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Low Pressure Cold Spraying of Tungsten Carbide Composite Coatings

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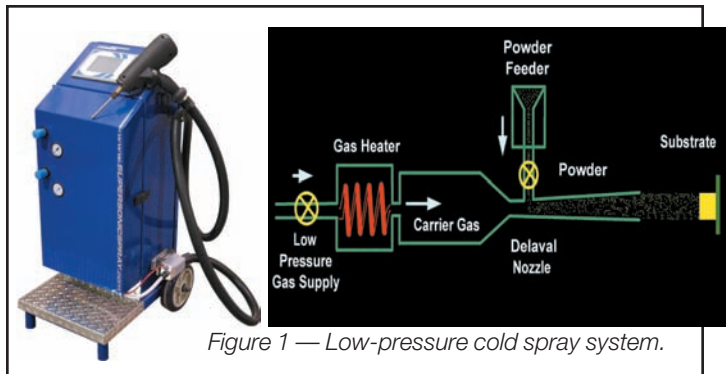
CenterLine (Windsor) Ltd., Windsor, ON, Canada

WC-Co coatings are used extensively for wear resistance applications. The hard WC phase provides wear resistance while the cobalt binder increases toughness. The recent implementation of regulations, such as the EU's Regulation of Hazardous Substances (RoHS), to eliminate the environmental impact of hexavalent chromium during traditional chromium plating processes has opened new applications for WC-Co coatings. Currently, WC-Co hard coatings replacing electrolytic hard chrome (EHC) coatings are sprayed by high velocity oxyfuel (HVOF). Cold spray processes can mitigate the possibility of WC-Co coating imperfections like cracks, blisters, and/or delaminations associated with HVOF process effects such as oxidation, decarburization, thermal expansion mismatch, and undesirable metallurgical transformations.

Cold spraying

Low pressure cold gas-dynamic spraying (low pressure cold spray) is a unique low temperature spraying process in which the spray materials are not melted in the spray gun; instead they are kinetically deposited on the substrate at low temperatures. Adhesion of the deposit is achieved through solid state bonding as particles are accelerated towards the substrate at supersonic speeds. As the first particles impact the substrate, they shatter the surface oxides and eject them from the bonding surface. Particle velocity control is critical for successful adhesion. When the right critical velocity for a substrate/particle combination is reached, there is a momentary high interfacial pressure at the impact site that allows the atomic structures to come into intimate contact. Subsequent particle collisions at the critical velocity cause the new particles to plastically deform, compact the already attached particles, and bond to the previously formed layer. When particle velocity is too low, the particles simply bounce off the substrate. If the particle velocity is too high, the particles pulverize on impact.

Key advantages of low pressure cold spray include portability and low operating cost. Unlike traditional thermal spraying processes there are no thermal effects such as oxidation, distortion, residual stresses, and/or metallurgical transformations. The process performs the functions of grit blast, spray coating, and shot peening in a single operation so a finished surfacing coating can be applied quickly and consistently. Also, the deposits are fully dense and exhibit exceptional bonding strength. Mechanical and/or metallurgical bonding is possible due to extensive and localized plastic deformation resulting from high velocity particle impact. A schematic of a



low pressure cold spray system is illustrated in Figure 1.

One characteristic of low pressure cold spray is the mixing of a percentage of ceramic particles into the metal powder to increase the bond strength and density of the metallic deposits. Although a portion of hard particles is left dispersed in the metal matrix, the mechanical properties of the resulting deposit are not enough to provide adequate abrasion resistance. Spraying mixtures that are primarily ceramic, such as WC-Co, using low pressure cold spray technology has proven particularly challenging. Evidence suggests that the presence of a minimum volume percent of ductile species is necessary for kinetic bonding to occur. Attempts to spray hard materials by mixing them with ductile species (such as aluminum, zinc, and copper) have met with limited success.

An alternative to mixing powders is to modify the surface chemistry of the powders. Chemical vapor deposition (CVD), electroplating, and electroless plating are techniques that can be used to modify the surface chemistry of metallic and non-metallic powders. Ductile metals such as copper and aluminum can be deposited on the surfaces of individual non-metallic particles, such as tungsten carbide. A ductile layer on the tungsten carbide particles may improve the ability to cold spray these materials while increasing the volume fraction of the hard phase in the as-sprayed deposit. Incorporating a higher volume fraction of hard phase in the deposit could improve wear and abrasion resistance of the deposits.

At Centerline, a study was undertaken to evaluate the feasibility of cold spraying surface modified tungsten carbide powders. The microstructure and mechanical properties of the composite coatings resulting from surface particles were compared with similar coatings produced by mixing of the precursor powders using traditional powder blending techniques.

Feedstock powders

A number of commercially pure powdered materials were used in this study, including aluminum (-325 mesh, Atlantic Equipment Engineers, USA), copper (-325 mesh, Acupowder International LLC, USA), and tungsten carbide (14-25 μm , Buf-

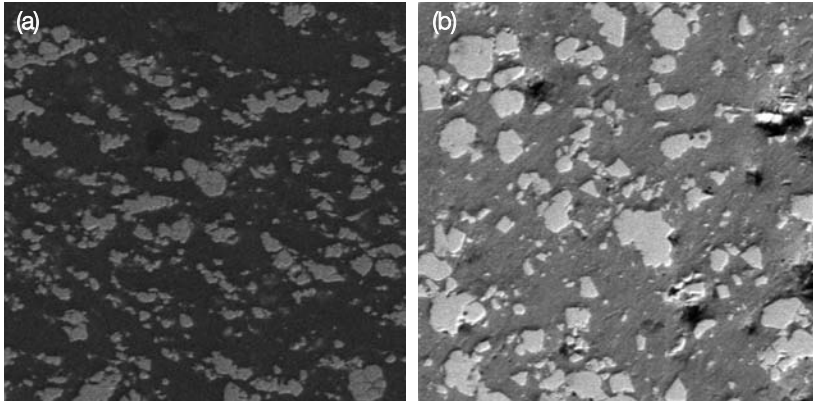


Figure 2 — Microstructure of cold sprayed (a) aluminum-coated WC and (b) copper-coated WC.

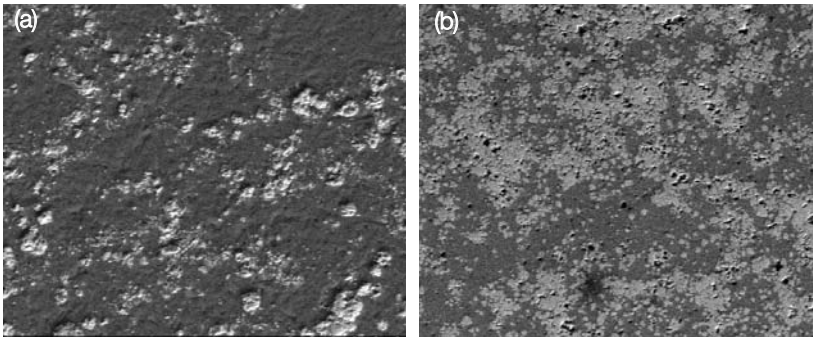


Figure 3 — Microstructure of composite coatings produced from mixtures of (a) WC-30wt % pure aluminum powder and (b) WC-30wt % pure copper powder.

falo Tungsten Inc, USA). The feedstock particles and compositions used in the study are listed in Table 1. The Al-WC and Cu-WC blends were produced by mechanical mixing of metallic and ceramic powders.

Table 1— Cold spray feedstocks and hard phase contents

Feedstock	WC composition (wt%)
Cu-coated WC	80
Cu-WC blend-1	20
Cu-WC blend-2	40
Al-coated WC	70
Al-WC blend-1	20
Al-WC blend-2	40
Al-WC blend-3	70

Tungsten carbide particles were coated with aluminum via a proprietary chemical vapor deposition (CVD) process. Wet coating methods are not feasible because of the high activity of aluminum. SEM inspection revealed that the aluminum did not deposit homogeneously over the surfaces of the WC particles. Rather, sub-micron and micron sized aggregated clusters of aluminum spheres were observed on the carbide particles. EDX analysis on the spheroids confirmed that the clusters were aluminum. The presence of aluminum as sub-micron spheres was expected to decrease the amount of aluminum available on the carbide surfaces, even though the overall aluminum content may have conformed to the nominal composition.

The proprietary CVD technique also was used to deposit copper on WC particles. However, the copper phase distribu-

tion and particle surface morphologies resulting from the CVD process were not significantly better than was achievable through mechanical mixing of the powders. Therefore, electroplating was selected as the preferred method to deposit copper on tungsten carbide particles. After electroplating, the carbide particles showed round edges indicating a uniform coating. Microstructural observations of cross-sections of selected copper-coated particles confirmed the presence of a uniform and continuous layer of copper around these particles.

Composite coatings

A Centerline SST portable low pressure cold spray system was employed to produce the composite coatings. A convergent-divergent (de Laval) round-section nozzle was used with an expansion ratio of 6.4 and divergent section length of 120mm. The substrate materials were 1018 carbon steel and 6061 aluminum; they were grit blasted with 80-grit alumina prior to spraying. Table 2 summarizes the cold spraying process parameters.

Table 2 — Cold spray process parameters

Carrier gas	Compressed air
Carrier gas temperature, °C (°F)	375-540 (705-1005)
Carrier gas pressure, MPa (psi)	0.5-0.6 (80-90)
Standoff distance, mm (in.)	15 (0.6)

Al-coated and Cu-coated WC feedstock powders were successfully cold sprayed, and typical microstructures of the composite coatings are shown in Figure 2. The addition of a layer of soft metal around the carbide particles appeared to provide suf-

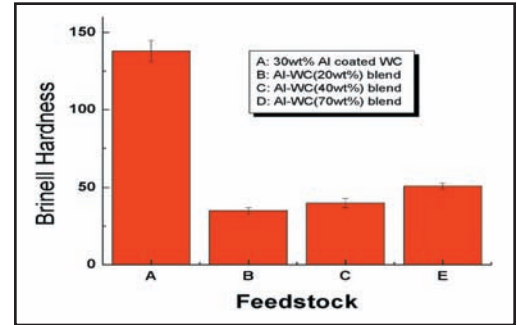


Figure 4a — The macro-hardness of the coatings from aluminum-coated WC powder and Al-WC blends.

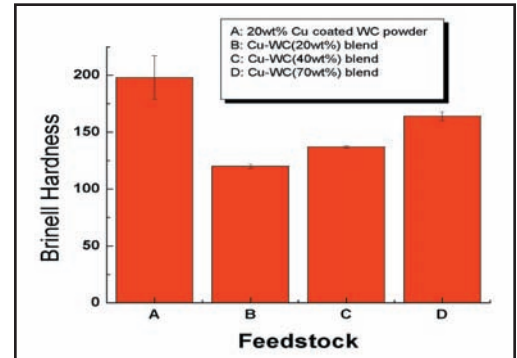


Figure 4b — The macro-hardness of the coatings from copper-coated WC powder and Cu-WC blends.

efficient surface with the necessary ductility to stimulate solid state particle-to-substrate and particle-to-particle bonding. The powders behaved similar to a regular soft metal powder on cold spraying. The volume percentage of dispersed carbide in the deposit was estimated at 55% for both Al-coated and Cu-coated powders. The coating resulting from the Al-coated WC feedstock appeared to have the carbide phase well dispersed within a pure aluminum matrix.

For comparison, Al-WC and Cu-WC blends with three different weight fractions of WC powder (20wt%, 40wt% and 70wt%) were cold sprayed using the same spraying system and process parameters (Table 2). The microstructures of deposits resulting from Al-WC and Cu-WC powder blends are shown in Figure 3. The volume fraction of carbide phase retained in the metal matrix reached a plateau that could be well below the amount of carbide present in the original metal-WC blend. For example, the maximum amount of carbide phase retained in the Al-70 wt% WC feedstock deposit was about 30 vol%. For Cu-70 wt% WC feedstock, the maximum amount of carbide retained was higher, about 65 vol%. In both cases, the carbide was not homogeneously dispersed in the matrix.

Hardness measurements indicated higher hardness values for cold spray deposits produced from metal coated carbide feedstock compared to cold spray deposits produced from metal-carbide powder blends (Figure 4a, 4b). This was attributed to better dispersion of the carbide phase in the aluminum or copper

matrix produced from metal-coated carbide feedstock as well as possibly less porosity.

This study demonstrated that metal coating of tungsten carbide feedstock is an effective means to cold spray otherwise unsprayable materials, such as pure tungsten carbide. Chemical vapor deposition of aluminum produced discontinuous clusters of sub-micron metal spheres on the carbide surfaces, however, the feedstock was still cold sprayable and produced enhanced coatings. Electroplating is more effective than CVD for coating WC particles suitable for cold spraying.

The deposits fabricated from coated particles were characterized by a high percentage of well dispersed, retained carbide phase, and low porosity. These characteristics yielded hardness values higher than equivalent deposits produced from traditional metal-ceramic blends.

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