POWDER DEVELOPMENT | Cold Spray Coatings for Cr and Ni Plating Replacement

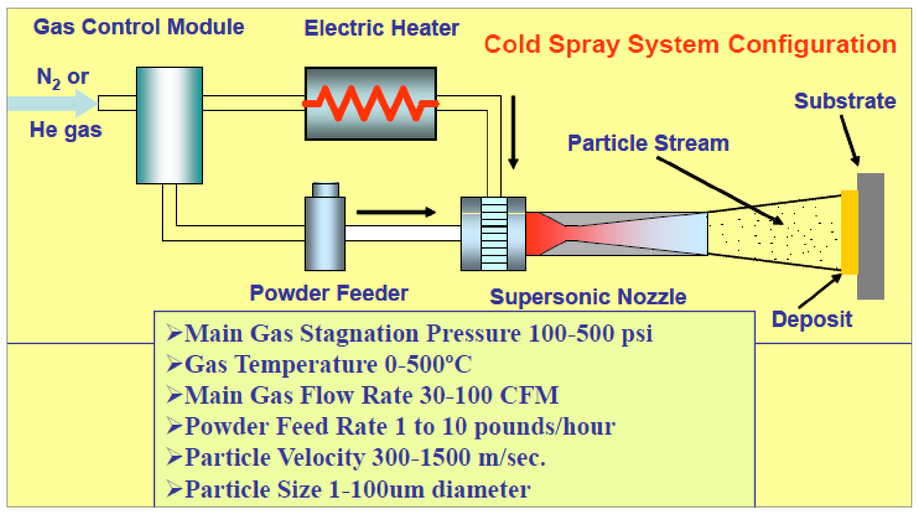
Blake Barnett, Victor Champagne, Anais Espinal, Dennis Helfritch, Daniel Kaplowitz, George Kim, Keith Legg, Aaron Nardi, Matt Siopis

OVERALL OBJECTIVE

Develop environmentally friendly processes to replace electrolytic Cr and Ni plating used on steel and aluminum alloys using Cold Spray technologies

OUR APPROACH

- The Cold Spray process achieves particle bonding through a process of high velocity impact and plastic deformation
- Powders used in Cold Spray must contain a "soft" plastic phase in order to properly consolidate
- To create hard coatings, a significant quantity of hard phase is required in the coating



SYNTHESIS OF COLD SPRAY (CS) POWDERS

a. Identify the appropriate types of soft and hard phases
b. Identify the best configuration of these phases within the powder particle
c. Identify the appropriate particle size
d. Develop the spray process parameters required to consolidate this material

Materials by Design

Hard Phases
- Tungsten Carbide
- Chrome Carbide
- Iron-based hard powders
  - Diamalloy 1008
  - Nanosteel

Soft Phases
- Nickel
- Stainless Steel
- Cobalt
- Chrome
- Tantalum
- Niobium
- Bronze
- Copper-Nickel

Methods of Combinations

- Blending
- High Energy Milling
- Powder Plating
- Small-Large Powder Granulation
- Spray Drying

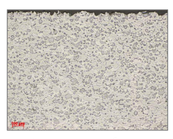
RESULTS

Blending

- Blending of powders can achieve high quality deposits with a variety of combinations of hard and soft phases
- Blending achieves harness limited to approximately 350-500 HV making it a potential solution for nickel plating replacement
- Several potential combinations of hard and soft phases have been successful

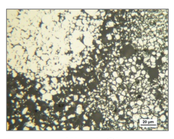
Chrome Carbide Nickel-Chrome

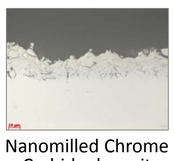
Iron hard face with Nickel


Iron hard face with Stainless Steel

High energy milling

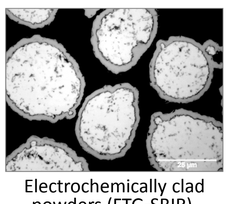
- Milling of powder has been unsuccessful to date
- Lack of transfer from soft powder to hard powder during the milling process
- Potential for improvements through the use of finer soft powders


Nanomilled Chrome Carbide powder


Nanomilled Chrome Carbide deposit

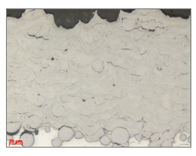
Plating

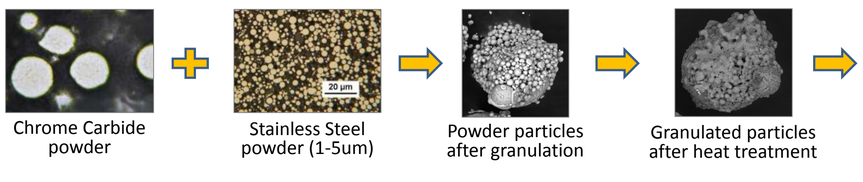
- Powders have been sent out for plating by nickel
  - Chrome Carbide
  - Tungsten Carbide
- First batch of plated powders received


Electrochemically clad powders (FTG-SBIR), as an example

Granulation

- Large core powders have been granulated with fine metal powders using aqueous PVP solutions
- Powders are then heat treated to sinter the fine powder to the hard core powder
- Fine powders create a coating around the core powder
- Potential for low cost high volume production

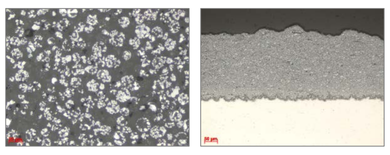

Cobalt-chromium-molybdenum alloy with Nickel | 656 HV



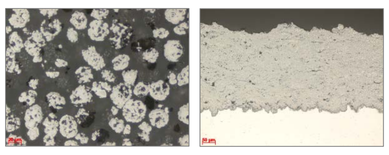
Spray Drying

- Several powders have been procured and specially designed for this application
- Development leads to the need for smaller carbides and smaller particle sizes
- Deposits greater than 850 HV have been achieved
- Both chrome carbide and tungsten carbide-based powders were sprayed
- The following powder characteristics lead to improved outcomes
  - Sphericity of agglomerates
  - Homogeneity of agglomerates
  - Finer constituents in agglomerates <2 microns
  - Small agglomerate size <20 microns lower preferred
  - Relatively low porosity of agglomerates
- Fewer chrome carbide powders were sprayed showing similar trends
  - One difference is that chrome carbide is lower density and therefore particle size is not as critical, but still important

Tungsten Carbide (powder and deposit)



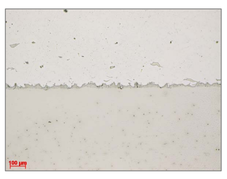
Chrome Carbide (powder and deposit)



Deposits hardness are >850 HV

FUTURE STEPS

- Nano-grained chromium alloy powder (MIT)
  - Need increased hardness
- Improve spray dried deposit quality
  - Lower particle size distribution
  - Modified chemical composition
  - Use of sub-micron carbides
- Improve spraying conditions for high energy milling powders
  - Spray with smaller particle size distribution
  - Combine with other finer soft powders


Deposit using conventional Chromium Powder | 338 HV

Partners of this project:

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PROJECT OVERVIEW | Cold Spray Coatings for Cr and Ni Plating Replacement

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PROBLEM STATEMENT (SERDP PROJECT # 16 WP 04-003)

- Cr and Ni electroplating operations must comply with environmental regulations (i.e. AERTA PP-2-02-04) and Executive Orders (i.e. 13148) to eliminate Chromic Acid. The EO requires the usage reduction of hexavalent chromium by 50%.
- Plating operations must also conform to the DoD Emerging Contaminates Directorate in the Memorandum from John Young, USD (ALT), to Secretaries of Military Departments, Minimizing the Use of Hexavalent Chromium.
- OSHA has proposed a reduction in the current Permissible Exposure Limit (PEL) established for water soluble chrome VI compounds from the current 5 micrograms per cubic meter to less than 1 micrograms per cubic meter.
- Eliminate $5M/yr. waste disposal costs collected from Watervleit and Rock Island Arsenals, Corpus Christi and Anniston Army Depot (CCAD). Based upon yearly production numbers from NDCEE Toxic Metal Waste Study.

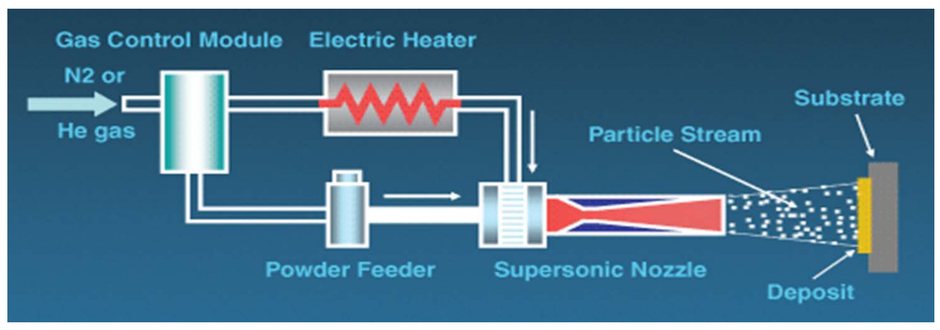
TECHNICAL OBJECTIVE

- This work will advance the state-of-the-art for CS by providing a better understanding of the particle/substrate interaction and bonding mechanism and result in novel CS coating powders/materials that can be used by DoD and industry to replace Cr and Ni electroplating.
- This will be accomplished by a 'Materials by Design" approach through proven modeling/simulation, innovative nozzle design, the synthesis and development of CS powders and process parameters that can produce protective coatings with properties comparable to those of Cr and Ni plating for production and/or field relevant performance characteristics.

PERFORMANCE CRITERIA

- Phase 1: Hardness (> 850 HV), bond, microstructure and wear
- Phase 2: Same as Phase 1 criteria plus strain to failure (> 0.7%) and fatigue

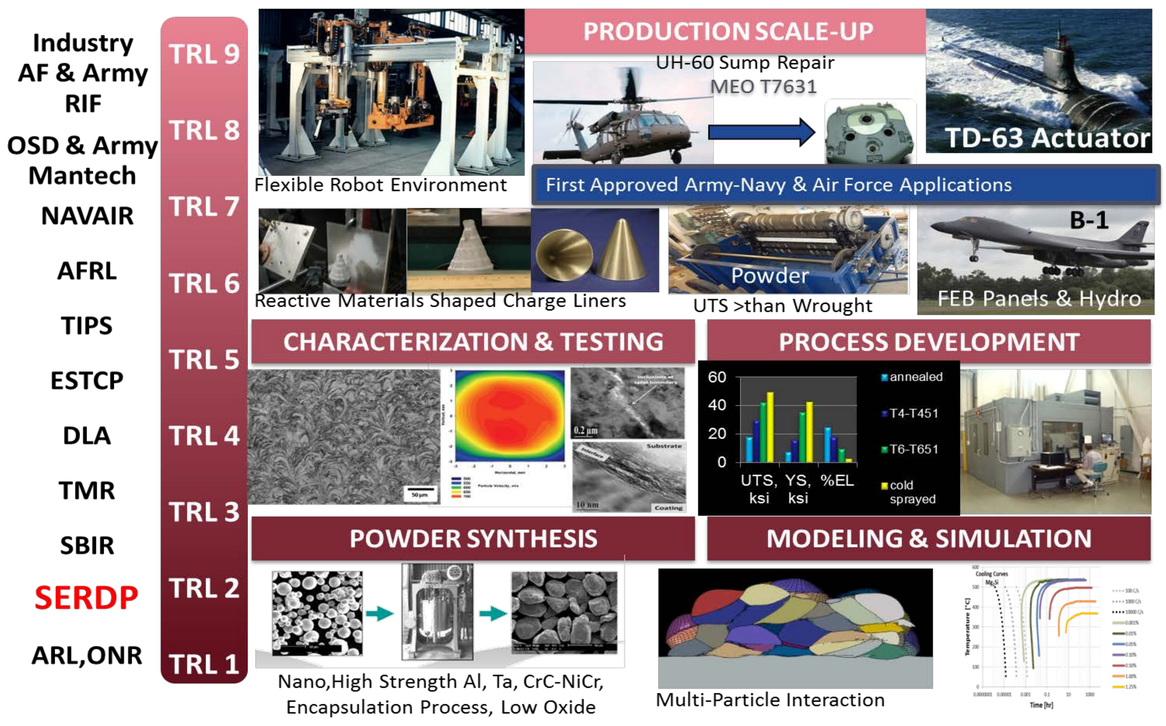
THE COLD SPRAY PROCESS



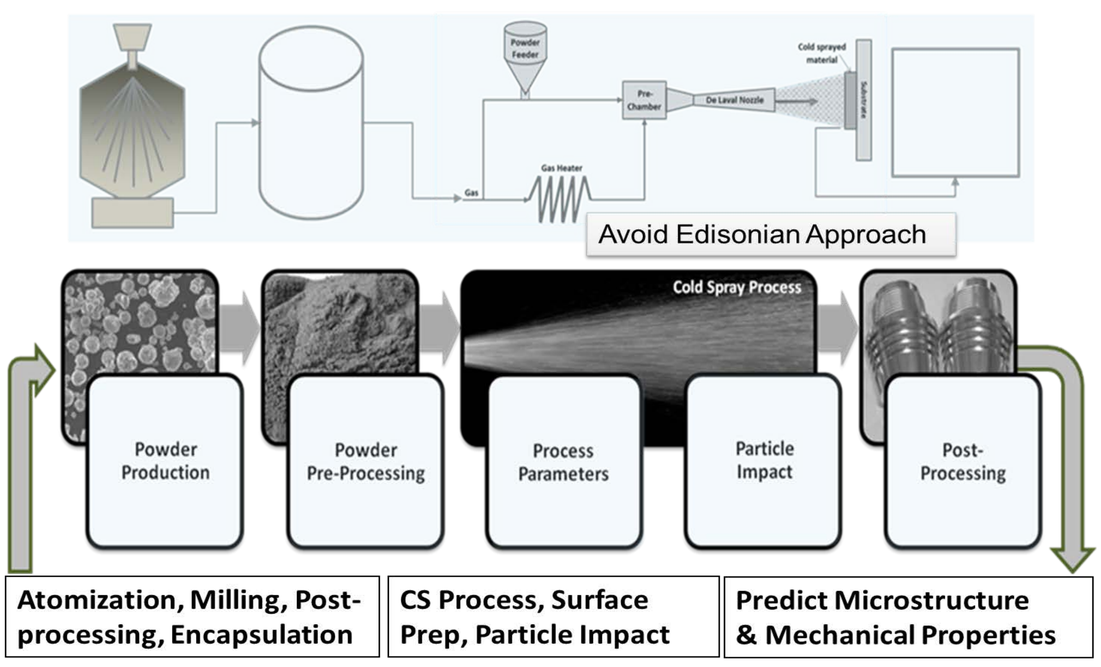
- Basic process is known – but the technology must be 'enabled' to allow development of new materials/coatings
- CS developed in Russia in mid 1980's but has yet to realize potential
- Cr plating replacement material not developed to date
- ARL Cold Spray Center has led R&D and applications development since 2000's
- "Materials by Design" Approach-Materials Science-Modeling-Hardware/Software

ARL COLD SPRAY RESEARCH

FROM **CONCEPT** TO **TRANSITION** 7 YEARS…2005-2012

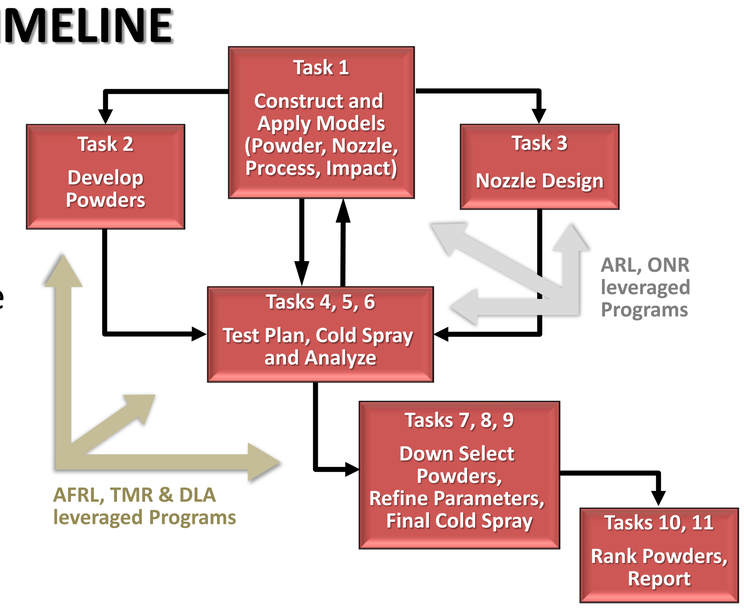


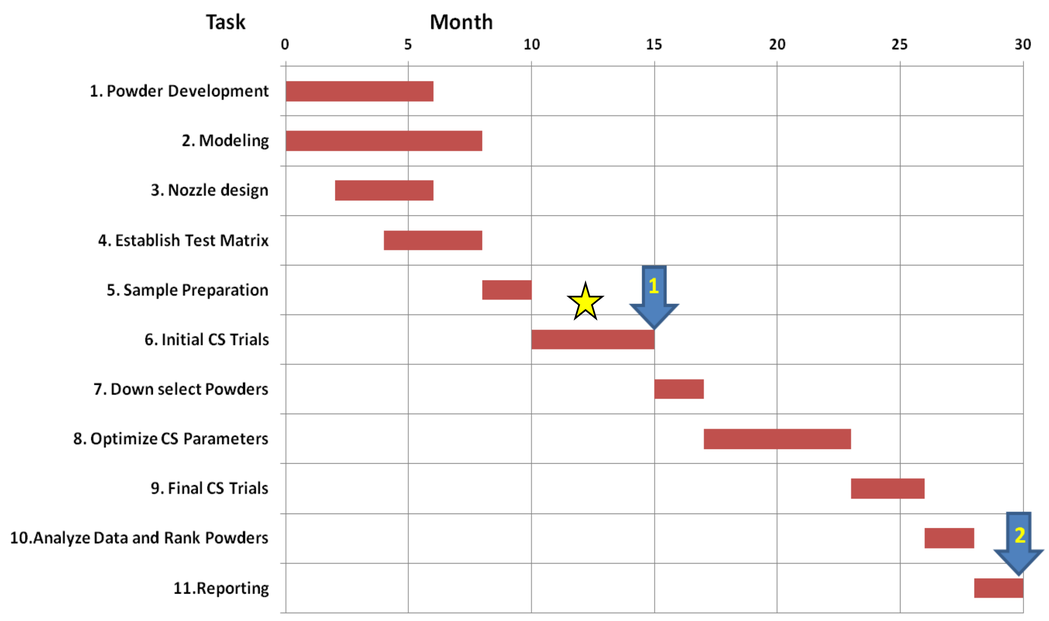
COLD SPRAY HOLISTIC THROUGH-PROCESS MODEL



PROJECT DELIVERABLES AND TIMELINE

1. Cold Spray powder for Cr & Ni
2. CS process for Cr & Ni replacement
3. Materials characterization results
4. Recommended CS nozzle and hardware for demo/validation in a follow-on ESTP Program





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PROCESS DEVELOPMENT & MODELING | Cold Spray Coatings for Cr and Ni Plating Replacement

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PROCESS DEVELOPMENT

Analytical and CFD approaches are used to predict particle velocity, temperature, and distribution within the stream

1 CS Conditions: Relative Critical Velocity Ratio Calculations

- Critical velocity ratio allows for comparison between varying velocities and temperatures
  - Should be used as a relative number not absolute
- Actual powder size distribution can be used to determine mass averaged velocity

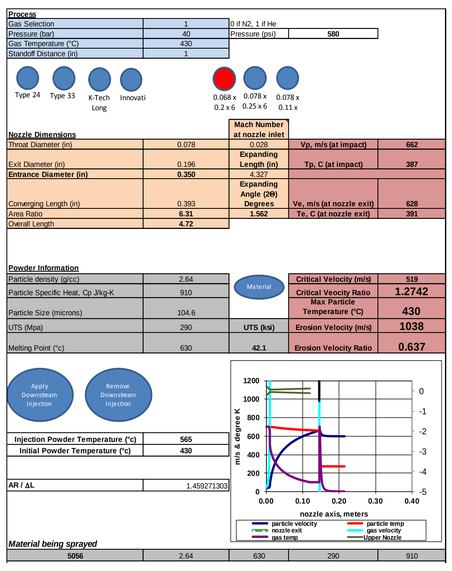
$$V_{crit} = \sqrt{\frac{4F_1\sigma_{uts}\left(1-\frac{T_i}{T_{MP}}\right)}{\rho} + F_2 C_p \left(T_{MP} - T_i\right)}$$

Particle Diameter (um)	Impact Temp (°c)	Impact Velocity (m/s)	Critical Velocity Ratio
104.6	387	662	1.3
88	376	726	1.4
73.99	362	794	1.5
62.22	346	867	1.5
52.32	326	944	1.6
44	304	1025	1.7
37	280	1109	1.8
31.11	254	1195	1.9
26.16	230	1283	1.9
22	210	1371	2.0
18.5	197	1459	2.1
15.55	196	1543	2.2
13.08	210	1623	2.4
11	239	1696	2.6

Average CVR
1.805

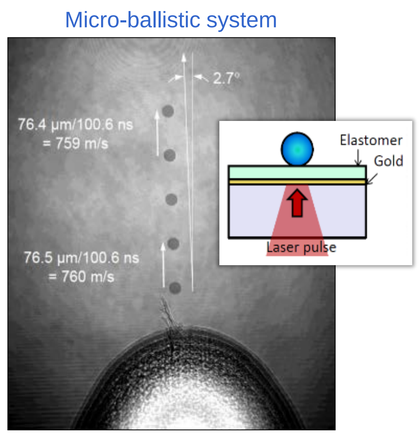
Average Velocity
1143

Average Temperature
271

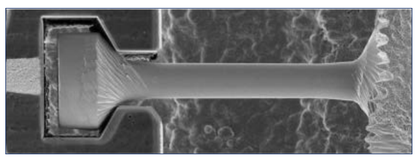


2 Advanced characterization to develop property data for powders

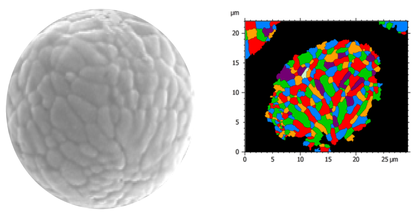
Laser-induced single particle impact



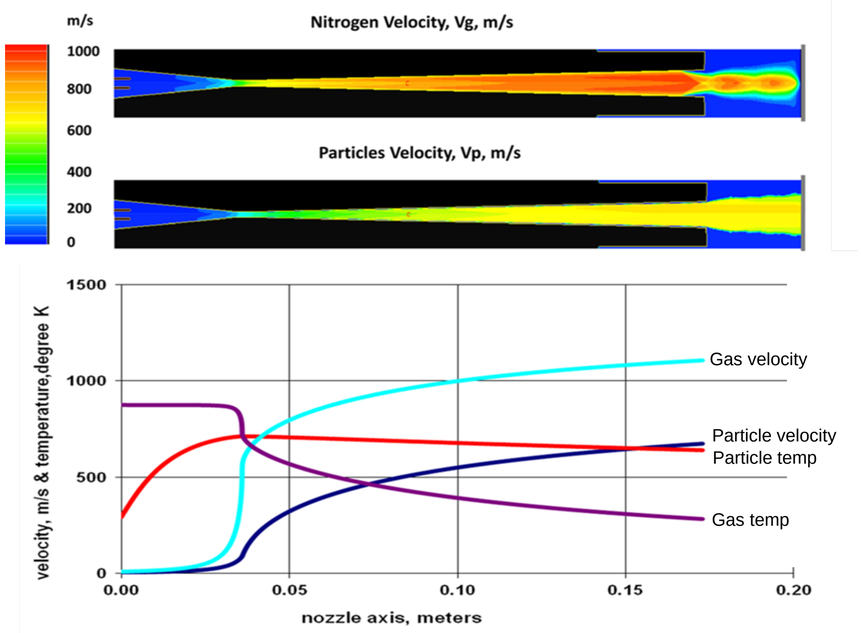
In-situ mechanical tests in SEM



Microstructure characterization



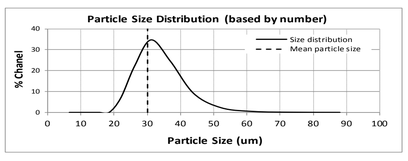
3 CFD: Nozzle and Process Modeling

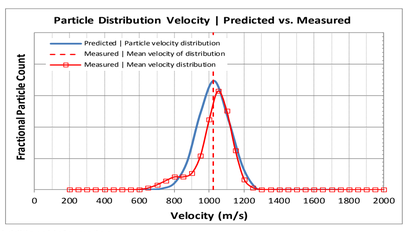


4 Validation: Velocity calculations calibrated with Laser Doppler Velocimeter

Under all spray conditions evaluated measured velocity was within 5% of predicted velocity

	Run ID	LDV-017
POWDER	Powder type	Al 5056
	Manufacturer	Valimet
	Classification	10 LPM
	Sieving	-400/+500
	Mean particle size, mm	30.08
	Powder density, g/cm3	2.618
COLD SPRAY CONDITIONS	System	CGT
	Nozzle material	PBI
	Nozzle	SM-0007, Type 33
	Throat diameter, in: 0.106; Exit diameter, in: 0.381	Converging length, in: 1.155; Expanding length, in: 7.39
	Gas 1	Helium, 100%
	Gas 2	---
	Distance from end of nozzle, in	1
	Pressure, bar	20
	Gun temperature, °C	300
	Nozzle temperature, °C	---
	Calculated | Nozzle Temperature, °C	291
	Gas flow, LPM	---
	Calculated | Gas flow, m3/h	182
	Predicted | Velocity of mean diameter particle, m/s	1056
	Predicted | Mean velocity of distribution, m/s	1029
	Measured | Mean velocity of distribution, m/s	1023
	Deviation, %	0.63%



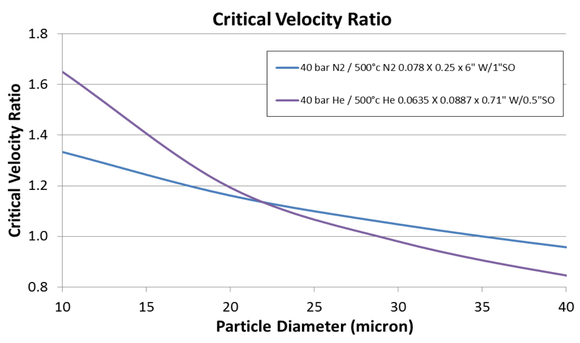


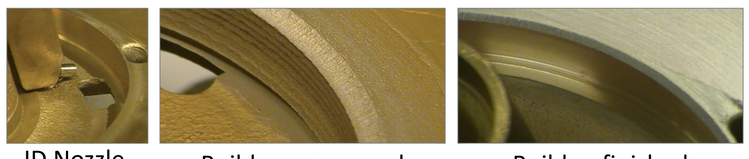
Legend:
- Calculated using rule of mixtures
- Predicted using 'Velocity Calcs 1.4 + Log Book' Excel file
- Measured values from LDV laser system
- Deviation between predicted and measured velocity

Additional information:
- * Particle size distribution was measured using Microtrak S3500
- * Powder density was measured using pycnometer
- --- : not available

Application example: Cold Spray deposition head developed for small gaps

- A nozzle and nozzle holder were designed based on the velocity prediction tools used at UTRC
  - Initial convergence in nozzle holder
  - Final converging and diverging in nozzle
- Validation testing performed
  - 31 micron mean particle diameter
  - Predicted velocity = 504 m/s
  - Measured velocity = 531 m/s

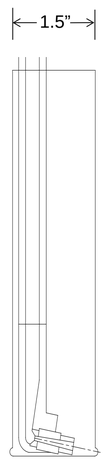




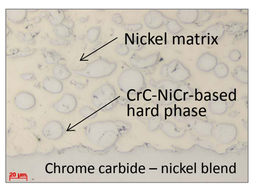
ID Nozzle bottom of travel | Buildup as sprayed | Buildup finished

Potential uses for small nozzle technology in chrome and nickel plating replacement

- Spraying blended powders such as those suited to nickel replacement
- Spraying cermets such as spray dried powders designed for chrome replacement
- Potential for spraying ID coatings in bores as small as 1.5 inches



ID Nozzle

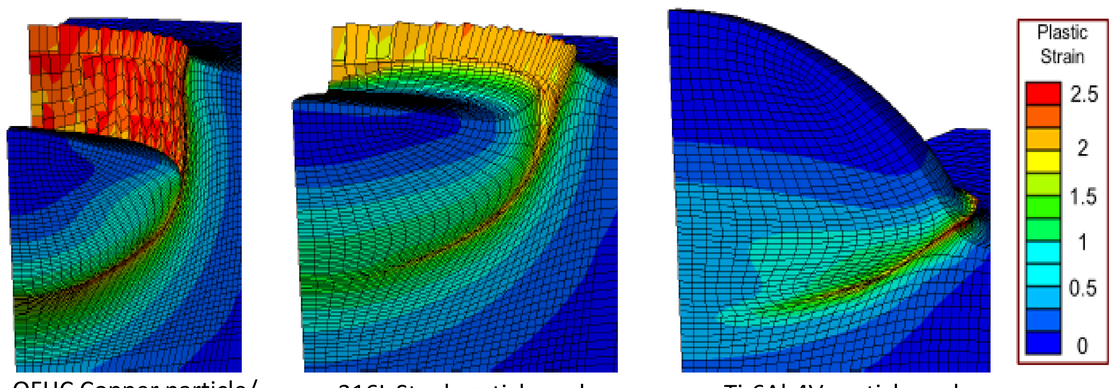


Hardness = 446 HV

Hardness = 866 HV

IMPACT MODELING

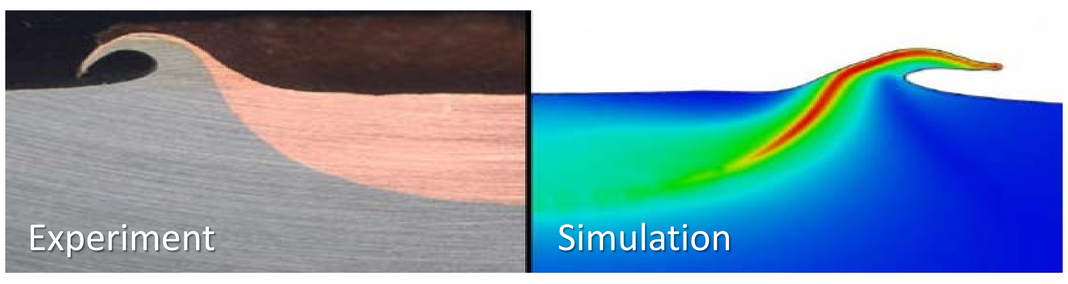
Single particle impact model



OFHC Copper particle/ Al 6061-O substrate, 600m/s | 316L Steel particle and substrate, 800m/s | Ti-6Al-4V particle and substrate, 800m/s

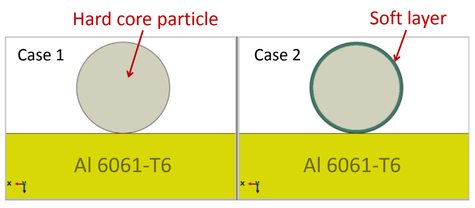
Impact modelling calculation for various 20 micron particles impacting onto dissimilar surfaces. Colors indicate plastic strain values | Abaqus/Explicit - Johnson-Cook flow stress model

Actual copper CS deposit

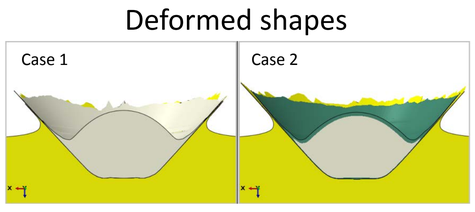


Particle impact of hard phase core particle with a shell of soft material

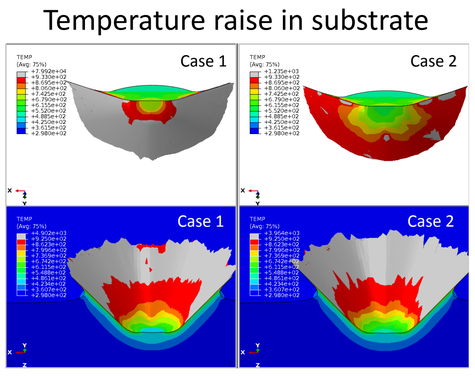
Undeformed shapes before impact



Deformed shapes



Temperature raise in substrate



Cases 1 and 2 show impact deformation (i.e., material jet, particle flatten ratio/penetration, etc.) and temperature rise in the substrate.

Higher temperature rise is observed at the contact surface of the particle without coating, comparing that of the coated particle.

All material data are from literature.

- *Gray, G.T. III, et al., LA-12669-MS, 1994*
- *Scheffler, Daniel R., ARL-TR-1417, 1997*
- *Grunschel, S.E., Dissertation, Brown University, 2009*

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