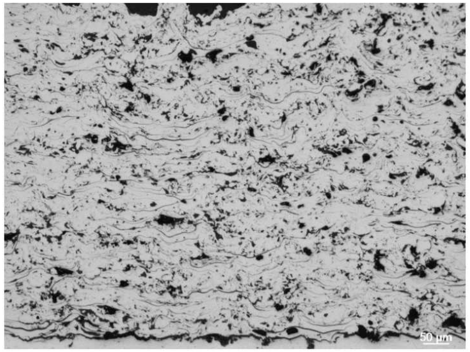
Twin Wire Arc (TWA) thermal spray

- Advantages
  - Cheap, effective way to cover large areas quickly (10s of lbs per hour)
  - Low, Medium, and High melting temperature metals (e.g., Zinc/Al, Ni/ Fe based alloys, Mo)
  - Transportable, large areas demonstrated (e.g., Bridges)
- Disadvantages
  - Brittle, Porous deposits
  - Tensile stresses during deposition



TWA process schematic
(Image from Oerlikon-Metco)

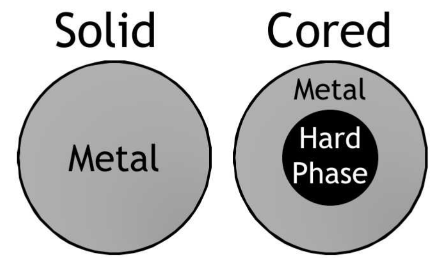
The Wuhan Junshan Bridge over the Yangtze River is covered with 35,000 m^2 (~8.5 acres) of thermal sprayed zinc coating



Porous, defect-laden microstructure

Low melting temperature materials able to be deposited on polymers, flammable substrates

Prospective Materials



Hard, high compression strength metalized surface desired

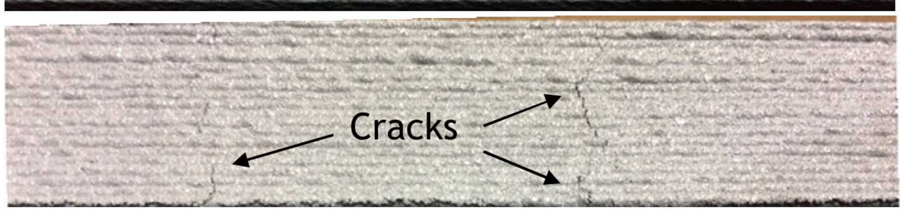
- Several Fe-based hard-facing alloys on market – Solid and/or Cored Wire
- Reported hardness range from 20-67 HRC (O1 Tool Steel HRC ~61-63)
  - TWA applications typically designed for wear resistance and/or restoration
- Medium melting temperatures, stiffness
  → Higher local deposition temperature, quenching stress

Fe-Based hard-facing alloy: severe cracking and delamination when applied directly to polymer BAAM

Low melting temperature bond coat

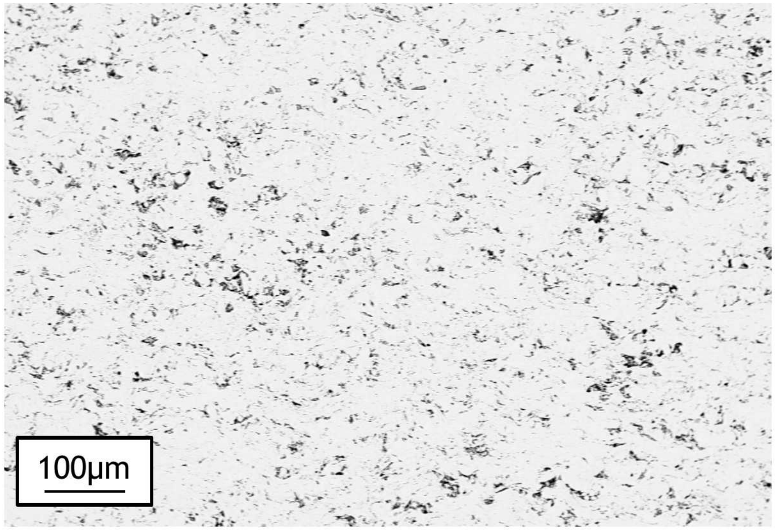
- Potential intermediate layer between hard-facing layer and BAAM
- <u>Zinc</u>, Aluminum, Copper

Zinc on BAAM: Continuous coating, no visible defects

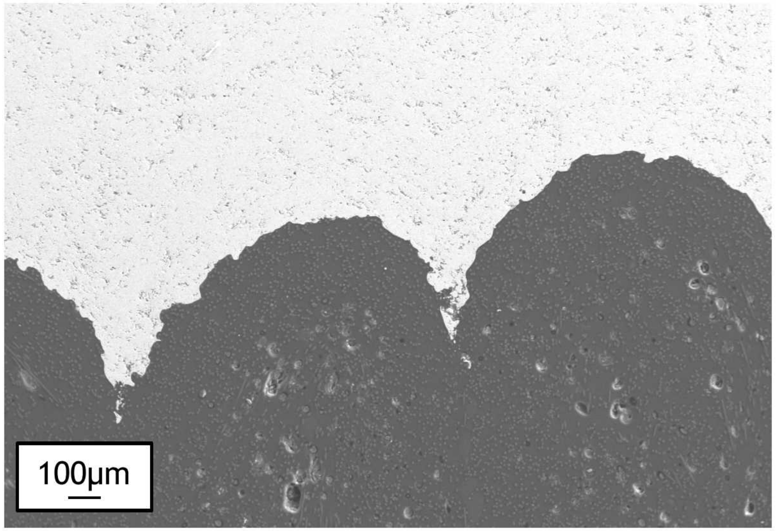


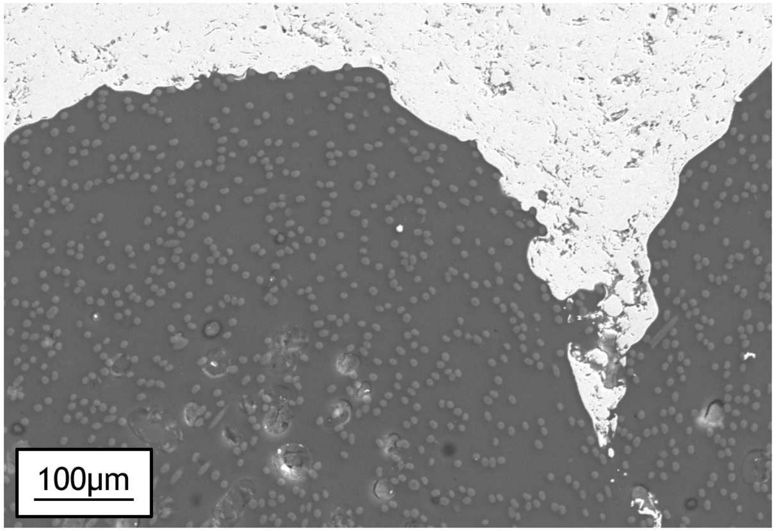
Aluminum on BAAM: Several large microcracks observed

Micrographs – Bond Coat and Substrate



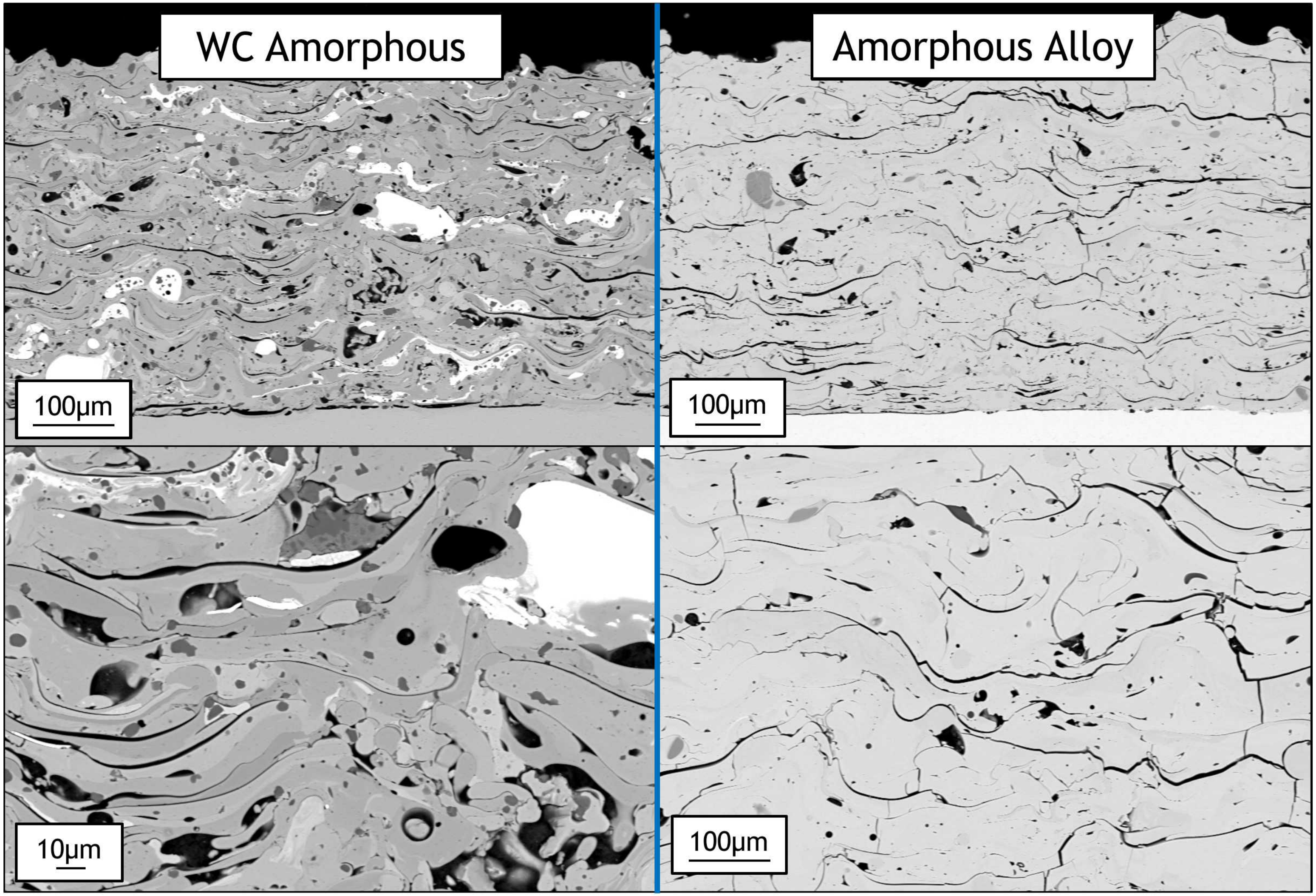
- Zinc bond coat on Polymer BAAM (20% CF-ABS and 50% CF-PPS)
  - Porous Zinc bond coat
  - Macroscopic roughness of Polymer surface thought to aid in adhesion
  - Zinc spray readily infiltrates troughs in polymer surface





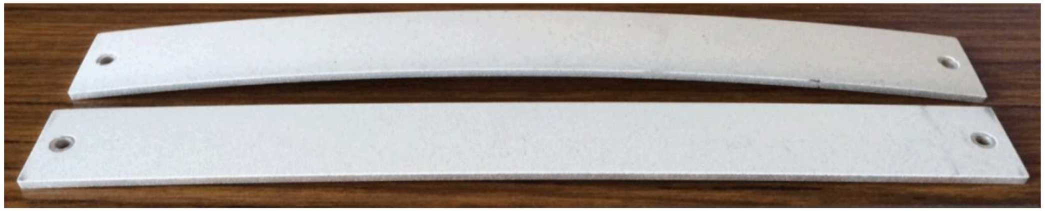
Micrographs – Top Coats

- "WC Amorphous" – Cored wire with WC and TiC particles in Fe-Cr-Ni amorphous matrix
- "Amorphous Alloy" – Cored wire with Fe-Cr-Ni-Mo amorphous matrix

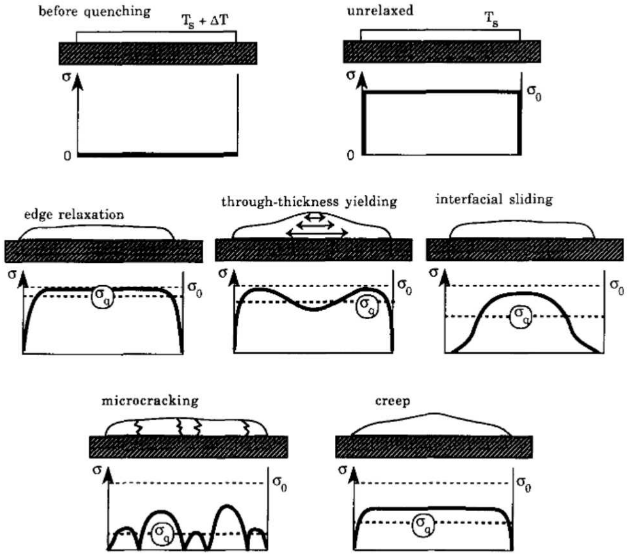


Residual Stresses in TWA Coatings

- TWA is a melt-deposition technology, therefore a maximum quenching stress of $\sigma = \alpha_d \Delta T E_d$ exists
- Multiple stress relief mechanisms – material yielding, micro-cracking, interfacial sliding/delamination etc.
- Further stresses induced by thermal expansion mismatch between coating and substrate
- Bonding to substrate is primarily mechanical
- Several ways to measure residual stress within TWA coatings
  - X-ray diffraction ($\sin^2\Psi$ method)
  - Neutron diffraction
  - Layer removal w/strain measurement
  - Substrate curvature



Air Plasma Sprayed Al2O3 on Aluminum substrate with different processing conditions



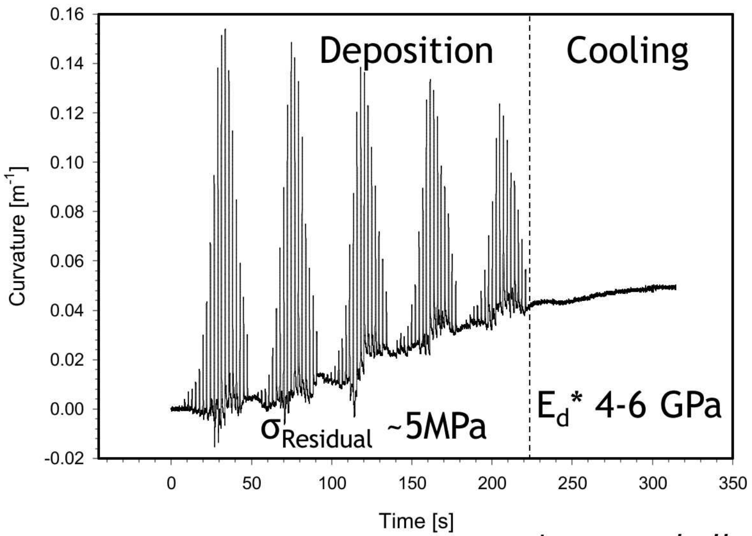
Kuroda, S., and T. W. Clyne. "The quenching stress in thermally sprayed coatings." Thin solid films 200.1 (1991): 49-66.

In-situ Substrate Curvature Measurements

- Real time substrate bending and back side thermocouple measurements during coating deposition and post-deposition cooling using In-situ Coating Property (ICP) sensor (*ReliaCoat Technologies LLC.*)
- Analysis of data gives residual stress and coating stiffness

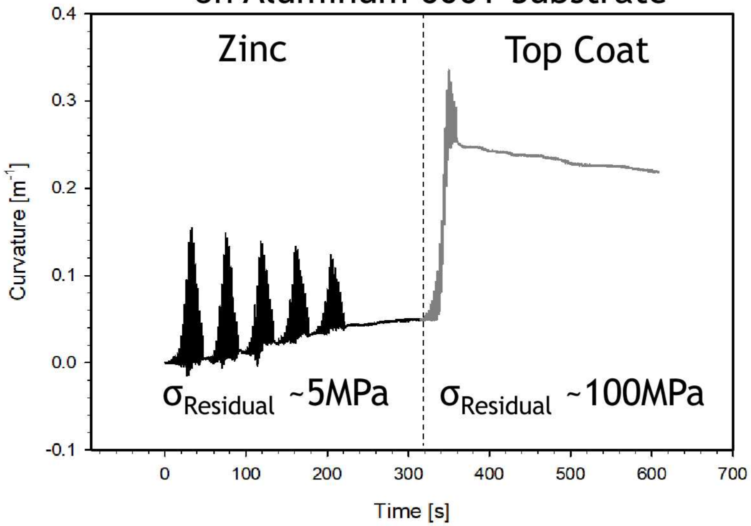
$$\sigma_{Film} = \frac{Es\, h^2\, \Delta\kappa}{6\, H} \qquad \Delta\kappa = \frac{6E_dE_shH(h+H)\Delta\alpha\Delta T}{E_d^2h^4 + 4E_dE_sh^3H + 6E_dE_sh^2H^2 + 4E_dE_shH^3 + E_s^2H^4}$$

TWA Zinc sprayed on Aluminum 6061 Substrate



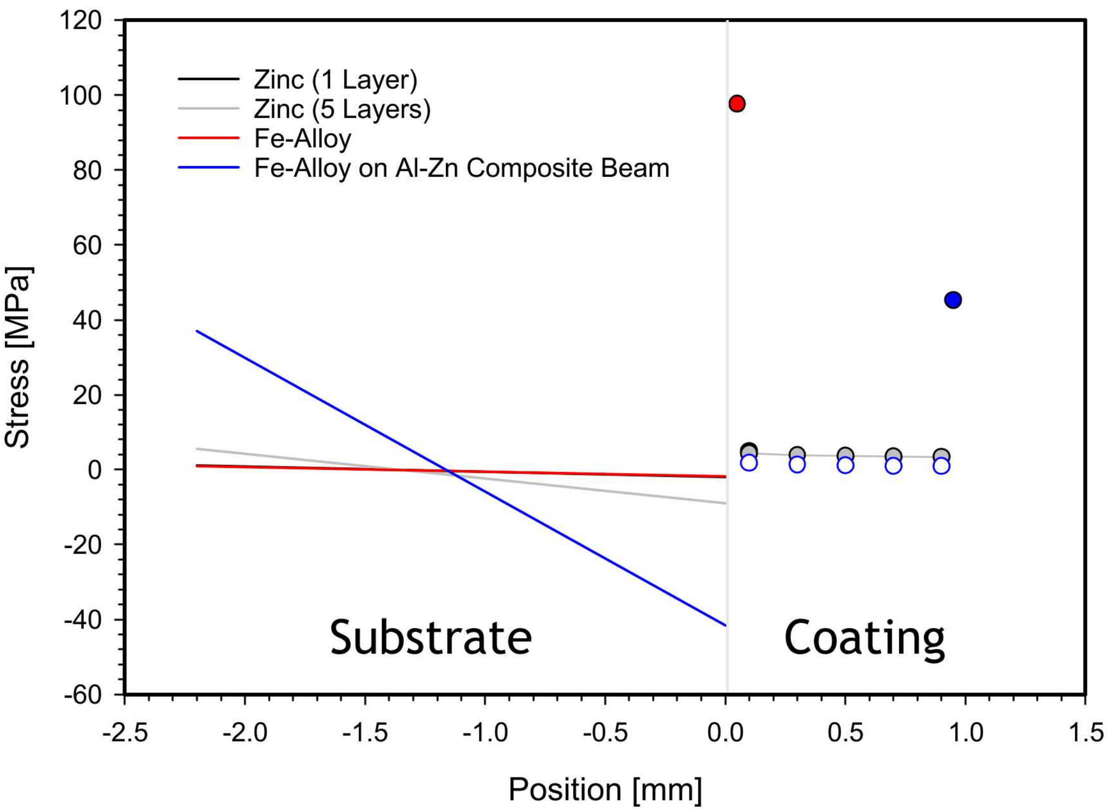
*assumes bulk CTE

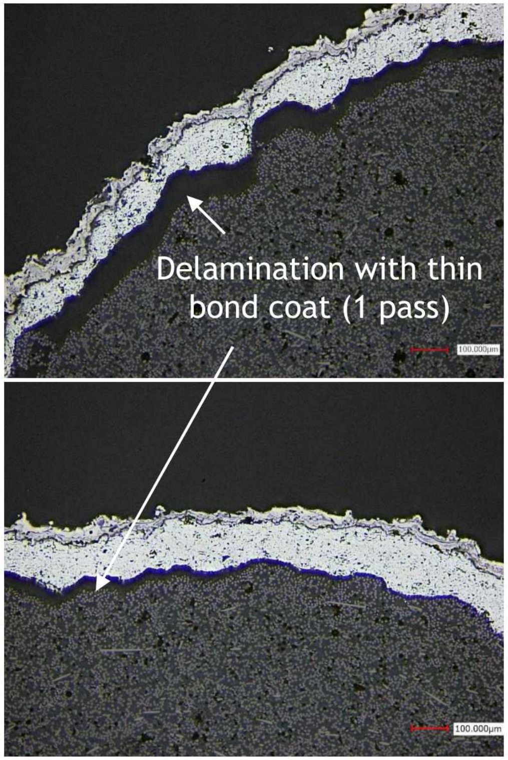
TWA Zinc + Fe-alloy Top Coat sprayed on Aluminum 6061 Substrate



Residual Stress Profiles using Tsui-Clyne analytical model*

- Both Zn and Fe-Alloy add little stress to substrate but vary in film stress; larger interfacial force
- A composite Al-sprayed Zn beam (with adequate Zn thickness) acts as a stress buffer for the Fe-Alloy, reduces interfacial force





* *Tsui, Y. C., and T. W. Clyne. "An analytical model for predicting residual stresses in progressively deposited coatings Part 1: Planar geometry." Thin solid films 306.1 (1997): 23-33.*

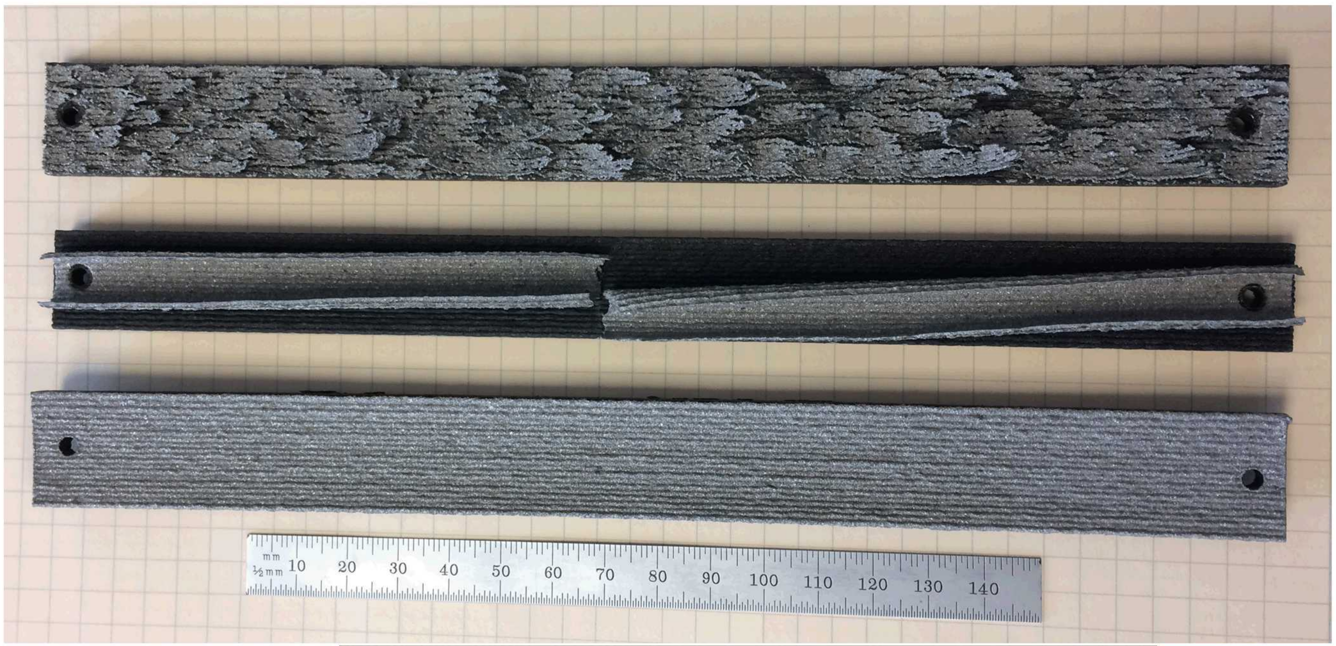
Multi-layer TWA coatings on polymer BAAM

- Applying Zinc stress buffer layer to reduce interfacial forces makes multi-layer metallization onto BAAM possible

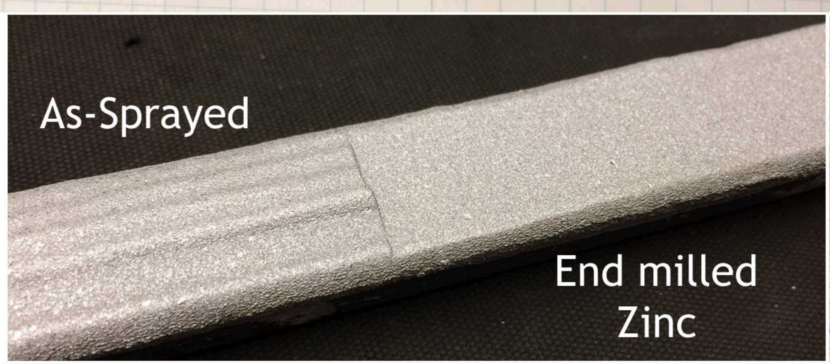
No Zinc

Thin layer of Zinc

Thick layer of Zinc

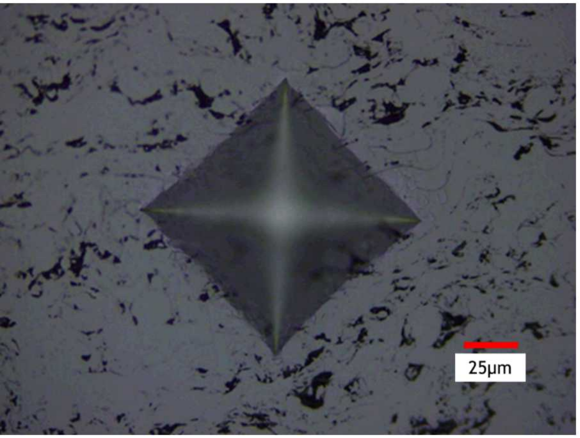


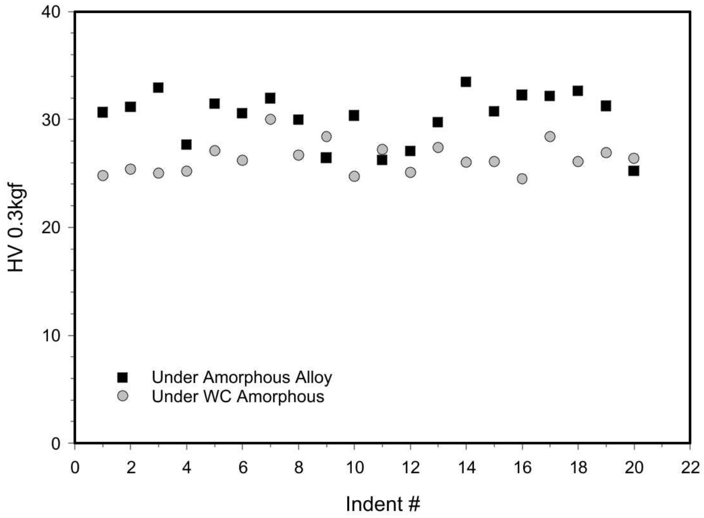
- Machining of Zinc surface before top coat application allows for macroscopically smooth surface

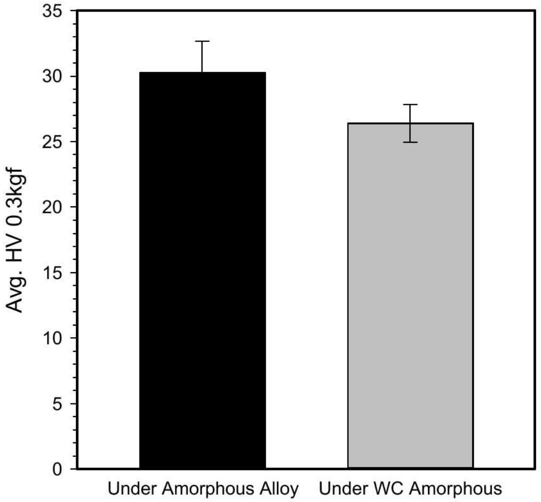


Vickers Hardness (Cross Section)

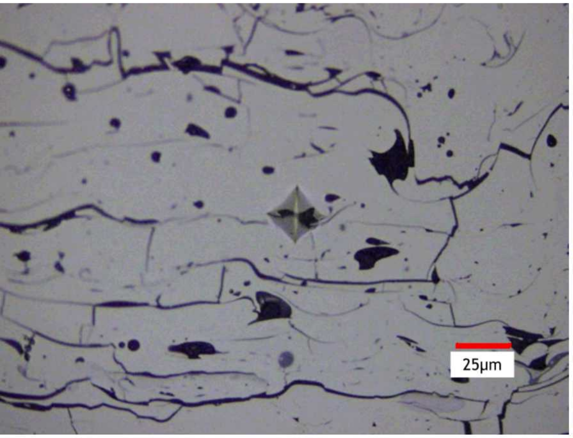
Zinc Bond Coat (on BAAM Substrate)

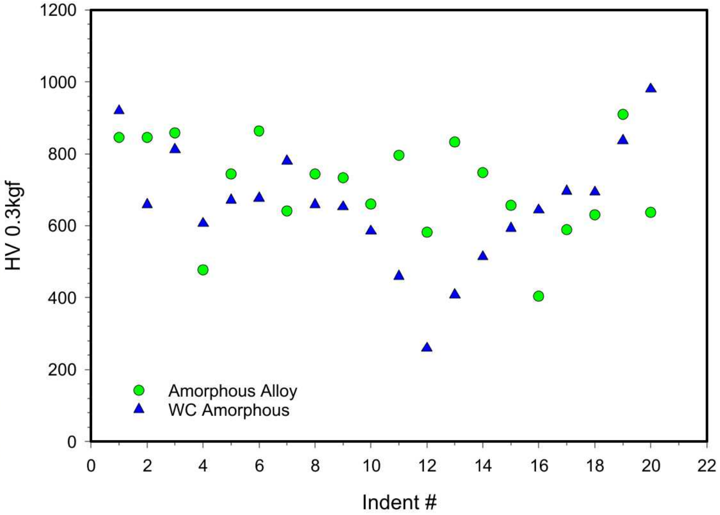


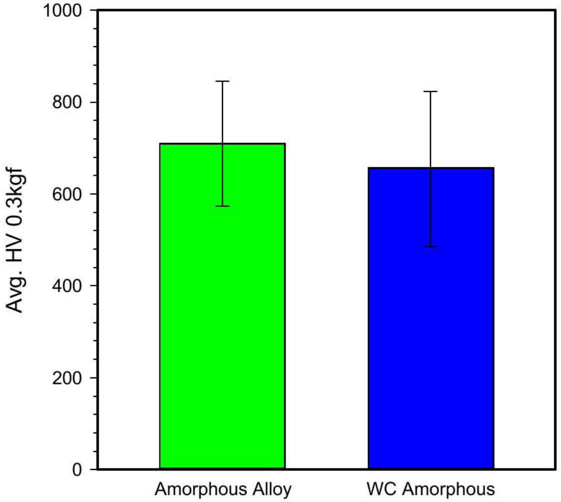




Hard Facing Top Coat (on Zinc + BAAM Substrate)

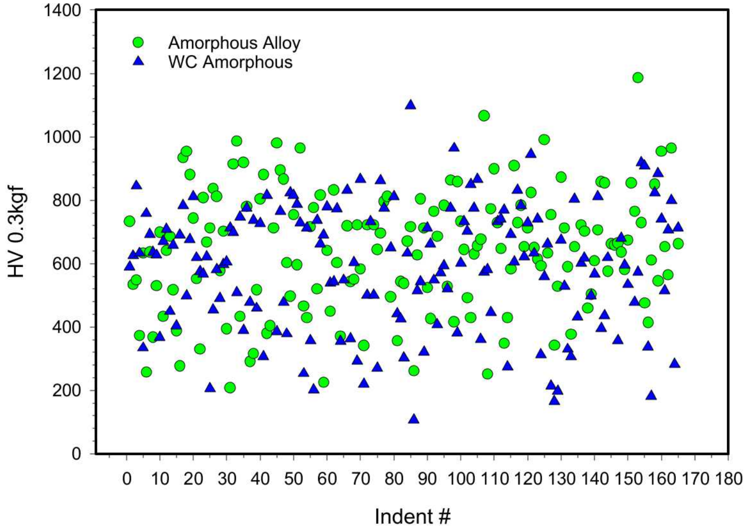


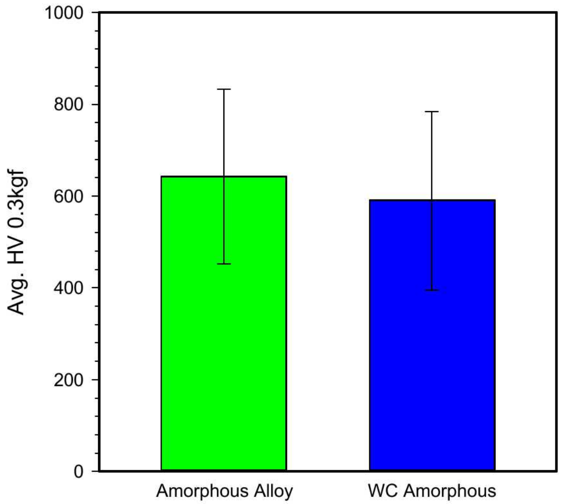


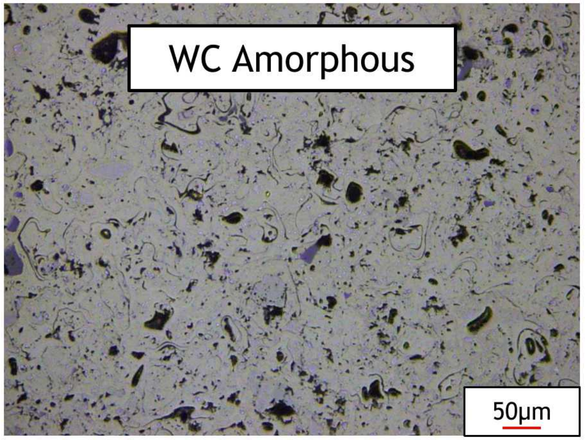


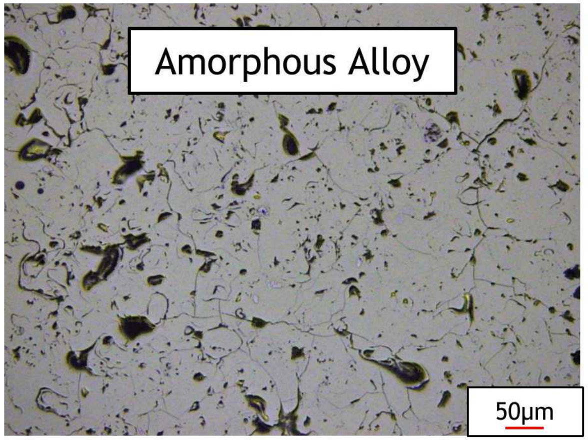
Vickers Indentation (Top surface)

- Significant scatter in hardness data fir both top coat materials



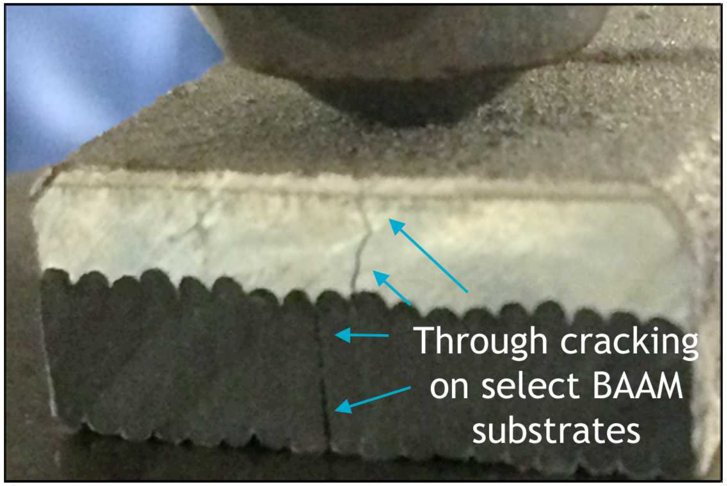


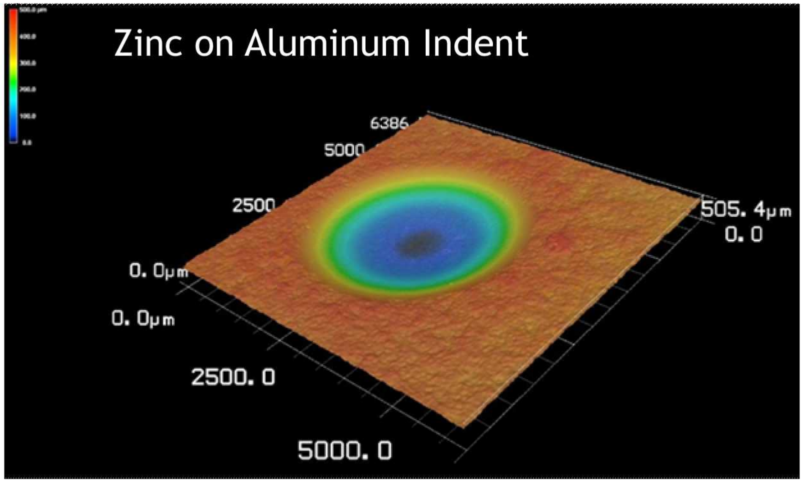


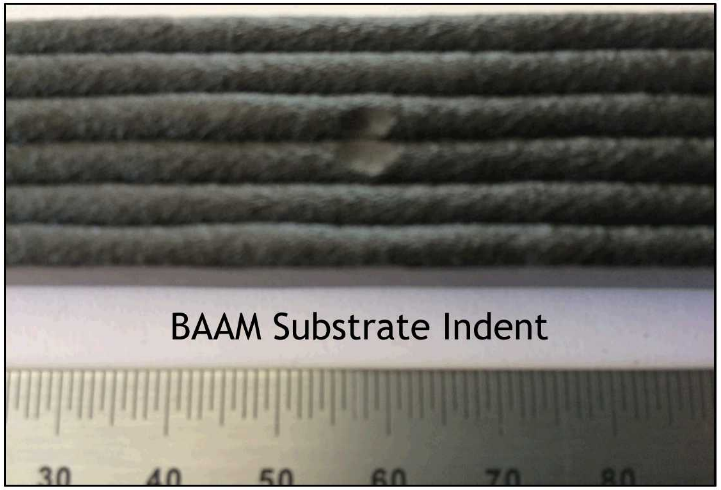


Brinell Indentation

- 500kg load with 10mm diameter ball on top surface of as-sprayed stack-ups: Comparison between Aluminum and BAAM substrates







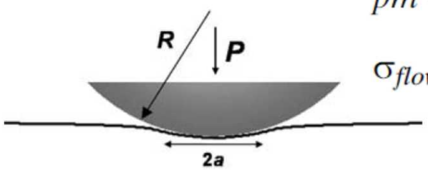
Tabor Method*

- Uses Brinell type indentation to determine inelastic stress-strain behavior over a series of indentation loads – Demonstrated for thermal spray coatings †, **
  - Representative Strain (ε_R) based on contact (a) and indenter (R) radii
  - Mean Pressure (pm) based on indentation load (P) and contact area
  - Flow Stress (σ_{flow}) empirically determined

$$\varepsilon_R = 0.2\frac{a}{R}$$

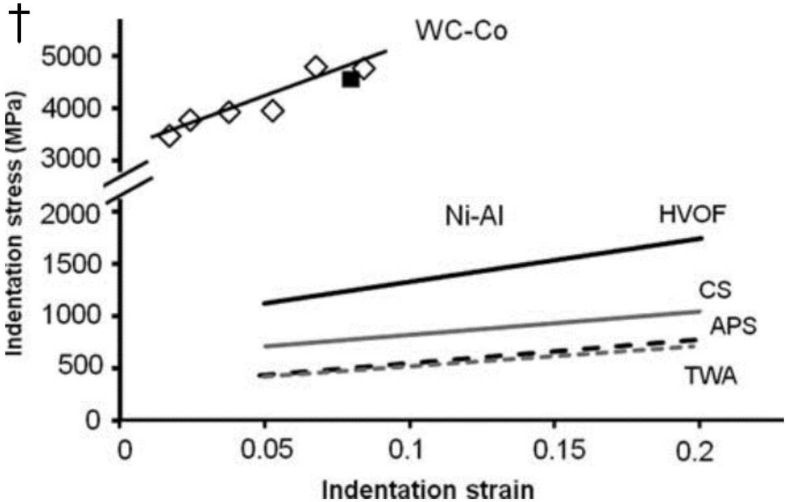
$$pm = P/\pi a^2$$

$$\sigma_{flow} = \frac{pm}{2.8}$$



- NiAl: Process dependence on indentation behavior
- Cold Sprayed Al: Work hardening from coating consolidation, softening with heat treatment

†



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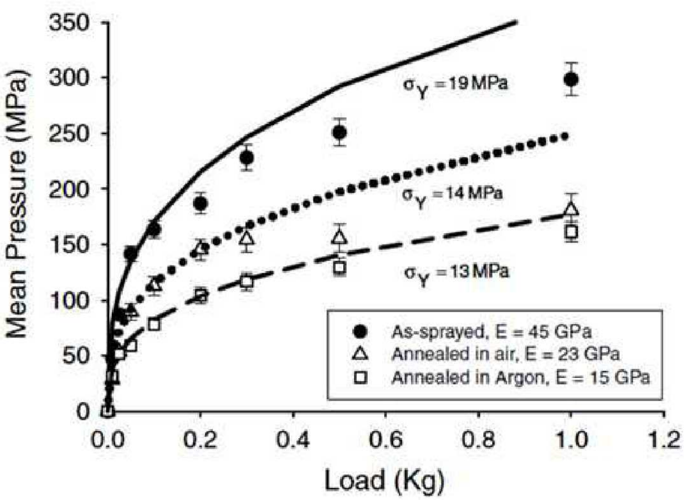
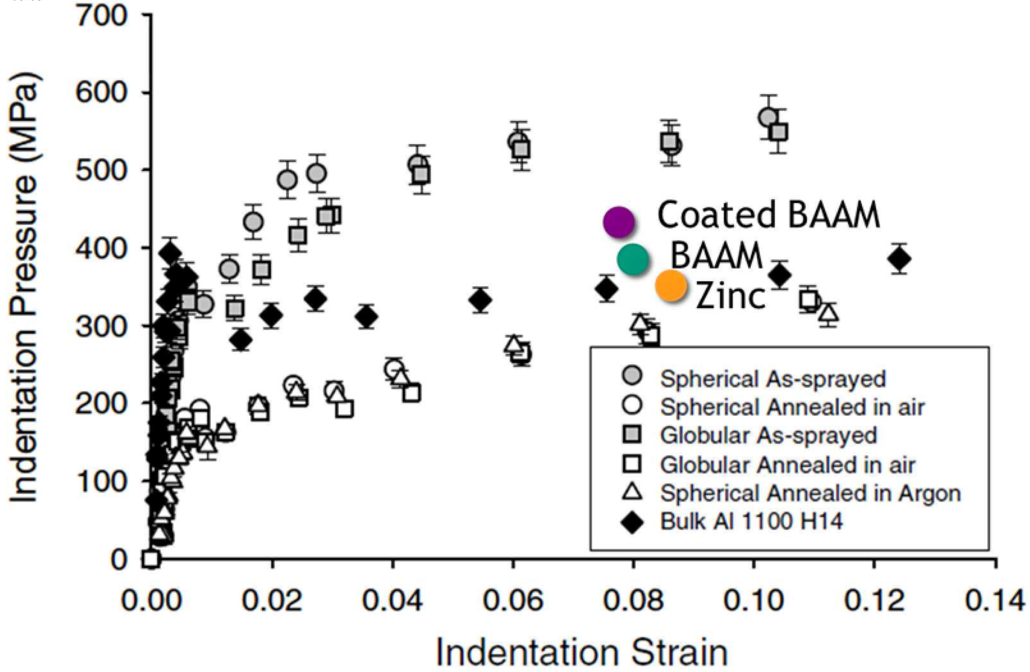


* Tabor, D. "The Hardness of Metals Oxford University Press." *New York* (1951).
† Choi, W. B., et al. "Indentation of metallic and cermet thermal spray coatings." Journal of thermal spray technology 18.1 (2009): 58-64.
** Choi, W. B., et al. "Integrated characterization of cold sprayed aluminum coatings." Acta Materialia 55.3 (2007): 857-866.

Metallized BAAM compared to other materials through Tabor indentation

- Zinc bond coat shows highest indention strain and lowest mean pressure
- Zinc + top coat shows lower indention strain, higher mean pressure than un-coated BAAM
- Cold Spray Aluminum in as-sprayed state may offer higher compressive strength than TWA coated BAAM – may be alternative pathway for stack up

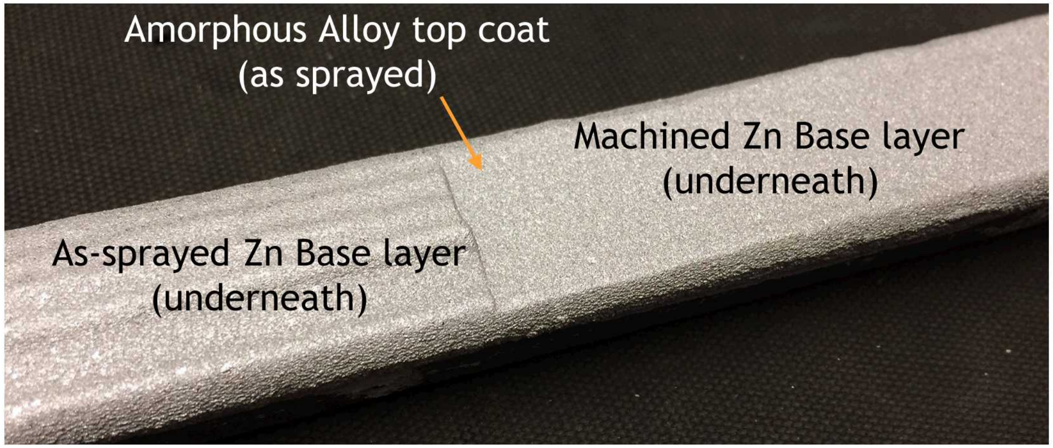
**



** Choi, W. B., et al. "Integrated characterization of cold sprayed aluminum coatings." Acta Materialia 55.3 (2007): 857-866.

Conclusions

- Metallization of Polymer BAAM possible through the use of low melting temperature and low stress bond coats (Zinc)
- Hard facing top coats able to be deposited onto Zinc bond coats, providing higher surface hardness than un-coated polymer BAAM
- Coating porosity and stresses limit mechanical strength and have adhesion limits, respectively
- Alternative high throughput spray processes and materials may provide harder surfaces as a top coat (e.g., cold spray)



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  - Deidre Hirschfeld, Pylin Sarobol, Jesse Adamczyk, Mike Clearwater, Tom Holmes, Joe Padilla, Carlos Silva, Joe Fonseca
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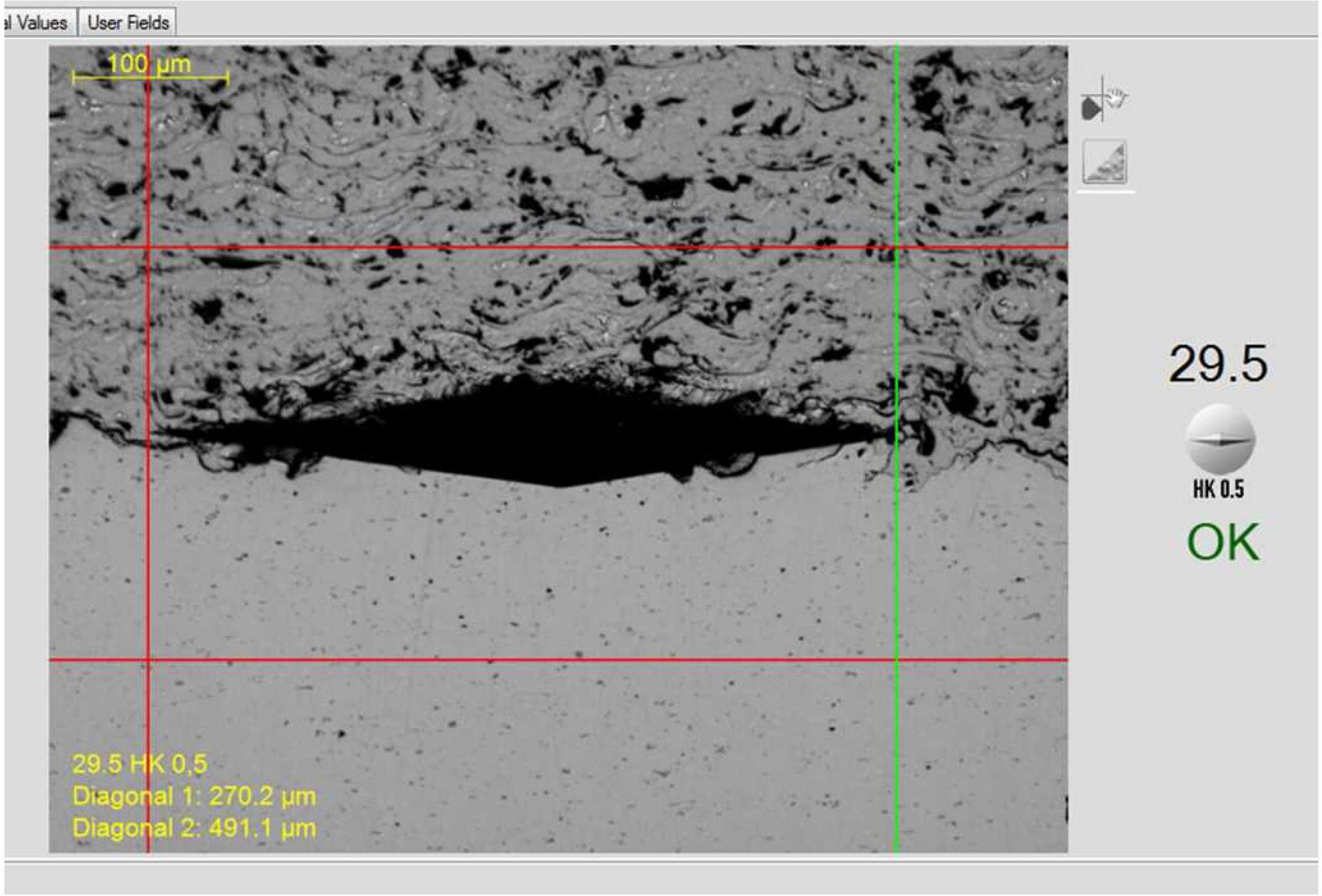
- Material Characterization
  - Christina Profazi, Alice Kilgo, Bonnie McKenzie

Questions?

Interface Indentation

Knoop indentation at Zn and Al interface up to 2kgf load did not result in de-bonding



Test sample synthesis?

Sample	Zinc Passes	Zinc Layer [µm]	Top Coat Passes	Top Coat [µm]
Zinc	5	880	-	-
Zinc + Amorphous Alloy	5	860	1	100
Zinc + WC Amorphous	5	850	1	100
Coarse Bead BAAM	-	-	-	-
Zinc + Amorphous Alloy	20	<3.5mm (milled after deposition)	5	~500
Zinc + WC Amorphous	20	<3.5mm (milled after deposition)	5	~500

Update with Brinell hardness #

Aluminum Substrate
BAAM Substrate

ICP on HDPE

- Non-uniform curvature due to slower heat transfer through substrate