SAND2015-10650PE

Cold Spray Coatings & Sandia's Thermal Spray Research Laboratory (TSRL)

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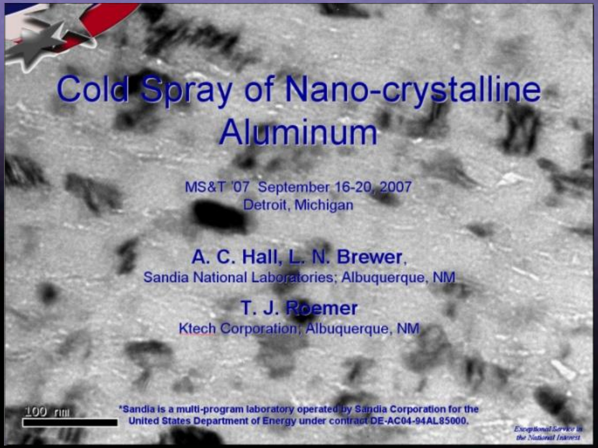

National Nuclear Security Administration

*Sandia is a multi-program laboratory operated by Sandia Corporation for the United States Department of Energy under contract DE-AC04-94AL85000.

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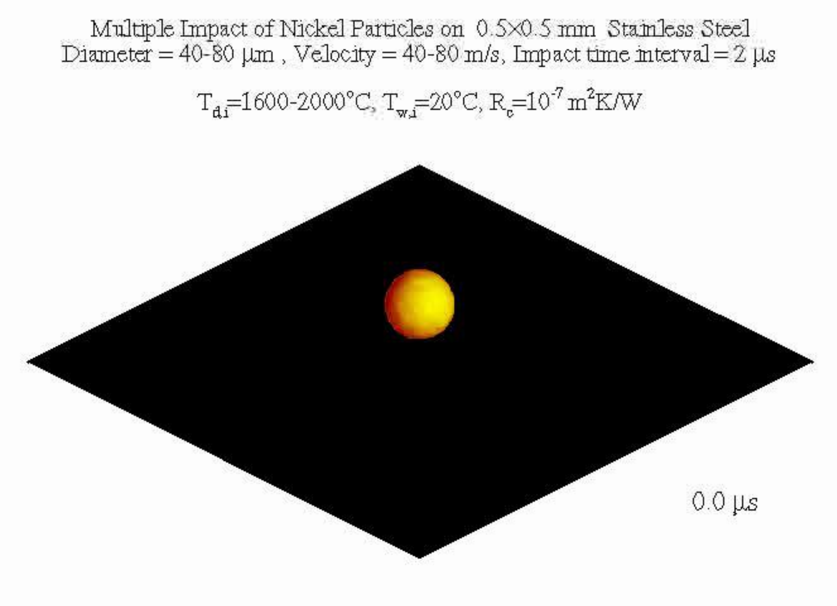
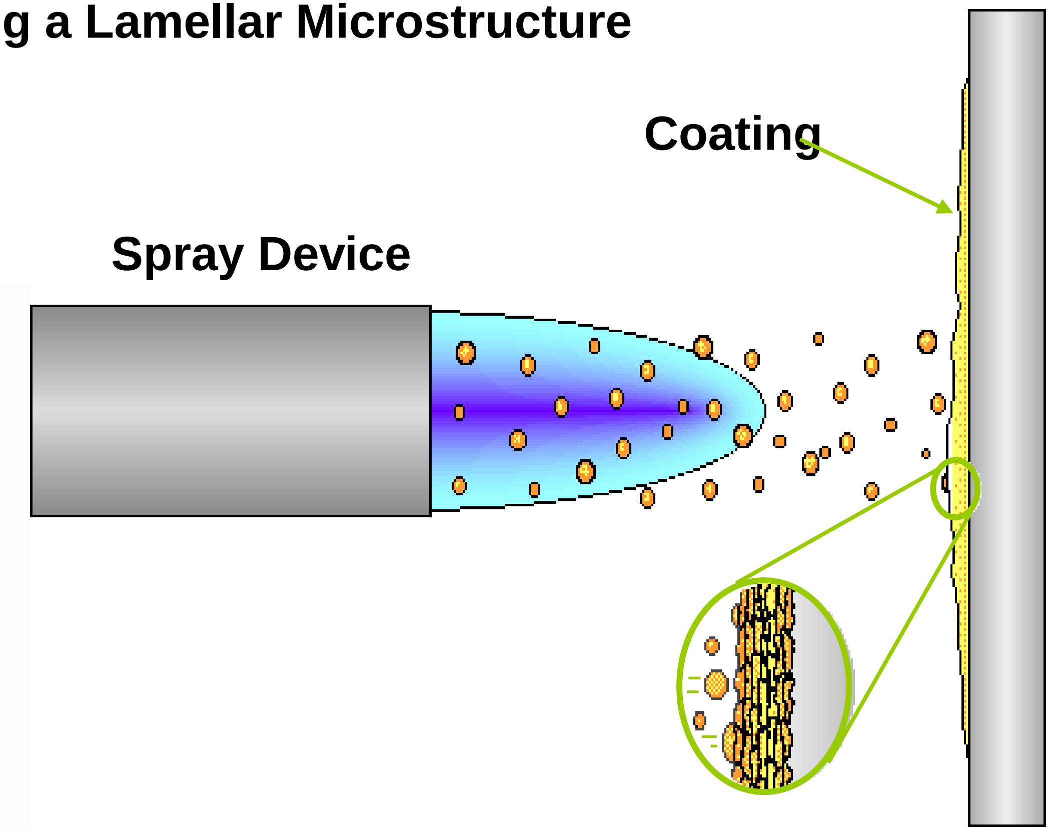
What is Thermal Spray?

~ 10 - 100 µm Molten or Semi-Molten Droplets are Sprayed onto a Target Surface Where they “Splat” Cool at Rates up to 10^4 -10^8 K/sec Forming a Lamellar Microstructure



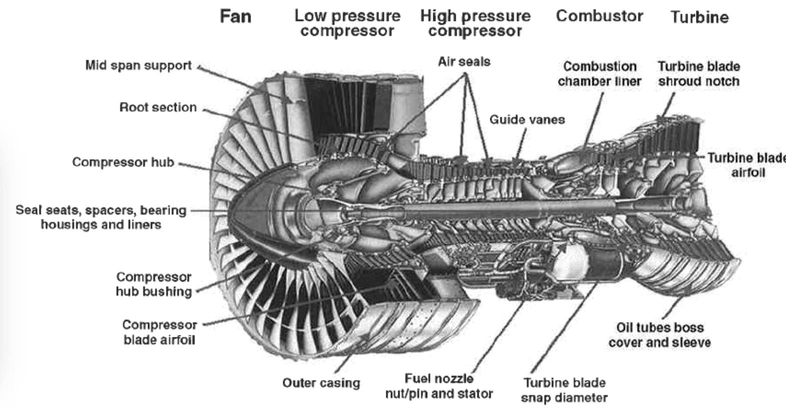


*Droplet Impact Simulation by Prof. J. Mostaghimi, et al, Univ. of Toronto, 1998.

What are Thermal Spray Coatings Used For?

- Aerospace
  - Gas Turbines
  - Landing Gear
- Automotive
- Biomedical
- Computers
- Electronics
- Infrastructure
- Marine
- Paper Making
- Petrochemical
- Power Generation
- Printing
- Textiles

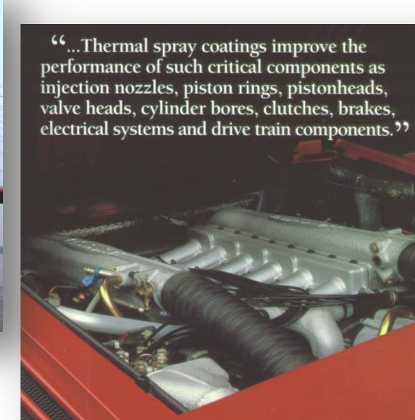
Hydroxyapatite coating on a hip implant



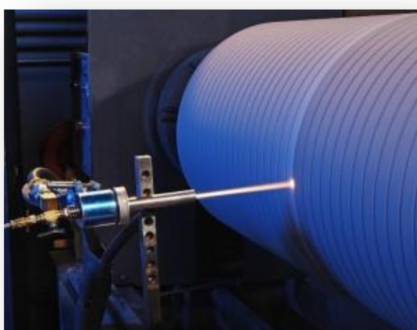
Gas Turbines are full of sprayed coatings!

Hard Chrome Replacement on a Landing Gear Strut

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



Auto applications include pistons, valves, cylinder bores, clutches, and drive train components.



Ceramic Coating a Printing Roll

Thermal Spray Coatings find niche surface modification applications in many, many industries!

Handbook of Thermal Spray Technology, 2005, ASM International

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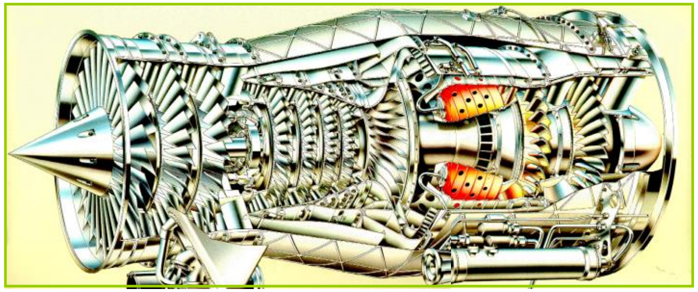
What sorts of materials can I work with?

- **Pure metals, most common alloys, and most refractory metals:**
  - Sn; Zn; Al; Cu; Ni; Fe; Mo; Ta; W, Nb,
- **Most traditional ceramics:**
  - Al_2O_3; TiO_2; MgO; YSZ; ZrO
- **Composite abradable seal materials:**
  - Al-Si-40Polyester; Ni-25Graphite; Al-Si-20BN
- **Iron Based Alloy Coatings**
  - 316 Stainless; Fe-Cr-Al-Mo-TiO2 (grindable wear resistance)
- **Ni Base alloys**
  - Ni-Cr-Al-Mo-Co-Ti-Zr-B (for use w/ Inconel)
  - Ni-Cr-Fe (machinable "stainless")
  - Inconel
- **MCrAlY's:**
  - Co-Ni-Cr-Al-Y (high temp erosion, corrosion, & oxidation resistance in gas turbines)
  - Ni-Cr-Al-Y (high temp erosion, corrosion, & oxidation resistance in gas turbines)
- **Blended cermets**
  - $MgZrO_3$+35NiCr; Al_2O_3 + 30(Ni-20Al) (abrasion & shock resistance)
- **Cobalt Based Alloys**
  - Co-Cr-Ni-W (abrasive wear and erosion in high temp environments)
  - Co-Ni-Cr-WC (surface restoration for combustors, airfoils, blades, and vanes in gas turbines)
- **Carbides & Metal / Carbide Composites**
  - MoC_3 , Cr_3C_2 , Cr_3C_2-NiCr (wear resistance & hard chrome replacement)
- **Tungsten Carbide Based Materials**
  - W_2C-12Co (hard chrome replacement)
  - (W_2C-12Co)+25(Ni Base Super alloy) Blend



and many, many more…

A wide variety of materials are commonly thermal sprayed!

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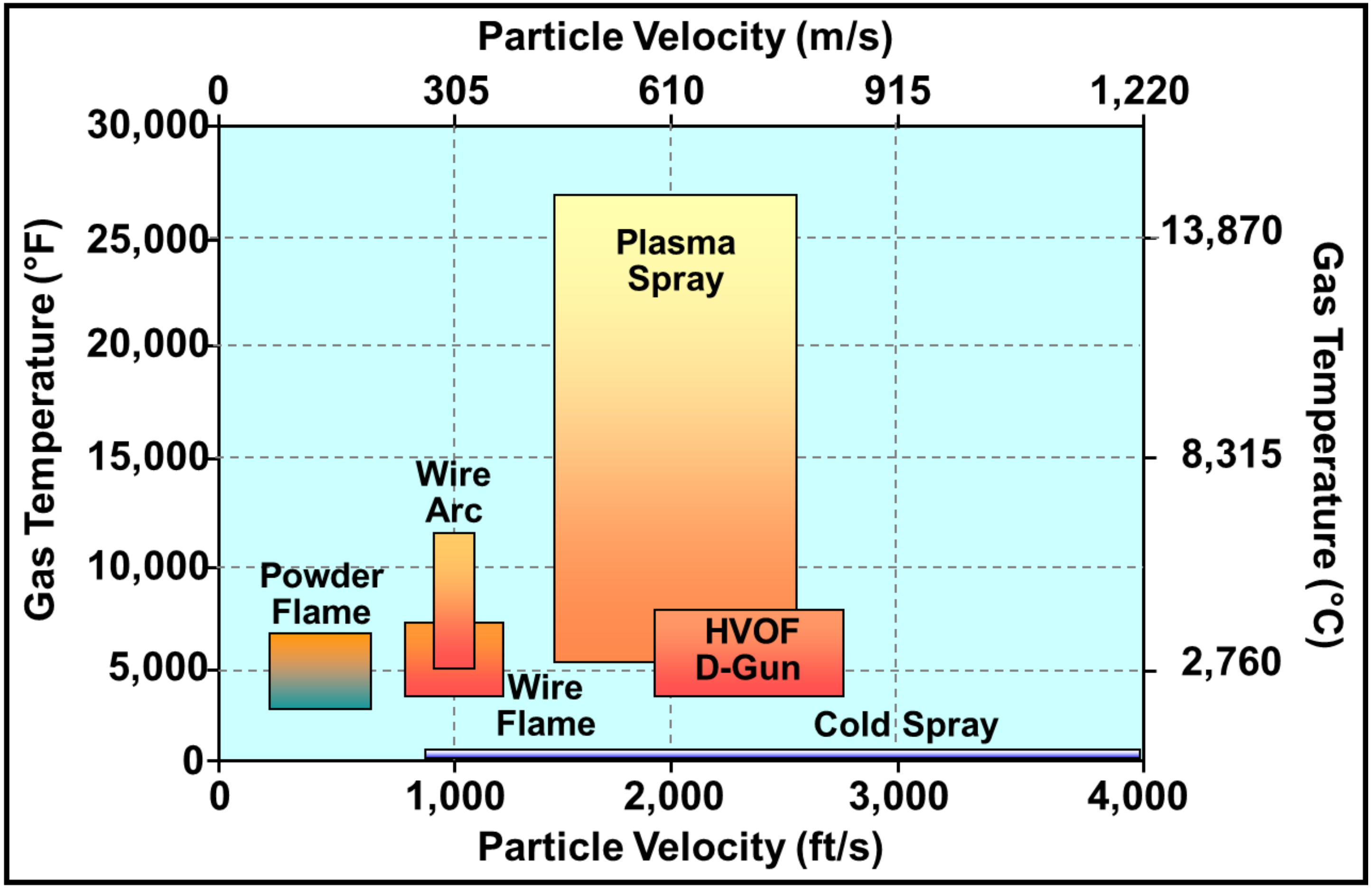
Like welding processes, there are many different thermal spray processes.



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

We choose a thermal spray process based on the properties of the feed stock and the requirements of the coating application.

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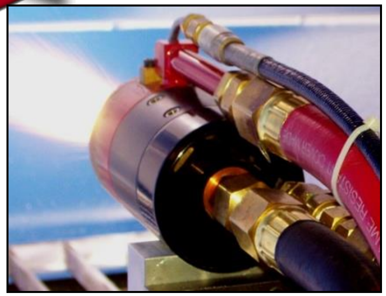
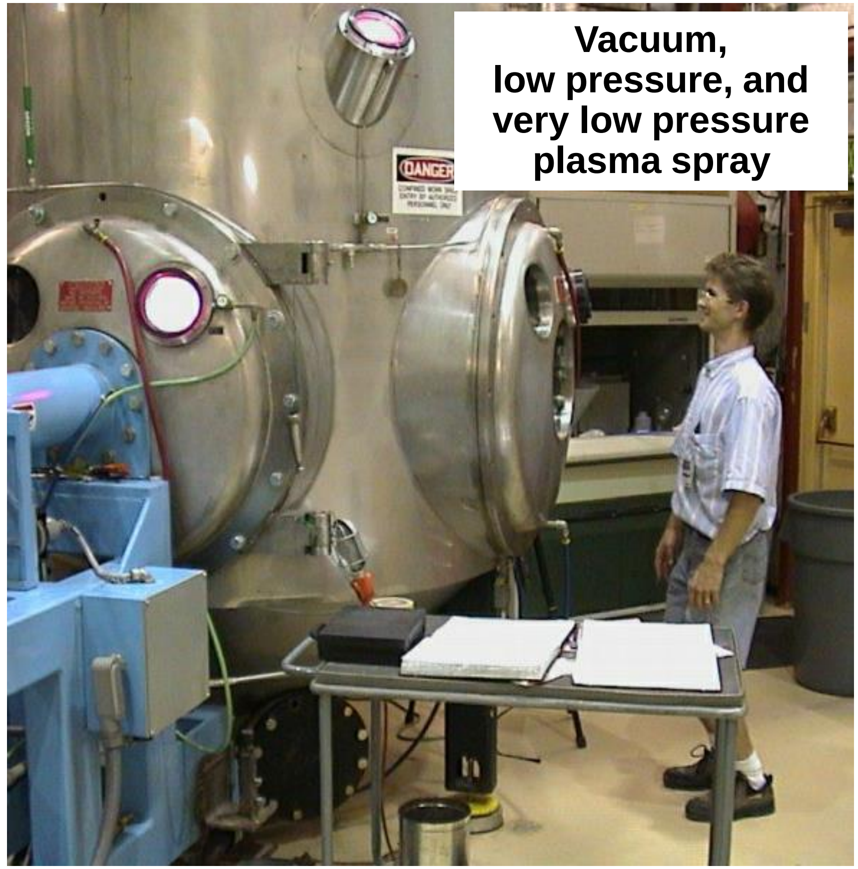
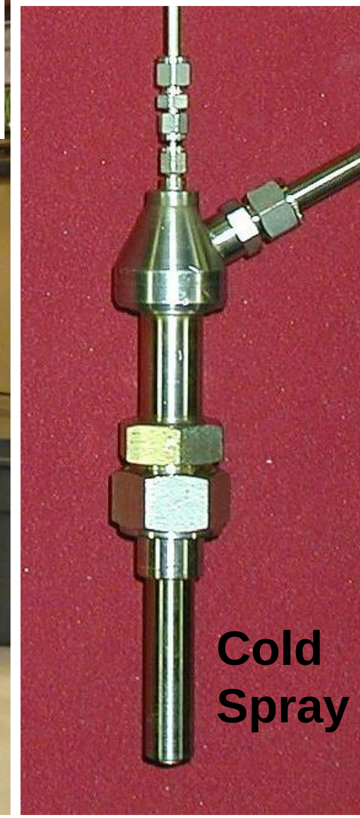
TSRL is a broadly capable development facility with experience operating at least one version of every major thermal spray process.



Atmospheric Plasma Spray

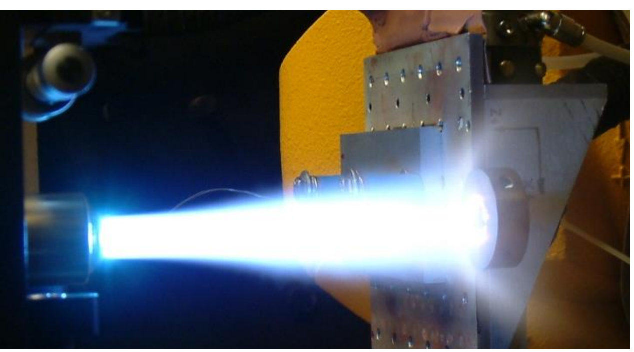


Vacuum, low pressure, and very low pressure plasma spray



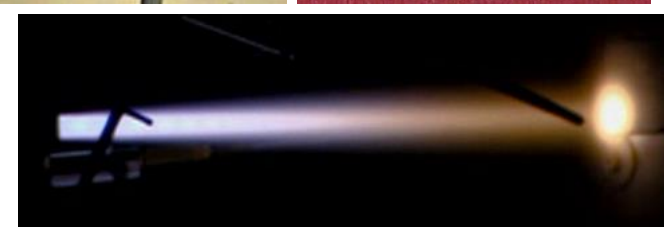
Cold Spray

Twin Wire Arc Spray



Powder Flame Spray

Wire Flame Spray



HVOF

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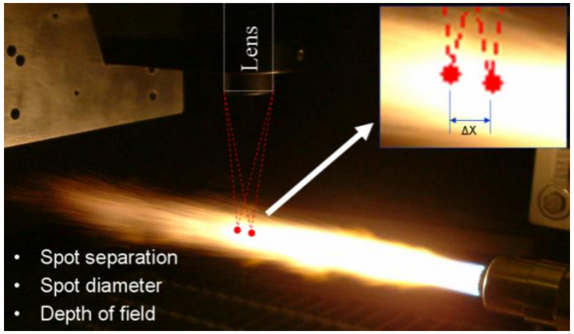
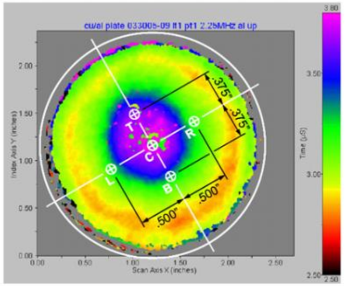
What makes the TSRL unique?

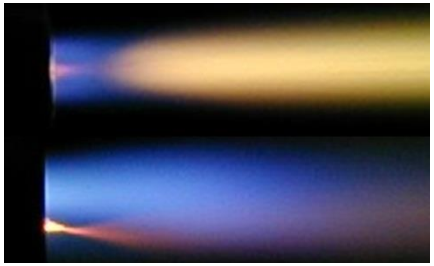
- **Focus on Process Diagnostics for Thermal Spray**
- **Materials Science Expertise and Analysis Capability**
- **Strong Ties to Materials & Process Modeling at SNL**
- **LPPS® Thin Film & Cold Spray**
- **Experience supporting spray processes across entire technical readiness scale**

Sensor based particle diagnostics measure particle temperature (Tp) and velocity (Vp).

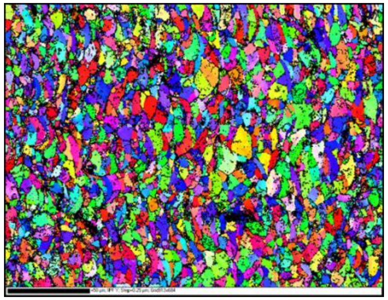




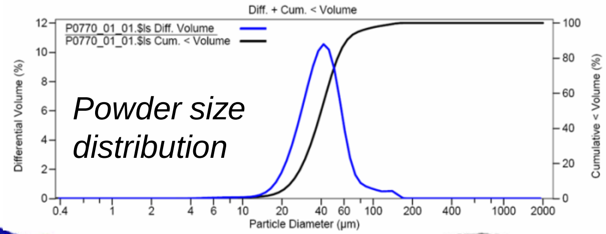
Non-Destructive Inspection



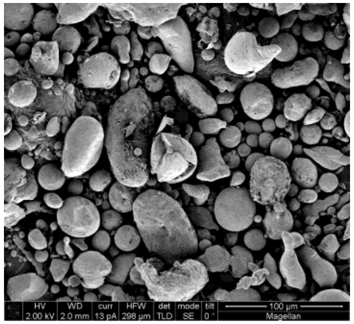
Wire tip imaging



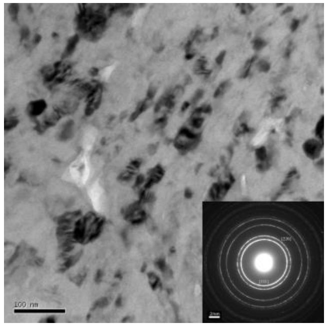
EBSD Mapping of Coating Microstructure



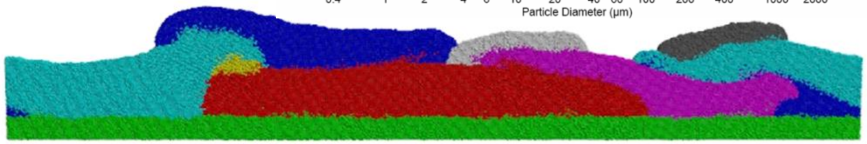
Powder size distribution



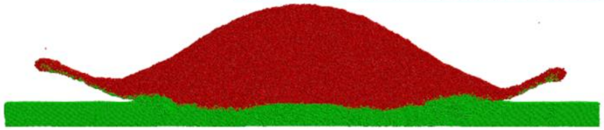
SEM for powder morphology determination



High Resolution TEM



Mesoscale coating build-up model



Complex chemical/physical phenomena such as wetting, solidification, and fragmentation captured in atomistic scale modeling.

We are fully equipped for Thermal Spray Process Development; and we happily do technology transfer!

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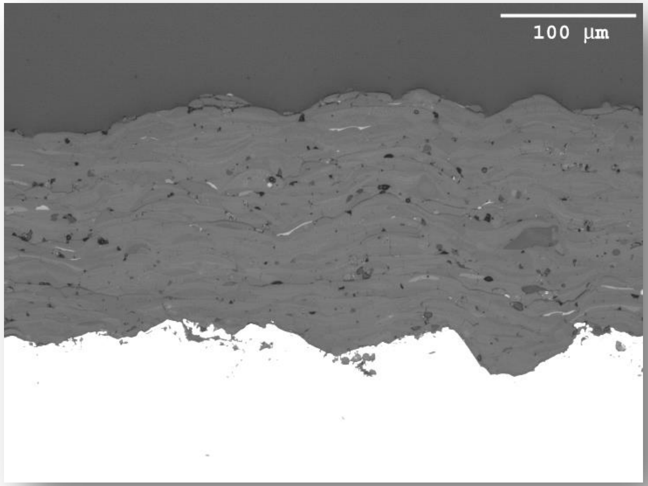
Particle Temperature (Tp) and Particle Velocity (Vp) directly affect coating microstructure and properties.

Tp: Particle Thermal energy
Vp: Particle Kinetic energy

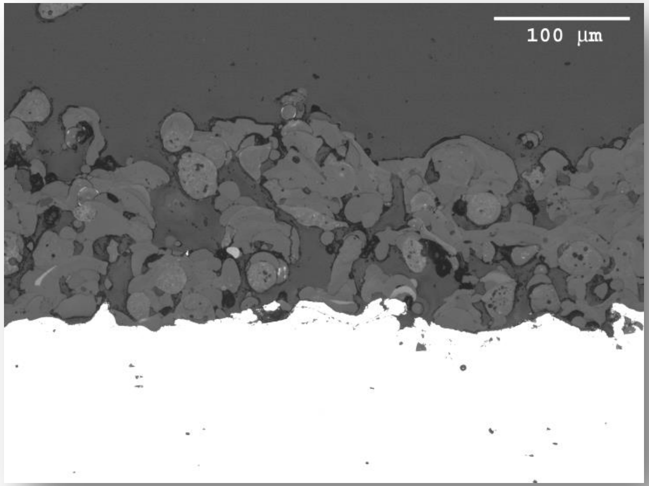
- *Are controllable*
- *Are measureable*
- *Make sense*

Increasing Tp or Vp

- *Increases deposition efficiency*
- *Reduces coating porosity*
- *May increase residual stress*
- *May increase substrate damage*



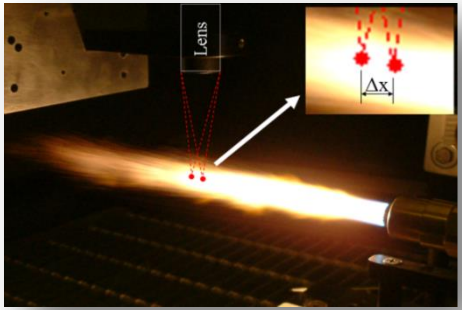
vs.



Sensor-Based Particle Characterization

- *Simultaneous time of flight and two color pyrometry measurement*

$$Vp = \Delta x / \Delta t$$
$$Tp = \lambda 1 / \lambda 2$$



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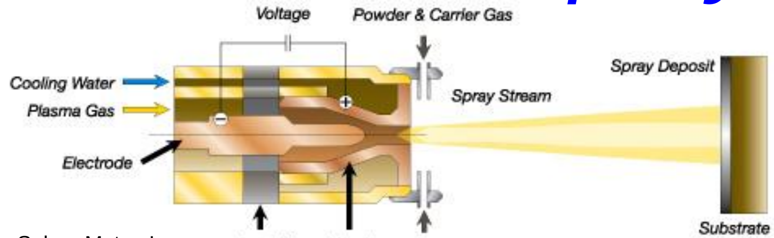
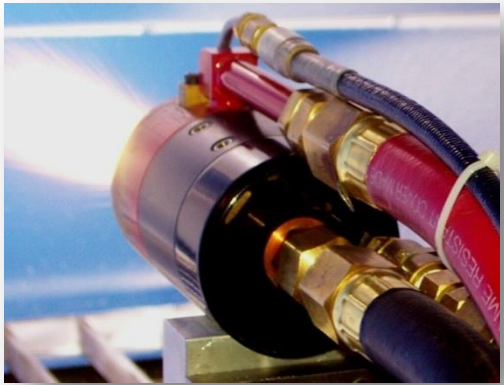
Plasma Spray



Sulzer-Metco Inc.


SG-100 Praxair-Tafa Inc.

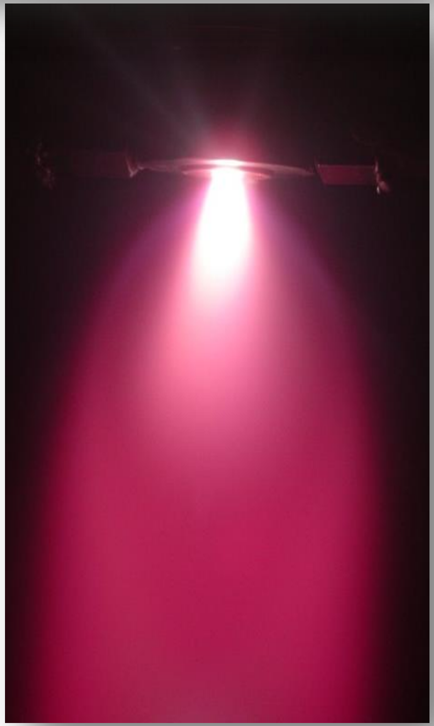

Triple cathode design

Triplex®Pro-200 Sulzer-Metco Inc.

Air Plasma Spray
- DC Plasma heat source
- SG-100, Triplex®Pro-200
- I, V, & Gas Composition affect T_p & V_p

"Vacuum" Plasma Spray
- Plasma spray at ~ ½ atmosphere (380 torr)
- Oxide-free coatings

Very Low Pressure Plasma Spray
- Plasma spray at 1.0 Torr (0.001 atm)
- Emerging Technology
- SNL has one of two systems in U.S.
- *Droplet Deposition*
- *Vapor Deposition!*
- *Thin coatings (< 50 microns)*


O3CA Metco Inc.

Plasma Spray

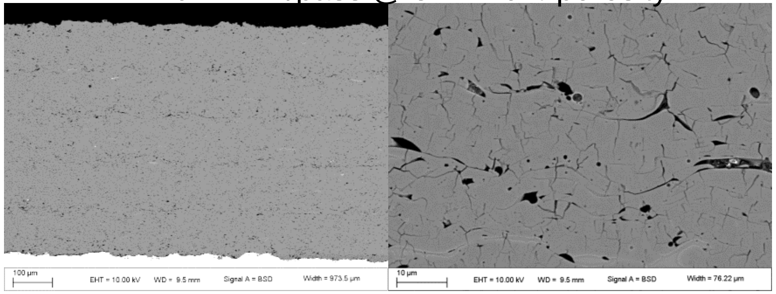
Air Plasma Spray

- Can deposit high melting point materials (ceramics, metals, composites, etc.).
- Droplet deposition
- Inherent porosity in coatings
- Coating microstructures highly depend on spray process parameters

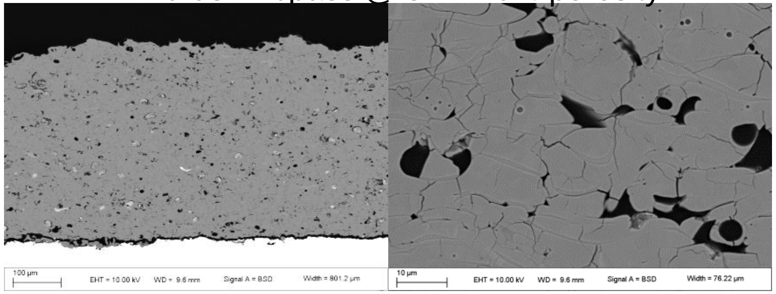
Short Standoff Distance | Long Standoff Distance

Low traverse speed

0.11mm/pass @ 5.4±1.6% porosity

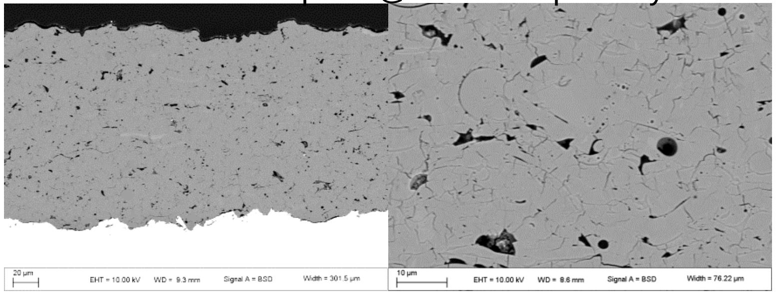


0.08mm/pass @ 8.4±2.0% porosity

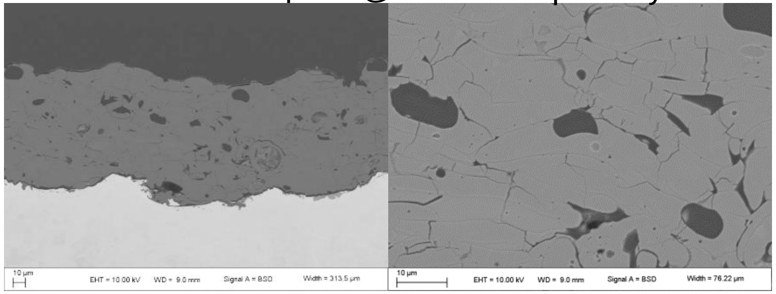


High traverse speed

0.03mm/pass @4.2±0.8% porosity



0.02mm/pass @11.0±2.6% porosity



Air plasma sprayed alumina coatings at different gun standoff distance and robot traverse speed resulted in different coating build rate and microstructures—surface roughness, porosity size and density.

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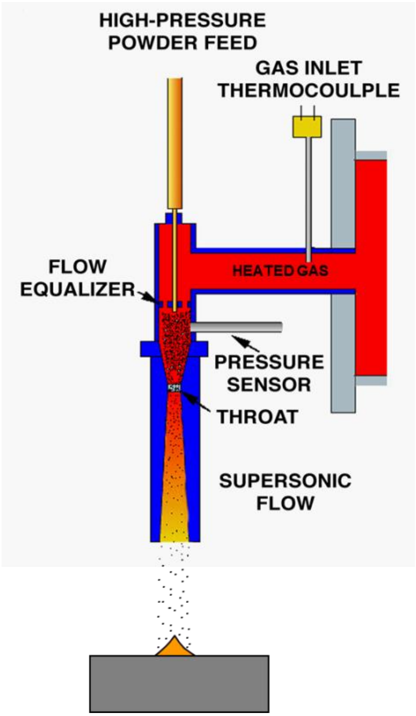
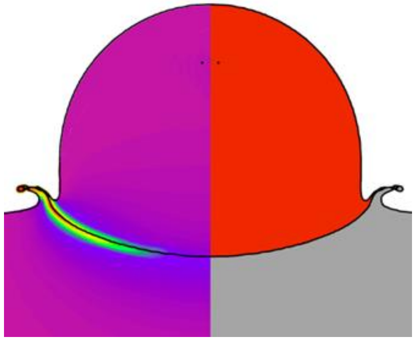
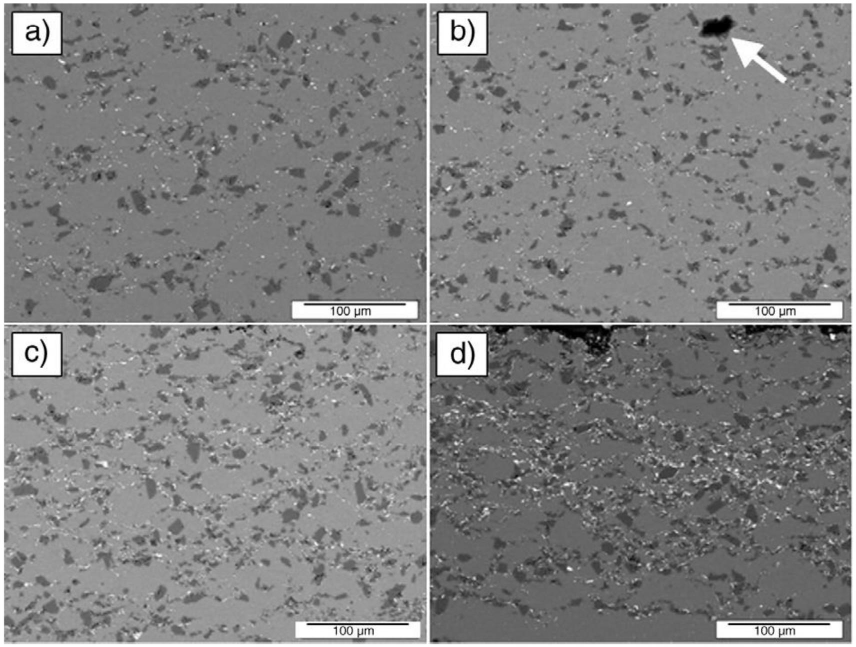
Cold Spray



Solid-state cold spray deposition is achieved through "miniature explosive welding" when a high velocity (~1000 m/s) metal particles (30µm) impact a substrate and consolidate to form a thick (inches) coatings.



Impacting cold spray particles undergo bonding phenomena similar to explosive welding



Cold sprayed Al-SiC composites with a) 20%, b) 30%, c) 40%, and d) 60% SiC by volume*

Cold spray is proven technology for creating metallurgically dense, conformal, Al-SiC deposits with considerable microstructure and property control.

*E. Sansoucya, P. Marcouxb, L. Ajdelsztajna, B. Jodoin; *Properties of SiC-reinforced aluminum alloy coatings produced by the cold gas dynamic spraying process*; Surface and Coatings Technology Volume 202, Issue 16, 15 May 2008, Pages 3988–3996

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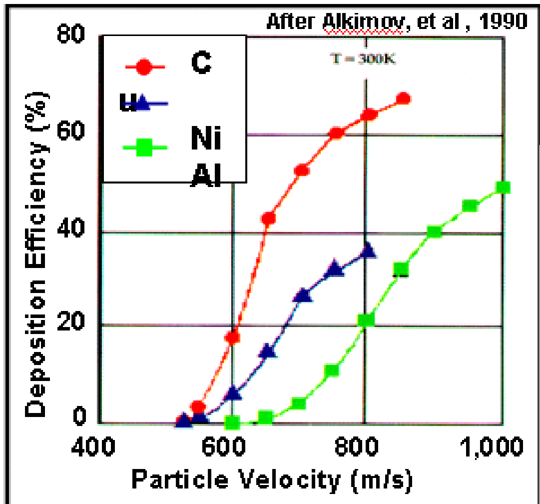
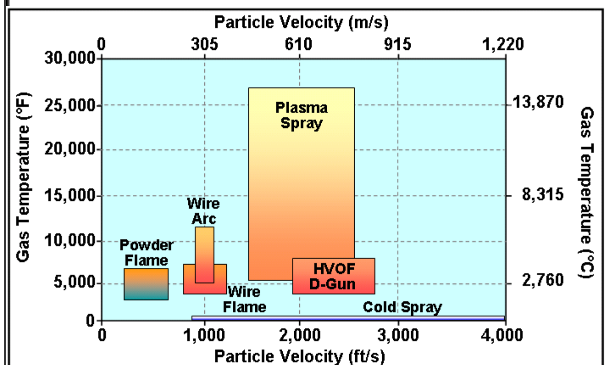
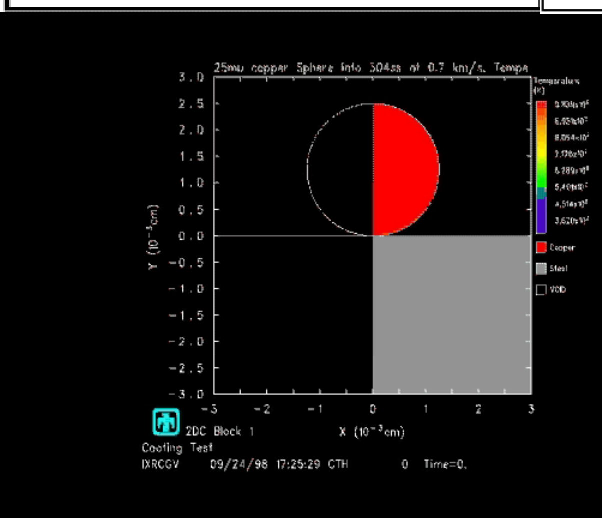
Cold Spray

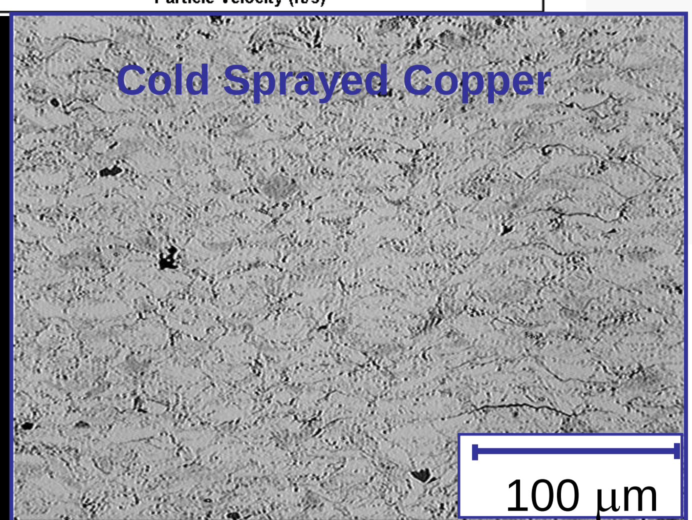
- Sold particle deposition
- High density metal coatings
- Low oxide content
- Compressive residual stress

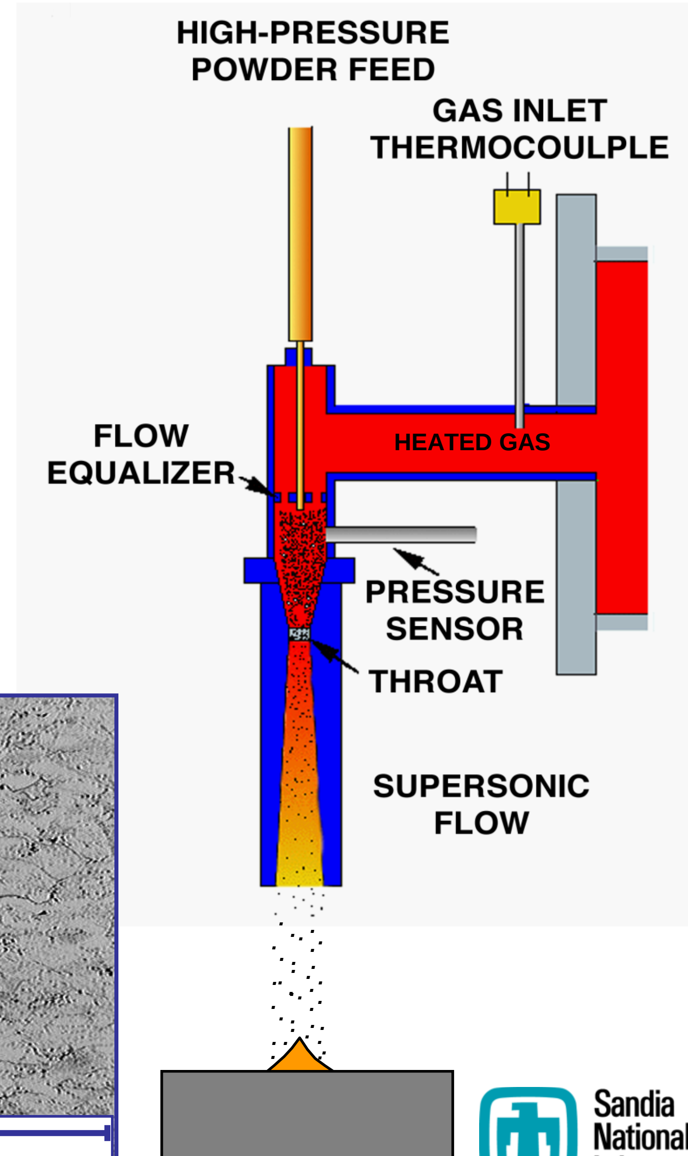
$$Vp \propto P + T$$











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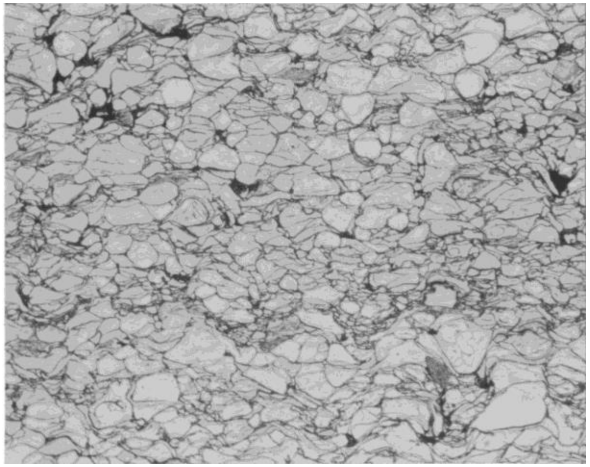
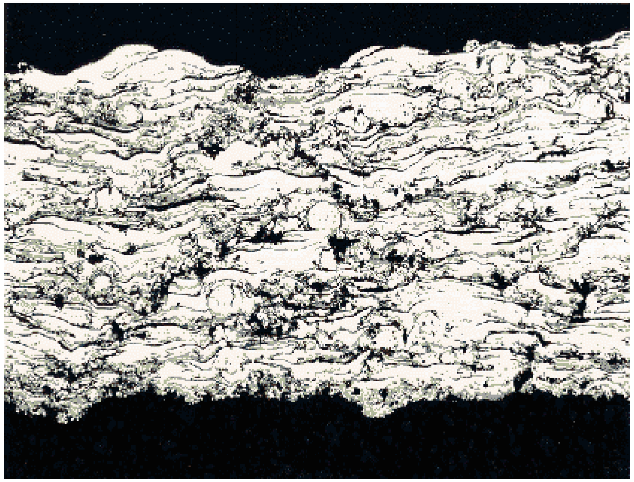
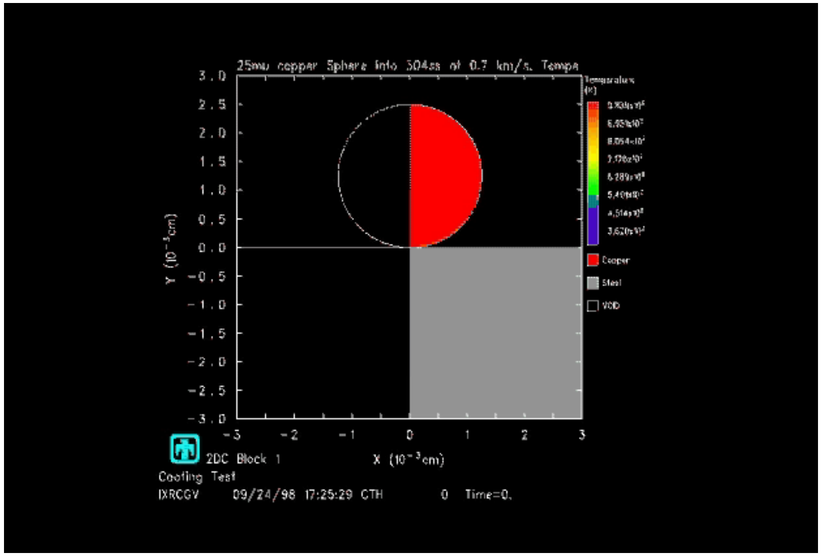
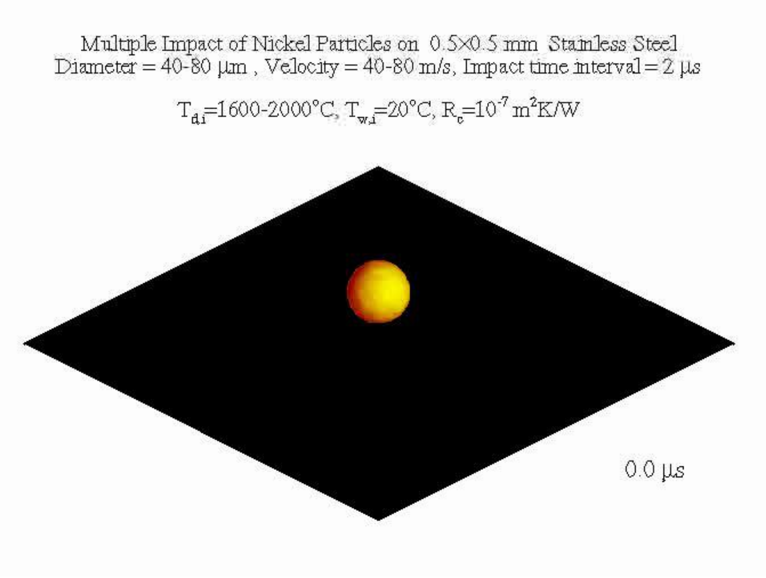
Cold Spray ≠ Thermal Spray









Solid particle impact

Liquid droplet impact

*Droplet Impact Simulation by Prof. J. Mostaghimi, et al, Univ. of Toronto, 1998.

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What Mechanical Properties & Mechanical Behavior Can We Expect From Cold Spray Coatings?

- It is well known that the cold spray process heavily cold works the coating material.
- There is very little published data on the properties of cold spray coatings.

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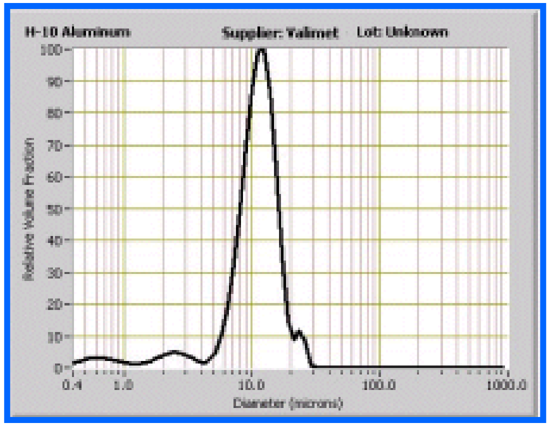
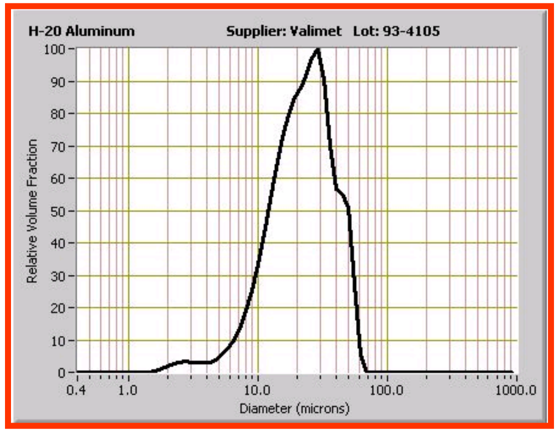
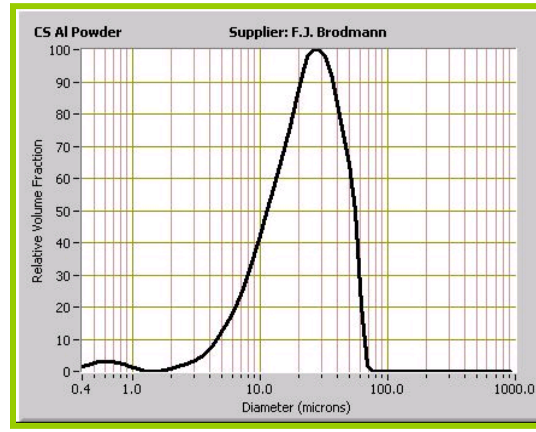
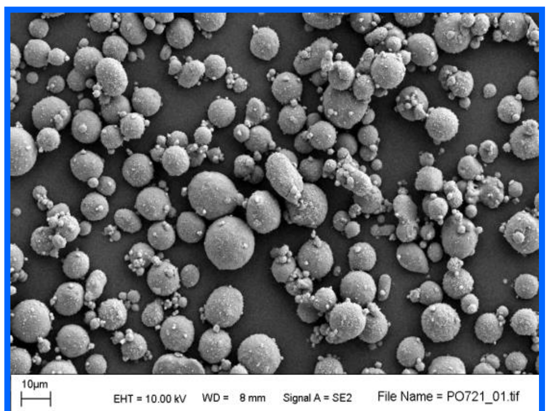
Three Different Aluminum Powders Were Investigated

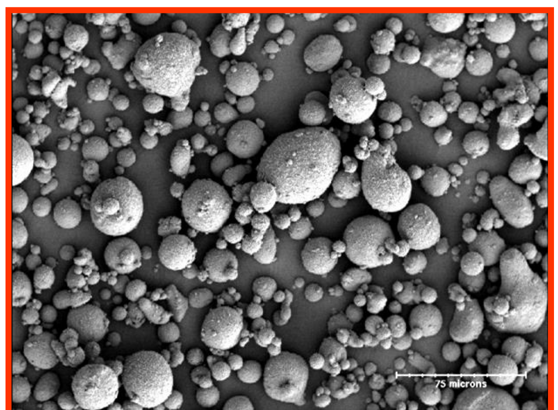
Material	H-10*	H-20	Broadman†
Manufacturing Proc.	Air Atomized	Air Atomized	Air Atomized + Oxidized
Mean Particle Size	11.77	25.87	26.38
Standard Deviation	4.90	13.23	15.10

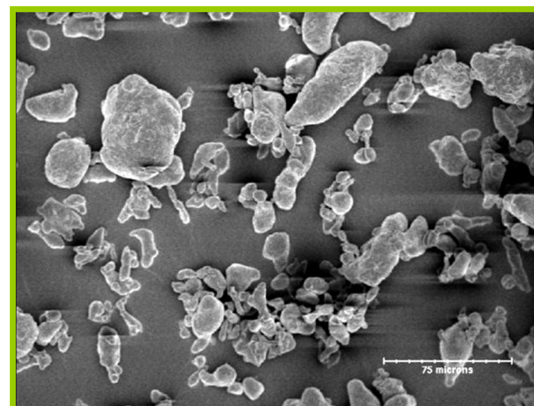












* This non-standard H-10 was sifted to reduce fines and improve flow properties.

† This powder had shown good results at Ktech when cold sprayed with nitrogen.

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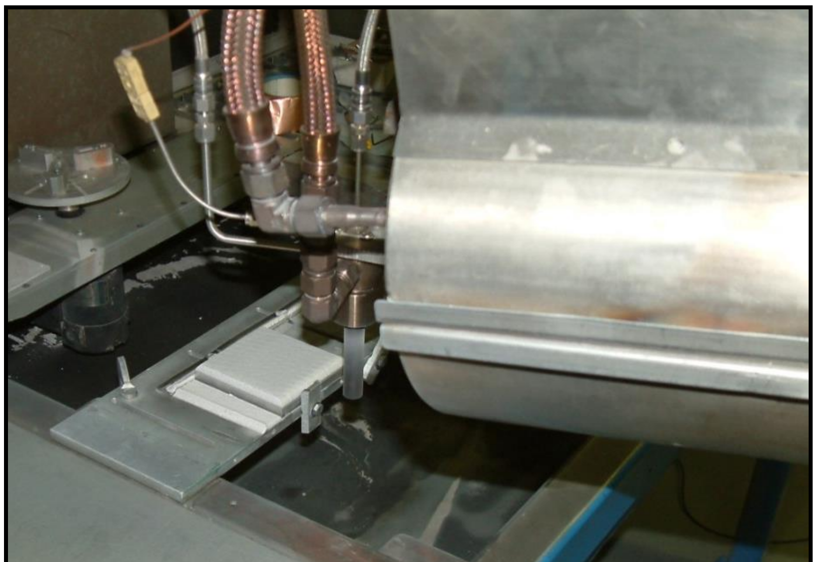
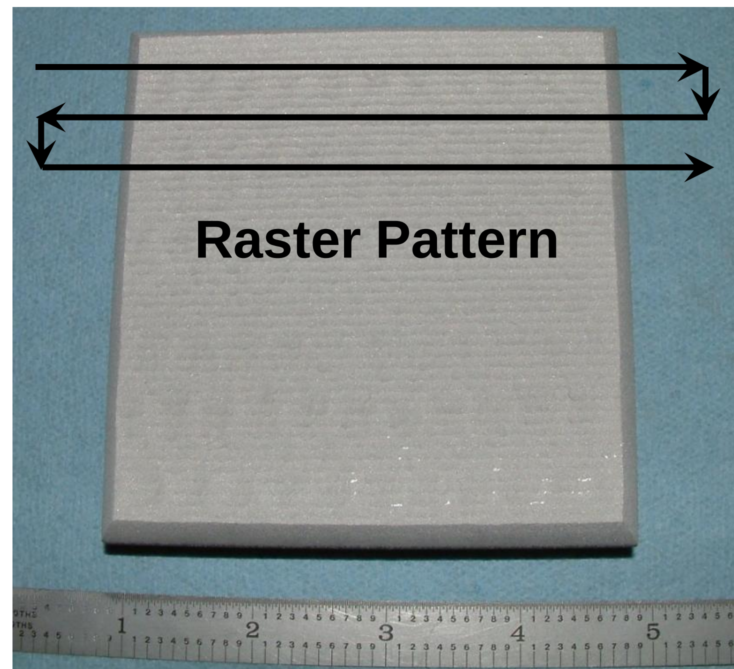
½ inch (1.27 cm) Thick Coatings Were Helium Sprayed with Each Powder

Powder	H-10	H-20	Broadman
Gas Pressure (psi / kPa)	250 / 1,724	325 / 2,241	225 / 1,551
Gas Temp. (°C)	350	375	400
Estimated V_p (m/s)	1117	880	871



Coatings being deposited onto 4x4 inch (10x10 cm) Al coupons at Ktech



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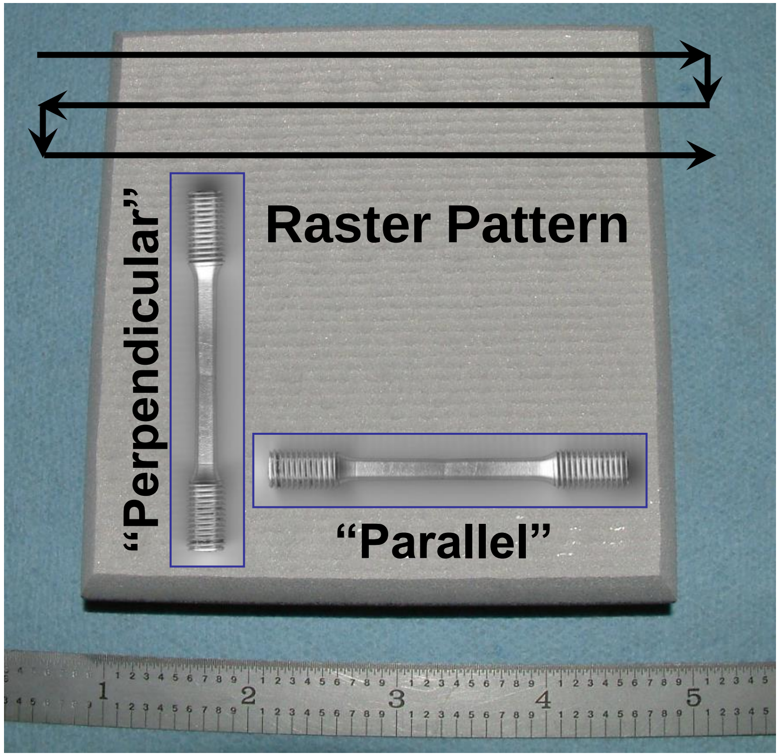
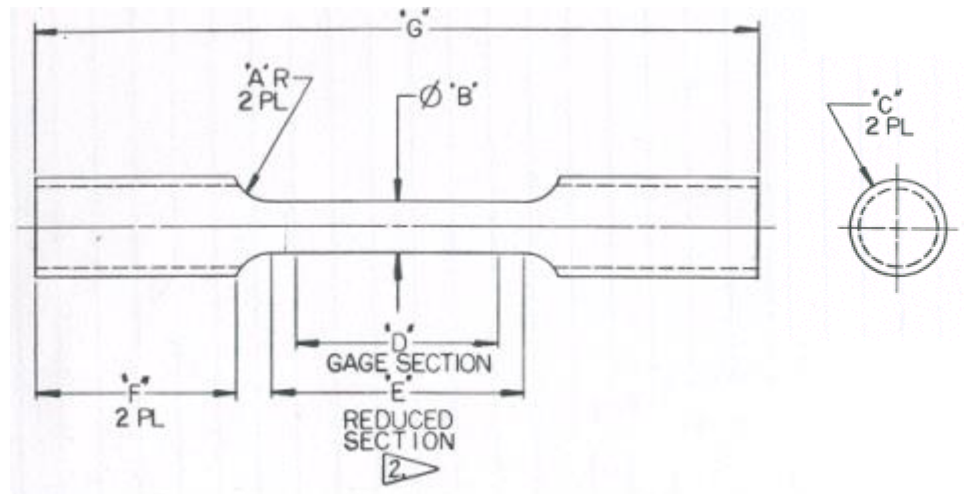
Modified* ASTM E8 Tensile Bars Were Machined from Coatings

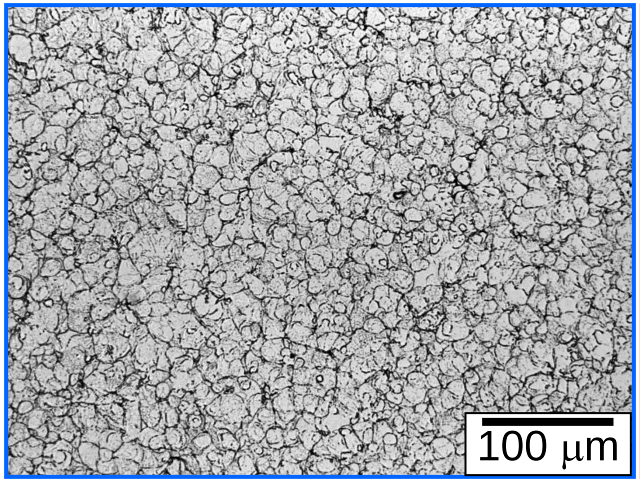


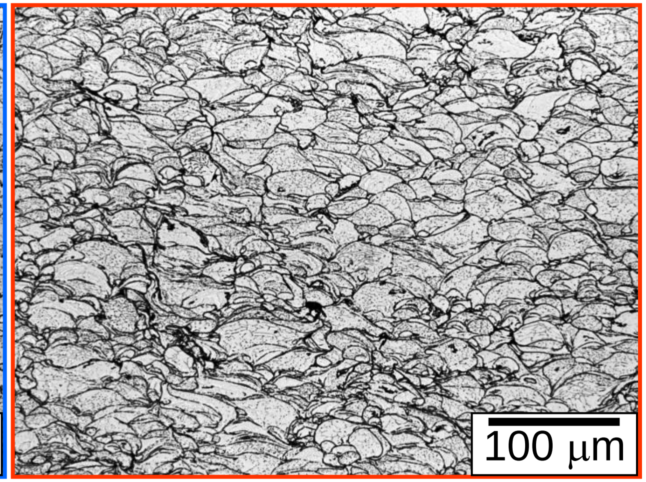
Radius (A):	**0.188 ± 0.10**
Gage Diameter (B):	**0.180 ± 0.005** ***(*Normally 0.250)***
Grips (C):	**5/16-24 UNF**
Gage Length (D):	**1.000 REF**
Reduced Section (E):	**1.250 ± 0.010**
Grip Length (F):	**0.500 ± 0.10**
OAL (G):	**2.625 REF**

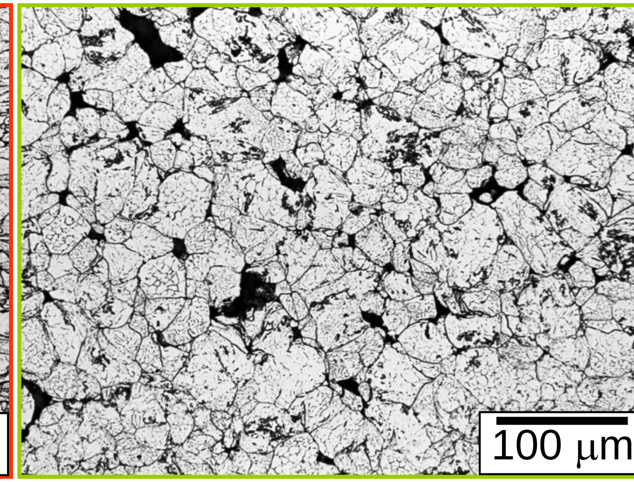


Annealed H-10 Sample After Testing

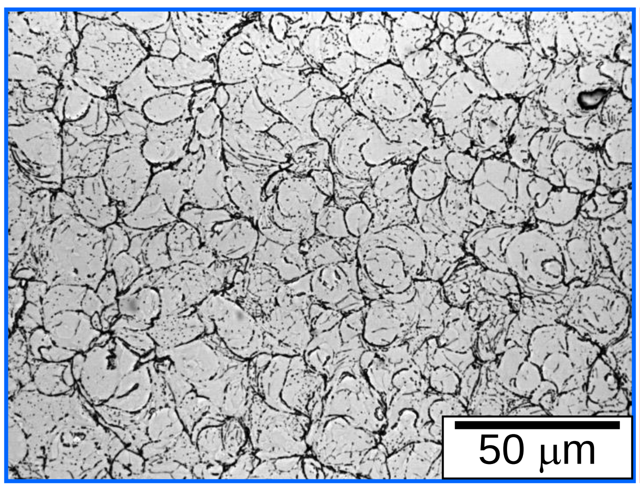
As-Sprayed Microstructures Reveal Some Obvious Differences

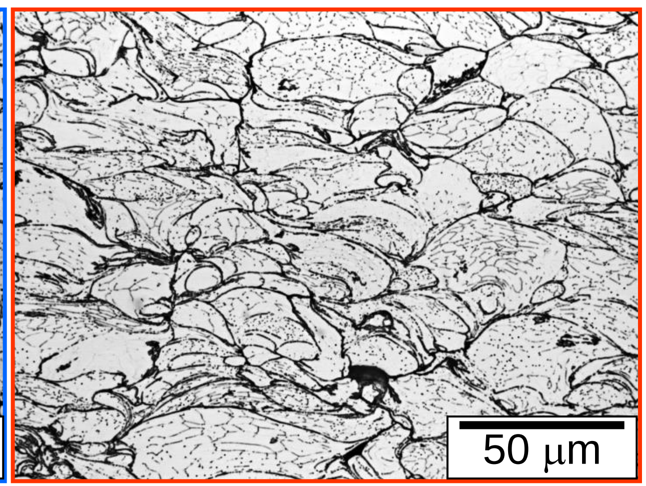


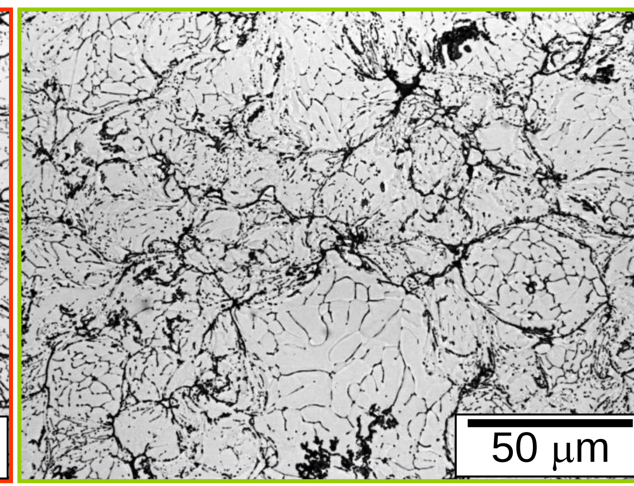




H-10 | **H-20** | **Broadman**







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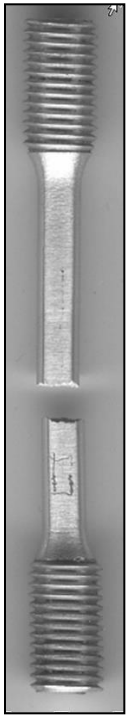
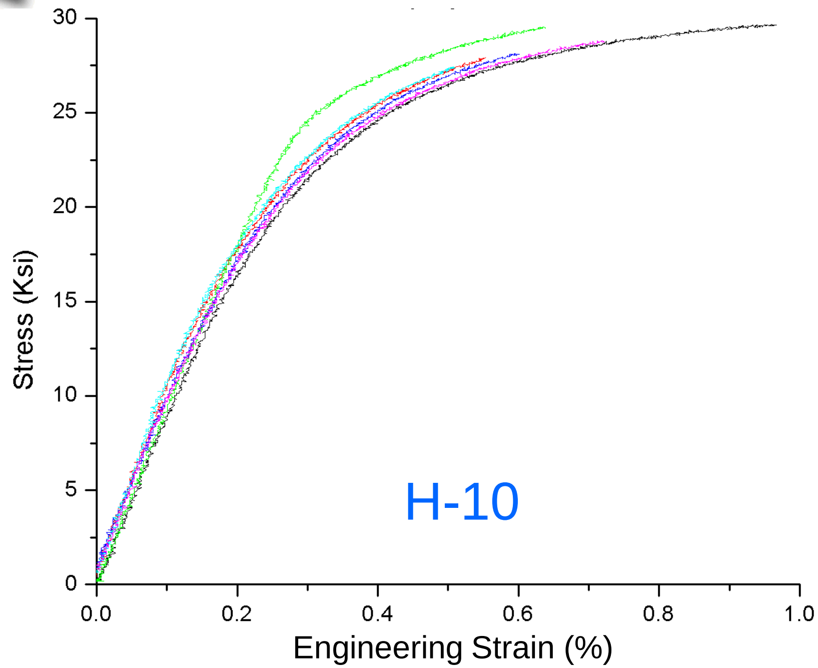
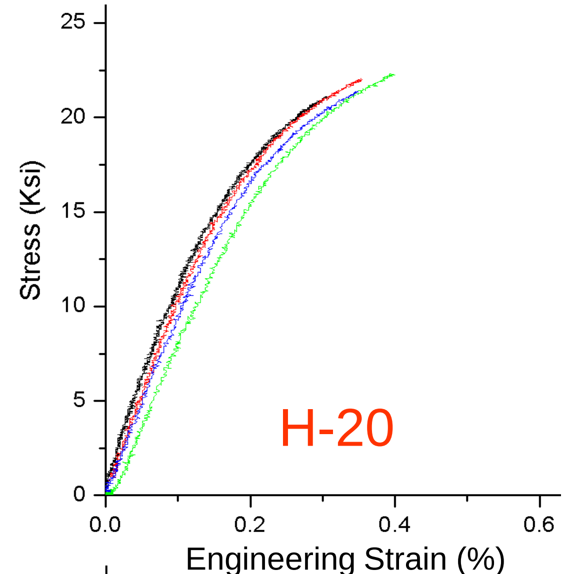
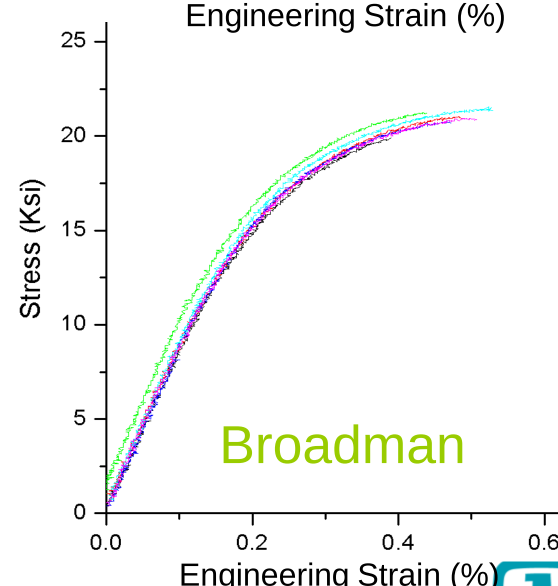
H-20 Compared to H-10 & Broadman



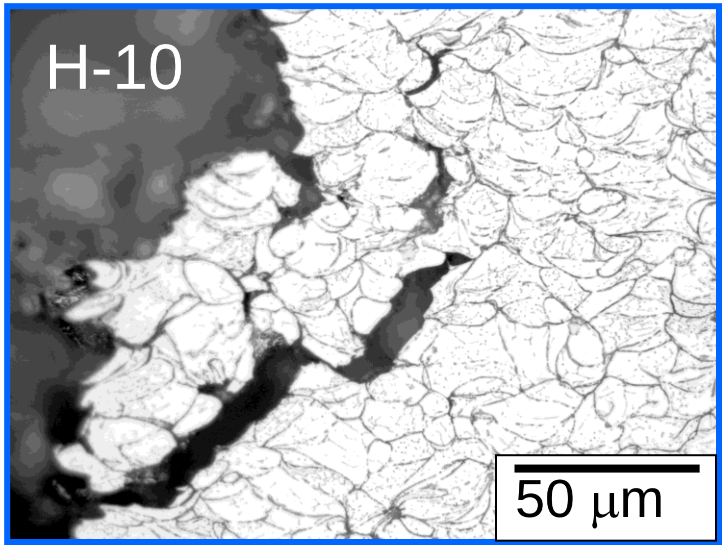


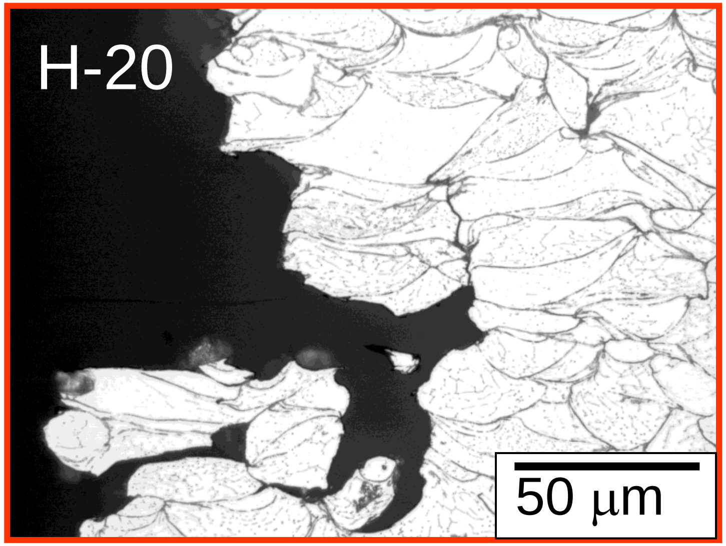




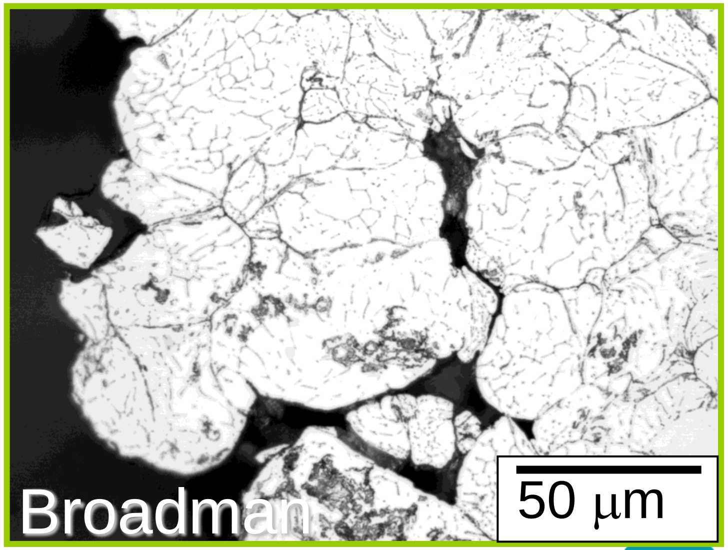
- H-10 significantly higher strain & UTS
- Broadman slightly more strain, similar UTS
- All are basically brittle as-sprayed

Cross Sections of As-Sprayed Failure Surfaces





- Separation primarily along splat/grain boundaries
- No indication of significant plastic flow
- Micrographs are consistent with stress/strain plots



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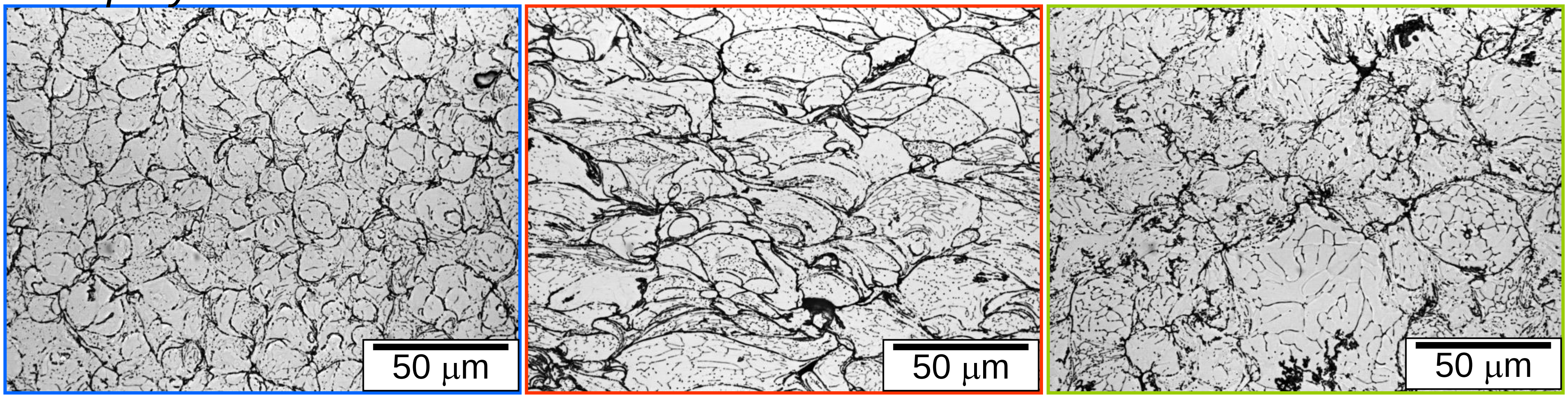
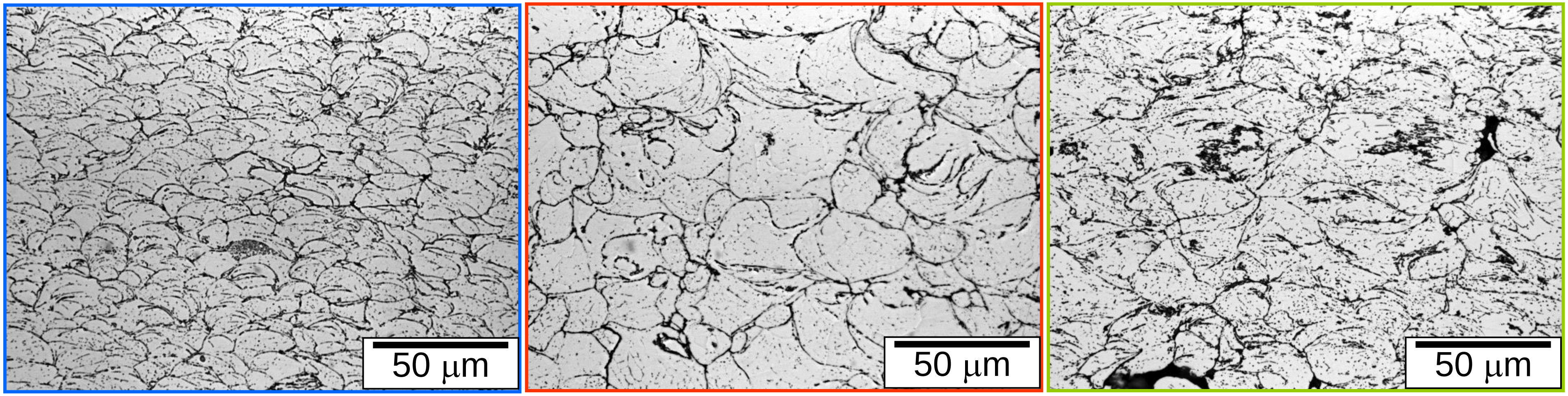
Samples Annealed 22 hours @ 300°C Look Much Like As-Sprayed Material

As-Sprayed



H-10 | H-20 | Broadman



Annealed

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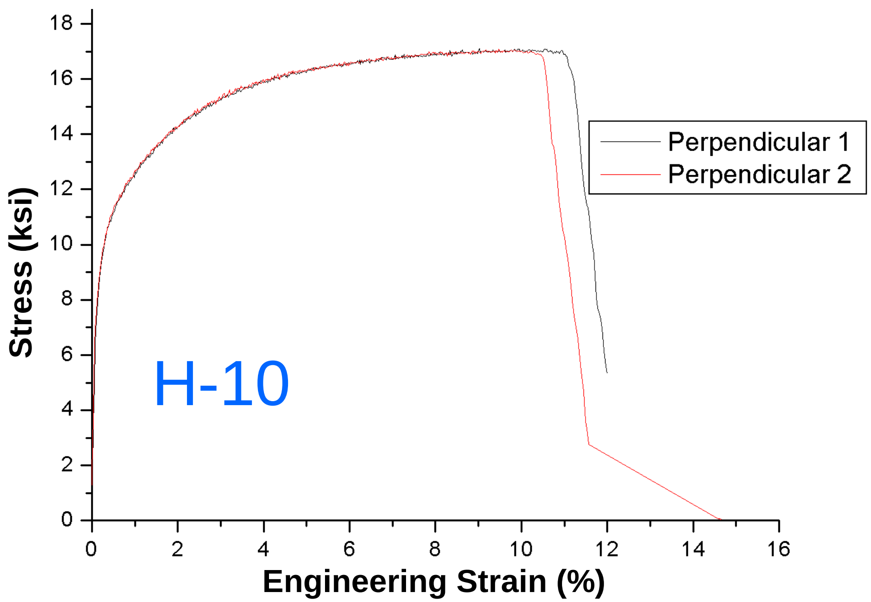
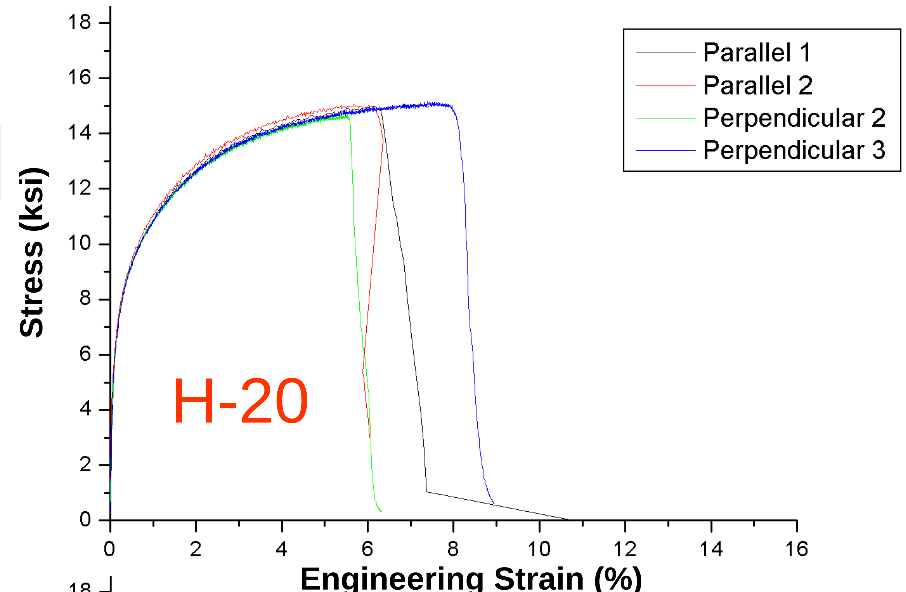
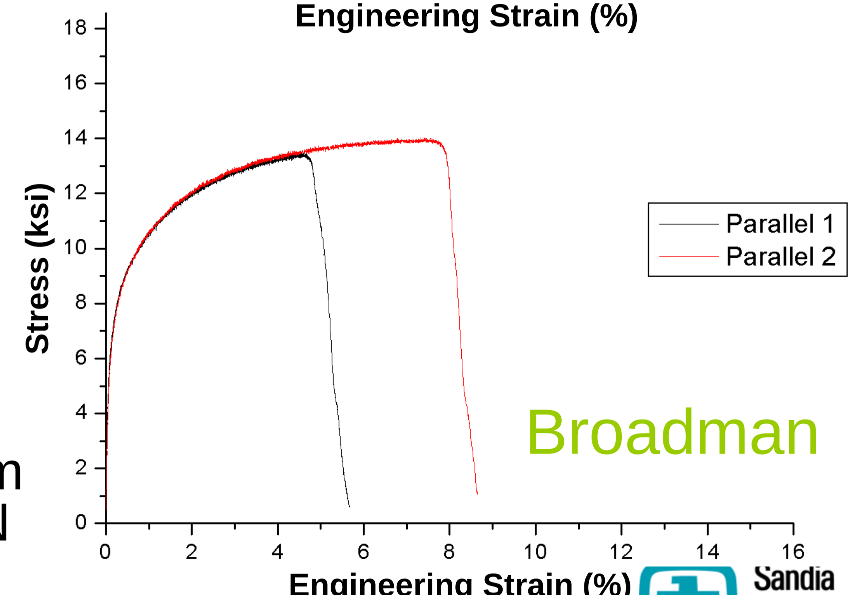
But, Annealing at 300°C for 22 hours Dramatically Alters Mechanical Behavior







- H-10 shows the greatest ductility and slightly higher strength
- Broadman very similar to H-20
- Strain-to-failure increased from ~ 0.4 - 0.6% AS to ~ 6 - 11% AN
- Ultimate Tensile Strength reduced from ~ 21 – 28 ksi AS to ~ 14 – 17 ksi AN

(AS = As-Sprayed AN = Annealed)

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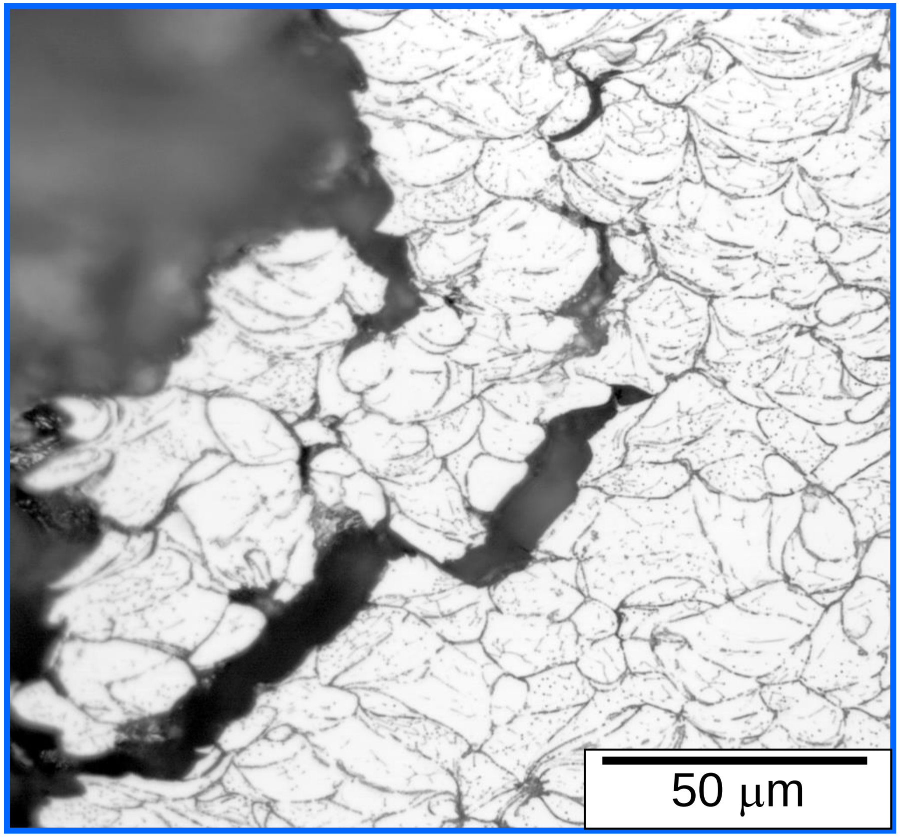
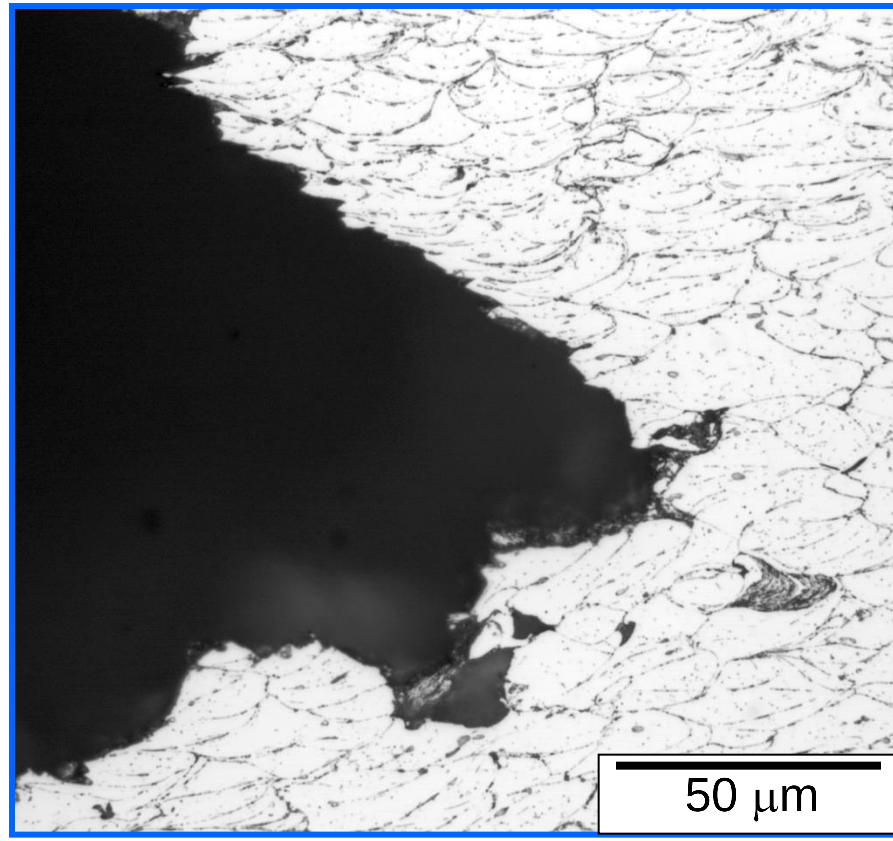
Cross Sections Clearly Reveal Change in Fracture Modes for H-10

As-Sprayed



- Little apparent elongation or flow
- Fracture primarily along boundaries

Annealed



- Elongation & flow very evident
- Trans-splat/grain fractures

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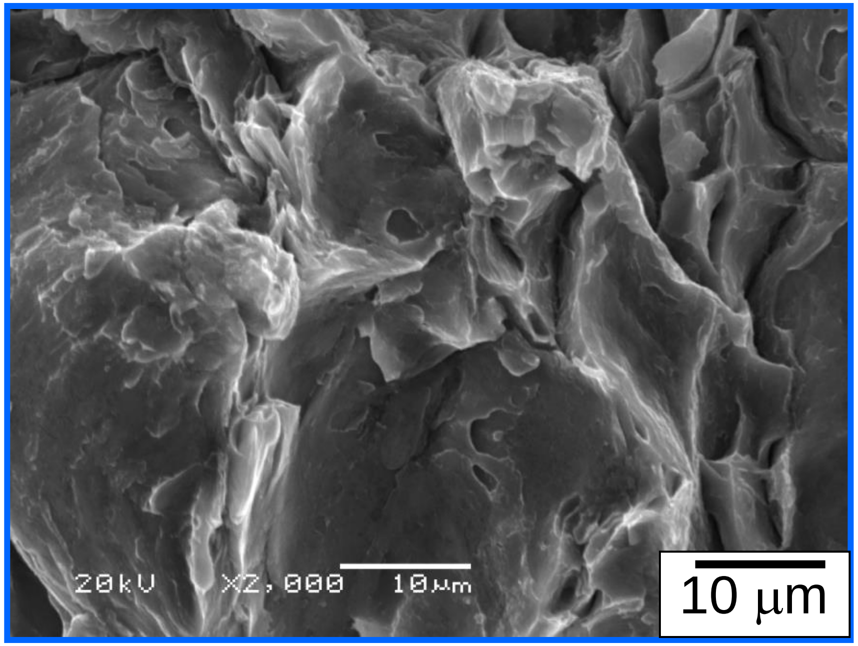
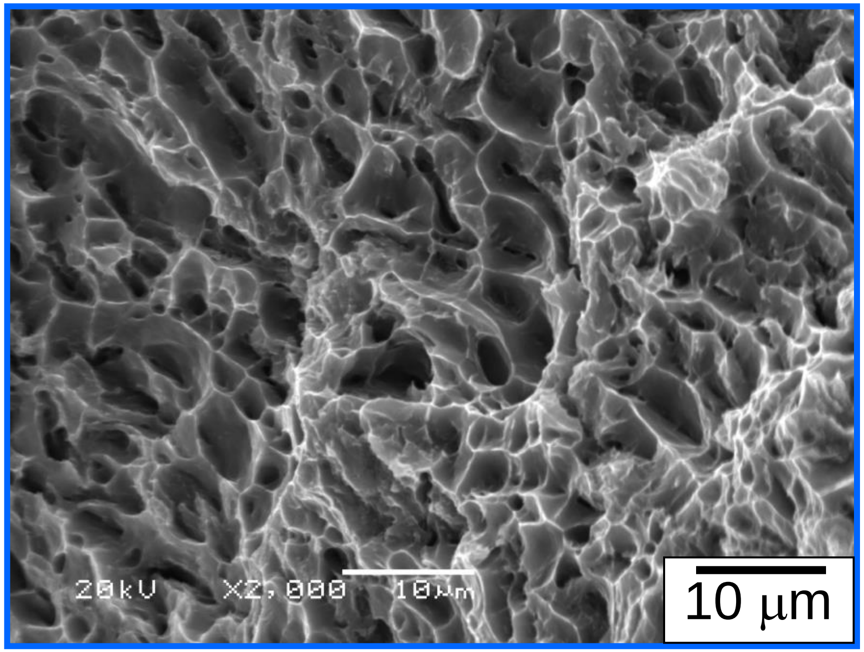
Examination of Fracture Surfaces also Reveals Obvious Differences

H-10 As-Sprayed



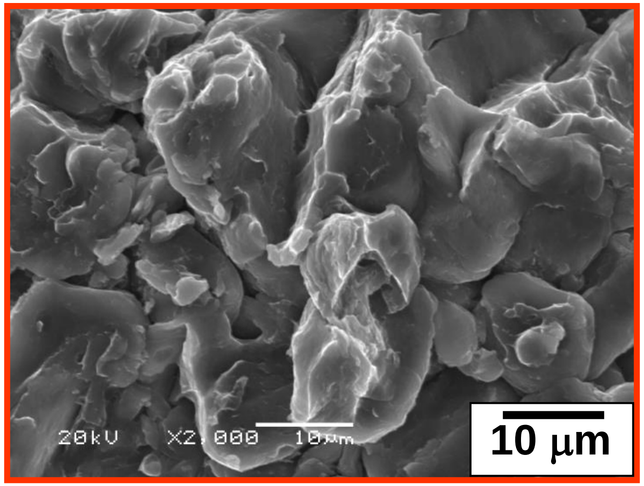
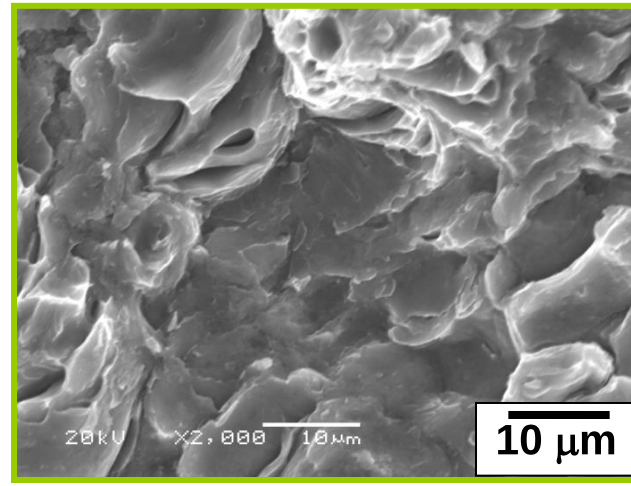
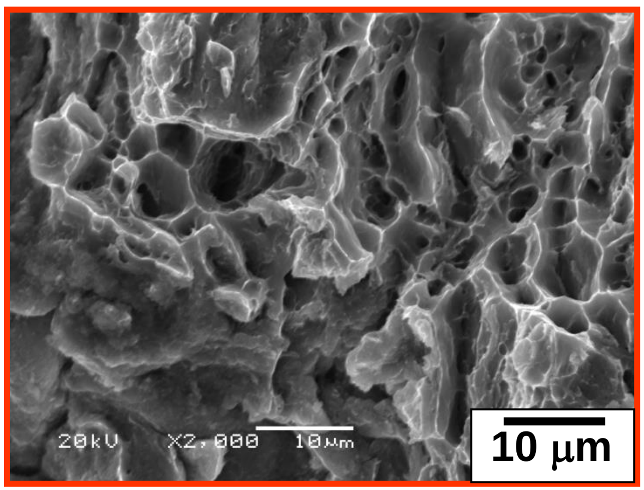
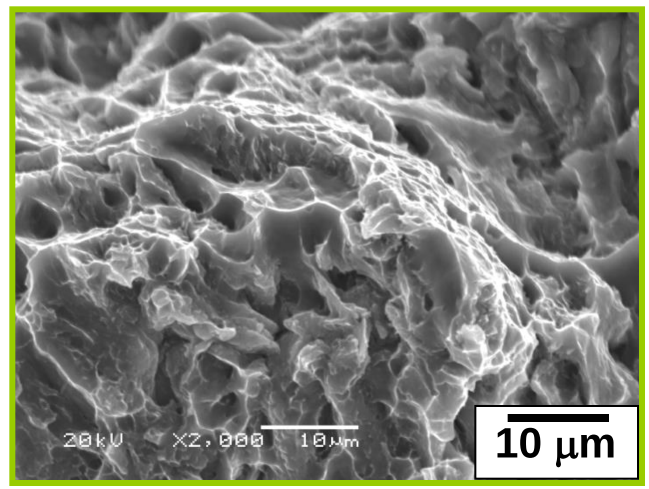
H-10 Annealed



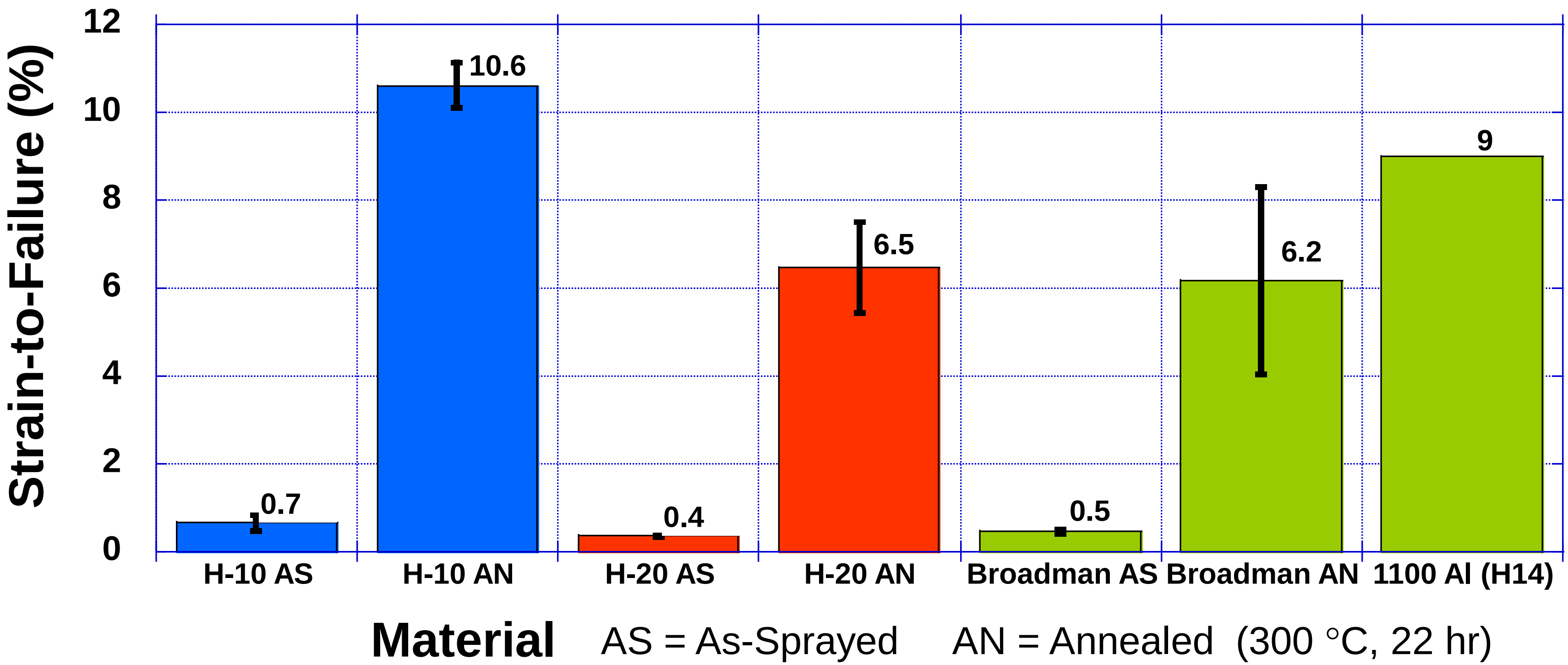
- Features on scale of original splats
- Relatively smooth, “blocky” surfaces
- Absence of classic ductile features

- Features much smaller than splats
- Rough surfaces with ridges or “lips”
- Classic ductile features

Similar Changes Observed with the Other Powders

	H-20	Broadman
As-Sprayed		
Annealed		

Strain-to-Failure Comparison



- Post-anneal elongation is dramatically increased for each powder
- H-10 shows greatest increase, exceeds ductility of wrought 1100 Al (H14)
- H-20/Broadman results are very similar, despite differences in powder and spray conditions

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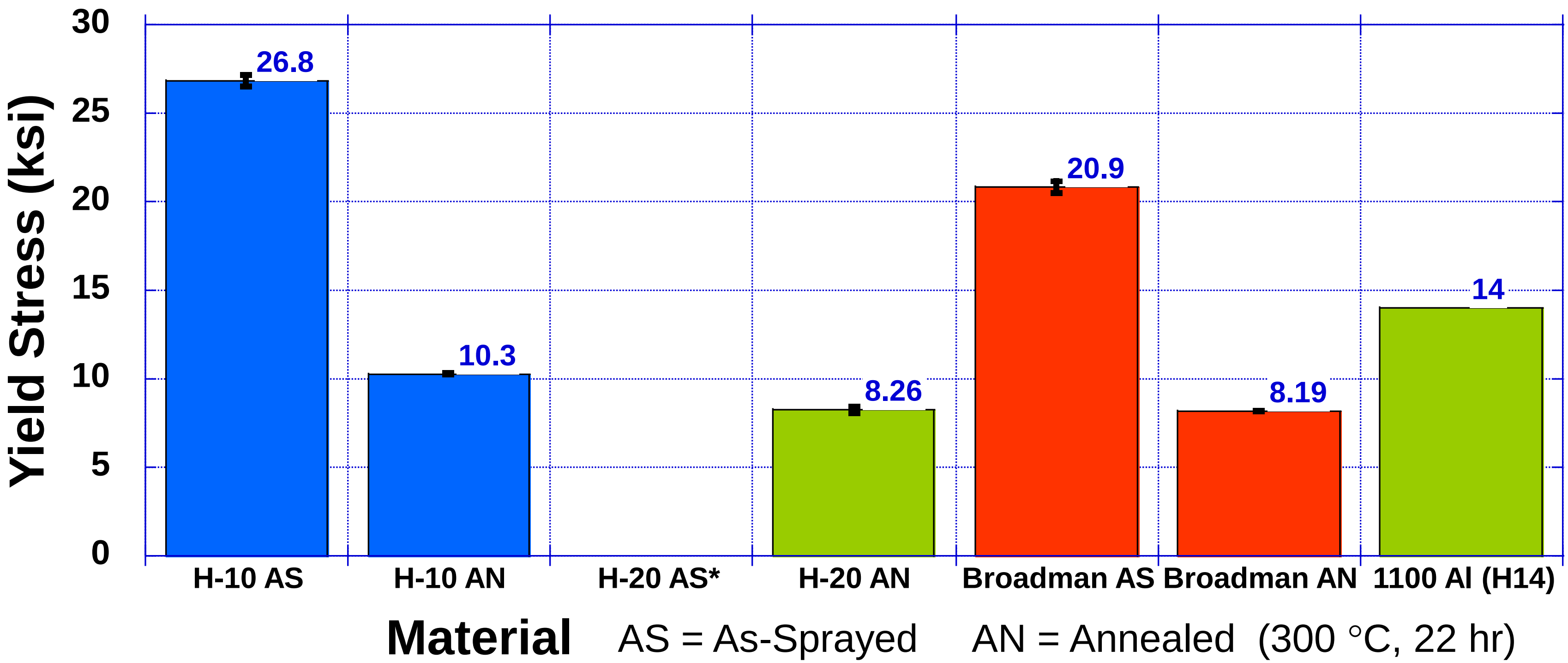
Yield Strength Comparison



AS = As-Sprayed   AN = Annealed (300 °C, 22 hr)

- H-20 was too brittle to determine as-sprayed Yield Stress (YS)
- Anneal reduced H-10 & Broadman YS by more than 60%
- Post-anneal H-20/Broadman YS very similar; H-10 slightly higher
- Pre/post anneal results bracket literature value for 1100 Al (H14 condition = ~50% of full potential strain hardening, no anneal)
- *No yield data available for H-20 AS, complete brittle fracture.

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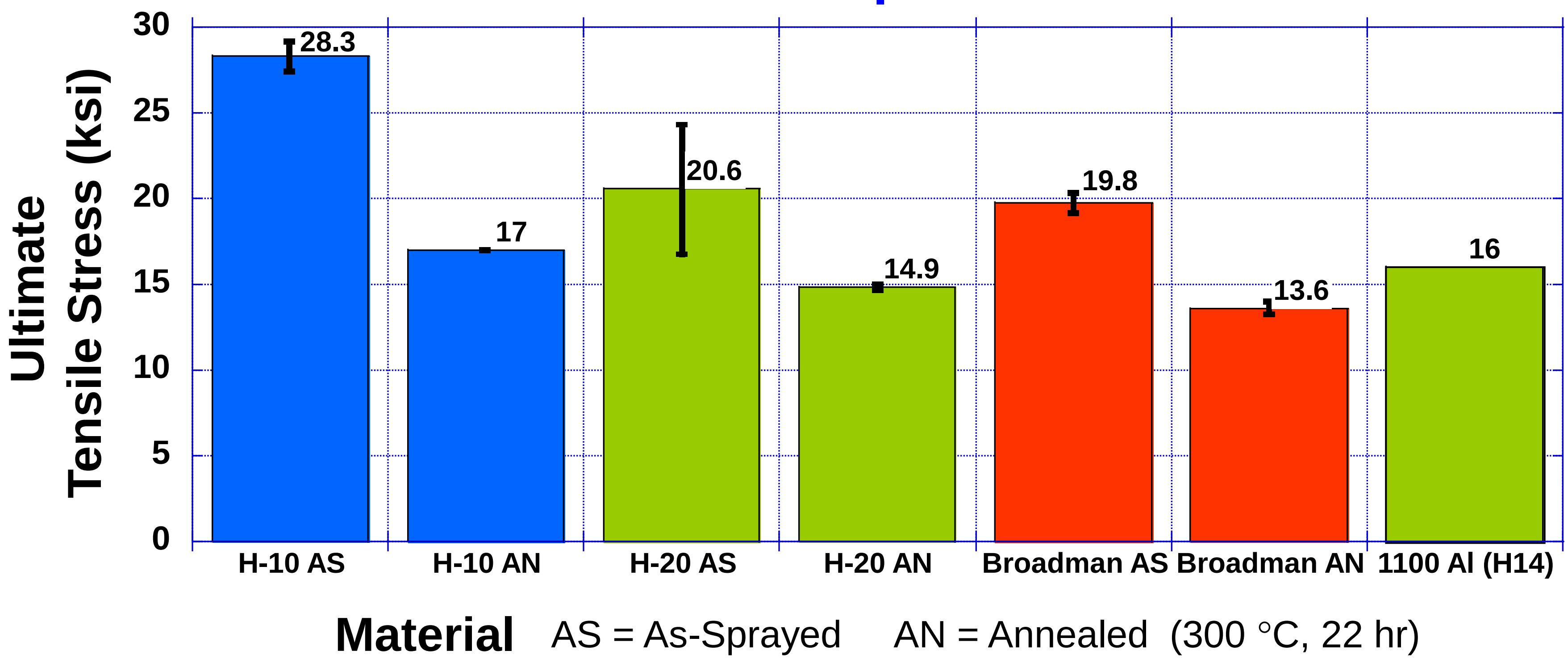
Ultimate Tensile Strength Comparison



- Post-anneal ultimate strength is significantly lower in each case
- H-10 results are somewhat higher than the other two powders
- H-20/Broadman results are very similar
- Results again look reasonable in comparison to 1100 Al (H14)

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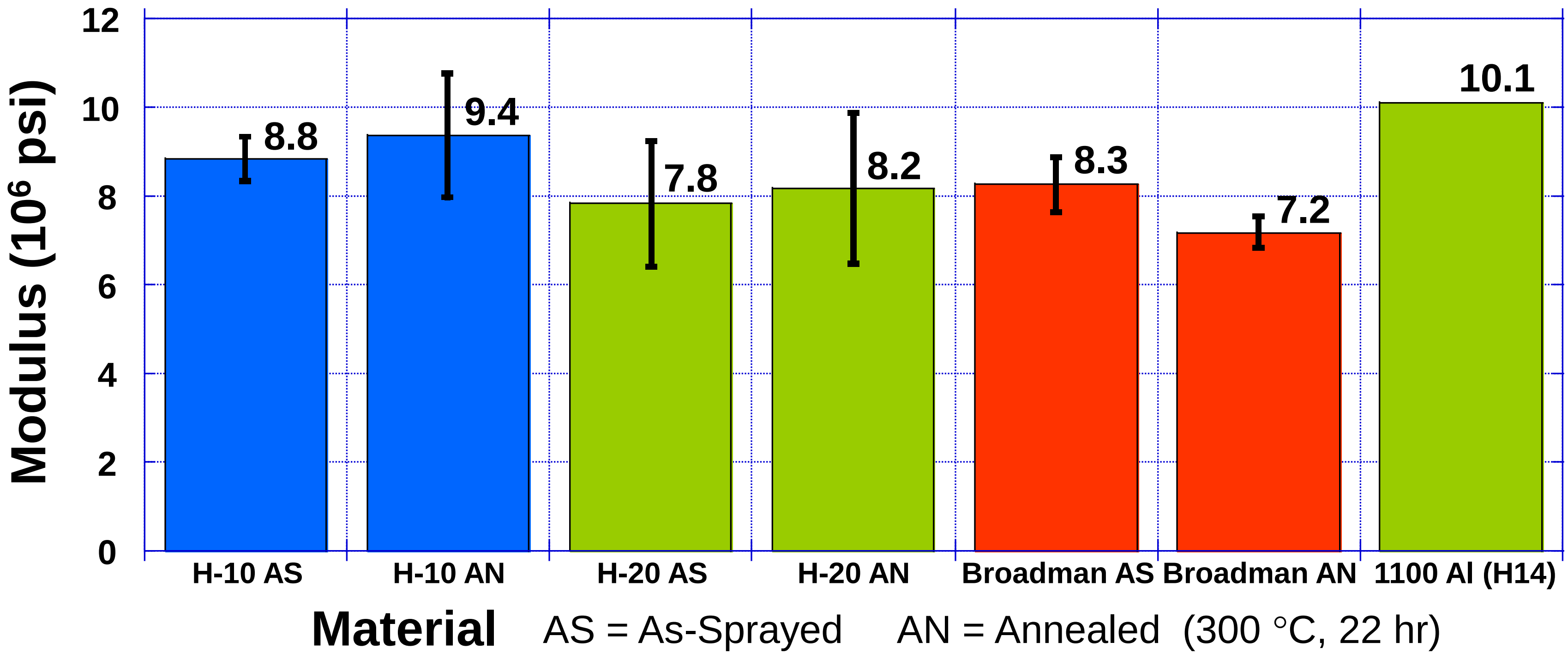
Comparison of Modulus Results



- Difficult to extract *accurate* modulus numbers from tensile plots
- Would not expect the anneal to affect true modulus
- Unlikely that small differences are real considering scatter in data (Overall Avg. ~ $8.3 \pm 0.8 \times 10^6$ psi or 57 ± 6 GPa)
- Average is slightly lower than the literature value for 1100 Al

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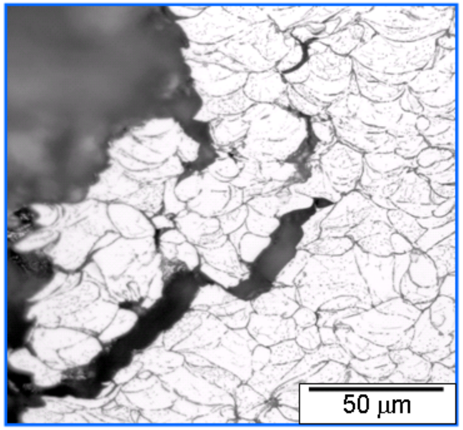
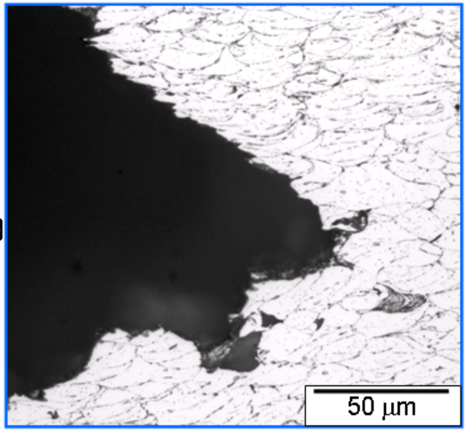
What is the mechanism for the observed change in ductility upon annealing?

- Bonding in cold spray coatings can occur by two mechanisms:
  - Mechanical Bonding
  - Metallurgical Bonding
- As-sprayed material fractures at particle boundaries.
- Annealed material fracture within particles.
- No significant change in apparent particle size upon annealing.
- Two possible mechanisms for increase in ductility:
  - Reduction of dislocation density in cold worked material
  - Strengthening of interparticle boundaries due to diffusion and / or recrystallization across splat boundaries.



Annealed



As-Sprayed

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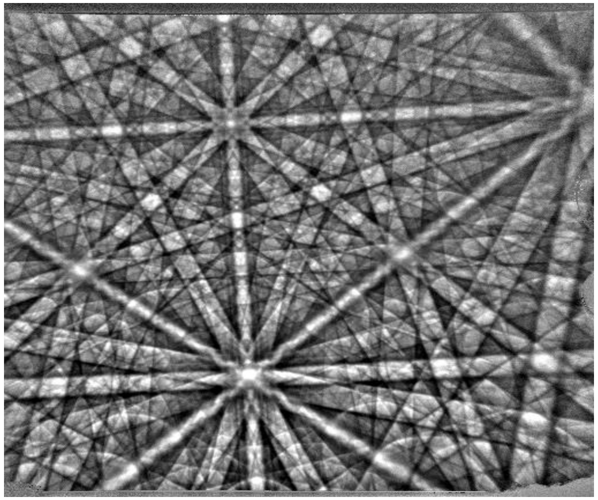
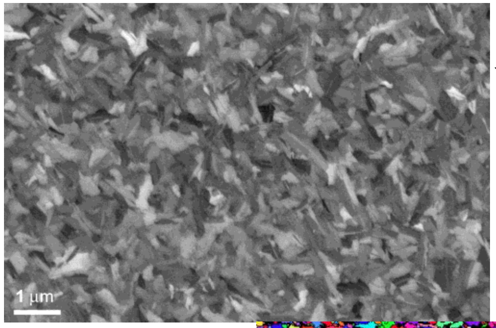
Electron Backscattered Diffraction (EBSD) or Kikuchi Mapping

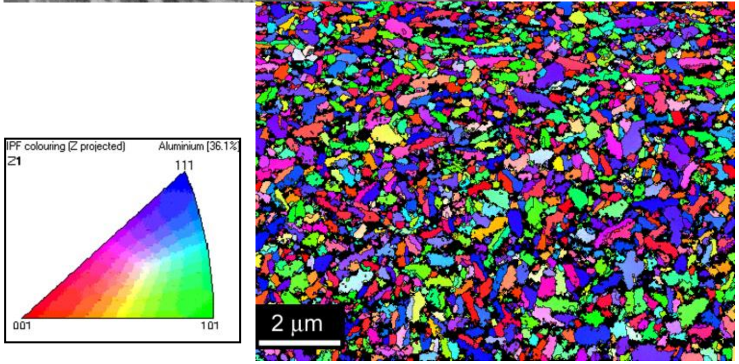
- SEM based technique to collect electron backscattered diffraction patterns
- Phase identification
- Orientation mapping
- Grain boundary identification

Electron Backscattered Diffraction Pattern



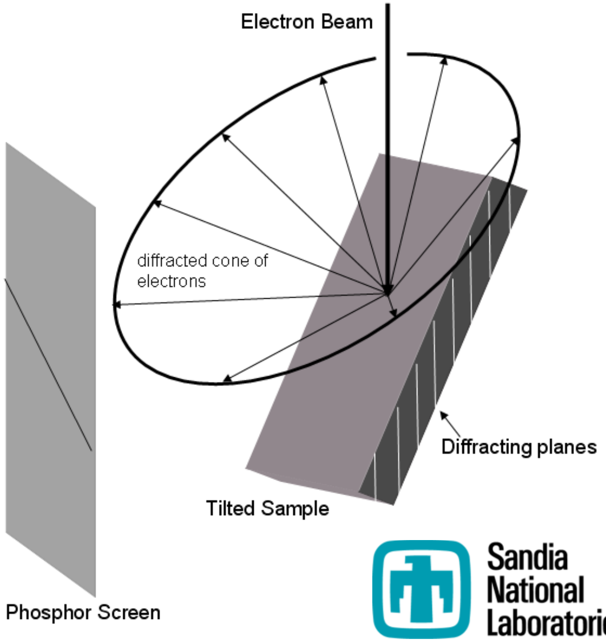


SEM Image of Polycrystalline Silicon



EBSD Map of Polycrystalline Silicon

EBSD Sample, Camera and Electron Beam Arrangement



** J. R. Michael; R. P. Goehner: Electron backscatter diffraction: A powerful tool for phase identification in the SEM; Conference: Materials Research Society Fall Meeting 29 Nov 1999 – 3 Dec 1999: Boston, MA*

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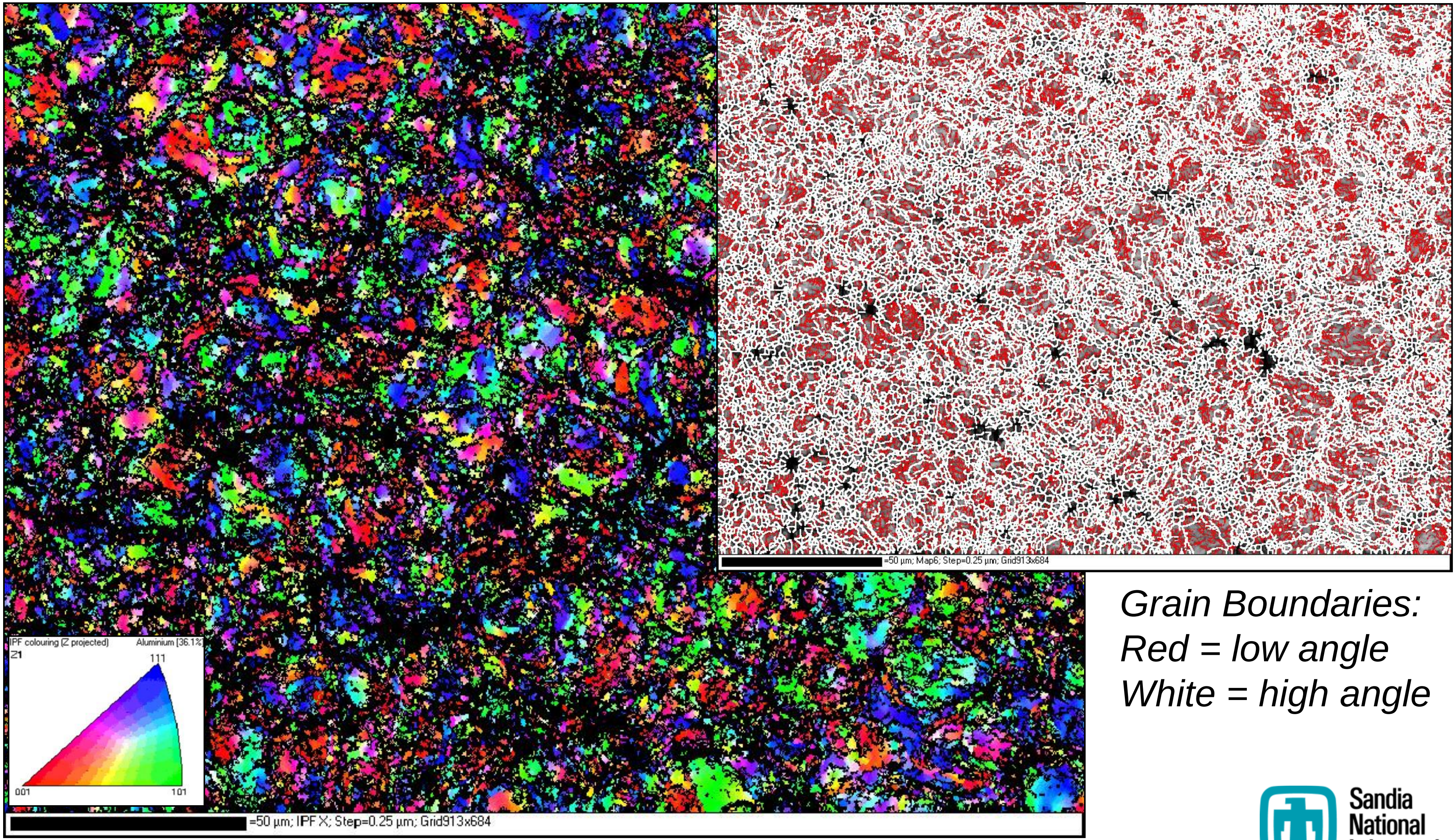
EBSD (Kikuchi) Map of As-Sprayed H-10 shows fine grain structure & high dislocation density due to heavy cold work.



Grain Boundaries:
Red = low angle
White = high angle

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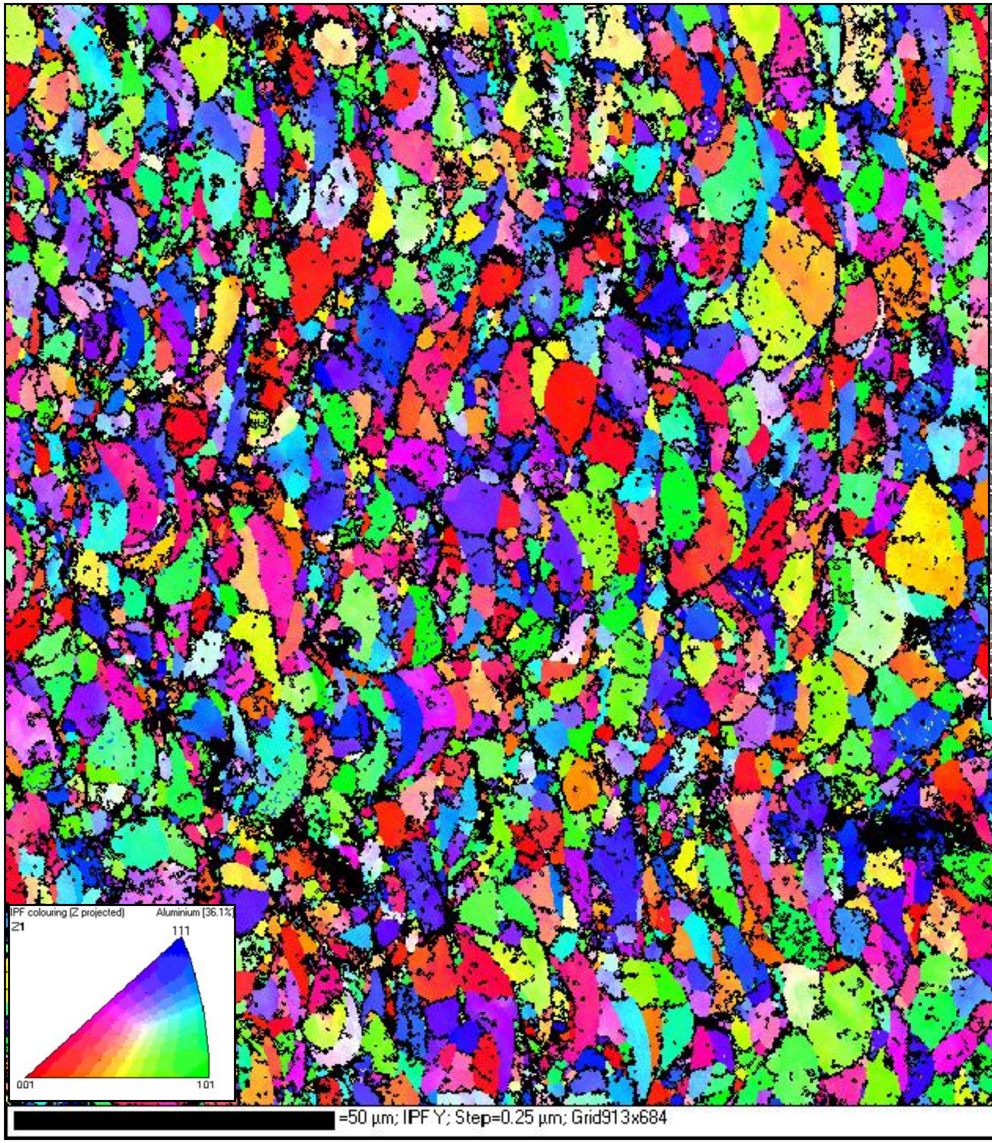
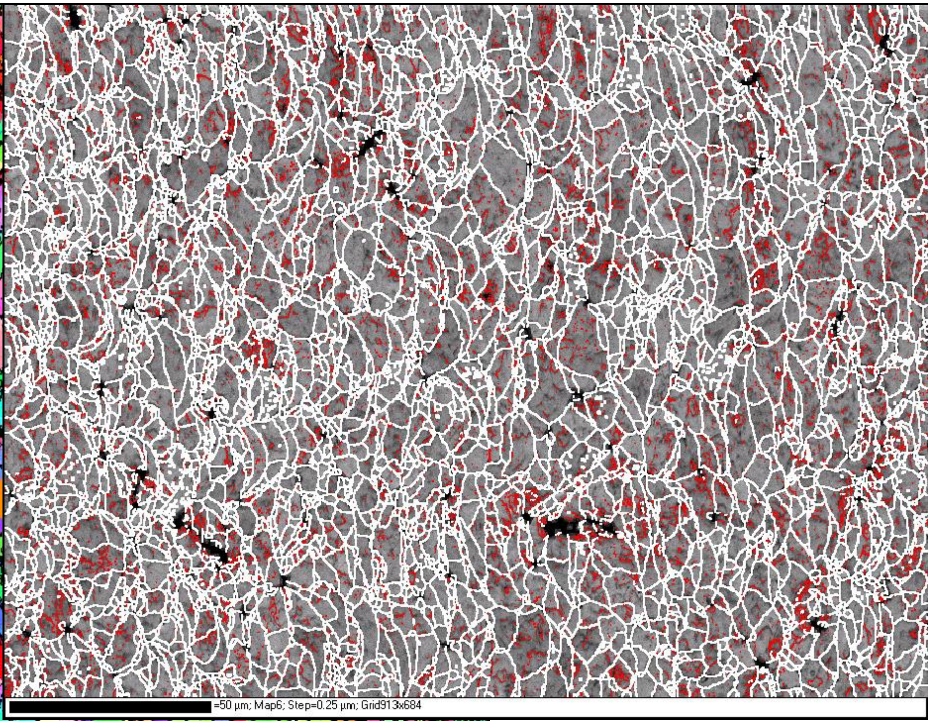
EBSD (Kikuchi) Map of Annealed H-10 shows significant recrystallization, grain growth, and reduction of dislocation density.





Grain Boundaries:
Red = low angle
White = high angle

Cold Spray of Nano-crystalline Aluminum

MS&T '07 September 16-20, 2007
Detroit, Michigan

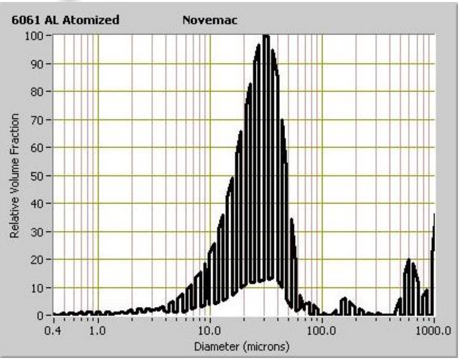
A. C. Hall, L. N. Brewer,
Sandia National Laboratories; Albuquerque, NM

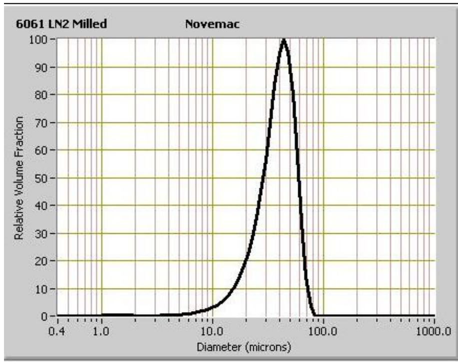
T. J. Roemer
Ktech Corporation; Albuquerque, NM

***Sandia is a multi-program laboratory operated by Sandia Corporation for the United States Department of Energy under contract DE-AC04-94AL85000.**

Exceptional Service in the National Interest

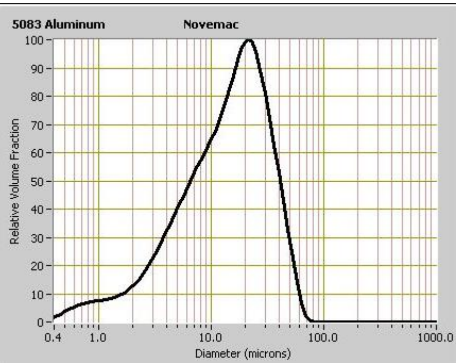
Spherical gas atomized 6061 & 5083 aluminum powders were LN_2 ball milled to create a feedstock with a nanocrystalline microstructure

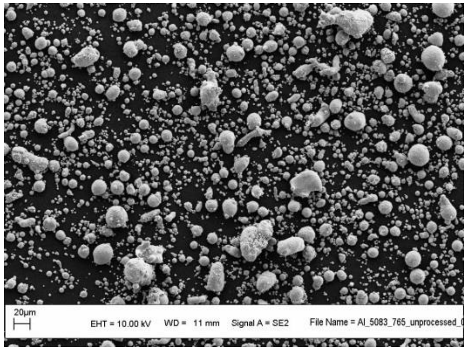


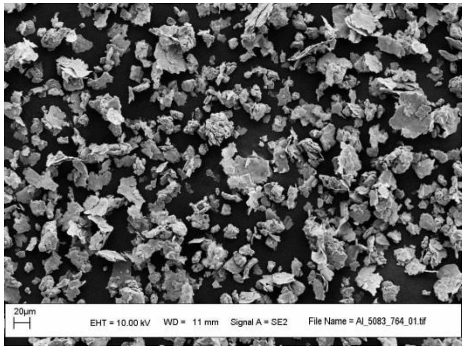


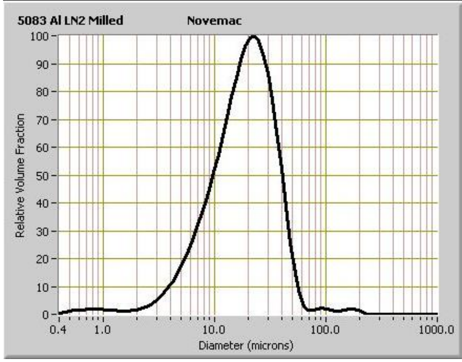
Gas Atomized (As-received)

LN_2 Ball Milled









Powder / Condition	Mean Size	Standard Deviation	Morphology
6061 Al / Gas Atomized (As-received)	27.8	13.67	Spherical
6061 Al / Gas Atomized & LN2 Ball Milled	40.7	14.44	Platelet
5083 Al / Gas Atomized (As-received)	18.2	13.6	Spherical
5083 Al / Gas Atomized & LN2 Ball Milled	22.6	17.8	Platelet

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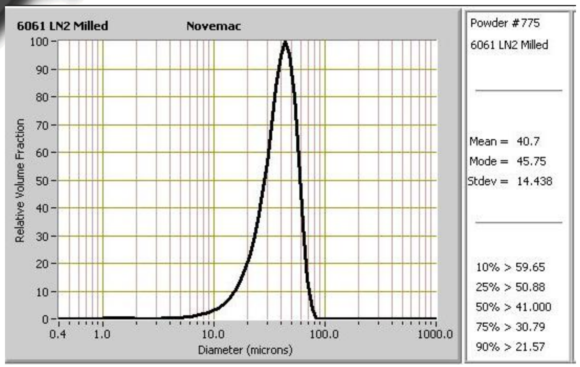
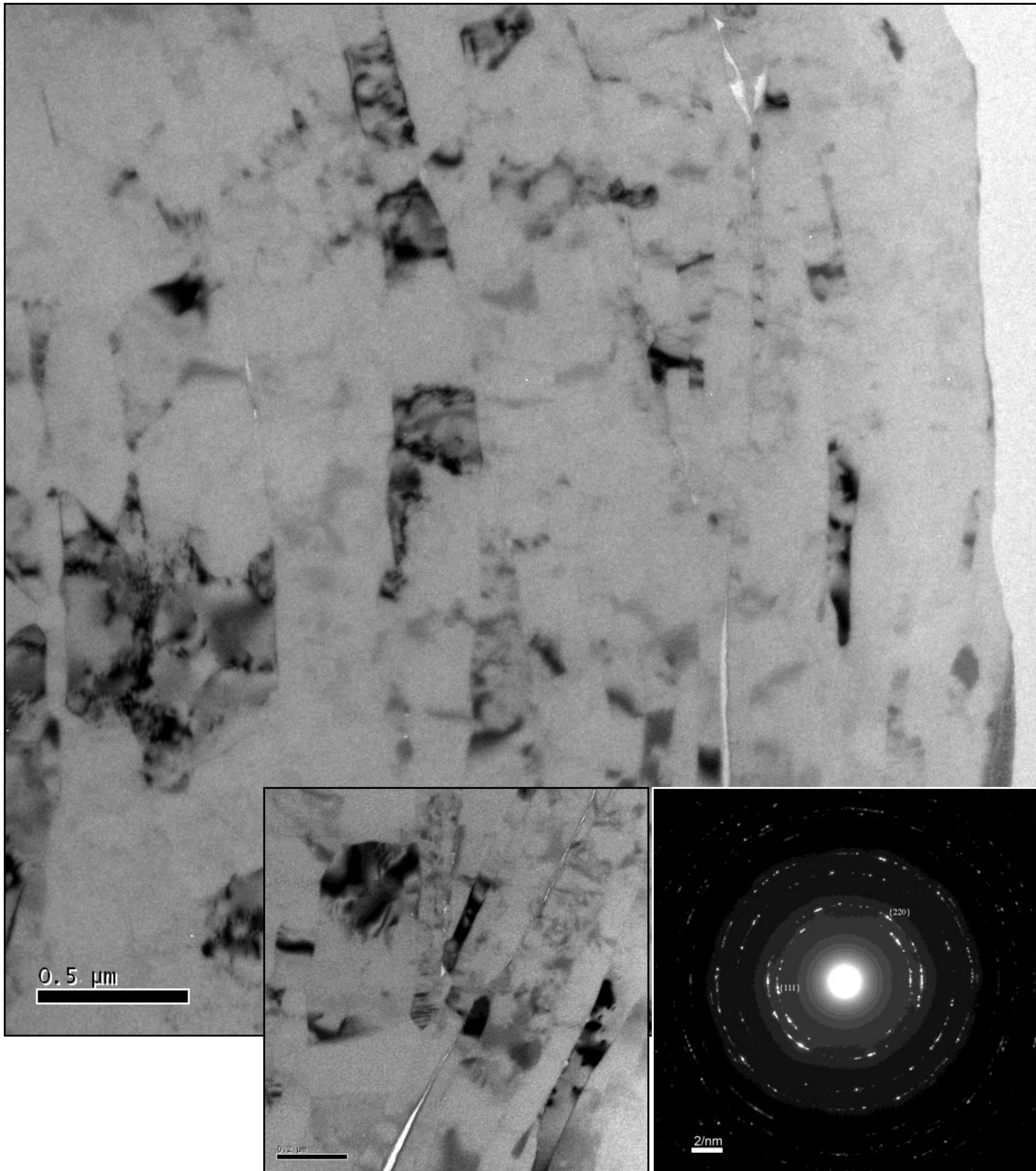
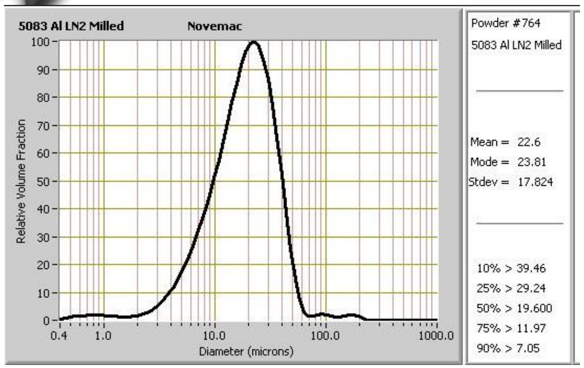
6061 Al powder contains 250-400 nm grains after LN_2 ball milling

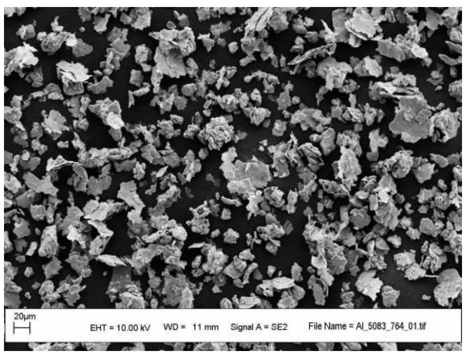




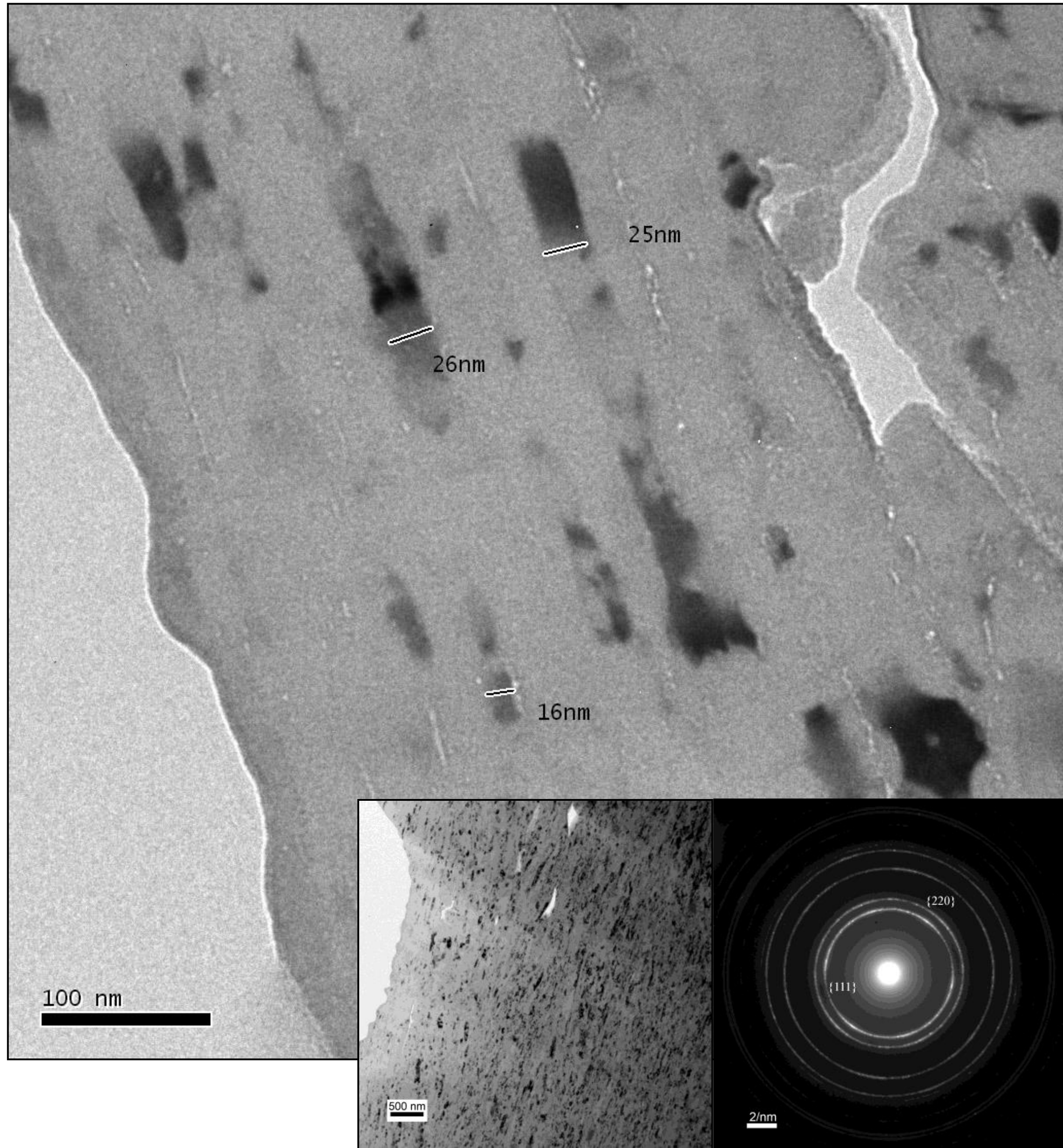
- 40 micron average particle size
- 14 micron standard deviation
- 250-400nm grains within particles (ultra-fine grain material)
- Lath-like grain structure w/ inter grain porosity,
- No strong crystallographic texture evident in SADP

5083 LN_2 ball milled Al microstructure similar to, but much finer than LN_2 milled 6061 Al

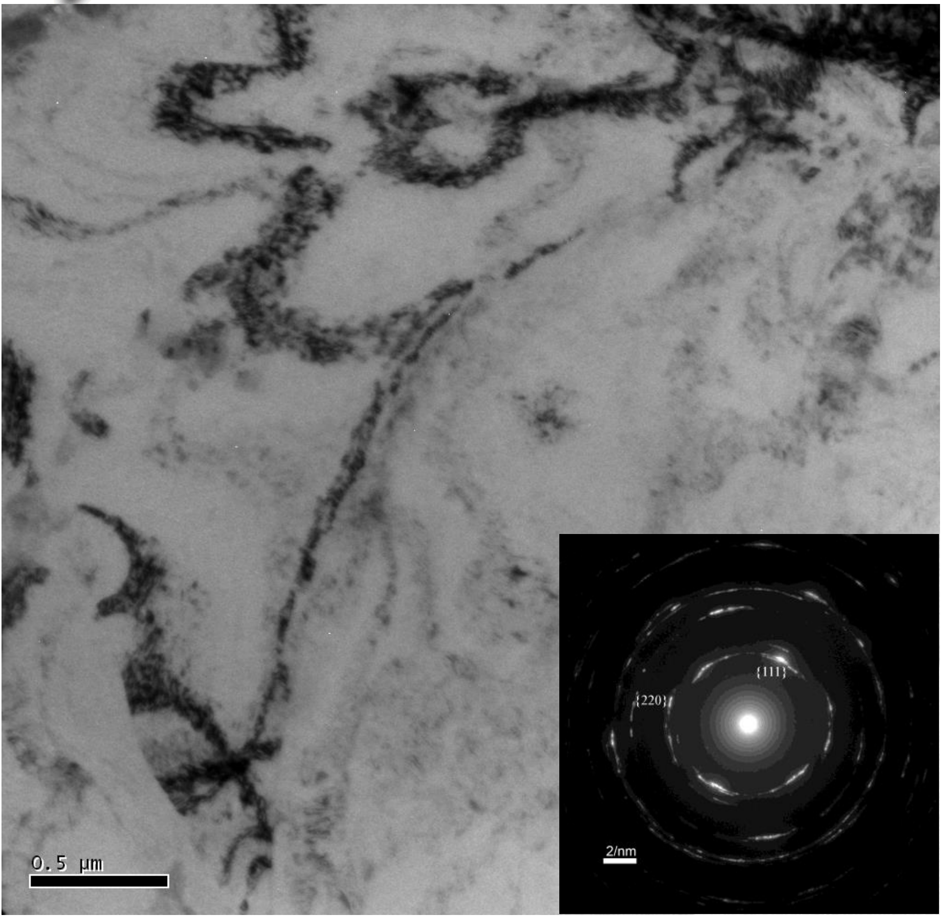




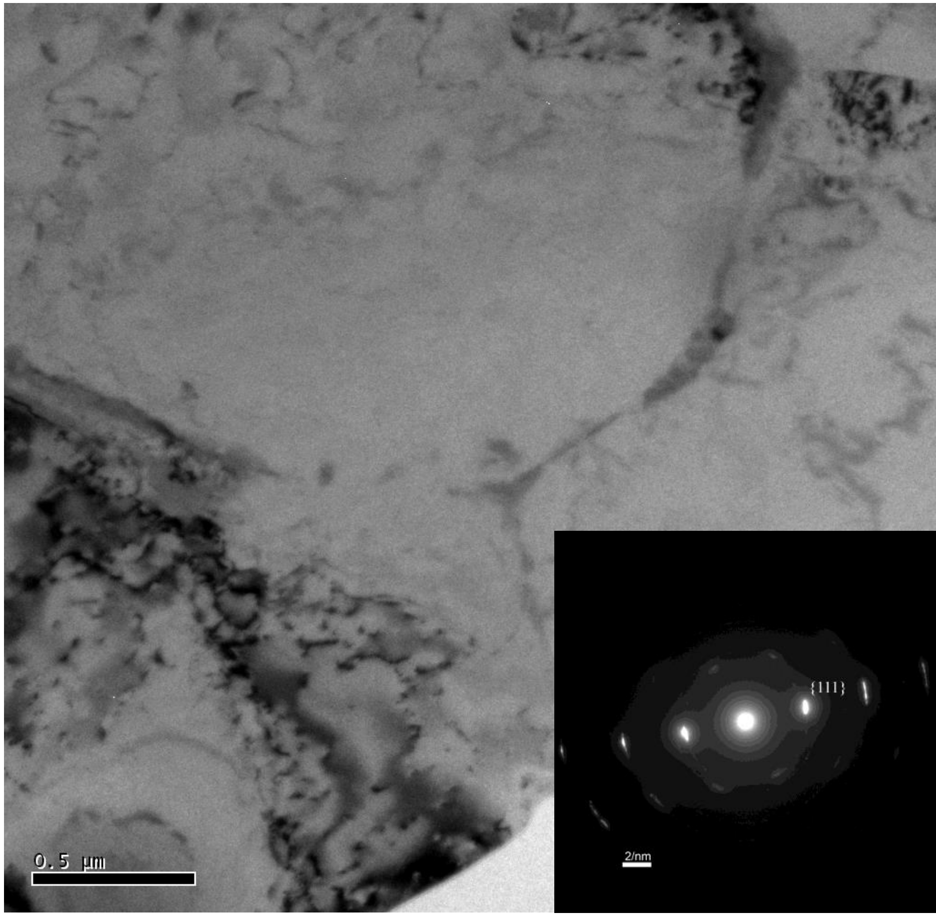
- 22 micron average particle size
- 17 micron standard deviation
- Microstructure comprised of elongated grains, parallel to surface of particle, with thicknesses <100nm
- Porosity visible, mostly at GB's
- SAD pattern shows ring pattern with very little texture (perhaps a slight amount for the {111} reflection)



Coatings prepared using as-received powders show "normal" sized grains



5083 as-received



6061 as-received

- **Large (>500nm) grains with heavy deformation**
- **SADP show smeared spots from deformed grains.**

- **Large grains (> 1µm) observed throughout 6061 as-received coatings**
- **SADP from single grain**

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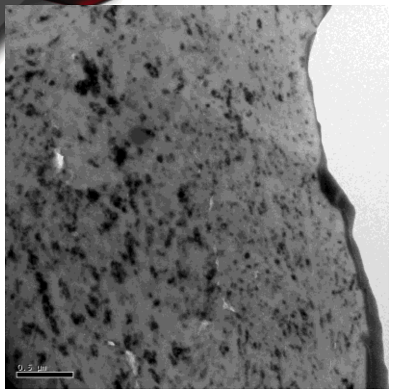
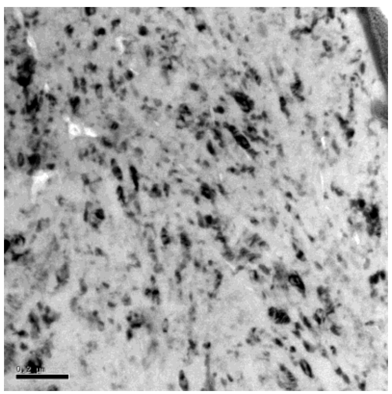
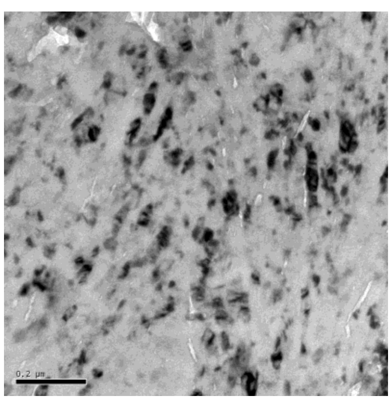
6061 LN_2 ball milled powder results in a truly nanocrystalline coating

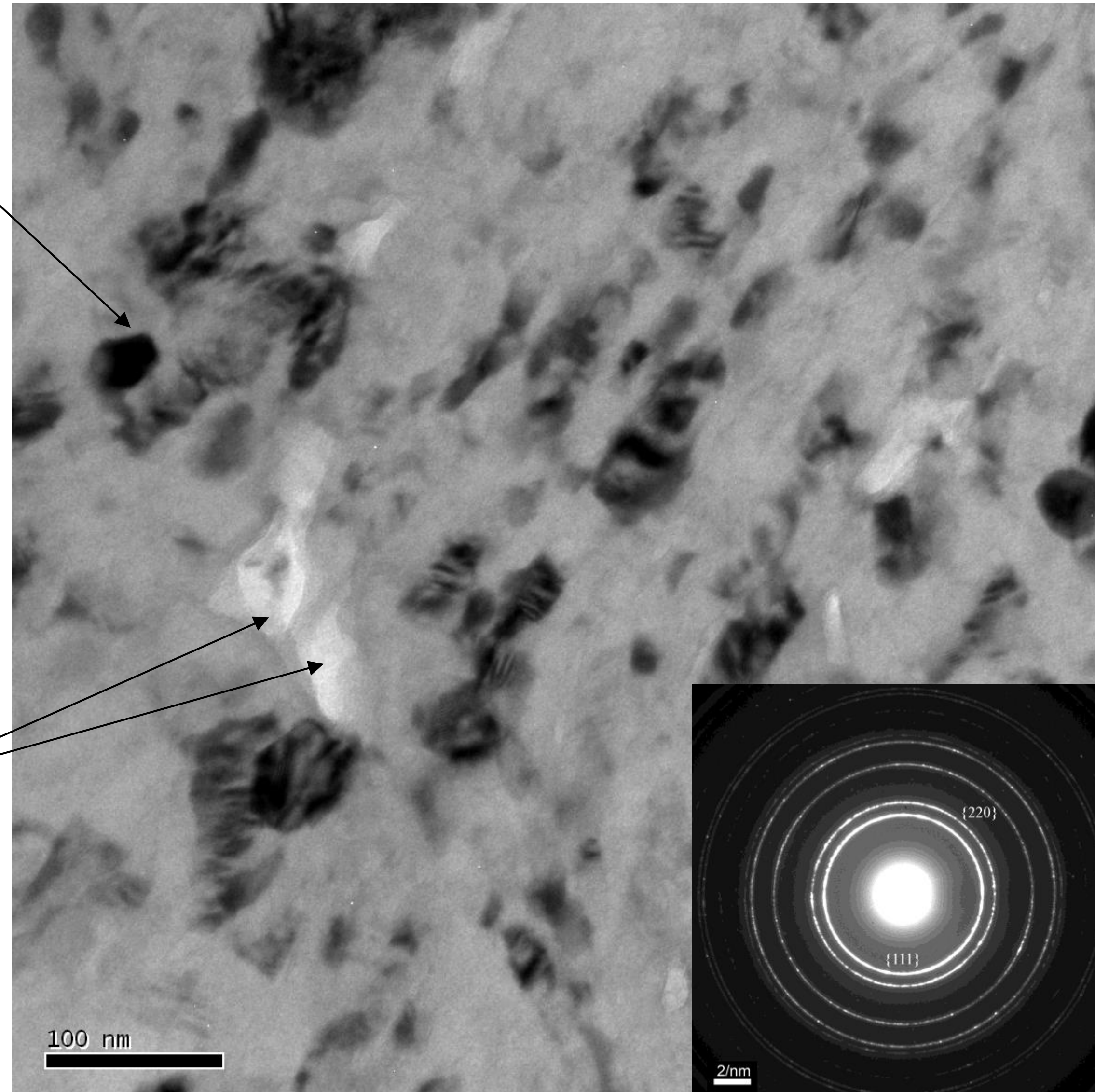






30 – 50 nm grains

Voids



No discernable texture!

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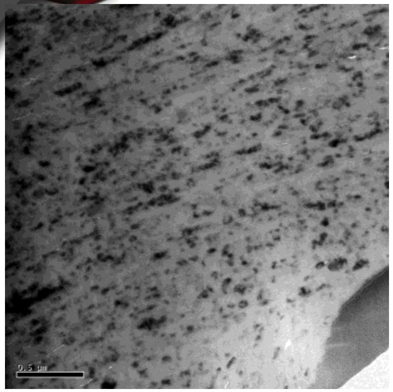
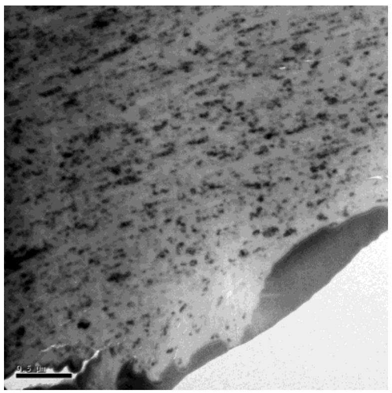
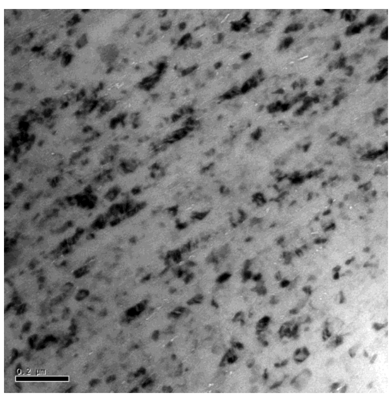
5083 LN_2 ball milled powder also results in a truly nanocrystalline coating

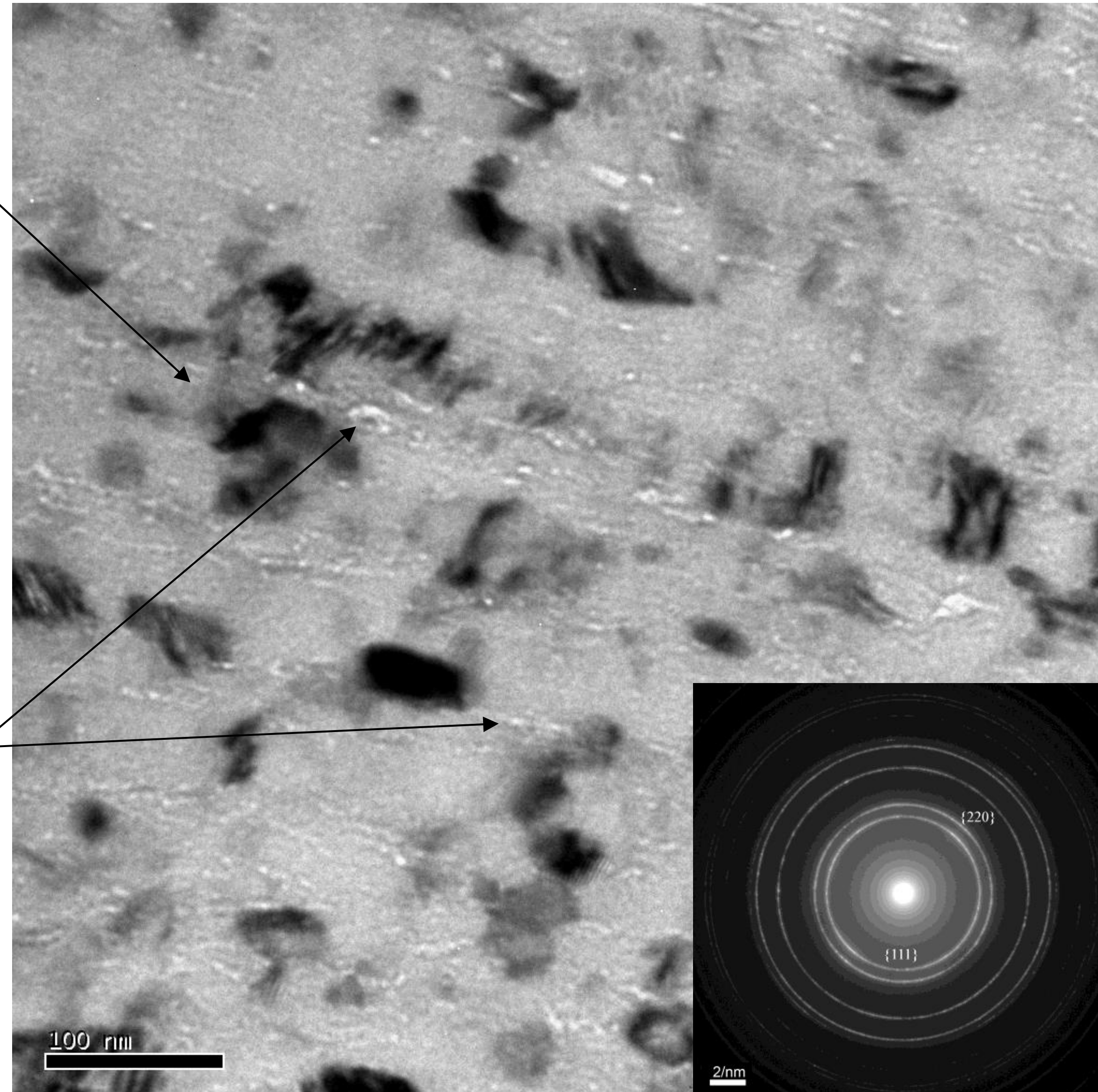






20 – 50 nm grains

Voids



No significant texture

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These microstructures are approaching the minimum grain size for aluminum

- Minimum grain size for Aluminum is ~ 20 nm
- Dislocations are unstable in Aluminum grains smaller than 18nm
- Plastic deformation is responsible for grain refinement in LN_2 ball milled and cold sprayed aluminum
- Both cold sprayed samples show grain sizes between 20 and 50 nm.
- Grain refinement through plastic deformation will not create Al grains less than ~ 20 nm in size.

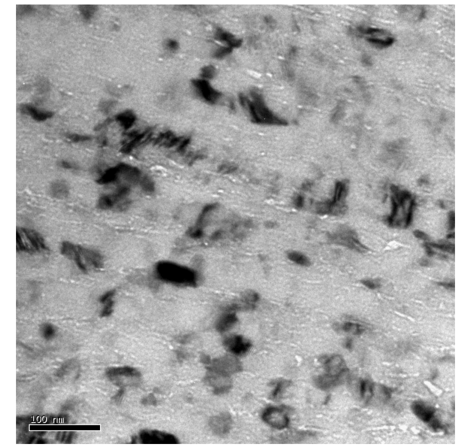


TABLE 1

Critical length of dislocation stability for metal nanocrystals with slipping interfaces

	Cu	Al	Ni	α-Fe
Elastic modulus G (GPa)	33	28	95	85
Lattice parameter b (nm)	0.256	0.286	0.249	0.248
Peierls stress σ_p (10^{-2} GPa	1.67	6.56	8.7	45.5
Λ (nm), sphere	38	18	16	3
Λ (nm), cylinder	24	11	10	2

A. E. Romanov, Continuum Theory of Defects in Nanoscaled Materials, *NanoStructured Materials*, 1995, 6(1-4) p 125-134

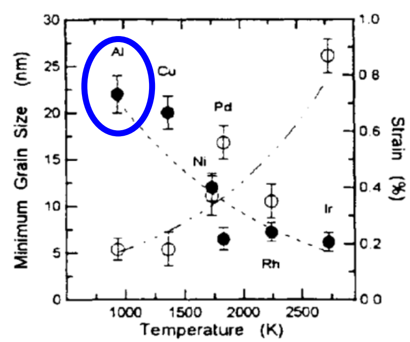
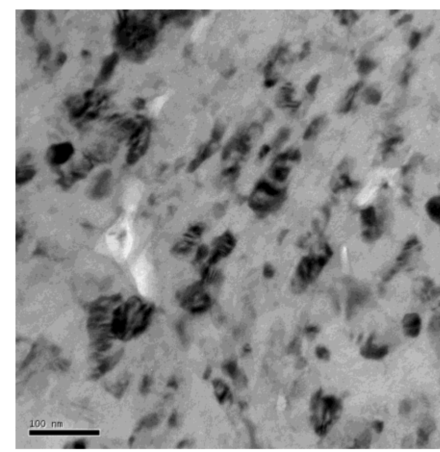


Figure 1. Minimum average grain size (filled symbols) and atomic-level strain (open symbols) for ball-milled fcc metals versus melting temperature.

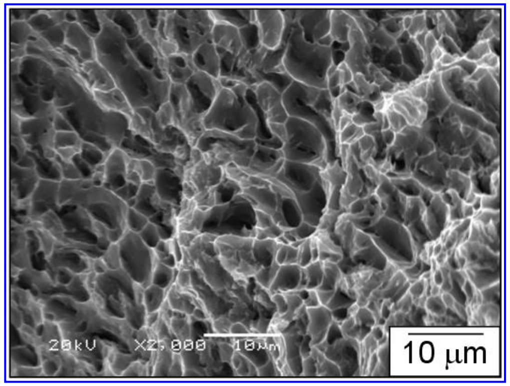
J. Eckert, Relationships Governing the Grain Size of Nanocrystalline Metals and Alloys, *NanoStructured Materials*, 1995, 6(1-4), p 431-416



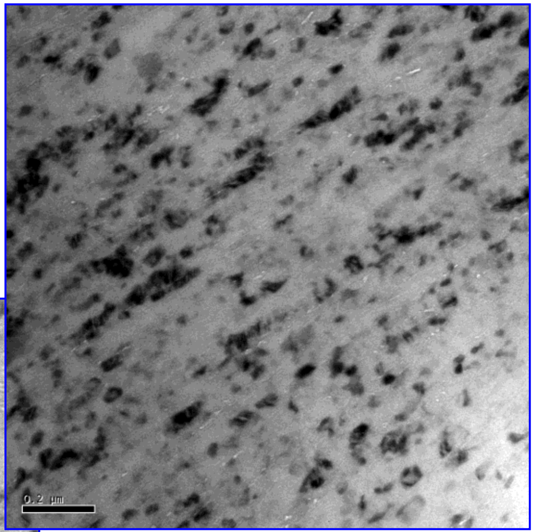
Void formation is likely due to large amounts of plastic deformation from ball milling and cold spray.

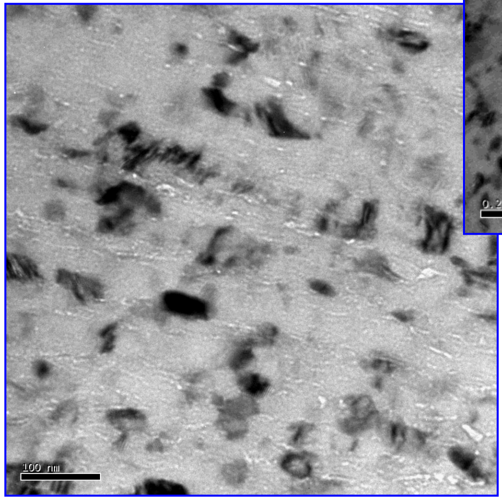
- Void formation is commonly associated with ductile fracture
- Homogenous void is nucleation possible*
- Heterogeneous void nucleation is more likely*
  - Within precipitates
  - At interfaces
  - At grain boundary triple points
- Both 5083 & 6061 contain precipitate forming elements
- Aluminum nitrates are known to form in LN_2 ball milled aluminum†.

Ductile fracture surface in cold sprayed aluminum



Cold sprayed nanocrystalline aluminum showing voids at grain boundaries





*S. H. Goods and L. M. Brown, The Nucleation of Cavities By Plastic Deformation, *Acta Metallurgica*, 1979, 27, p 1-15

†L. Ajdelsztajn, B. Jodoin, G. E. Kim, J. M. Schoenung, J. Mondoux, Cold Spray Deposition of nanocrystalline Aluminum Alloys, *Metallurgical and Materials --Transactions A*, 2005, 36A, p 657-666

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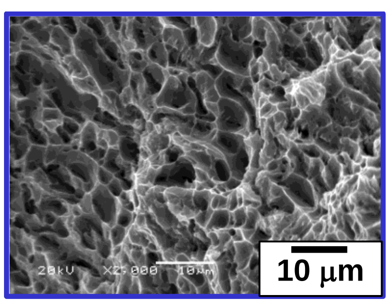
Summary

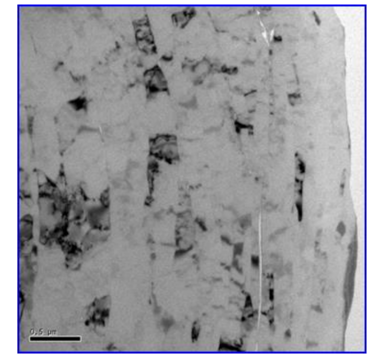
As-Sprayed

Annealed

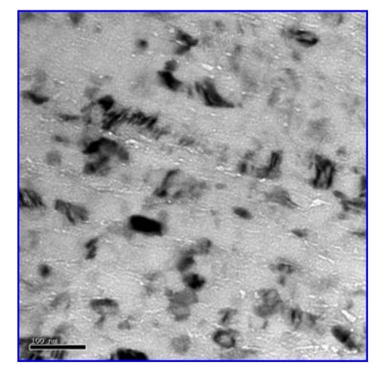


- Cold sprayed aluminum is brittle as-sprayed
- Annealing dramatically improves (>10x) ductility & changes fracture mode.
- Cold Spraying LN_2 ball milled aluminum is effective for preparing nanocrystalline aluminum
- Significant grain refinement can occur during the cold spray

LN_2 ball milled powder containing 250 - 400 nm grains



Cold Spray coating containing 20 - 50 nm grains



Questions

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