Cold Spray Coatings for Chromium and Nickel Plating Replacement

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The objective of this project was to develop cold spray coating as an environmentally benign process to replace hard chromium and nickel electroplating used for localized repair of weapons system components. The approach that the Cold Spray Team has taken was not just to develop a specific coating or set of coatings to replace Cr and Ni electroplates, but also to develop and deploy a holistic approach to cold spray development that would employ all the modern computational an analytical tools at our disposal to develop and optimize the powders, spray equipment, and deposition conditions to bring cold spray coating technology to production rapidly and reliably.

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LIST OF ACRONYMS

AERTA - Army Environmental Requirements and Technology Assessment

ARL - Army research Laboratory

CFD – Computational Fluid Dynamics

CS – Cold Spray

DoD – Department of Defense

EHC – Electrolytic Hard Chrome (Engineering Hard Chrome)

EO – Executive Order

ESOH – Environmental Safety and Occupational Health

ESTCP – Environmental Security Technology Certification Program

FEA – Finite Element Analysis

HAP – Hazardous Air Pollutant

OCP – Open Circuit Potential

OEM – Original Equipment Manufacturer

ONR – Office of Naval Research

OSHA – Occupational Safety and Health Administration

PEL – Permissible Exposure Limit

SBA – Sea-Based Aviation

SERDP – Strategic Environmental Research and Development Program

SON – Statement of Need

UTRC – United Technologies Research Center

VOC – Volatile Organic Compound

KEYWORDS

Cold spray, wear, WC-Co, WC-CoNi, Cr_3C_2-Ni

ABSTRACT

Objectives

The objective of this project was to develop cold spray coating as an environmentally benign process to replace hard chromium and nickel electroplating used for localized repair of weapons system components.

Technical Approach

The approach that the Cold Spray Team has taken was not just to develop a specific coating or set of coatings to replace Cr and Ni electroplates, but also to develop and deploy a holistic approach to cold spray development that would employ all the modern computational an analytical tools at our disposal to develop and optimize the powders, spray equipment, and deposition conditions to bring cold spray coating technology to production rapidly and reliably. We have therefore developed modeling and computational methods to determine the optimum powder design, gun design and process parameters.

We have also developed the necessary infrastructure for successful production of additional equipment, powders, and coatings for fully industrializing cold spray.

This work has utilized the capabilities of a diverse team led by ARL.

Results

The resultant coatings have been evaluated in wear tests, and several tungsten carbide and chromium carbide composite coatings have been shown to be superior in performance to hard chrome and nickel electroplates.

In addition to improved wear, these cold spray coatings appear to be able to be built up in thicknesses that would allow them to be used directly for repairs that would replace the current sulfamate nickel/ hard chrome coatings currently used to bring badly worn or corroded components back to print dimensions.

Finally, not only have powders been developed and demonstrated, but also new applicator and nozzle designs have been developed which are ideally suited to the materials of interest, but can also deposit coatings in hard to coat areas. Specifically, short nozzles and specialty applicators have been produced which can get coatings into gaps or bores as small as 2 inches in diameter, and has the potential to coat bores as small as 1.5 inches.

Benefits

The primary benefit of the cold spray development approach that we have created in this program is the capability of designing, not just the coatings, but the powders, equipment and deposition processes to bring viable coatings to the market rapidly and successfully. This will make it easier for organizations to increase the speed with which changes can be made in response to environmental and market drivers. Specifically, as regulatory requirements change powder and coating composition changes can be made to accommodate the new requirements.

The improved performance of composite cold spray coatings will reduce sustainment cost and increase readiness by producing repairs that are more reliable and long-lasting, while reducing

the ESOH burdens on the sustainment community. The powders and equipment developed have furthermore been evaluated using COTS (Commercial Off-The-Shelf) Cold Spray systems that have or are planned to be installed at several military depots including Corpus Christi, Letterkenny, Pearl Harbor, and Puget Sound as well as several contractor and supplier facilities which support the DOD.

1. Objective

The work reported here addresses the call in WPSON-16-04:

> *The objective of this Statement of Need (SON) is to develop environmentally benign processes that replace electrolytic chromium and nickel plating used on maraging steel, corrosion-resistant steel, and aluminum alloys in localized areas of weapons system components. The proposed technology should meet the following requirements:*
> - *Eliminates the use of hexavalent chromium and contains low or no volatile organic compounds (VOCs) and hazardous air pollutants (HAPs).*
> - *Does not promote embrittlement in the substrate material.*
> - *Eliminates or reduces part masking, bond coats, and flashings.*
> - *Provides equivalent or better deposition rates as compared to traditional electrolytic plating.*
> - *Is suitable for a wide variety of common military parts and substrates, to include internal and external diameters, surfaces, complex shapes and blind holes, in an economically feasible manner.*
> - *Operates in versatile environments from high volume production floors to portable and unpredictable field conditions.*
> - *Allows for spot repair.*

The approach used to meet this objective is based upon the development of Cold Spray (CS) technology. The CS deposition of protective coatings is an environmentally friendly and field-deployable replacement process for Cr and Ni electroplating. Cold spray has already proven to be a replacement for coatings used to restore dimensions, and it is currently being used on a number of weapons systems. Electrolytic Hard Chrome plating (EHC) is an electroplating technology based on hexavalent chromium. It is widely used throughout DoD for build-up and repair of subsystems subject to wear, such as landing gear and hydraulics.

The research focused on

- Synthesis of CS Powders
- Innovative Nozzle Design
- Development of Optimized CS Process Parameters.

CS will enable the DoD to comply with environmental regulations (i.e. AERTA PP-2-02-04) and Executive Orders (i.e. 13148) to eliminate Chromic Acid used in the current process, a hazardous substance containing hexavalent chrome, a known carcinogen, and Nickel, also known to be an environmental and occupational pollutant, while adhering to the DoD Strategic Sustainability Performance Plan. The EO requires the usage reduction of hexavalent chromium by 50%. Moreover, 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.

2. Background

Previous powder spray technologies were developed before tools were available for understanding the physics and chemistry of the deposition process. Consequently materials and processes were developed by the slow Edisonian approach of trial and error. The result has been a generation of thermal spray coatings that are often far from optimal for their applications, while the difficulty of developing new materials has resulted in the wide use of a few materials, far better solutions could be found for different applications.

The work reported here is part of a broad overall project to develop cold spray technology as a valuable tool for manufacture and sustainment of defense articles. The role of the SERDP program has been central to this effort by funding the evolution of a modern development methodology for materials and process design for cold spray materials. This design methodology has been applied to the development of alternatives to hard chrome plating.

In this approach, illustrated in Figure 1, cold spray development is a holistic process that integrates starting powder feedstock, powder processing, powder characterization, process optimization, and post deposition characterization, all of which are connected through modeling and simulation. The technology is then fit into the DoD environment for both OEM production and depot level sustainment.

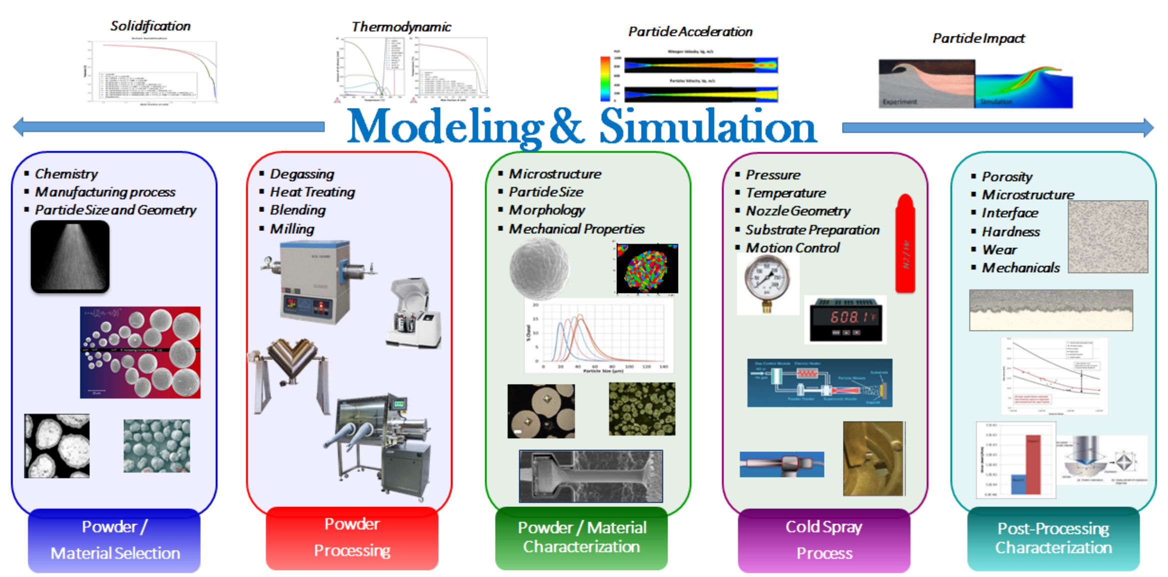


Figure 1. Holistic Cold Spray material and process development.

In this project we have combined all major aspects of this Holistic Approach including modeling of materials, computational fluid dynamic (CFD) and analytical modeling of gas and particle flow and temperature, modeling of particle-solid interactions, materials selection by chemistry and morphology, powder processing to improve deposition characteristics, spray process development and nozzle design, characterization by electron microscopy and other methods, and characterization and evaluation of the final materials and their performance. This approach has made it possible for us to design the materials and their manufacturing and processing methods to obtain the optimum performance in the minimum time. Figure 2 illustrates how all of the different modeling techniques have been combined with experimental validation to predict the final properties of the material and guide the powder and process development.

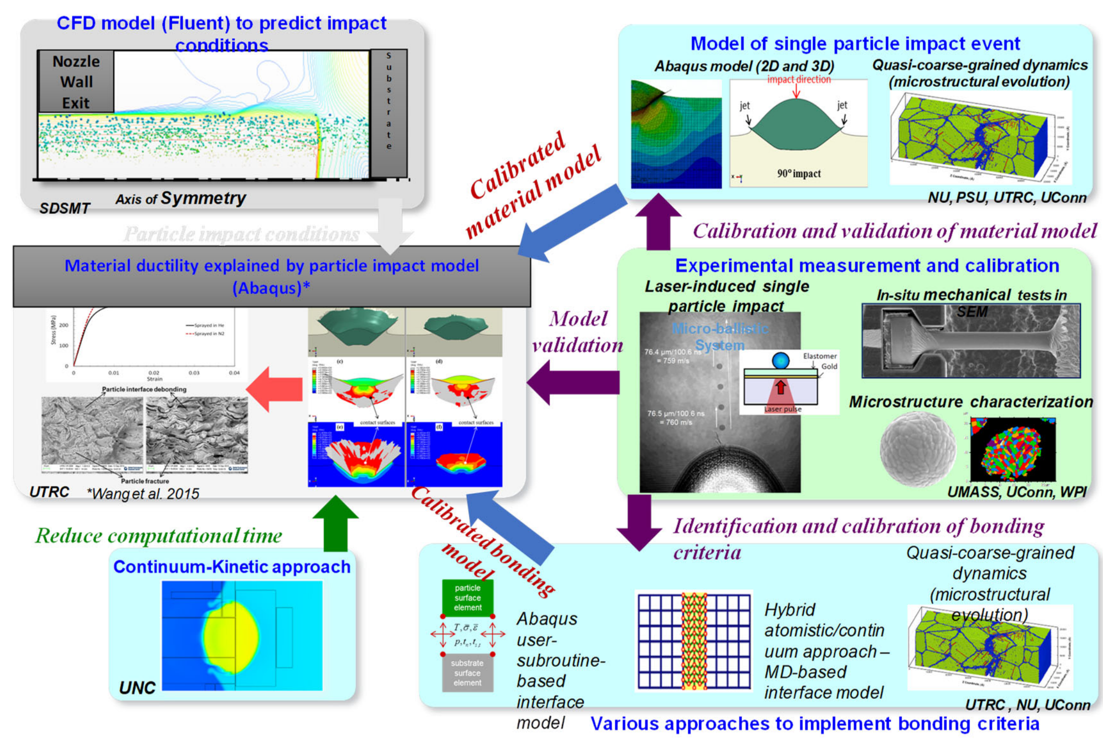


Figure 2. Physics-based material property prediction modeling framework, showing models used and team members involved.

3. Materials and Methods

Hard chrome is a single-element material applied by electroplating. It is a relatively simple process in which the coating is determined by the chemistry of the electroplating bath and the deposition parameters (primarily potential, current density, temperature). Cold Spray is a process in which particles are accelerated to extremely high velocities (Mach 2-Mach 4) at which point they impact a substrate and deform though plastic deformation. The plastic deformation causes the particles to bond in a similar manner to cold welding or explosive cladding. Cold spray hard chrome alternatives, are therefore by necessity very complex materials that typically combine a wear-resistant hard phase which cannot plastically deform, such as a carbide, with a soft phase that can plastically deform and will additionally provide toughness. The properties of the final coating are a function of the hard and soft phase materials, their morphology and loading, the manner in which they are combined, particle mean size and distribution, the gas used, gas temperature, velocity, design of the nozzle, and a host of other variables.

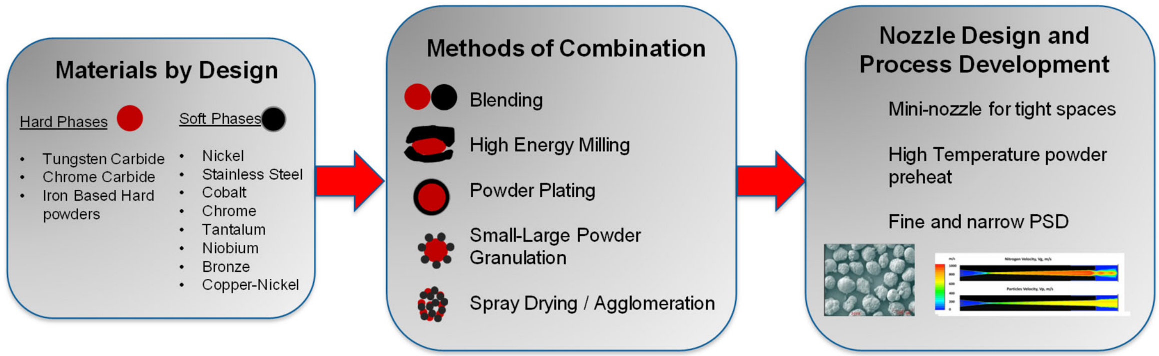


Figure 3. Materials by Design approach.

In order to obtain an optimized process, a unique Materials by Design approach was used in this program, combining materials modeling, process modeling, and experimentation. The methodology involved three primary steps, as shown in Figure 3:

1. Choose the materials for the hard and soft phases
2. Optimize the method of combining them to produce the optimum material, particle morphology, etc.
3. Optimize the deposition process through the nozzle design, heating methods, particle size distribution, and spray parameters such as standoff between nozzle and substrate, spray gas chemistry, temperature, pressure, and velocity.

3.1. Modeling Methods

The Materials by Design approach makes extensive use of modeling to understand the details of the process physics and to use that knowledge to guide the development of equipment, powders, and deposition process conditions. Spray models have been developed by ARL and the cold spray team, calibrated to both Computational Fluid Dynamics (CFD) models of the particle acceleration process and laser Doppler velocimetry data. These models have then been used for determining process conditions, to achieve impact velocity and impact temperature conditions adequate to achieve material consolidation. Finite Element Analyses have been carried out with Abaqus multi-physics simulation software from Dassault Systèmes in order to understand the particle impact and deformation processes. Finally, phase fraction analyses have been developed to understand the relative proportions of hard and soft phases required in a typical cold sprayed bondcoat.

3.2. Cold spray Equipment and Technology

The cold spray processing shown schematically in Figure 4. Unlike thermal spray processes such as HVOF and plasma spray, the cold spray powder is not injected into a heat source to bring it near the melting point. The carrier gas such as helium (for high velocity cold spray) or nitrogen (for lower velocity spray) is heated and powder injected into the heated gas stream.

This avoids the phase changes and decarburization commonly found in thermal sprays, and the energy in the process comes primarily from the kinetic energy of the particles, which become essentially cold welded or explosively clad to the surface.

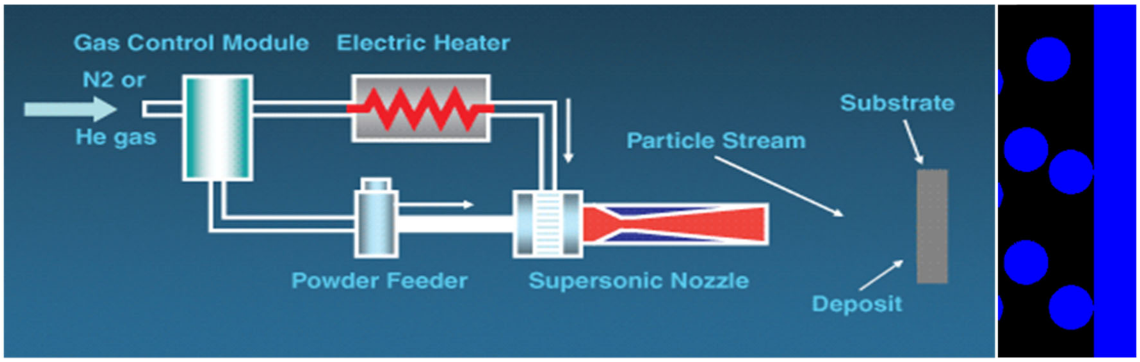


Figure 4. Cold spray system schematic

The process of gas acceleration occurs due to the high pressures inside the applicator creating a choked flow through the nozzle. The nozzle is a DeLaval style nozzle with a converging section, a flow restricting throat causing choked flow, and a diverging portion where the gas stream is expanded causing supersonic gas velocities. The relative lengths of each section of the nozzle as well as converging ratio, throat size, and diverging ratio all play a critical role in determining particle velocity and temperature on impact.

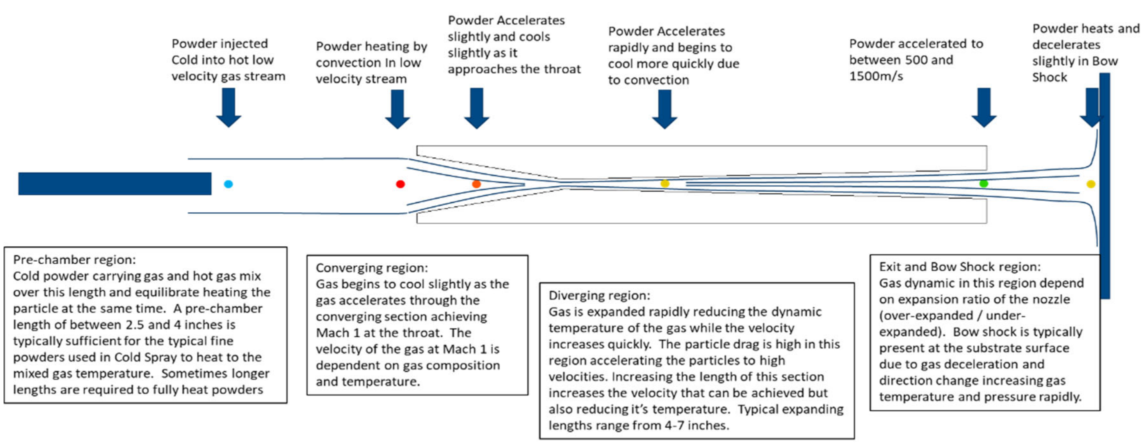


Figure 5. Schematic representation of Cold Spray DeLaval type nozzle with critical powder effects

The schematic representation in Figure 5 describes the various portions of a Cold Spray nozzle and the influence of the process on the powder in each portion. In most cases higher velocities are the key to improving Cold Spray deposit properties. In the case of multi-phase carbide containing materials, there is a critical balance between impact velocity and impact temperature due to the relatively low proportion of ductile phase present, and the propensity for the materials to overwork.

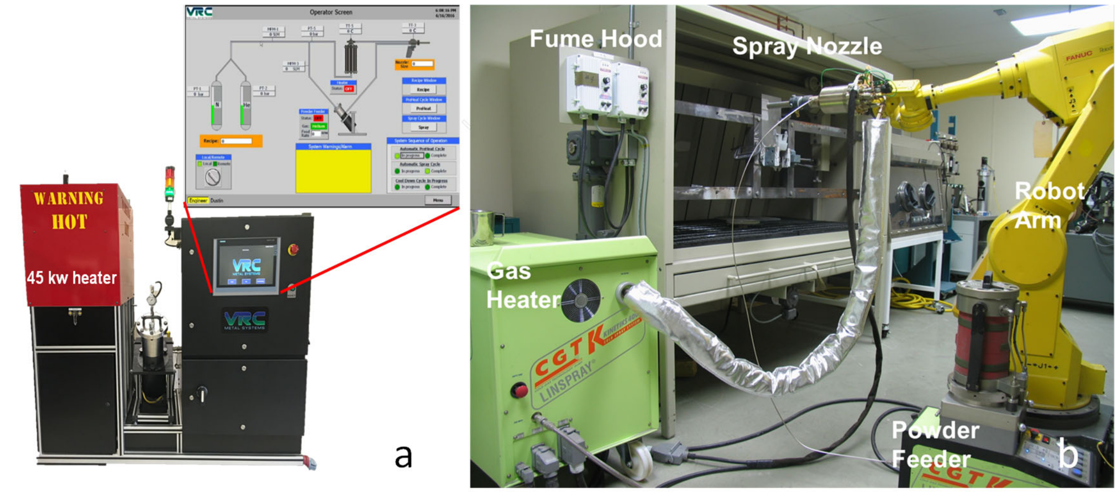


Figure 6. Cold spray equipment used in program (a) VRC Gen III Max Cold Spray System (b) R&D system at ARL

Several pieces of equipment were used in this work. Figure 6 shows an R&D unit installed at ARL and a commercial VRC Gen III hybrid cold spray system designed for commercial processing. The VRC equipment is the same type of system as that being installed at Honeywell, Letterkenny Army Depot, and Corpus Christi Army Depot. Both of these CS systems are high pressure and high temperature capable systems. The VRC system design also features the ability to spray at lower temperatures and pressures and using a wider variety of nozzle designs. This provides a versatility to spray not only Chrome replacement coating with one nozzle design and setup, but also structural aluminum or steel repair, or even tantalum deposition.

3.2.1. **Powder development**

A critical element of how CS coatings are formed is the dynamics of particle interactions with surface to create good adhesion, and with each other as the coating builds up to create good cohesion and develop mechanical properties. The physics was modeled by Finite Element Analysis (FEA) using Abaqus.

3.3. Sample Production and Test Methods

Samples and coupons were made, tested, and evaluated by various team members.

3.3.1. **Material characterization**

Powders were characterized by optical and electron microscopy (SEM). In addition some powders were characterized for particle size distribution through sieving or through microtrac evaluation.

Coatings were characterized by a combination of optical metallography and SEM, as well as X-ray diffraction to determine crystal structure.

Hardness was measured by ASTM E 384 Vickers hardness indentation.

3.3.2. Adhesion

Adhesion was measured by lug shear testing similar to Mil-J-24445. This applies a thick buildup (typically about 0.25 inches) of deposit to the panel then lugs are machined in and sheared from the substrate. This shows that not only can the material be built up sufficiently thick, but also provides for measuring strength above the strength of a typical polymeric adhesive.

3.3.3. Wear

Wear was measured by two methods:

1. Taber abrasion, which is an abrasive wear test
2. Reciprocating ball-on-flat wear testing using an alumina ball for abrasive wear and a 52100 ball for adhesive wear.

3.3.4. Electrochemistry

The polarization curves of the cold spray coatings and the Induplate hard chrome were measured in a standard flat cell under 3.5% NaCl bulk solution, following the ONR SBA Best Practices. They were deconvoluted into their underlying reactions using CUVFIT software, and inserted in Corrosion Djinn™ to permit galvanic analysis.

4. Results and Discussion

4.1. Modelling of Cold Spray Powders and Deposition Process

4.1.1. Nozzle design

One of the most critical aspects of the cold spray deposition method is the design of the converging-diverging nozzle to optimize particle impact velocity while balancing particle impact temperature.

Nozzle design was aided by quasi-one-dimensional isentropic (or inviscid) analysis.[1] While (CFD) can model viscous effects, it is computationally not well suited for efficiently evaluating multiple designs. Therefore we have added viscous effects empirically to the isentropic calculation, developing a finite difference program that includes viscous effects to calculate optimum nozzle dimensions. This has been calibrated not only to CFD analyses, but also experimental measurements from Laser Doppler Velocimetry

An example of the fluid dynamics calculations is shown in Figure 7. In this figure the orange line indicates the nozzle wall where the dotted orange line is the real wall, and the solid line indicates the core flow (subtracting the boundary layer thickness) or effective wall used for calculations of particle velocity. Notice that the gas velocity increases rapidly beyond the converging section of the nozzle, dragging the particles with it and increasing their velocity to about Mach 2. In this same region the gas temperature cools rapidly which also tends to reduce the particle temperature. This plays a critical role especially in the cermets evaluated here as we found that for the highest concentrations of ceramic or hard phase particles in the resulting deposits, the temperature needed to be higher while the velocity could be lower.

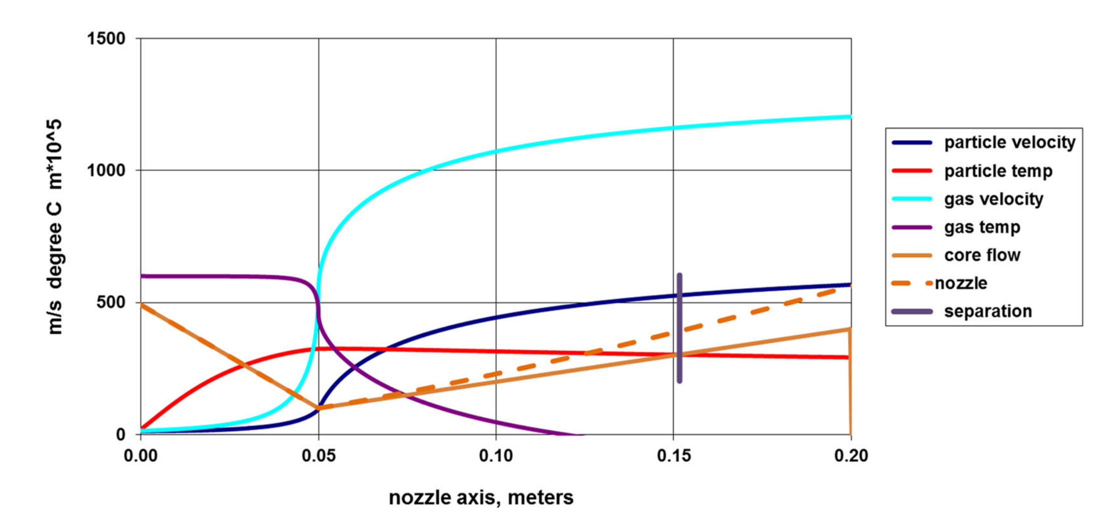


Figure 7. Numerical analysis and process modeling for CS nozzle refinement.

4.1.2. **Process modeling**

Another critical aspect of the cold spray process is the particle-solid interaction at the surface of the substrate and of the growing coating. FEA modeling has shown that there are a number of critical requirements for a CS particle to adhere well to the substrate as well as creating a coating that has high hardness coupled with high toughness and low porosity. Primarily, the bonding and densification processes can be summed up in one critical physical process, plastic deformation. It is plastic deformation of the particle and of the substrate at the interface between the two which causes bonding, and it is bulk plastic deformation of the particle that aids in densification.

HVOF coatings such as WC-Co or WC-CoCr used as an option for chrome replacement in the past are very hard and far more wear resistant than hard chrome in most cases, but they suffer from the drawback that they can have low strain-to-failure, and as a result they tend to fail in high strain environments. Furthermore when these coatings fail they tend to spall from the substrate due to a failure of the bondline of the coating. Chrome is also prone to cracking at low strain levels, but the cracks are less likely to create a spall location leaving the substrate susceptible to wear, or damaging mating surfaces such as seals. [2]

To improve on this performance it is important to understand what governs the particle-solid interaction when a high velocity particle impinges on a solid surface, and to do that it is important to understand the physics of deformation of the particle, and how that is governed by its structure. As a result, powder design and process design are very strongly coupled. We cannot simply take standard powders developed for thermal spray and expect them to perform well in cold spray. For this reason modeling was carried out both for powder development and for the development of processes using those powders.

Modeling the effects of particle porosity was a key focus of this effort. Porosity is important due the typical manufacturing process of many cermet powders. Spray drying and sintering is a common process in which fine carbide particles are combined with a metal using a polymer binder and spray dried, forming spherical powders. The powders are then sintered to remove the polymer, leaving behind only the carbide and metal bound together. These powders have porosity levels measured as high as 30%. This porosity tends to be very fine and randomly distributed.

Initial indications from a literature review suggested that increasing porosity would increase deformation and strain within the particle as well as surface temperature.[3] Figure 8 shows an example of the effect of different particle porosity on the way that particle heats and embeds into the surface. As the porosity of the particle is increased the surface temperature rises during the impact and the plastic strain within the particle and at the interface increases, making the coating more dense and well bonded. Figure 8 shows that increased porosity increases the temperature at the impact site.

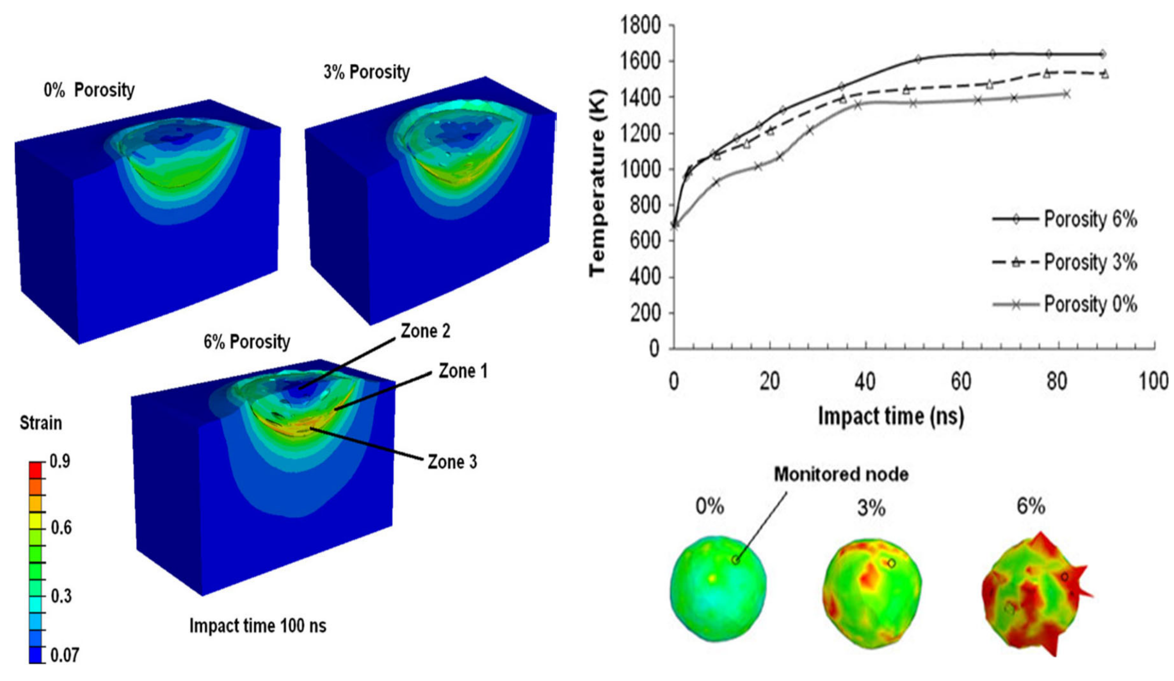


Figure 8. Effect of particle porosity on impact temperature excursions[3].

An in-house analysis was performed to confirm results from literature as well as better understand the effects of particle porosity. For simplicity, this modeling was performed with uniform and slightly larger than typical pores. In this study, the impact and penetration of particle with and without porosity was compared, as can be seen in Figure 9. This comparison shows how the presence of porosity dissipates more energy, reduces penetration of the particle into the substrate, increases particle flattening, and increases the rise in interface temperature. The results suggest that the presence of porosity allows a particle that otherwise acts like a rigid body to behave in a semi-plastic or pseudo-plastic manner.

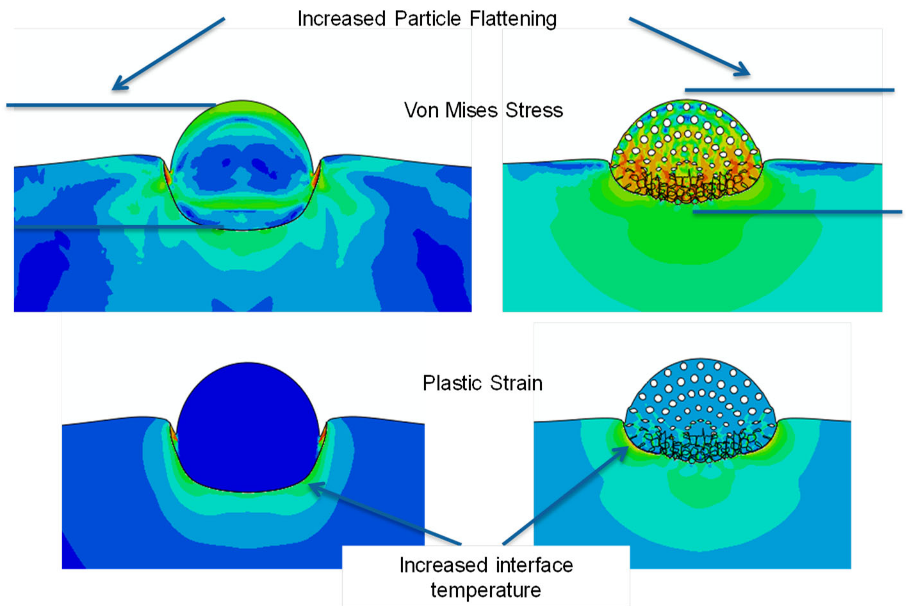


Figure 9. Increased Von Mises stress and plastic strain with more porous particles.

Impact modeling also showed that using hard but deformable particles with a soft outer layer increases temperature uniformity and produces higher interface temperatures, forming a better coating. Our modeling shows that when a particle strikes the surface, its kinetic energy is rapidly turned into thermal energy via plastic deformation and can result in localization of strain at the particle-substrate interface. The particle then flattens and becomes partially buried in the surface where it bonds. The uniformity of the strain and temperatures at the interface drives the bond strength.

When the hard particle has a soft coating, the coating can more easily deform and the shear of this softer material flowing at the interface provides a more uniform heating of the particle surface and the substrate surface. Figure 10 shows the difference in temperature and thermal effects due to impact by a hard particle and hard particle with a soft shell. When the particle itself is more porous it becomes better incorporated into the surface, with higher surface temperatures and a more uniform stress field. This can then be combined with the benefits of coating of the particle to further improve bonding and to add to the total metal content of the deposit in an attempt to improve the overall toughness of the material.

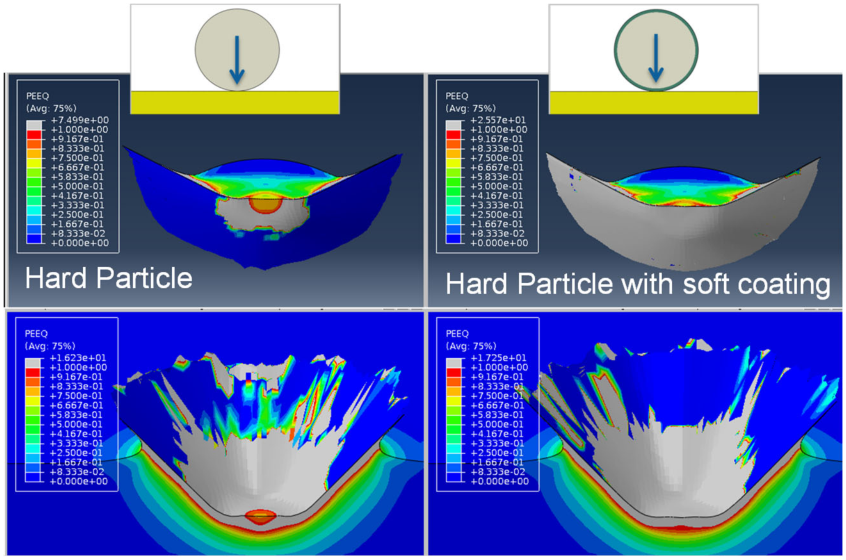


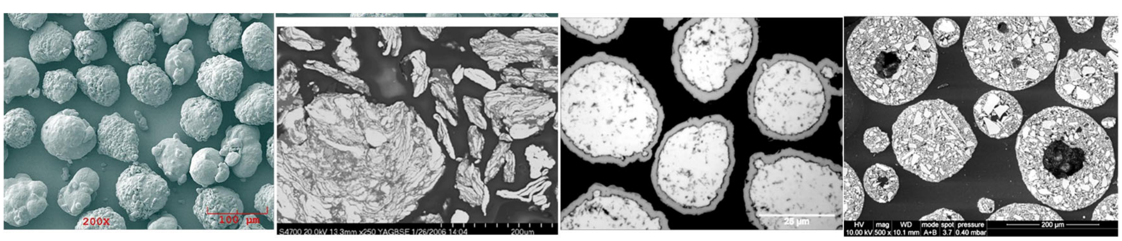
Figure 10. Effect of soft shell on hard particle.

4.2. **Powder Development**

Based on our finite element modeling results, powders were designed and developed to optimize the mechanical properties of the coating. As we have noted above, CS powders for the most hard and wear resistant surfaces, must include hard and soft phases, and an optimum porosity. This involves identifying the best particle morphology and processing techniques for cold spray, remembering that powder processing is a strong cost driver.

4.2.1. **Powder manufacturing process development**

In this program several different methods were evaluated for producing composite powders (i.e. powders with a hard phase and a soft binder phase). Examples of powders produced by several of these methods can be found in Figure 11.



Mechanically Clad Mechanically Alloyed Chemically Clad Spray Dried and Sintered

Figure 11. Multi-base powder production techniques.

Blending

Various combinations of hard and soft phases have been evaluated. The best results have included Cr_3C_2 + Ni, Cr_3C_2 + Ni20Cr, as well as Fe based hard powders such as Nanosteel and Iron Based hardfacing powders blended with nickel and stainless steel. Blending achieves hardness that are limited to approximately 350-500 HV, making it a potential solution for nickel plating replacement, but not for most hard chrome replacement. This said due to the mixed phase microstructure (large hard phase well bonded into a softer phase) in some wear environments these can even perform similar to or better than chrome. In addition, due to the high metals content, these materials can build up with no real limit in thickness (up to 0.75 inches has been demonstrated), and they have a high toughness (impact resistance).

High Energy Milling (Mechanical Alloying)

High energy milling has not proved to be very successful for combing hard and sof phases together. This type of powder processing has been useful for combining two soft phase materials such as nickel and aluminum in the past. For soft phase-hard phase combinations, the soft powder does not transfer well onto hard powder during the milling process. There may be potential for improvement through the use of finer hard powders or with agglomerated/sintered powders.

Spray Drying Agglomeration and Sintering

This is a common method of manufacturing cermet powder. It uses a spray nozzle to atomize a slurry of very fine constituents (typically less than 10 micron) particles in a polymer binder solution like PVA or PVP into a heated gas. The droplets formed dry quickly forming powder particles. These powder particles are then sintered to remove the binder leaving the fine constituents sintered together as porous spherical powder. In thermal spray the size of the hard particles in the powder, such as carbides, tend to be 3-10 microns. Finer carbides would generally be considered better, as they are in WC-Co hard metal tooling, but they are not preferred due to degradation in the flame of the thermal spray system. Cold spray does not have the same issues and as such performance has been found to improve by using smaller carbides as well as smaller particle sizes. Cold Spray deposits with hardness between 700 and 1300 HV have been achieved with coating compositions of WC-Co, WC-Ni, and Cr3C2-Ni20Cr. Examples of powders and deposits are shown in Figure 12.

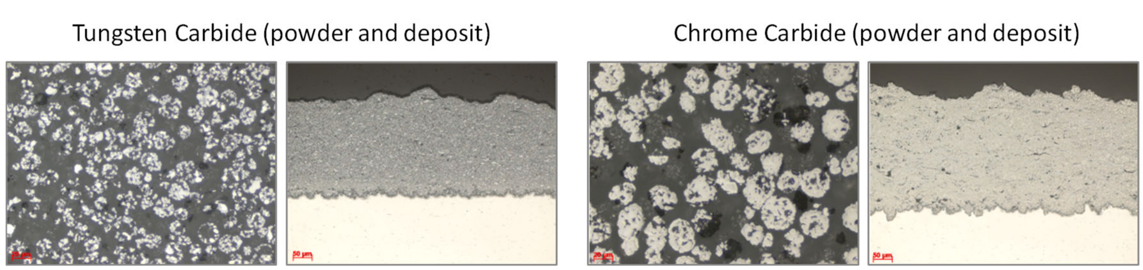


Figure 12. Spray dried and agglomerated particles and resultant coating microstructures.

The following powder characteristics lead to improved outcomes:

- Sphericity of agglomerates
- Homogeneity of agglomerates
- Small agglomerate size <20 microns lower preferred (related to density)
- Finer constituents in agglomerates <2 microns

Chrome carbide and Tungsten Carbide powders have shown similar trends. One difference is that chrome carbide is lower density than tungsten carbide, and therefore particle size, although still important, can be larger. Once the ideal characteristics of the WC based powders were determined, several special order powders were created to explore the chemistry design space. A list of the powders evaluated are shown in Table 1.

Table 1. WC Powders produced by HC Stark.

Powder #	Powder Formulation	Powder Name	As received Particle Size
1	WC-12Co	Amperit 519.059	-30/+5
2	WC-17Co	Special Order	-30/+5
3	WC-17Ni	Special Order	-30/+5
4	WC-25Ni	Special Order	-30/+5

Granulation

Clad powders were produced using a granulation developed by UTRC for the Cr_3C_2-Ni and Cr_3C_2-NiCr CS powders. The granulation approach is quite common and many companies have large batch production capabilities using this method. In the UTRC method fine soft cladding particles are cladded to hard larger core particles by the granulation technique. Images of example powders produced are shown in Figure 13.

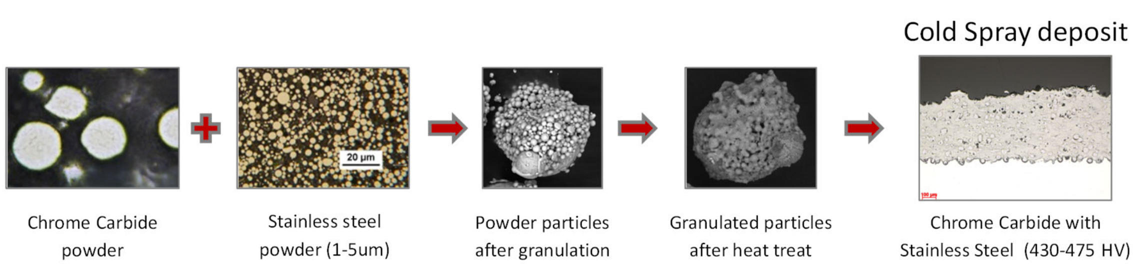


Figure 13. Granulation process for CrC+410ss.

This technique uses a PVP solution portioned out in order to create a layer of fine particles attached to the outside of the core particle. The resulting clad powders were then heat-treated to create adherent layers.

Spray drying / Granulation

The combination of spray drying and granulation, using high hardness spray dried powder with the addition of a soft metal phase to reduce peak hardness, increases deposition efficiency (DE) and sprayability. In addition the benefits of using the spray dried powders as described earlier with regards to modeling were that the core particle experiences pseudo-plasticity allowing the powder to deposit and bond and for the soft outer layer to help improve the bonding of the particles. The granulation process generally and more specifically the process used with spray dried powders is shown in Figure 14.

The general deposit properties are given below:

- Deposits in the 650-750 HV range have been achieved using two different WC spray dried powders with fine nickel granulation (resulting in higher hardness and increased DE)
- DE is more than double that of carbide powder alone
- Buildups as thick as 1mm have been demonstrated with no evident limits and requiring no special nozzle designs.

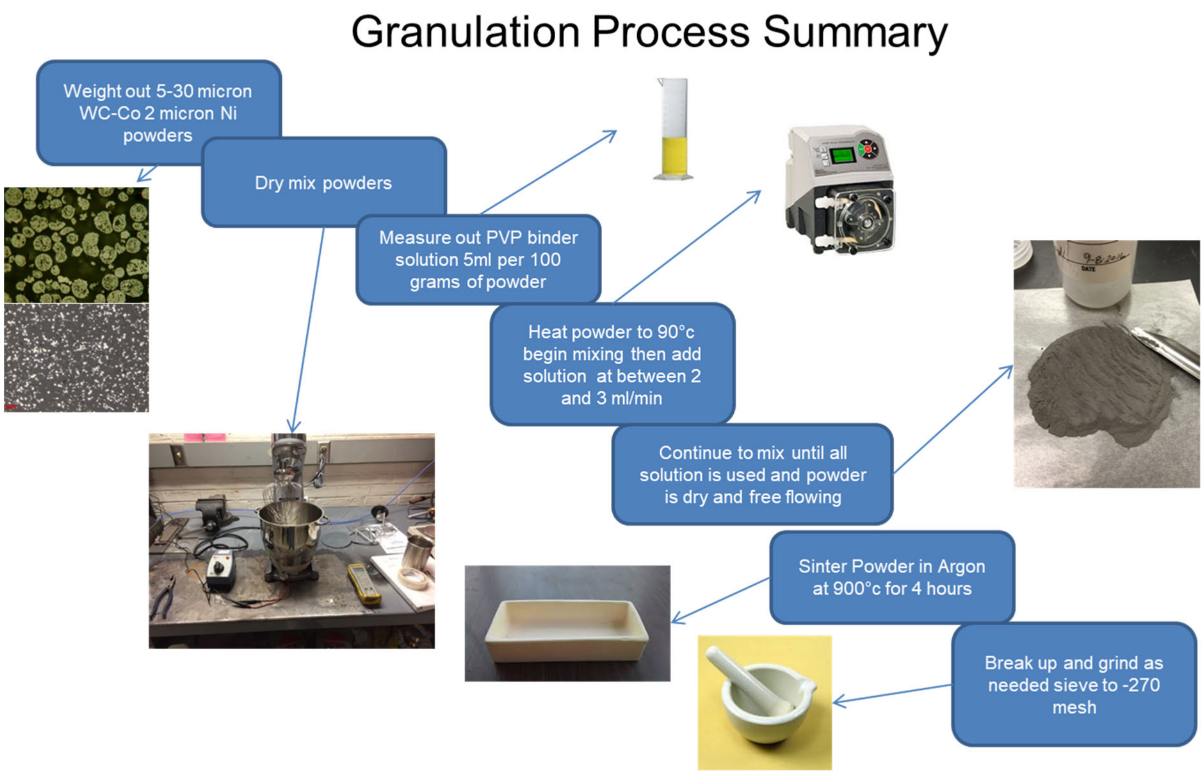


Figure 14: The granulation process of spray dried WC-12Co powder with fine nickel

An examples of a WC based spray dried + Granulation powders produced which later sprayed successfully are shown in Figure 15.

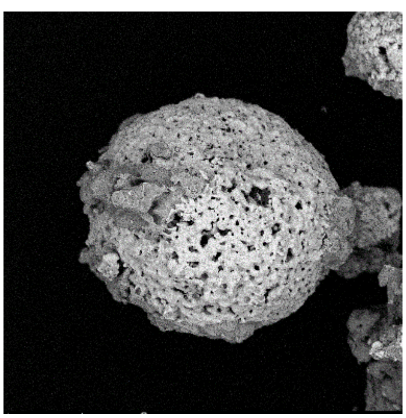


Figure 15. WC-12Co+18Ni produced by granulation.

Two WC based powders were found to produce excellent coatings after granulation and both were also found to deposit well even before granulation. These were Amperit 519.059 powder from HC Stark and PComp W-611 from Mesocoat. Examples of the deposits produced are shown in Figure 16.

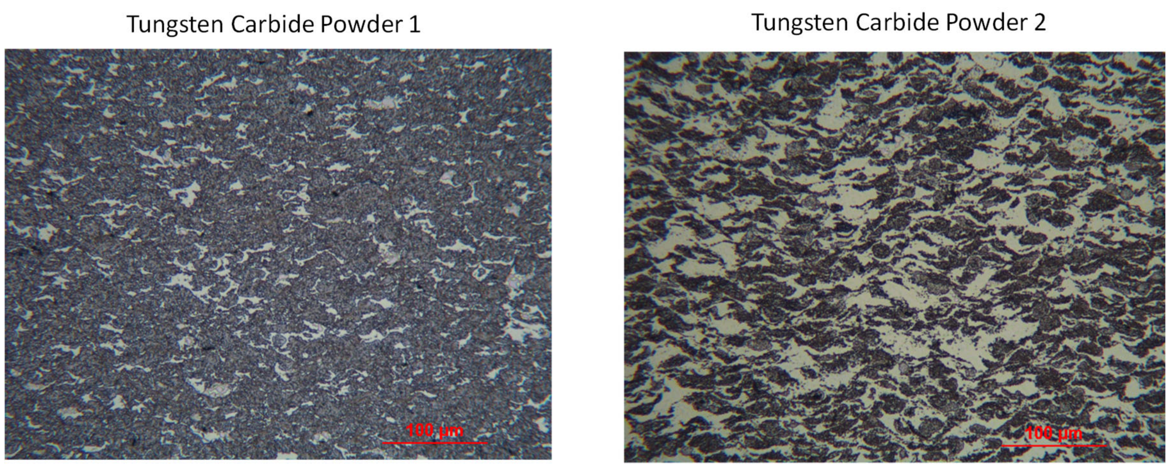


Figure 16. Two tungsten carbide cross sections made with spray dried and granulated powders.

4.3. Coating Properties

4.3.1. Chemistry and Microstructure

The chemistries and microstructures of coatings deposited during the program are shown in Table 2. These materials are all composites comprising a hard phase in a relatively soft matrix. The hardness values depend on the type of coating and percentage of binder versus hard phase. All of the high hardness and medium hardness coatings are comparable in heartedness to hard chrome. Figure 17 shows cross-sections of three of the cold spray hard coatings compared with hard chrome.

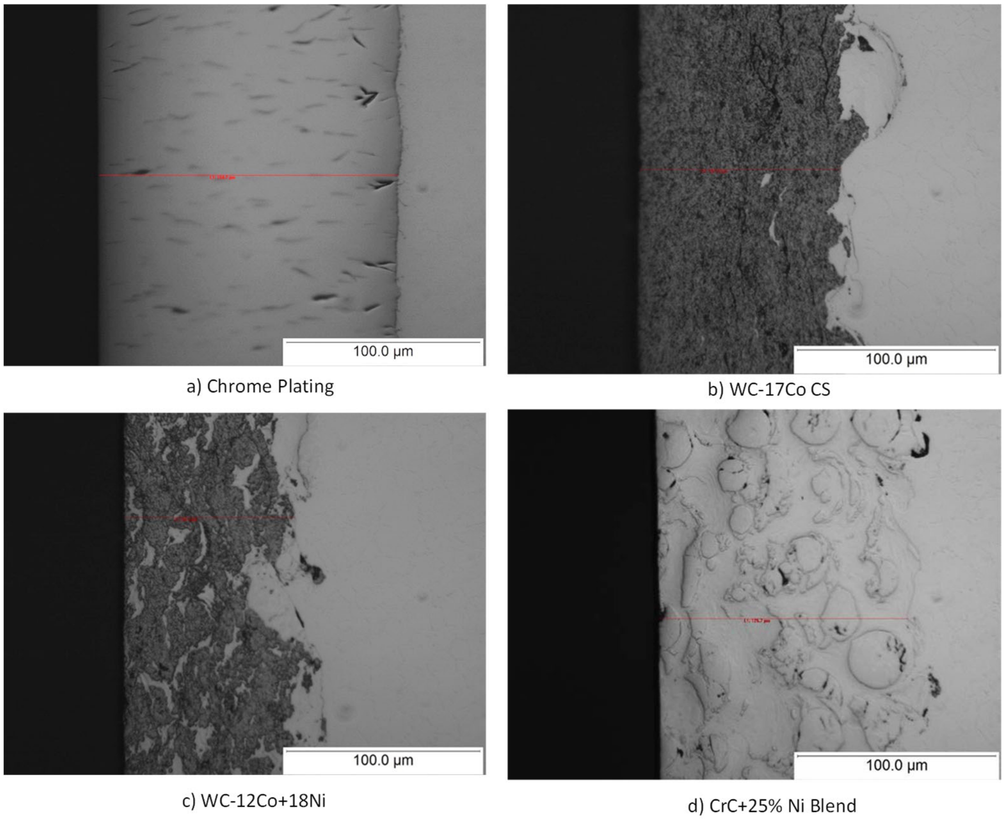
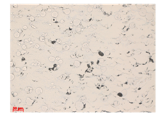
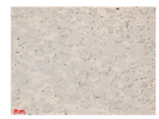
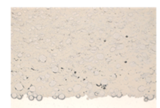
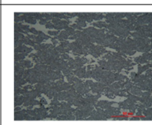
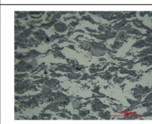
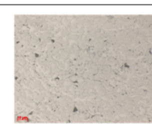
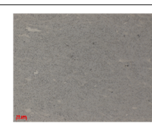
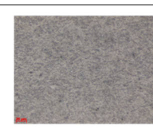
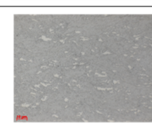
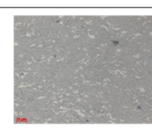


Figure 17. Cross-sectional microstructure of hard chrome and CS coatings.

Table 2. Cold spray coatings, powders and hardness values.

Coating Type	Sample ID	Simple Name	Composition	Gas Used	Nozzle Used	Potential N2 coating	Hardness Range (HV)	Representative Micrographs
Low Hardness Coatings <500 HV	CS-16-093-5	CrC-NiCr-NiCr	Blend, CRC-410-1 + 25% Ni-105-7	N2	Long	yes	400-500	
	CS-16-112	CrC-NiCr +Ni	Blend, CRC-410-1 + 25% Ni-914-3	He	Short	yes	400-500	
	CS-16-133	Fe Hard Phase + Ni	Blend Diamalloy 1008 + 10% Ni-914-3	He	Long	yes	400-500	
	CS-16-134	Fe Hard Phase + 420SS	Blend Diamalloy 1008 + 10% Fe-211 Ar HT	He	Long	yes	400-500	
	CS-16-211	CrC-NiCr +20%Ni	CrC 410-1 -400 mesh granulated with 18% Ni(5 μm)	N2	Long	yes	400-500	
Medium Hardness Coatings 700-800 HV	CS-16-222-3	WC-12Co+18Ni	Amperit 519.059 granulated with 18% Ni(1.5 μm)	He	Medium	yes	700-800	
	CS-16-222-4	WC-17Co+19Ni	Mesocoat Pcomp W611 -500+635, granulated with 18% Ni(1.5 μm)	He	Medium	yes	700-800	
High Hardness Coatings >800 HV	CS-16-209-5	Cr3C2-35NiCr	Amperit 587 -325/+400	He	Short	?	900	
	CS-16-209-10	WC-12Co	Amperit 519 -635 mesh	He	Short	?	1200-1300	
	CS-17-030-1	WC-17Co	Similar to old Amperit 527-635	He	Short	?	900	
	CS-17-030-2	WC-17Ni	Similar to old Amperit 527-635 but using Ni instead of Co	He	Short	?	1150	
	CS-17-030-3	WC-25Ni	Similar to old Amperit 527-635 but using Ni instead of Co and increasing Ni to 25%	He	Short	?	800	

4.3.2. **Adhesion**

As discussed previously, in Cold Spray plastic deformation is the key to both bonding to the substrate and bonding between layers or particles. When a soft particle is therefore sprayed onto a hardened substrate (e.g. soft pure nickel on hardened steel) the soft particle will deform and flatten however the substrate will not deform and as such a strong bond will not form. We have found that by blending hard particles and soft particles together the bond strength can be improved. This occurs due to the hard particle impacting the soft material at the same time as the soft material impact and sticks to the substrate. This forces plasticity to occur in both the particle and substrate.

In the current project blended materials were evaluated for their improvements in wear, but similar blends can be used to enhance adhesion for a variety of hard materials. The key in to select hard particles of the correct hardness and size that they will cause plastic deformation then either incorporate as a second soft particle impact the surface (this is the case when wear resistance is required), or bounces off because the larger particle is too large to capture (this is the case with many bondcoats). In either case the bond effectiveness is governed by the likelihood of impact of the hard phase just after the soft phase has bonded.

As illustrated in Figure 18, soft particles tend to flatten, which increases their effective area on the surface, while hard particles deform less reducing their effective area relative to their nominal diameter.

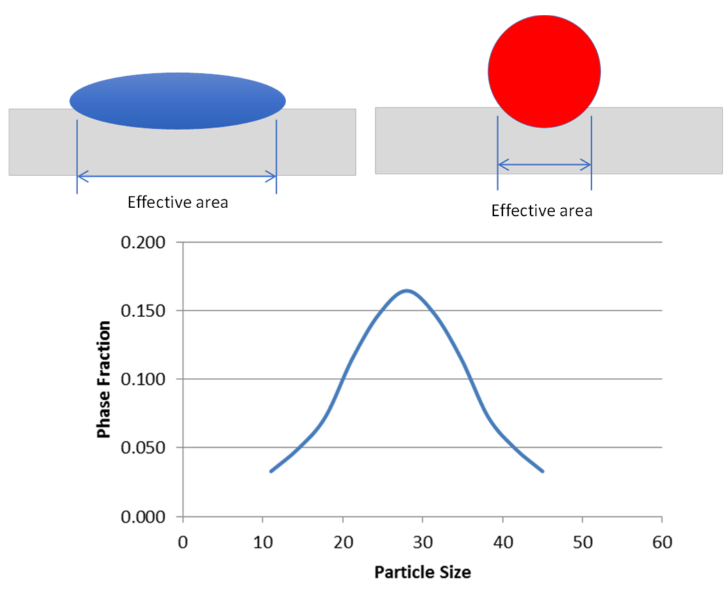


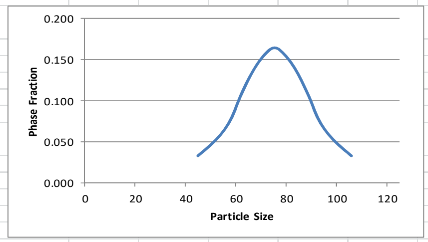
Figure 18. Projected areas of hard and soft particles due to flattening – Cr_3C_2-Ni bond coat and buildup coating.

A semi-empirical model was developed that correlates bond strength with particle size and density. The idea comes back to the projected area of the particle relative to its mass. Since for instance volume is a cubic function of particle radius while projected area is a squared function, this suggests that hard phase particles with a larger mean particle size would tend require a higher mass fraction in the blend in order to have a sufficient probability that all soft particles would be impacted after bonding. Once developed this model was calibrated empirically using bond data generated with two different particle size hard phases at two different percentages. The results of the model are shown in Figure 19 and show that a projected area ratio or "Overlap ratio" of greater than 4 provides a high quality bond.

Optimization of Blend Ratios to Achieve high Bond Strength

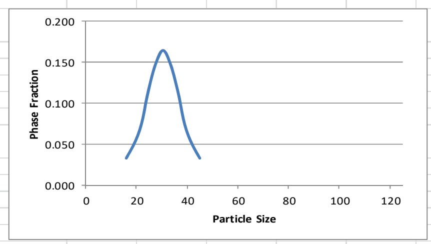
Hard Particle	
Density (g/cc)	6.971
D10 Particle Size (um)	45
D90 Particle Size (um)	106
Blend Mass Percentage	90
Particle Hardness (HV)	1000
Total projected area in 1 gram of blend	2671454758

Assumed PSD		
Size (um)	Fraction	Projected Area (um^2)
106	0.033	60097892
100	0.049	95651299
94	0.072	149411816
88	0.115	254233955
82	0.148	351307529
76	0.164	421879240
69	0.148	413064760
63	0.115	352232509
57	0.072	245014482
51	0.049	186997354
45	0.033	141563923



Soft Particle	
Density (g/cc)	8.9
D10 Particle Size (um)	16
D90 Particle Size (um)	45
Blend Mass Percentage	10
Sprayed Particle Hardness (HV)	240
Total projected area in 1 gram of blend	585776288

Assumed PSD		
Size (um)	Fraction	Projected Area (um^2)
45	0.033	12320126
42	0.049	19753171
39	0.072	31114604
36	0.115	53455093
33	0.148	74695376
31	0.164	90886177
28	0.148	90392230
25	0.115	78559509
22	0.072	55949197
19	0.049	44000451
16	0.033	34650355



Overlap Area Ratio	4.56

Figure 19. Model of projected particle areas for hard and soft particles.

Using this coating design information a bondcoat of 90% of a large (45-90 micron) CrC particle blended with 10% of a smaller (10-50 micron) pure nickel powder. This bondcoat provides sufficient plasticity to create high bond strength, while not incorporating significant amounts of the harder CrC phase. The combination of this bondcoat with the standard blended CrC-NiCr and CrC-Ni are shown in Table 3 for a nitrogen sprayed deposit. It should be noted that helium deposits always exhibit even greater bond strength than nitrogen deposits due to the significantly higher velocity of the particles. The same bondcoat is typically used on all of the coatings developed under this effort. It is also notable that this bond strength must be measured by lug shear testing because the coatings have an extremely high bond strength that results in only adhesive failures in the typical ASTM C633 bond test typically used for thermal spray coatings.

Table 3. Cold spray coatings bond strength.

Substrate	Coating	Bond Strength (ksi)
17-4 Stainless	CrC-NiCr (WIP-C2)	28
17-4 Stainless	CrC-Ni (WIP-C1)	26
40 HRC Alloy Steel	CrC-Ni (WIP-C1)	25

4.3.3. **Hardness**

As expected, increasing percentages of binder reduced the hardness, but higher levels of binder typically increase the toughness of sprayed coatings. Hardness values of several coatings systems evaluated are shown in Table 2. With the blended hard phase soft phase materials it is important not to understand the mass or volume percent of hard phase in the powder blend, but rather in the final deposit. For instance, with the CrC-Ni, the common blend used very successfully is 75% by weight CRC particles with 25% pure Nickel. Both powder size distributions are similar at roughly 20-45 or 50 microns. The mechanism of capture is to have a hard particle impact causing some penetration, then having a metal particle capture it before the elastic energy in the particle forces it to rebound from the surface. Generally the phase fraction in the coating after deposition is between 35 and 40% for this blended powder. This capture efficiency is therefore the reason for the hardness values of 400-450 HV in the blended powders and the reason for the lower apparent deposition efficiency of between 25 and 35%. All of the particles that impact then rebound from the surface impart plastic deformation even if they do not bond in place which is why we get a high quality deposit and high bond strength even with nitrogen or air with most of these materials.

4.3.4. **Electrochemistry, corrosion**

Figure 20 shows the polarization curves in bulk 3.5% NaCl solution for Induplate EHC, cold spray WC-CoNi and Cr_3C_2-Ni, vs the metals they would be most commonly used on – 4340 high strength steel and 7075 Al. Clearly, the Cr_3C_2-Ni (green curve) is far more cathodic, with an Open Circuit Potential (OCP) of -0.22V in contrast to the OCPs of -0.56 and -0.50 for EHC and WC-CoNi respectively. This is what we would expect since Ni is far more noble (cathodic) than Co, and it is the matrix metal that determines the electrochemistry.

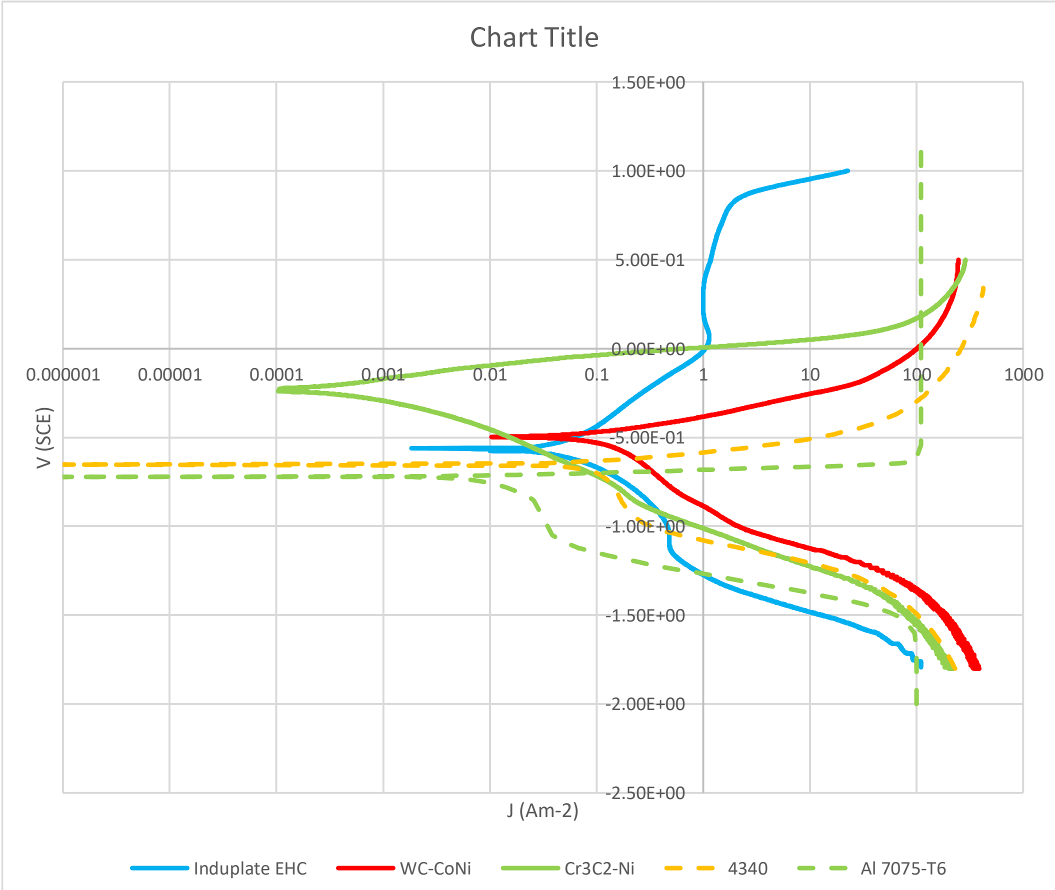


Figure 20. Polarization curves in 3.5% NaCl of cold spray materials and EHC vs high strength steel and Al.

According to MIL-STD-889B this would be expected to result in strong galvanic corrosion of high strength steel and Al. However, as the ONR SBA Team has clearly established, what matters is not the OCP difference, but the galvanic current at the point where the polarization curve of the cathodic material crosses the anodic curve of the anode, which will be incorporated into the next version of MIL-STD-889. The crossing point for Cr_3C_2-Ni and 4340 is about the same value as the EHC crossing point. Thus it will cause no more galvanic corrosion on high strength steel than EHC does, which is about 120µm/yr – similar to the self-corrosion rate of 4340 steel. WC-Co-Ni will cause two to three times this galvanic corrosion rate.

The conclusion of this analysis is that Cr_3C_2-Ni will not cause excessive galvanic corrosion on high strength steels when the coating is damaged while the WC-Co-Ni may show an increased galvanic corrosion rate. With this said, many corrosion tests have been performed with similar composition materials deposited by HVOF and have shown a variety of different results depending on the specifics of the corrosion environment. Further testing with real world corrosion evaluations are necessary to understand the expected field performance of the coatings.

4.4. **Coating performance**

4.4.1. **Wear**

Taber abrasion testing provides a measure of abrasive wear resistance, which is important for applications where a component may be exposed to abrasive particles such as sand – this a common situation for landing gear and aircraft hydraulics. Figure 21 shows that the cold spray WC-12Co-18Ni (WIP-W1) is somewhat more abrasion resistant than hard chrome, while CrC-Ni (WIP-C1) is less resistant to pure abrasion.

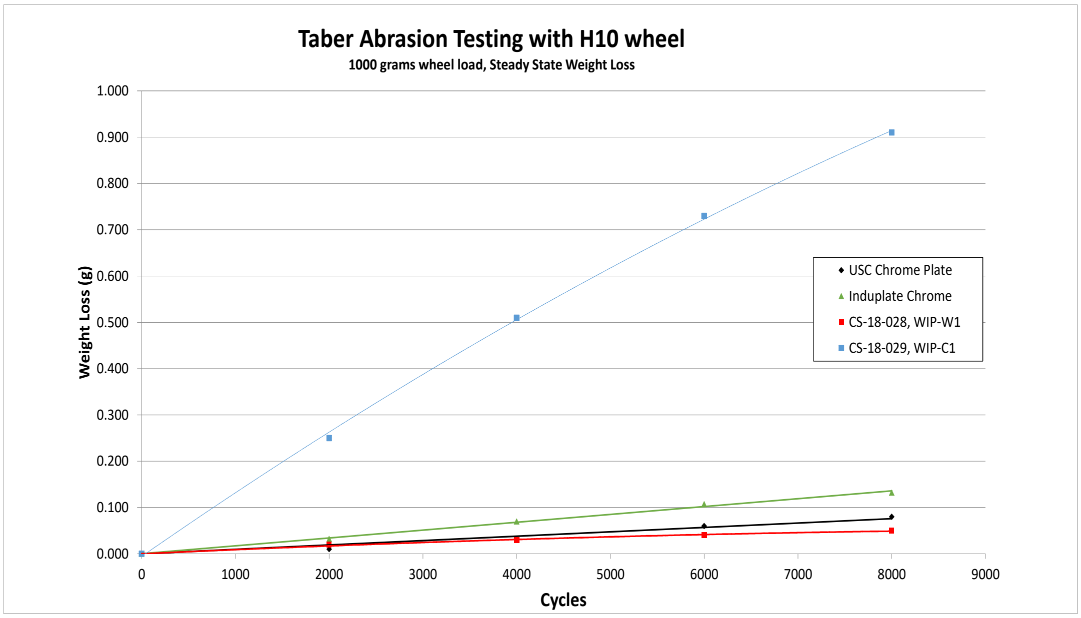


Figure 21. Taber wear of WC-12Co-18Ni (WIP-W1) vs hard chrome.

These abrasion results are not completely unexpected for the CrC-Ni (WIP-C1) due to the relatively low hardness of this material. In fact, this level hardness coating would generally be considered for applications replacing electrolytic nickel platings where far less abrasion resistance is expected. It is notable that the WC-12Co-18Ni (WIP-W1) Cold Spray coating does show an improvement over chrome as this has a hardness of roughly 700 HV in comparison to 850-900 HV for typical Chrome Plating.

Reciprocating ball on flat tests provide a measure of adhesive wear when a metallic ball is used, and abrasive wear using a ceramic ball. UTRC performed lighter load and lower speed G133 testing using both 52100 and alumina ball bearings. Chrome plate and CrC-Ni were evaluated at 10, 20, and 30 N loads and were found to increase in wear rate proportional to load. Based on this information all other materials were only tested at 30N. Wear rates of coatings tested against alumina bearings are shown in Figure 22. In this figure, the label 'Amperit 519 + AA Nickel 2-3 APS' corresponds to WC-12Co-18Ni and 'PComP W611 + AA Nickel 2-3 APS' corresponds to WC-17Co-19Ni.

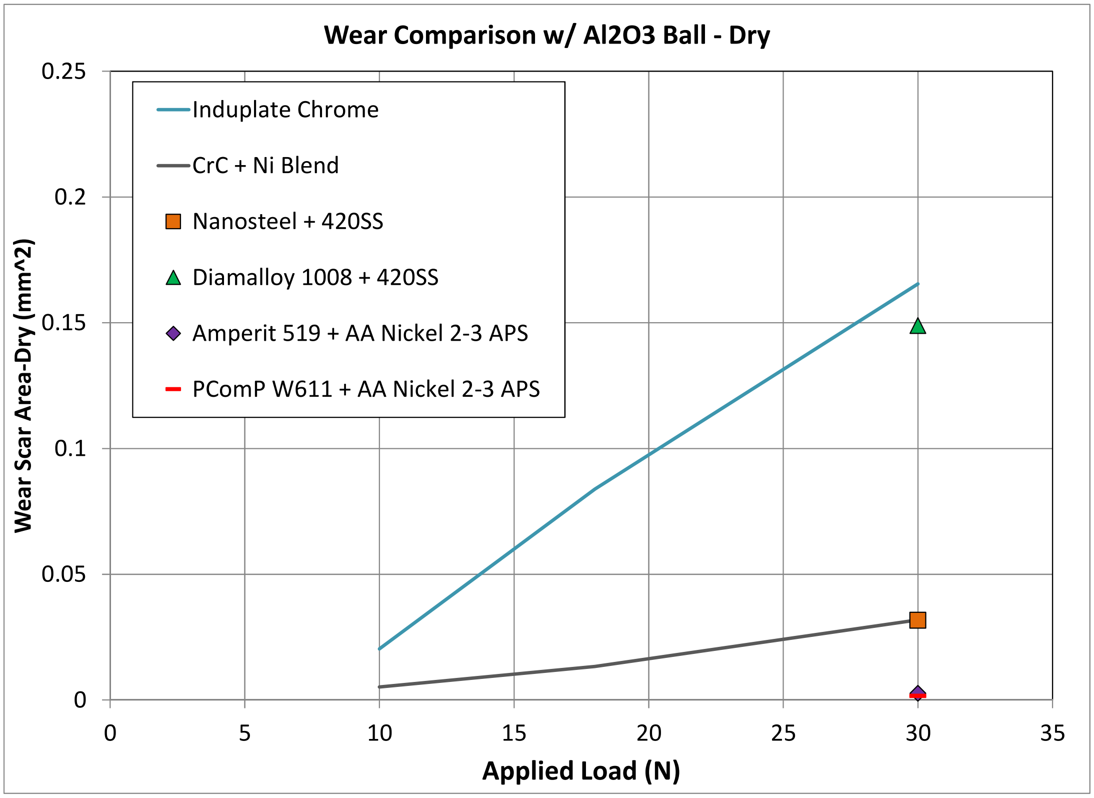


Figure 22. Coating scar area for Al_2O_3 ball on flat reciprocating wear test on various SERDP coatings (UTRC).

It is clear from this data that all Cold Sprayed coatings including the lower hardness blended deposits (CrC-Ni, Diamalloy 1008 + 420SS, and Nanosteel + 420SS) outperformed chrome plating in tests against an alumina ball.

In tests against a 52100 ball under these loading conditions, the chrome plating was found to perform very well. This data is shown in Figure 23. In this case only the higher hardness WC-12Co-18Ni (Amperit 519 + AA Nickel 2-3 APS) and WC-17Co-19Ni (PComP W611 + AA Nickel 2-3 APS) spray dried and granulated coatings performed comparable to chrome while the blended material performed more poorly.

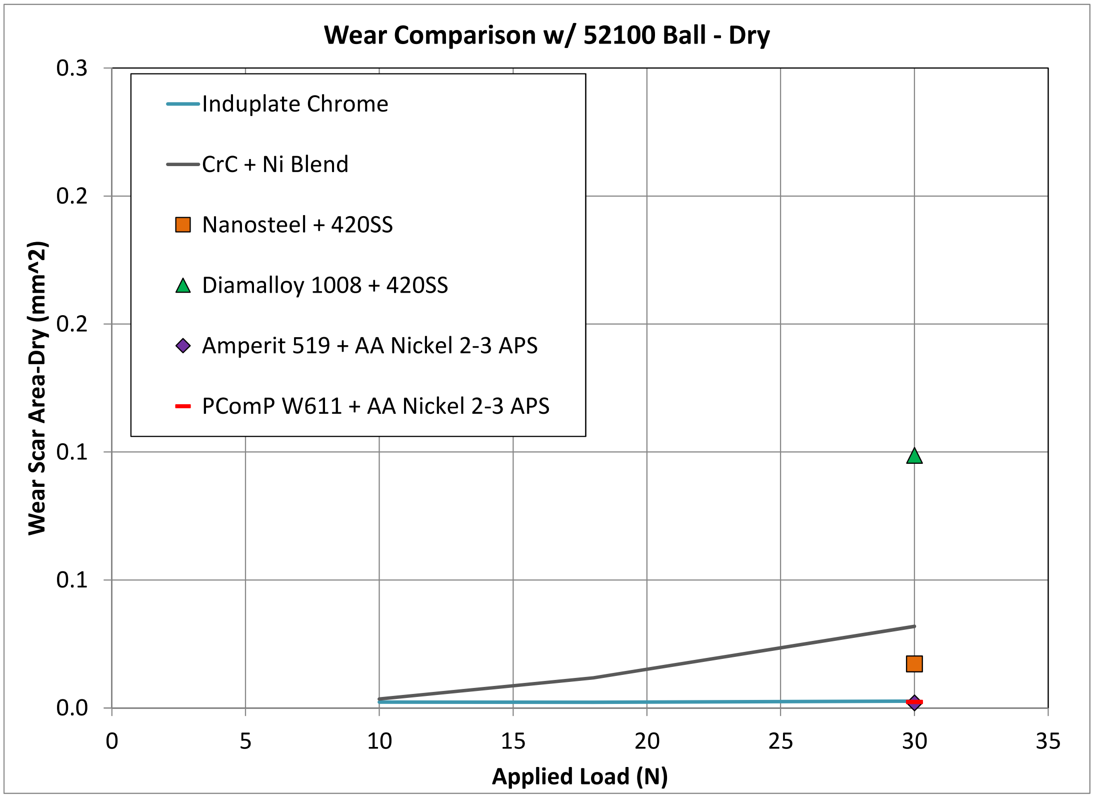


Figure 23. Coating scar area for 52100 ball on flat reciprocating wear test on various SERDP coatings (UTRC).

4.5. Cold Spray Equipment and Process Development

4.5.1. Thick Build-up Coatings

One of the shortcomings of HVOF WC-Co coatings such as WC-CoCr is that they have low strain-to-failure and tend to crack and delaminate close to the yield point of most high-strength steels. This means that in many applications, such as landing gear, thick coatings needed to return the component to print dimensions require a combination of a relatively low hardness, high toughness build up coating capped with a hard tungsten carbide. As we have noted in Section 4.2.1, tungsten carbide coatings deposited using spray dried and granulated powders can be built to millimeter thickness. In this program we have not acquired fatigue data on these coatings, and therefore do not yet know whether there are practical limitations on their thickness.

4.5.2. Nozzle design

Using the modeling approach described in Section 4.1, nozzle geometries have been designed for different applications. Figure 24 shows an example of a nozzle design for CS of internal diameters. This approach makes it possible to spray diameter as small as 4 cm, even down the entire length of a blind hole. The design similar to that of Figure 24 has been successfully used for spraying the IDs of gun barrels for hard chrome placement.

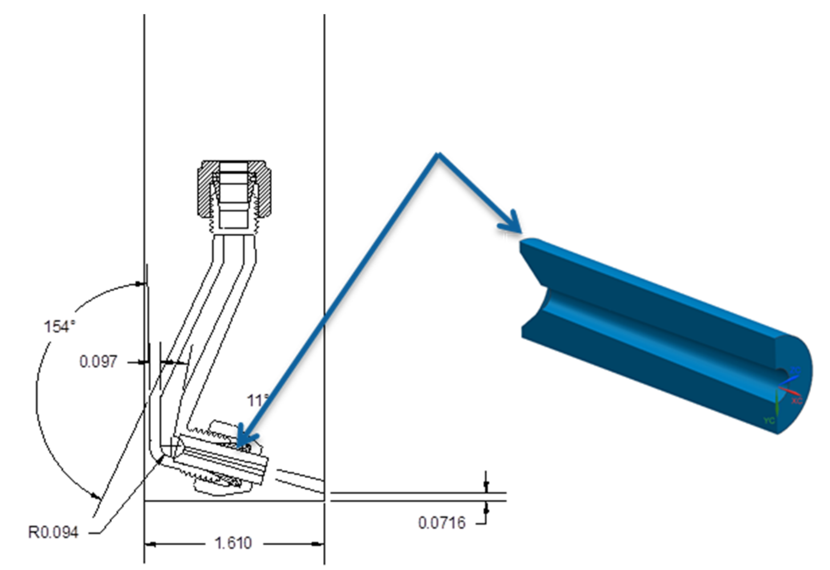


Figure 24. Computationally-designed nozzle for ID coating

Other nozzle designs are shown in Figure 25. The right angle nozzle design can be used to spray areas that are not easily accessed with a standard gun. The capillary nozzle design makes it possible to spray very small areas at a high build-up rate.

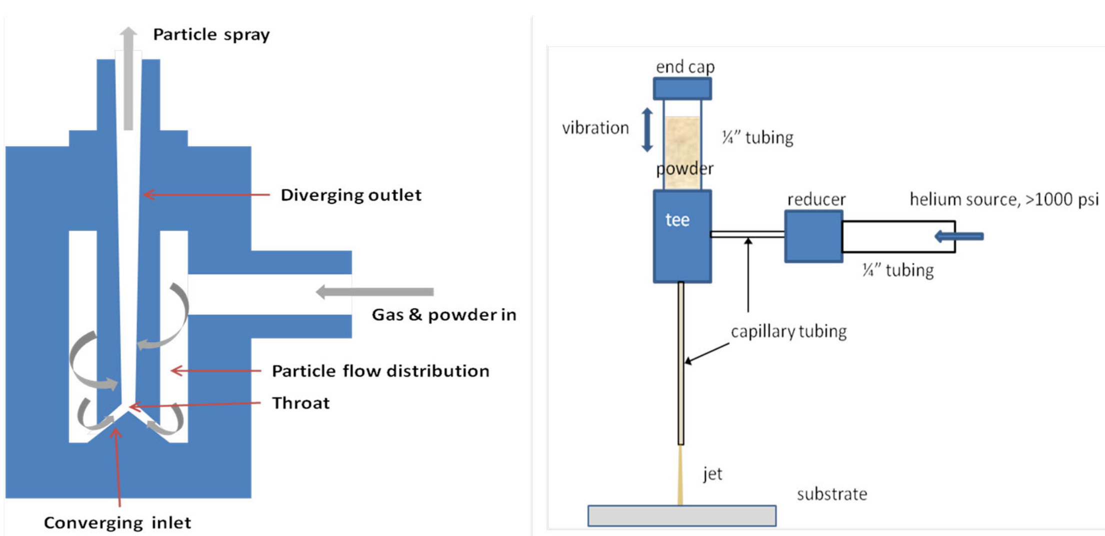


Figure 25. Left - right angle nozzle design; Right - Capillary nozzle design.

4.5.3. **Fielded Cold Spray Applications**

A number of cold spray repair applications have been brought to production, including:

- Fielded SH-60 Seahawk with Cold Spray Mg repair, operating since August, 2009- Australian Navy (ARL/JSF/DSTO Collaboration)
- Three Fielded Blackhawk Medvac Units with Cold Spray Al repair, operating since August, 2009 (ARL/AMCOM/Ft. Hood Collaboration)
- Fielded B-1 Bomber with Cold Spray Ti and Al repair operating since September 2009 - Tinker AFB (ARL/Tinker and Ellsworth AFB/HF Webster/SDSM Collaboration)
- Apache Intermediate Gear Support, production part-casting defect repair, fielded in 2014
- Two Expeditionary Fighting Vehicles with CS Mg Repair, fielded and operating since September, 2008 (ARL/Allison Transmissions Collaboration)
    - Power Transfer Module, 10 magnesium castings
    - Transmission, 13 magnesium castings

5. Conclusions and Implications for Future Research/Implementation

The focus of this project was to demonstrate the utility of cold spray as a hard chrome replacement. In order to do this we have developed and demonstrated a **Holistic Cold Spray Material and Process Development Approach.** In this approach, for the first time, we have applied modern computational modeling methods to the development of cold spray powders and processes in a manner that optimizes the performance of the process as a whole. The adoption of this approach is a milestone in the development of cold spray technology because it makes it possible to develop new materials, new processes, and new equipment, all designed and optimized for specific applications. In the past powder was developed essentially independently of gun design, and often not for Cold Spray at all. The equipment was then forced to operate with available powders often not performing optimally. It is now possible to use computational modeling methods to optimize the entire process for a specific application as needed including design of the powder. This makes cold spray of far more efficient process, and process development may now be able to keep pace with the changing requirements of the marketplace, especially ESOH and REACH requirements.

Using this holistic development approach we have developed and demonstrated several powders and applicator / nozzle designs capable of producing wear resistant alternative coatings that meet or exceed the performance of hard chrome and nickel. This now makes it possible to use cold spray coatings for applications which would have been unthinkable a few years ago, including directly spraying the internal diameters of gun tubes, or hydraulic cylinders, or spraying complex shapes where direct access to all of the areas would be extremely difficult with typical thermal spray equipment.

At the same time that we have been developing a holistic approach we have also been developing the infrastructure needed to put that approach into practice. By working closely with powder producers to create powders to our design, and by creating equipment that can work seamlessly with Commercial Off-the-Shelf Cold Spray systems, the infrastructure is in place to scale up the materials developed and carry out the Cold Spray process reliably and reproducibility on a commercial basis.

The capability for rapid and accurate design of the entire process, its equipment and materials puts us in a very good position to develop specific applications for replacing hard chrome on DoD equipment. Indeed, we have already developed an approach for cold spray as a hard chrome replacement inside gun tubes with Technology Transfer Agreements in place with Watervliet Arsenal. We have also developed an AH-64 mast support repair that replaces hard nickel plating and has been approved by the US Army Aviation Army Directorate.

The Storage, Analysis, Failure Evaluation, and Reclamation (SAFR) building at CCAD contains numerous transition applications in the form of BER (Beyond Economic Repair) components that could be reclaimed by the use of cold spray (Figure 26). Among these is a T55 engine compressor shaft that is currently hard chrome plated and has a value of $142,413 and a 3rd turbine shaft assembly valued at >$2.6 million. We also plan to transition spot repairs on shafts and bearing areas that currently use a combination of nickel silver plating. The advantage of cold spray is that it avoids the need for hydrogen bakeout and it can be more wear resistant than is realistically feasible with nickel electroplating and requires minimal masking in most cases.

It is very common practice for DoD to rebuild equipment such as landing gear by a combination of sulfamate nickel electroplate for buildup, capped with hard chrome for wear. Nickel can easily be built up by cold spray, and capped with WC-Co-Ni, Cr_3C_2-Ni or an alternative composite cold spray; in fact it appears to be quite possible simply to use the composite for both buildup and wear resistance, since the cold spray materials evaluated appear not to suffer the low strain-to-failure problems associated with HVOF WC-CoCr coatings.

Much of the groundwork has been laid for rapid demonstration and validation of the coatings developed with the introduction of Military process standards and powder standards for Cold Spray generally, and working to develop the industrial base for powders and equipment.

Figure 26. Examples of items that could be reclaimed using Cold Spray.

However, in order to industrialize these cold spray coatings the next stage of development must be to acquire all of the engineering data necessary for qualification, including corrosion and fatigue, and develop the engineering specifications to ensure reliable deposition and performance.

REFERENCES

[1] J.D. Anderson. "Modern Compressible Flow With Historical Perspective, 3rd Ed." McGraw-Hill, 2003.

[2] "Replacement of Chromium Electroplating on Landing Gear Components Using HVOF Thermal Spray Coatings", COST & PERFORMANCE REPORT ESTCP Project: PP-9608, B. Sartwell, K. Legg

[3] "The Influence of Powder Porosity on the Bonding Mechanism at the Impact of Thermally Sprayed Solid Particles", DOI: 10.1007/s11661-010-0488-8

APPENDIX A. SUPPORTING DATA

No additional data to report

Appendix B. List of Scientific/Technical Publications

1) CSAT 2017 Brief "Multi-Directional Properties and Hard Coating Development", 6/14/2017, A. Nardi
2) CSAT 2018 Brief "Cold Spray (CS) Coatings for Cr and Ni Plating Replacement" 6/2018, A. Nardi
3) ASETS Defense Brief "Cold Spray (CS) Coatings for Cr and Ni Plating Replacement", 12/2016, V. Champagne
4) ASETS Defense Brief "Cold Spray (CS) Coatings for Cr and Ni Plating Replacement", 8/2018, A. Nardi
5) Practical Handbook for the Cold Spray Process, book manuscript, Chapter 4 – Powder, Chapter 5 – Material Properties, to be published by Springer

APPENDIX C. OTHER SUPPORTING MATERIALS

None to Report