Cold Sprayed Refractory Metals for Chrome Reduction in Gun Barrel Liners

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Abstract

Modern gun barrel technology faces a number of challenges related to the use of chrome-plated steel at the interior bore surface. The amount of allowable chrome has been significantly reduced due to environmental, health, and safety concerns. Furthermore, current munitions and propellants lead to erosion and condemnation of gun barrels well before their 10,000 round expected lifetime. This has precipitated a search for longer-lasting bore liners, such as refractory metals deposited by explosive bonding. The cost and difficulty associated with shaping these materials have made them impractical choices to date. Gas Dynamic Cold Spray consolidation of refractory metals and alloys was selected as an alternative to extrusion for additive manufacture of donor tubes. Tantalum-10 Tungsten alloy donor tubes have been produced by Cold Spray and tested for compatibility with the cladding process. A 1-meter (3-foot) long tube was produced to test scalability.

Introduction

The liners typically used for the manufacture of gun barrels, selected for their low cost and relative ease of manufacture, are ill-suited to withstand the thermal cycling and hot gas corrosion caused by most propellantsⁱ. Chrome plating, long used as a surface coating to line and protect steel gun barrels, has been shown to provide insufficient protection for the expected lifetime of modern systems. Thermal cycling, hot corrosion, and mechanical wear all contribute to early wear and failure of chrome-based coatings, leading to the search for more durable materials. Moreover, mandates from environmental, health, and safety organizations such as the EPA for reduction of chrome exposure have made chrome unattractive for continued productionⁱⁱ. Therefore, numerous research efforts^{iii,iv,v,vi} have been made to find suitable alternatives to chrome plating as a liner material that can offer extended gun barrel life and comparable or increased performance while maintaining competitive costs.

As munitions become more advanced, the trend has been towards higher energy rounds, which require higher temperature propellants that often produce corrosive exhaust. This has directed research efforts towards refractory based, high hardness alloys that will be able to withstand hot corrosion environments, thermal cycling, and the various stresses caused by compression cycles and erosion. The coating process is ideally also compatible with gun steel, demonstrating high adhesion, thermal protection, and the ability to integrate with current manufacturing processes and standards.

Refractory alloys possess many of the desired material qualities, but their high strengths present unique manufacturing challenges that can lead to high costs and long lead times. This has been especially true for tantalum-based alloys, which have been identified as materials of interest

for scale-up testing by Benet Laboratories^{vii}. While one-foot sections of Cold Sprayed donor tubes had been investigated in other studies^{viii} for gun barrel linings, large scale (three feet or greater) testing had not been attempted. Benet Labs and ARL have collaborated to develop the capability and manufacturability of Cold Spray for the production of long 10W-Ta donor tubes for evaluation as an alternate means of production.

Gas Dynamic Cold Spray

Gas Dynamic Cold Spray is a thermal spray type process that was issued a U.S. Patent in 1994 for coating applications^{ix}. Like thermal spray, Cold Spray directs powdered material towards a substrate in order to build up successive layers of particle “splats” from the impingement of the powdered material (Figure 1). However, contrary to thermal spray, the Cold Spray process is designed to keep the powdered material in the solid state, and achieves particle splatting through the application of kinetic energy as opposed to thermal energy. The use of converging-diverging nozzles (DeLaval nozzles) along with high stagnation pressures results in solid particles moving at supersonic speeds (800-1200 m/s). At these speeds, upon impact with the substrate, the particles deform, mix mechanically with the substrate and each other, and form metallurgical and mechanical bonds. Through the application of successive layers of particles, a dense, highly adherent coating can be built to significant thickness. These coatings can serve in a number of applications, based on their composition and shape. Most notably for the present work, careful design of the substrate and application of coating thickness can yield near net shape, additively manufactured parts with unique properties.

Figure 1: Schematic of the Cold Spray Process

Due to the high strength and toughness of refractory alloys, conventional fabrication methods of production such as machining or extrusion can prove difficult and costly. Powder metallurgy approaches are often used with refractory alloys due to their reduced temperature requirements compared to ingot metallurgy; Cold Spray can be thought of as a type of impact-mediated sintering operation. However, due to the effects of the impact process, cold-sprayed parts typically have high ultimate strengths (near and sometimes beyond wrought strength) but low elongation. This is a direct result of the impact process, as particles essentially undergo 100% cold work as they form splats in the solid state. Resultant residual stresses are typically compressive^x which can have repercussions on substrate geometry and as-sprayed material properties for near net shape applications.

Experimental Procedure

Process Modeling

A model previously developed by Helfrich et al was used to predict the powder size(s) required and optimum cold spray parameters of Ta-10W alloys and blends based on prior work with pure tantalum^{viii}. The model relies on assumptions based on material properties such as density, modulus and yield strength and has been used to accurately predict the deposition efficiency (DE, a measure of process waste) of copper and aluminum particles as a function of particle size. Investigations were also made into the effects of using Nitrogen as a process gas as opposed to Helium. Figure 2 shows the calculated DE for Ta-10W using Helium and Nitrogen as a function of pressure. Due to the greater mass of molecular Nitrogen compared to Helium, higher pressures are required when using Nitrogen to achieve the same particle velocity (and thus the same deposition efficiency). However, it should be noted that this calculation does not account for the physical properties of the deposit, such as residual stress or porosity. Although Helium was used for this particular study, the potential for comparable efficiencies with Nitrogen show promise for additional cost savings in the future. Deposition efficiency is calculated as a function of cold spray nozzle inlet parameters, and subsequently verified experimentally. Using an isentropic gas flow and associated particle drag models (described below), highly efficient spray parameters can be selected to yield DE's greater than 80%, which is particularly critical when using high cost refractory feedstocks. The DE model enables pre-selection of cost-effective process parameters while reducing the need for multiple iterations of time and feedstock intensive spray trials.

Figure 2: DE model as a function of temperature for Ta-10W at 1000 C

Deposition efficiency is calculated as a function of Mach number, temperature, and pressure at the inlet of the cold spray nozzle, which is then iteratively used to calculate gas velocity along the nozzle, through the gas exit from the nozzle and its impact with the substrate with associated bow shock. Particle size, size distribution, and shape are used to calculate particle velocity as a function of drag and heating in the gas stream, and a fraction of the particle population that will impact the substrate at or above the critical deposition velocity is calculated assuming a log normal size distribution around a user-supplied mean particle diameter. The critical deposition velocity is given by the formula from Assadi et al^{xi}

$$v_{cr} = 667 - 14\rho + 0.08T_m + 0.1\sigma_u - 0.4T_i \quad (1)$$

Where ρ is the material density in g/cm^3 , T_m is the melting temperature in $^\circ\text{C}$, σ_u is the ultimate strength in MPa and T_i is the initial particle temperature in $^\circ\text{C}$. These parameters summarize the onset of adiabatic shear instability in the impinging particles.

Particle velocities as a function of gas flows are determined using 1-d isentropic gas dynamic equations for gas stagnation conditions in a given nozzle geometry (inlet, throat, and expansion areas), as well as beyond the nozzle and through the bow shock preceding the substrate. Once gas conditions and velocity are characterized within and beyond the nozzle, particle velocity is iteratively calculated down the length of the nozzle through the use of a solid rocket nozzle particle drag relationship:

$$m \frac{dV_p}{dt} = C_D (\pi/8) \rho_g d^2 (V_g - V_p)^2 \quad (2)$$

Where V_p and V_g are particle and gas velocities, m is particle mass, ρ_g is gas density, and d is particle diameter. Additional considerations are made for particle heating in the gas stream through the application of a gas-particle heat transfer under forced convection:

$$c_p \frac{dT_p}{dt} = (N_u k / d) (A_p / m) (T_g - T_p) \quad (3)$$

Where c_p is the particle heat capacity, T_p and T_g are the particle and gas temperatures, N_u is the Nusselt number, k is the gas conductivity, and A_p is the particle surface area. Values for either nitrogen or helium can be used depending on the process gas to be used for deposition.

These particle velocity, temperature, and material property inputs are used iteratively prior to cold spray to calculate initial process parameters, which are optimized to yield a maximum deposition efficiency as shown in Figure 2. The resultant deposits are then characterized to evaluate coating quality with respect to performance criteria such as porosity, density, and hardness. Typical process parameter development cycles balance maximum DE, which typically occurs at the highest gas temperatures and pressures, against various processing issues, such as coating costs, residual stress from overworking of deposited particles, the erosion velocity of the particles for the substrate in question.

Powder Characterization

Powder size, shape, and oxygen content were identified as key parameters that affect the feasibility of consolidation. Received powders were characterized by SEM for size and morphology. Two sources of powder were tested: the first was a blended powder made at ARL from off the shelf Tantalum (HC Starck Amperit 151.065, -30/+10 micron) and Tungsten (Buffalo Tungsten, 5 micron) powders, the second was a custom Ta-10W alloy powder produced from a custom ordered ingot through HC Starck. While specific oxygen contents are proprietary to the deposition process, reduced interstitial oxygen content for tantalum, tungsten, and their alloys enables increased ductility of the cold spray feedstock, which promotes plastic flow on impact and higher consolidated material integrity. Feedstock with too great of an oxygen content will consolidate, but at lower efficiencies, and is at risk for cracking and failure as-sprayed through combined residual stresses, thermal shock, coating-substrate coefficient of thermal expansion (CTE) mismatches, and oxygen embrittlement. A summary of donor tube chemistries with qualitative oxygen content and associated hardnesses is shown in Table 1 for both cold sprayed feedstocks as well as a commercially available extruded tube. Note the increased deposit hardness and oxygen content for the as-received Starck powder. After these tests, the Starck powder was returned for additional processing including oxygen reduction and size classification

Table 1: Summary of Donor Tube Chemistries and Hardnesses

Average	ARL Blend	HC Starck Alloy	Extruded Commercial Tube
Hardness Vickers	264.77	448.31	287.49
Hardness Rockwell C	45.1	55.7	47.5
Density	16.54	16.48	16.95
Oxygen (%)	X	4.5X	1/8 X
Tungsten (%)	8.61	10.1	9.48
Silicon (%)	0.018	0.019	0.026
Tantalum	Balance	Balance	Balance

Cold Spray Deposition

Samples were sprayed using a CGT 4000 Cold Spray system that was manipulated over the substrate using a 6-axis robot with helium as the process gas. Test sprays were performed on flat panels and tubular aluminum mandrels in order to yield general deposition characteristics and donor tube test specimens, respectively. For all powders, samples were consolidated with a baseline parameter set of 400° C operating temperature and 25 bar stagnation pressure. Deposition Efficiency was determined by calculating the ratio of weight gain of the substrate to powder loss during the spray operation. After consolidation the samples were metallographically prepared and examined through optical microscopy. Donor tube samples, and full scale three foot tubes, were consolidated on tubular aluminum mandrels, then removed and post-processed for explosive cladding.

Post Processing

Consolidated tubes were removed from their aluminum mandrels through machining of the aluminum inner diameter followed by soaking of the donor tube in a dilute sodium hydroxide solution. Once all the aluminum was removed, the donor tube was annealed for stress relief and to restore the material's ductility and toughness to ensure component integrity through handling, final machining, and for explosive cladding.

Results and Discussion

Figure 3 shows SEM micrographs of the Ta-10W powders. While the ARL blend has a narrow particle size range, the atomized ingot powder shows a wide range of particle sizes, which can be challenging to consolidate because different sized particles achieve different velocities in the process gas stream due to varying drag and mass considerations. Particles moving too slowly fail to consolidate at all while particles moving too quickly erode the substrate as opposed to depositing on it. Therefore, the Starck alloy powder was returned to the vendor for classification into coarse and fine powder cuts, as well as to be treated in a reducing atmosphere to lower the amount of oxygen present in the powder. Both tantalum and tungsten are sensitive to interstitial oxygen, which can reduce the ductility of the deposit even after heat treatment and affect the ability of the tube to be explosively clad.

Figure 3: 500x SEM Micrographs of ARL Blend (A) and as-received HC Starck Alloy (B) powders

Figure 4 shows the alloy powder after classification into coarse and fine powder cuts. Note the separation of the fine powder from the large angular particles; this allows each powder set to be sprayed at its optimum process parameters.

Figure 4: 250x SEM Micrographs of Coarse (A) and Fine (B) alloy powders (250x)

Figures 5-8 shows metallographic specimens of the ARL blended powder, as well as the HC Starck alloy powder both before and after refinement.

Figure 5: Cold Sprayed ARL Blended Ta-10W

Figure 6: Cold Sprayed As-Received HC Starck Ta-10W Alloy Powder

Figure 7: Cold Sprayed Refined HC Starck Ta-10W Alloy Powder (Coarse)

Figure 8: Cold Sprayed Refined HC Starck Ta-10W Alloy Powder (Fine)

Note the homogeneously distributed two-phase microstructure of the blended “pseudoalloy” deposit in figure 5, as well as the improvement in microstructure of the fine refined true alloy.

The presence of large, angular particles in the unrefined and coarse alloy powders seem to have inhibited consolidation, whereas spherical particles of similar diameter in the blended powder did not lead to cracks in the deposit. It is likely that the spherical particles, while having larger cross-sectional areas than nominally similar angular particles, have enough increased drag to achieve critical velocities under similar process parameters. This resulted in a denser, more uniform coating with DE's above 85% for both the ARL blended and fine refined powders. In addition to coating integrity concerns, both the as-received and coarse refined powders demonstrated inferior DE's of less than 60%, even at maximum operating conditions. Based on the consolidation of the Ta-10W powders on flat samples, parameters were transferred to spraying donor tube sections onto tubular mandrels. A number of specimens were prepared to test the feasibility of production of Ta-10W donor tubes by Cold Spray with respect to residual stresses from impact and thermal expansion mismatches. Residual stresses were of particular concern due to the limited ductility of the deposit in the as-sprayed condition. It was found that cracking from thermal stresses was rate-dependent; samples that were cooled in air ($\sim 10^{-1}$ °C/s) occasionally developed internal cracks, whereas samples that were insulated upon the completion of spraying ($\sim 10^{-3}$ °C/s) did not. Figure 9 shows samples of un-insulated (cracked) donor tube sections as well as an insulated (un-cracked) section.

Figure 9: Cracked (A) and Uncracked (B, with mandrel) Donor Tube Sections, Outer Diameter .75"

Mandrel removal is a critical process to prevent the formation of intermetallic species during annealing of the donor tube. If the mandrel is not completely removed, residual aluminum could contribute to the formation of brittle tantalum aluminides which could interfere with final machining as well as the explosive cladding processes. In order to do this, mandrels were machined out of the inner diameter of the donor tube using deep drilling and honing techniques, followed by a brief soak in dilute sodium hydroxide. It was determined that the risk of intermetallic formation was greater than the potential for hydrogen embrittlement from the reaction products due to the ability to remediate hydrogen embrittlement with thermal treatment. After soaking, the donor tube was rinsed thoroughly with DI water and dried in preparation for heat treatment. Heat treatment was performed in a vacuum furnace in accordance with parameters used in previous studies with pure tantalum donor tubes^{viii}. After heat treatment donor tubes were sent for explosive cladding. Figure 10 shows a 3-foot section after mandrel removal

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4 and annealing. The section shown was successfully clad in May 2015 with acceptable bond line
5 integrity and with adhesion along all but the outermost sections of the donor tube length
6 (approximately 0.5” per side, typical of cladding operations and deemed acceptable by both the
7 cladding performers and Army gun barrel subject matter experts). The successful cladding
8 demonstrates cold spray technology feasibility and scalability as an alternative to extrusion for
9 refractory donor tubes, with the flexibility to create robust single-material, multi-material, and
10 potentially graded structures compatible with existing barrel liner fabrication and emplacement
11 practices. Post-cladding characterization and testing of the cold sprayed donor tube will be
12 performed by Benet Laboratories through FY15 to ascertain acceptable material properties
13 including adhesion, hardness, machinability, and cyclic hot-gas corrosion.
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35 **Figure 10: 3-Foot Donor Tube Section Prior to Explosive Cladding**

36 37 **Conclusions**

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39 Gas Dynamic Cold Spray has been found suitable for additive manufacture of refractory
40 tantalum-based alloy donor tubes for the explosive cladding of gun barrel liners. Powder and
41 process development enabled repeatable, reliable production of donor tubes in lengths of up to
42 three feet. Future work includes further process optimization to enable cost reduction through the
43 use of Nitrogen gas as opposed to Helium, functionally graded tubes for improvements in cost,
44 weight, and performance, and the use of mold release compounds to avoid the risks and expenses
45 of small-bore high aspect ratio machining operations.
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