TANTALUM AND NIOBIUM POWDERS FOR COLD SPRAY APPLICATIONS

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Cold Spray Technology

Cold spray is a variation of thermal spray technology where fine metal powders are carried by a supersonic gas stream to strike a substrate and form a conformal coating. Unlike thermal spray, cold spray particles impact the substrate as solids rather than liquids, and bond due to solid flow and interlocking of the particles with each other, and with the substrate. Layers can be built to almost any thickness and the varieties of materials and applications are numerous. The unique bonding interface and lower temperature interaction is opening the door to new material systems and opportunities. In many applications, heating from weld repair or traditional thermal spray can be detrimental to the substrate, giving cold spray an advantage as an *in situ* build or repair method. Many excellent references such as Practical Cold Spray[1] can provide overviews and detailed studies of cold spray. Figure 1 shows a general schematic of the cold spray equipment and process.

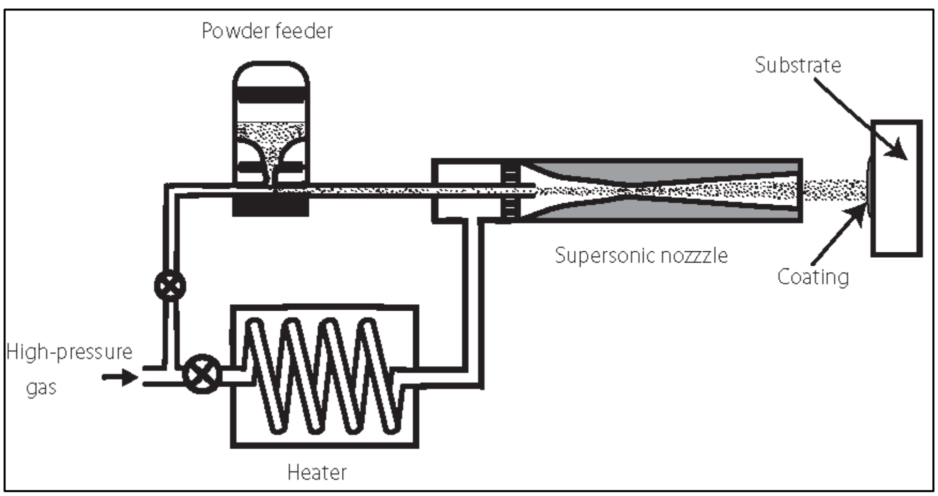

Fig. 1 General cold spray schematic[2].

Cold spray of metals onto surfaces is finding many advantages. As mentioned above, cold spray enables the ability to perform repairs with minimal thermal impact, eliminating the need for post-repair heat treatment. Eliminating thermal treatments permits point-of-use repair, making cold spray extremely attractive in applications such as keeping military vehicles in service[3 4]. As many legacy military programs face the challenge of component obsolescence, it is becoming imperative to sustain critical component inventories; however, cold spray has the potential to reduce the need to replace components with new, impacting obsolescence[5]. Cold spray is demonstrating the unique ability to combine materials with different properties (e.g., yield strength, melting point, corrosion resistance) to form graded layers[6] or a blended mixture such as a hard-phase / soft-phase composite for the replacement of electroplated hard coatings[7]. Cold spray processing and materials have been developed for aerospace[8], a large number of military applications[9] [10], and to address extreme environments in energy generation[11] [12] [13]. As cold spray becomes a standard repair and build technology, the number and variety of applications and materials will increase.

Applications for Tantalum and Niobium

Tantalum (Ta) and Niobium (Nb) are well known for their corrosion resistance and refractory properties. They are commonly used unalloyed in electronics, semiconductor manufacturing, medical, and specialty chemical processing applications where superior properties are required. Tantalum has a long history in medical applications[14] and its use continues growing due to its low toxicity[15] [16], osteointegration capability[17], and radiopacity[18]. In military applications, tantalum is used in durable electronics capacitors, munitions[19], and has also been tested to extend the life of gun barrels[20]. Tantalum fills important roles in defense and is considered a critical strategic material[21].

A review of literature shows continued testing of cold sprayed Ta and Nb in critical military[22] and energy applications[23]. Due to the nature of these metals, they are easy to forge and roll at low temperature using traditional metal forming methods. This workability has translated to ideal cold spray deposition performance, achieving near fully dense materials with strong, cohesive layers with superior mechanical and corrosion resistant properties[22] [24] [25]. Forming surface coatings via the cold spray process captures the benefit from tantalum's and niobium's corrosion and thermal resistant properties while maintaining the strength, lower weight, and lesser costs of the underlying substrates. For example, an iron-based or nickel-based plate or pipe can be coated with Ta to allow more economical use in acid processing. Many applications for Ta and Nb are known and the general expansion of cold spray will assist in growing the use of these metals and their alloys.

Powder Requirements for Cold Spray

Cold spray is a straightforward process; particles impact a surface at velocities high enough to deform and flatten the particles, expose nascent surfaces for bonding, and fill the surface topography to prevent porosity. A number of operational and material parameters influence this process, and need to be carefully controlled to repeatedly create strong, dense, and continuous coatings with high deposition efficiency (DE = the amount of sprayed powder that is incorporated to the deposit; ~yield). The key powder characteristics for unalloyed metals include: 1. powder flowability, 2. particle diameter and shape, 3. particle microstructure and porosity, 4. gas impurities, and 5. the powder surface.

1. Powder flow is important for controlled feed into and through the cold spray system, though the standard flow measurement methods are not perfect indicators of usability[26]. For a given material, powder flowability is a function of particle size distribution (PSD), shape, and surface. Narrower size distributions flow more readily[27]; equiaxed shapes like spheres and cubes flow easier than irregular particles[28] [29]; and rough, dirty, or damp

surfaces increase interparticle friction and inhibit motion[26 30]. Superior cold spray powders will have consistent PSD and particle shapes, low and controlled gas contents, and clean, dry surfaces.

2. Particle size and shape also influence particle acceleration in the cold spray gas stream and the impact energy at the substrate. For a given particle diameter (diameter is used, even for nonspherical particles) there is a critical velocity[31] resulting in impact which deforms the particle sufficiently to create fresh metal surface and fill voids, while not being excessive and causing substrate damage. It is obvious that a very wide size distribution will result in particles moving both faster and slower than the optimal spray parameters resulting in less desirable deposit density and surface conditions. Particle shape provides a similar effect with more and less aerodynamic particles having different critical velocities (and deposition efficiencies) and causing similar variations in deposit quality. Maintaining consistent size and shape of the particles is critical for maintaining optimized parameters and material characteristics.
3. Particle microstructure and porosity have a measurable effect on the deposition efficiency of cold sprayed materials. The presence of inter-particle pores can lead to lower interfacial mixing and therefore weakening the inter-layer bonds as well as between the deposit and substrate. The microstructure and porosity of the powder translate directly to the deposit material and can directly influence the mechanical performance of the bulk material[32].
4. Higher gas impurities increase the metal's yield strength and thereby increase the critical velocity[33 34]. It is preferred to keep oxygen levels below 300 ppm, though the overall measurement is a combination of internal, dissolved oxygen and the inherent surface oxide layer. Finer powders, with a higher surface-to-volume ratio, will naturally have higher oxygen content overall. The control of oxygen in these finer particle applications becomes an equilibrium challenge between the particle size desired and the minimum surface oxygen present.
5. The surface of a particle influences its flowability (see above), the deposition efficiency, and coating properties[26 30]. Particle surfaces with excess moisture, hydroxides and other contaminants, and extreme oxide layers will cause variation in flow through the system, lower DE, and poor coating strength due to less particle deformation and the incorporation of contaminants, oxides, etc. in the coating. Powders for cold spray should be processed, handled and stored to prevent contamination and surface reactions; where possible they should also be dried and packaged under an inert atmosphere for optimal quality and shelf life. Tantalum and niobium surface oxides are stable at room temperature, however, additional care and preventative measures are recommended for fine (<25 micron) and ultra-fine (<10 micron) particle sizes due to their high surface-to-volume ratio.

Global Advanced Metals Ta and Nb Powders

Global Advanced Metals (GAM) has a well-known history of producing high-quality Ta and Nb products including flake and agglomerated powders for capacitors, and angular met-grade powder as feed for mill products. GAM has applied the knowledge and capabilities used to develop powders for the semiconductor and capacitor industries now to produce powders with optimized and controlled particle size distributions and chemistry for cold spray applications. The micrographs in Figure 2 show examples of angular tantalum, tantalum-alloy, and niobium powders developed for cold spray applications.

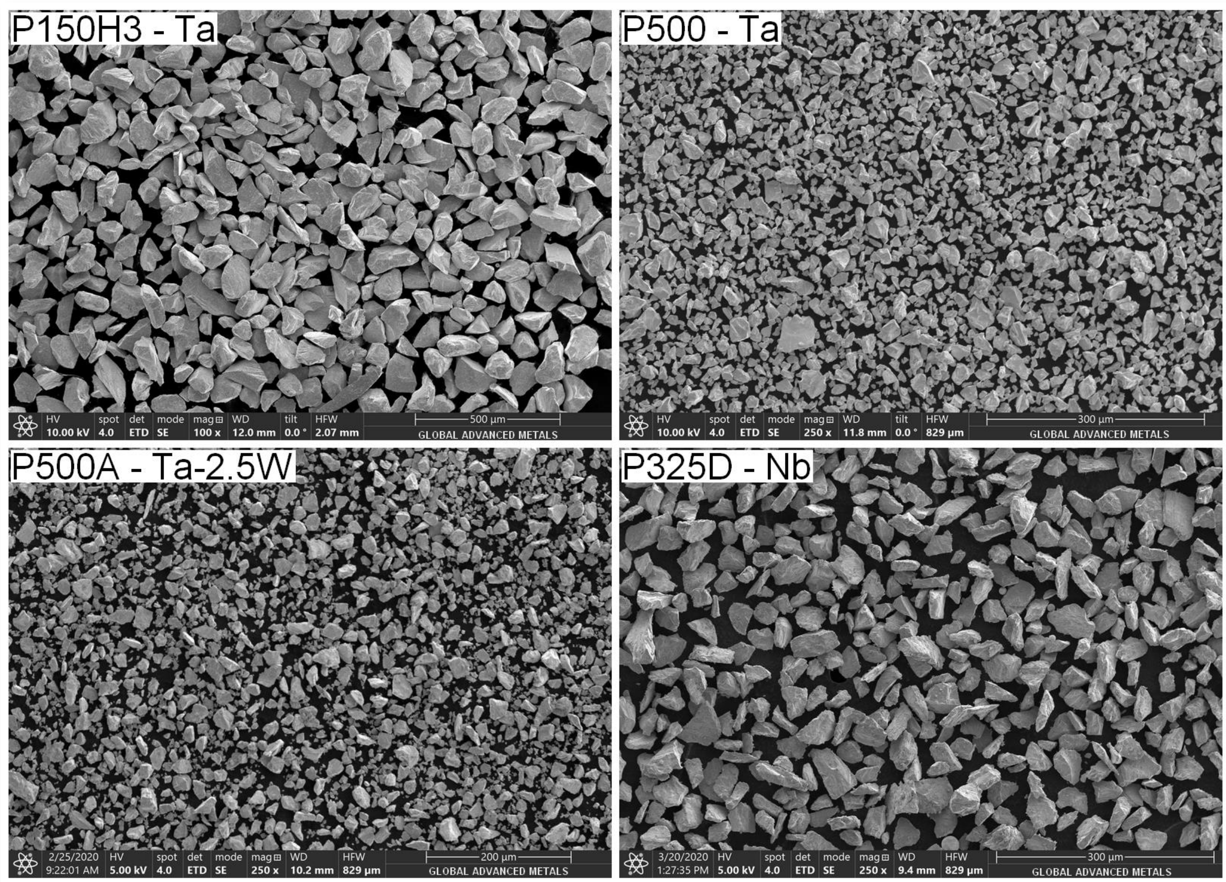

Figure 2. GAM angular powders designed for cold spray. Clockwise from top-left: 45-125µm Ta, 10-25µm Ta, 10-25µm Ta-2.5W, and 15-40µm Nb.

Early cold spray development testing of GAM tantalum powders have demonstrated consistent dense coatings with good bonding and low porosity. The powders used for these tests were larger, spherical particles (A), larger angular particles (B), and smaller angular particles (C). Table 1 shows the powder attributes and Figure 3 shows the feed powders. Cold spray deposition was performed by a collaborator to produce flat coupons, tensile bars, as well as coatings on interior and exterior curved surfaces. Figure 4 shows macro photos of various part geometries. With only preliminary parameters established, good bonding and low porosity were achieved as shown in the SEM photos and EBSD images in Figure 5.

Table 1. Cold spray Ta powder attributes

Powder	Shape	D10 (µm)	D50 (µm)	D90 (µm)	Bulk density (g/cc)	Hall Flow (s)	O (ppm)	N (ppm)	H (ppm)	C (ppm)	Purity (% Ta)[1]
A	spherical	20	39	77	9.86	5.24	61	<10	<10	<10	>99.99
B	angular	19	32	55	6.25	11.6	187	11	<10	10	>99.99
C	angular	9	16	28	5.63	N/A[2]	328	<10	<10	<10	>99.99

[1] *Does not include gases.*

[2] *N/A indicates powder did not flow through Hall funnel.*

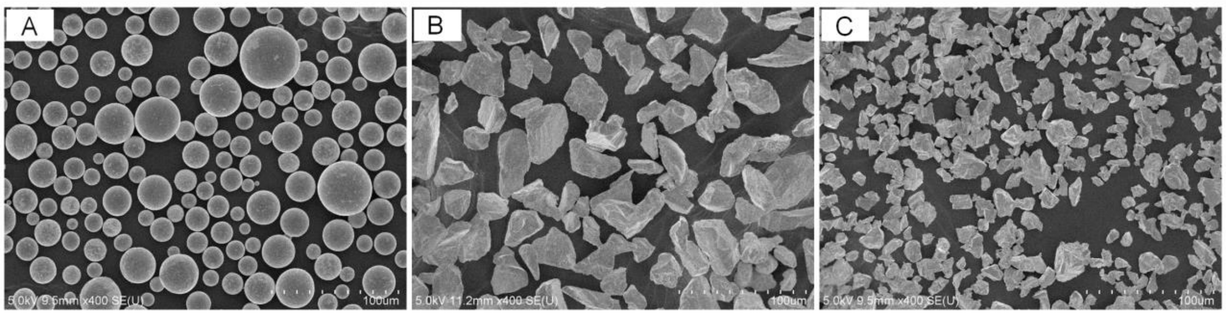

Figure 3. Micrographs of powders A, B, and C used in cold spray testing (left to right).

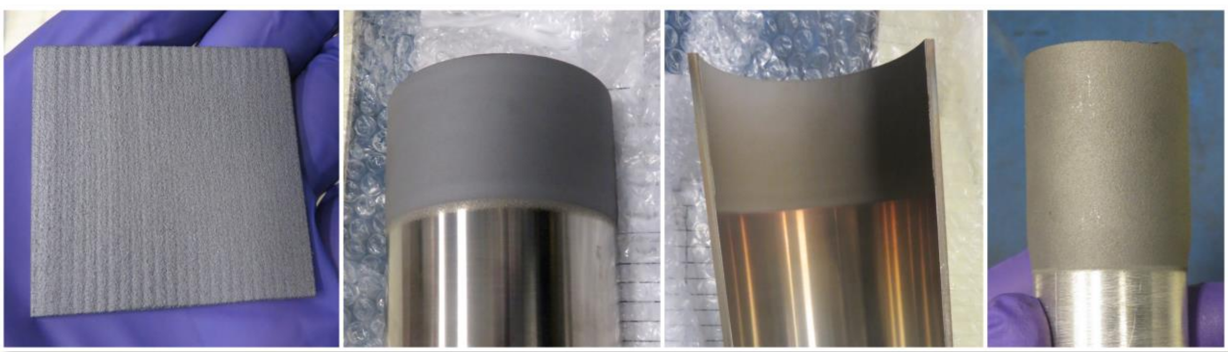

Figure 4. Macro photos of Ta cold spray samples (dimensions are approximate), left to right: 50x50 mm flat coupon, 50 mm radius outer curve, 50 mm radius inner curve, 30mm diameter cylinder.

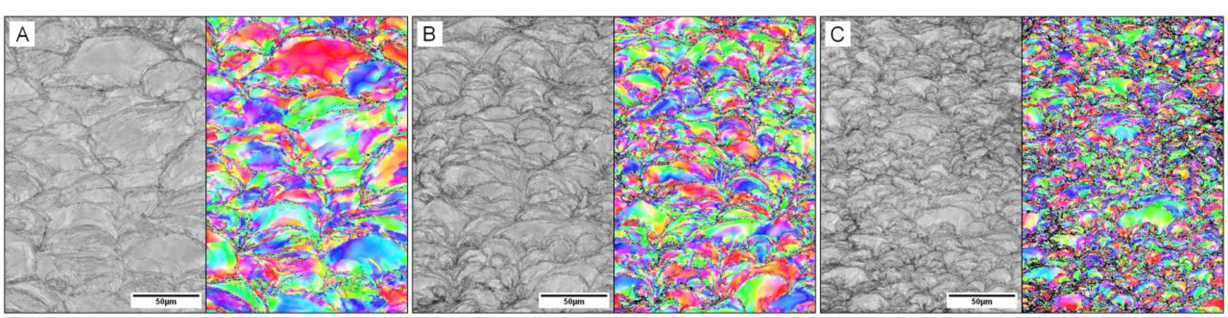

Figure 5. SEM and matching EBSD images for (left to right): Powder A coupon section, Powder B section, Powder C section. Growth direction is vertical in all cases.

Summary

As previous and emerging research have shown, careful control of powder properties is critical for success in cold spray applications. Early testing has demonstrated that the positive results seen in tantalum and niobium cold spray literature holds true for the high-quality powders produced by GAM. GAM has extended well-established processing techniques commonly used in the manufacturing of capacitor-grade and metallurgical-grade powders to the tantalum, tantalum alloy, and niobium cold spray powders thus providing superior performance in the form of consistent and controlled particle size distributions, excellent flow, and industry leading chemistry. Further material development and cold spray testing have been performed and additional results will be shared in future presentations and publications. GAM continues to invest in the development and production of powders designed for cold spray and additive manufacturing and thus will be well positioned to support the anticipated growth in this industry.

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