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Fabrication of erosion resistant WC-Ni based coatings using cold gas dynamic spaying

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COLD GAS DYNAMIC SPRAYING OF WEAR RESISTANT WC-BASED COATINGS

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ABSTRACT

This paper provides a review on cold gas dynamic spraying (CGDS) and its application to produce WC-based wear resistant coatings. CGDS is a deposition technique, in which fine, solid powder particulates are accelerated to supersonic speeds by means of a pressurized carrier gas. The high velocity particles are impacted onto a surface to form dense coatings. Severe plastic deformation of the particles during deposition is required to achieve sufficient adhesion and coating build-up. This process involves limited to no melting during coating deposition, thus, the chemical composition and bulk properties of the coatings typically remain identical to the feedstock powders. Substrate and particle adhesion occur as a result of highly localized adiabatic shearing, and the formation of a material jet of the ductile material, allowing for material interlocking and mechanical bonding. Deposition of WC-based coatings has been achieved using high pressure CGDS systems, with dense coatings having thickness and hardness values comparable to HVOF coatings. It is generally challenging to achieve the adhesion of WC-based coatings using low pressure CGDS systems; the addition of a ductile binder metal such as Cu, Ni and Al in the form of a MMC is generally required to facilitate deposition. Limited studies have been done on the wear resistance of cold sprayed WC-based coatings. To date it has been shown that WC-based coatings deposited using both high and low CGDS systems, possess higher sliding and abrasive wear resistances compared to coatings deposited using some HVOF techniques. The typical wear mechanisms observed are plastic deformation of the ductile metal matrix with minimal damage of the hard WC grains. Changes in wear mechanisms during wear have also been noted and appear to be influenced by the amount of WC present.

Keywords: Cold Spray, Coatings, WC, Cemented Carbides, Wear

NOMENCLATURE LIST

Abbreviation

CGDS	Cold gas dynamic spray
MMC	Metal matrix composite
HVOF	High velocity oxy-fuel

1. INTRODUCTION

Coating application is a surface modification technique that protects the underlying substrate against wear, corrosion, thermal degradation and premature damage (ed. Davis, 2004). WC-based coatings are ideal for protection against wear and corrosion due to the hard, high strength and chemically resistant nature of the WC compound. Carbide materials are seldom deposited without a softer binder material to facilitate adhesion. Cobalt (Co) is the best known binder metal for high wear resistance performance, as it offers moderate fracture toughness and good transverse rapture strength (Sarin, 1981) and (Upadhyaya, 1998).

WC-based coatings are conventionally deposited onto metal substrates using high temperature deposition techniques, such as high velocity oxy-fuel (HVOF), high velocity air fuel (HVAF), plasma transferred arc welding (PTAW) and spray fusion (SF). These high temperature processes involve the heating and melting of the high velocity powder particles, in order to achieve good particle-substrate adhesion (Jacobs, 1 998), (Kear, 2000), (Kulu, 2002), (Qiao, 2003), (Sahraoui, 2010), (Watanabe, 2006) and (Zikin, 2012). The elevated temperatures used during the deposition of WC-Co cemented carbide coatings typically lead to the formation of hard and brittle phases such as W_2C, W, $Co_xW_yC_z$ and WO_3 (Stewart, 1999)**,** (Stewart, 2000) and (Usmania, 1997). W_2C (3000 HV), which has been found to have a higher hardness and strength compared to WC (1300-2300 HV) , is brittle, and has been shown to decrease the wear resistance of the coatings (Marple, 2007) and (Stewart, 2000). Stewart et al (1999) also reported that the sliding wear rate of HVOF sprayed coatings increases with an increase in decomposition products, especially W_2C (Stewart, 1999). The high temperatures also lead to the formation of residual stresses, which if they are tensile, tend to propagate fatigue cracks within the coatings (Padilla, 2002). HVOF is the most commonly used high temperature deposition technique, as it has been found to give coatings with a high fraction of retained WC within the coating, low levels of porosity and a low decomposition of WC. This is attributed to the fact that lower process temperatures and higher velocities are used in HVOF compared to other high temperature spray techniques (ed. Davis, 2004).

Although the high temperature processes are known to produce effective wear resistant cemented tungsten carbide coatings, researchers have been investigating the deposition of WC-based coatings using cold gas dynamic spraying as an alternative to the high temperature deposition processes (Kim, 2005) and (Lima, 2002). The use of cold spraying is seen to be energy efficient, and it may eliminate the detrimental phases formed at high temperatures. This paper provides a review of cold gas dynamic spraying, and its application in producing WC-based wear resistant coatings.

2. COLD GAS DYNAMIC SPRAYING

CGDS is a deposition method in which fine, solid powder particulates are accelerated to supersonic speeds by means of a carrier gas and are impacted onto a surface to form dense coatings (Papyrin, 2006). Severe plastic deformation of the particles during deposition is required to achieve sufficient adhesion and coating build-up. The high pressures generated during impact onto the substrate allow for adiabatic shearing and the formation of a material jet of the ductile material, causing material interlocking and mechanical bonding (Hussain, 2009). The cold spray process involves limited to no melting during coating deposition, and the chemical composition and bulk properties of the coatings typically remain identical to the feedstock powders, as illustrated by the XRD patterns of WC-Co materials in Fig. 1 (Lima, 2002) and (Papyrin, 2006). The advantage of CGDS of cemented WC coatings over HVOF spraying is that some of the undesirable effects associated with thermal spraying processes are prevented. These include detrimental phase transformations, high temperature oxidation and recrystallization (Jacobs, 1998), (Kear, 2000), (Qiao, 2003), (Sahraoui, 2010), (Stewart, 1999), (Usmania, 1997), (Stewart, 2000) and (Watanabe, 2006). CGDS forms coatings with low porosity, good wear and corrosion resistances comparable to HVOF coatings, and compressive residual stresses which have shown to influence the coating hardness (Kim, 2005). The CGDS process also has significantly lower energy requirements compared to high temperature deposition processes (Papyrin, 2006).

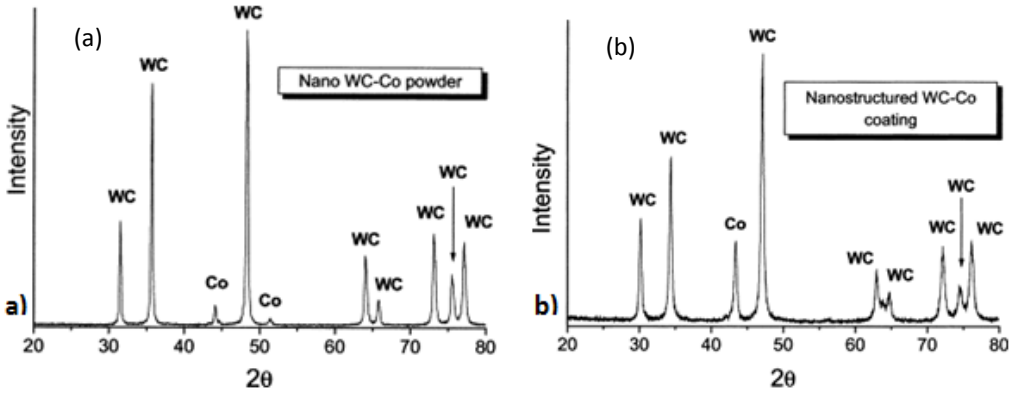


Figure 1 XRD of WC-12wt%Co (a) feedstock powder and (b) coating (Lima, 2002)

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There are currently two types of cold spraying systems available, namely low and high pressure, in which operational parameters such as pressure, temperature and the carrier gases differ. In low pressure cold spray systems, relatively low pressures between 0.550 - 0.695 MPa are used for coating deposition. Air or nitrogen is used as a carrier gas, which can also be preheated up to 500 C. The carrier gas containing the suspended powder particles is propelled through a nozzle onto the substrate to be coated, reaching velocities up to 600 $m.s^{-1}$. High pressure systems typically use nitrogen or helium gas as the propellant gases, to attain higher gas velocities. Pressures ranging up to 6.9 MPa can be attained, to accelerate the gas flow to the supersonic regime (1000 $m.s^{-1}$). The propellant gas can also be preheated to temperatures of about 1000 C (Papyrin, 2006).

2.1 Cold spraying of WC-based coatings

It is generally challenging to deposit WC particles using CGDS, due to its hard and brittle nature. The particles tend to shatter on impact and may erode the substrate, resulting in an effect similar to grit blasting (Karthikeyan, 2007) and (Ang, 2010). Since the successful deposition and adhesion of the cold spray coatings are significantly reliant on the deformation of the powder particles, the deposition of carbide materials can be achieved by the addition of a suitable ductile metal matrix to facilitate adhesion. Ductile metals such as Cr, Ni, Cu and Al have been spray deposited in combination with WC, however Co remains the most commonly used binder for wear resistance applications (Dosta, 2013), (Melendez, 2013a) and (Wang, 2009).

Some of the factors which influence the deposition efficiency of WC-based coatings include spray parameters, such as gas temperature and pressure, standoff distance (SOD), substrate properties, powder particle size and morphology, and binder content (Lima, 2002), (Melendez, 2013a) and (Wang, 2009). These process variables also have a significant effect on the critical particle velocity required for adhesion. If the particle impact velocity, Vp, is too low, no deposition will occur, as the feedstock particles rebound and may erode the substrate. By varying the process parameters, Vp for a given coating-substrate combination can increase, to be equal to or greater than the critical velocity, in which the particles can deform plastically and adhere to the substrate to form a coating (Wang, 2009) and (Schmidt, 2006). This substantiates the theory of a window of deposition for particles during CGDS, as illustrated in Fig. 2 (Schmidt, 2006).

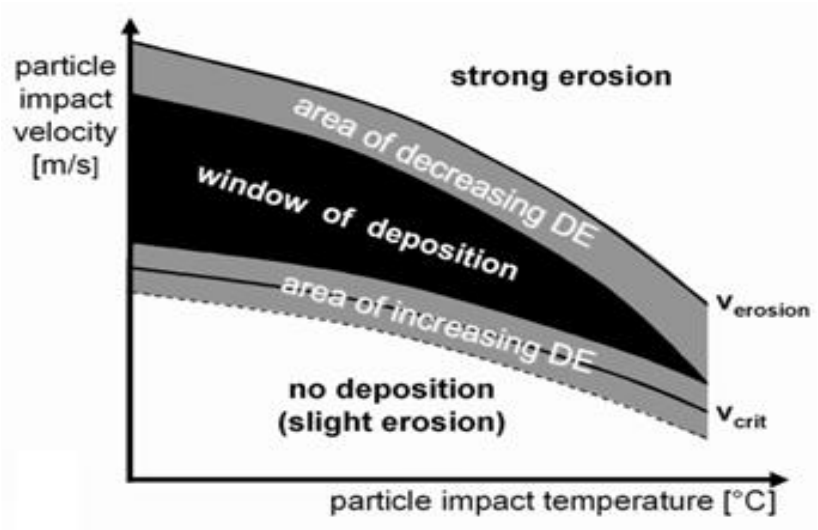


Figure 2 Window of deposition for CGDS (Schmidt, 2006)

The mechanism for the deposition of WC-based coatings differs from that of ductile metal coatings. For the WC-based coatings, the first coating layer is formed from the deformation and bonding between the metallic binder phase and the metal substrate, as well as the embedding of the hard WC particles into the substrate upon impact. In order to build up the subsequent coating layers, strong cohesive forces between the deposited WC-binder layer and the incoming WC-binder particles are required. Since it is the binder phase which plastically deforms and facilitates cohesion, coating build-up is strongly dependent on the amount of the binder phase present (Ang, 2010).

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2.1.1 High pressure CGDS of WC-based coatings

The deposition of WC-Co coatings has been achieved using high pressure CGDS systems, forming dense coatings with thickness and hardness values (300 µm and 1135 $HV_{0.3}$ respectively) comparable to HVOF coatings (He, 2000). Ang et al (2010) studied the effect of powder particle size on the deposition efficiency of WC. Three WC-17wt%Co powders, differing in particle size and morphology, were cold sprayed onto mild steel substrates using a high pressure cold spray system. A coarse grained powder (PM17) with a grain size of 2-3 µm, and two nano-structured WC-17wt%Co powders (IN17 and BN17) with grain sizes of 40-700 nm and 80-800 nm respectively, were used in the study. It was found that the nano-sized particles had superior deposition efficiencies, and formed coatings with higher hardness values, and fewer pores and cracks. The mechanism of deposition of the three powders is depicted in Fig. 3. The coating thickness of the PM17 powder was limited to about 20 µm, however the nano-structured IN17 and BN17 powders achieved coating thicknesses greater than 500 µm. The lack of coating build-up of the PM17 powder was attributed to the WC particle size, which was said to influence the formation and cohesion of the coating layer. The erosion of the substrate and deposited coating layers was more pronounced for the PM17 powder particles compared to the two nano-structured powders, thereby contributing to the lack of coating build-up. In such instances, a higher content of Co binder phase is required to increase the ductility of the powder, and to allow for more deformation, which facilitates cohesion between the interacting interfaces. The micron sized PM17 particles underwent particle refinement upon impact with the substrate, resulting in coatings with a refined microstructure. This was evident in the WC and Co diffraction peaks of the coatings that had broadened significantly compared to their feedstock powder diffraction patterns. The nano-structured IN17 and BN17 powders underwent particle refinement to a lesser extent. No evidence of decarburization or phase changes was observed in the resultant coatings (Ang, 2010).

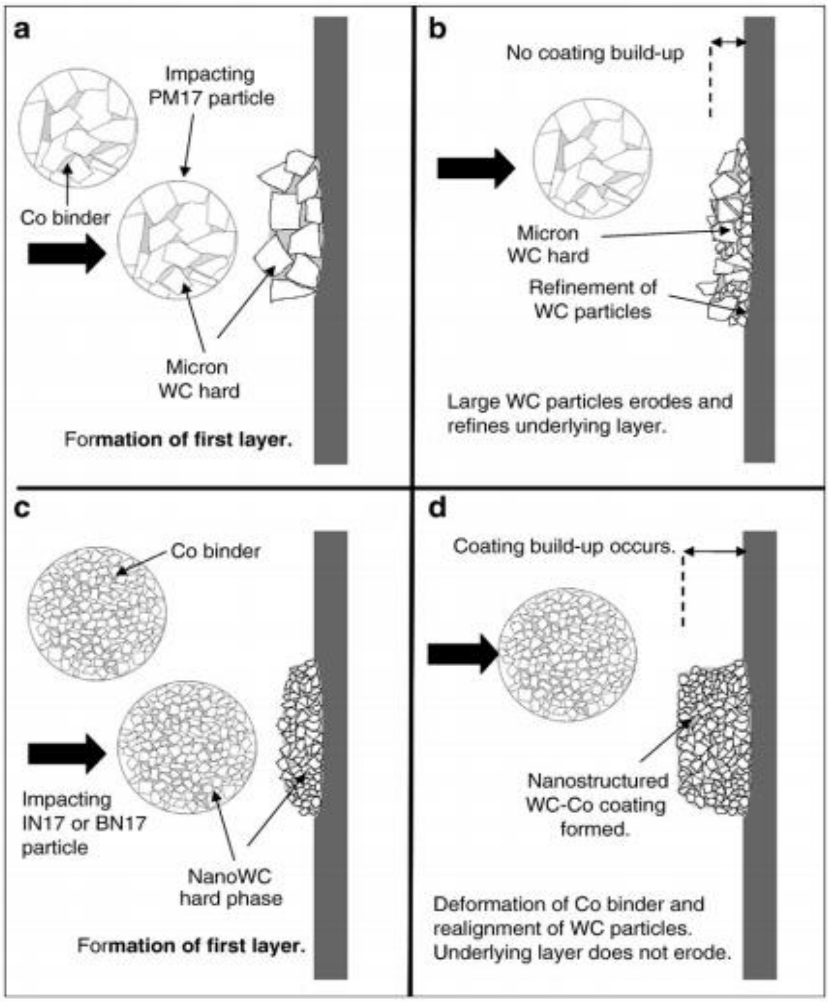


Figure 3 Coating formation of cold sprayed WC-17wt%Co powders differing in particle morphology (Ang, 2010)

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The porosity of the parent powders also plays a significant role in the deposition behaviour of WC-based powders. Gao et al (2008) investigated the effect of feedstock porosity on the formation of cold sprayed WC-Co coatings deposited using a high pressure system. Three nano-structured, agglomerated and sintered WC-12wt%Co powders, differing in porosity were used for the study; the high (HP), medium (MP) and low porosity (LP) powders had porosity levels of 43.8 %, 29.8 % and 4.9 % respectively. The study revealed that a certain degree of powder deformability is required to deposit hard WC-Co cermet coatings by high pressure cold spraying. The HP WC-12wt%Co particles experienced extensive deformation on impact as a result of the disintegration of the porous structure, and the collapse of the powder particles during flight and upon impact. The LP particles experienced less deformation during impact, making it difficult to deposit onto the substrate. Both the HP and MP powders were able to deposit thick coatings, compared to the thin coatings formed by the LP powders. The cermet powder particles therefore need to be carefully designed, with a certain degree of deformability suitable for deposition using CGDS. Porosity is required to assist with the deformation of the particles during impact, yet the particles should also possess sufficient cohesive strength, to minimize the disentegration of the particles during flight or impact (Gao, 2008).

2.1.2 Low pressure CGDS of WC-based coatings

It is challenging to achieve the adhesion of WC-based coatings using low pressure CGDS systems due to the hard and brittle nature of the WC compound (Dosta, 2013). To overcome this challenge, sintered and crushed, and spherical and agglomerated, WC-Co powders have been co-deposited with ductile metal binders such as Cu, Ni and Al, to form a metal matrix composite coating (Wang, 2009) and (Melendez, 2013a). Prior to deposition the feedstock powders can be blended either by mechanically mixing the WC-Co and metal binder, or by using metal binder encapsulated WC powder particles. Both methods were used in a study by Wang et al (2009) who produced WC-Al and WC-Cu blends by mechanical mixing, and coated WC particles with Al and Cu by means of chemical vapour deposition (CVD). It was found that the coated WC feedstock powders retained higher percentages of the WC phase in the resultant coatings, compared to the mechanically blended powders. The addition of a ductile metal layer around the hard, brittle carbide particles appeared to improve the solid state particle-to-substrate and particle-to-particle bonding, and as a result, the encapsulated hard WC particles behaved like regular soft metal powders during impact (Wang, 2009).

Melendez et al (2013a) successfully deposited sintered and crushed WC-12wt%Co powders, mechanically mixed with varying amounts of Ni, to form dense coatings, and compared the content of WC in the coatings to that of the original mechanically blended powder. The authors found a non-linear increase in the WC content of the coating as the WC content in the original powder increased, as illustrated in Fig. 4 (Melendez, 2013a). It was noted that the WC-12wt%Co particles were inhomogeneously distributed in the coatings, as some areas were rich in Ni, while other areas had high concentrations of WC grains. The inhomogeneous structure was attributed to the difference in the deposition characteristics of the constituent powders. Ni was preferentially deposited compared to the WC-12wt%Co particles, due to its softer, more ductile nature. A higher WC content in the feedstock powder was found to decrease the porosity of the final coating, which was attributed to the hard impacting action of the WC during deposition, resulting in the formation of a denser coating (Melendez, 2013a).

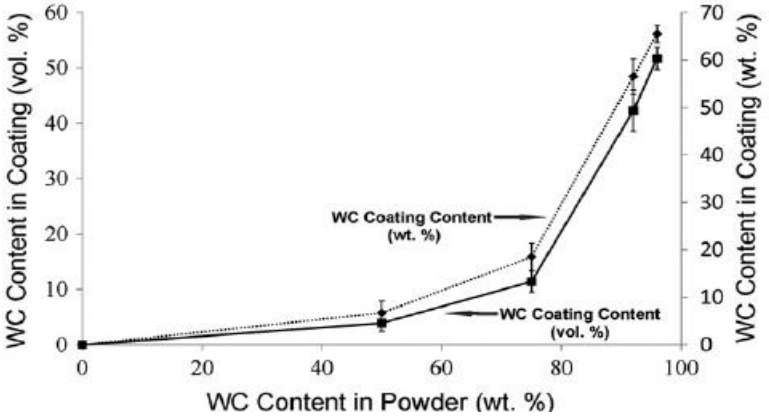


Figure 4 Comparison of the WC content in the coating and feedstock powder (Melendez, 2013a)

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In a recent study, the current authors (Lioma, in press) observed results similar to Melendez (2013a). In the study, Ni was able to successfully co-deposit dense, oxide-reduced WC powder (Fig. 5 a) and agglomerated and sintered WC-12wt%Co (Fig. 5 b) powder. The particle morphology significantly influenced the deposition behaviour of both powder types. The dense oxide-reduced WC particles experienced no deformation and tended to fracture within the Ni matrix, as a result of the high energy impact process (Fig 6 a). The porous structure of the spherical, agglomerated and sintered WC-12wt%Co particles was more deformable, thereby allowing for particle densification and elongation during deposition, which also resulted in a higher carbide retention within the Ni matrix (Fig 6 b). The WC-Ni coatings gave rise to less porous coatings with a higher hardness, compared to the WC-12wt%Co-Ni coatings, due to the more pronounced 'shot peening' effect experienced during deposition (Lioma, in press).

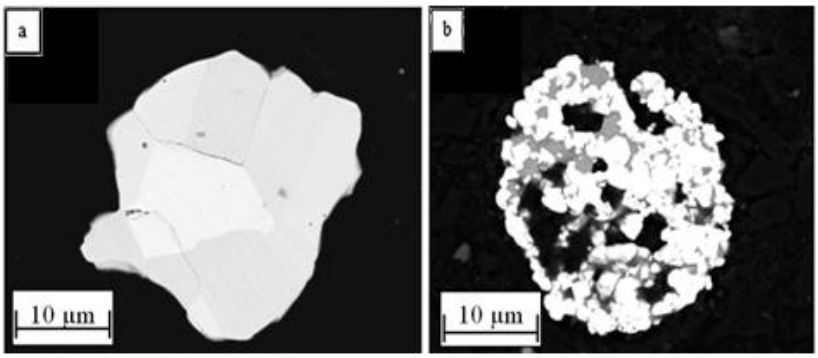


Figure 5 Cross sections of the (a) WC and (b) WC-12wt%Co feedstock powder particles (Lioma, in press)

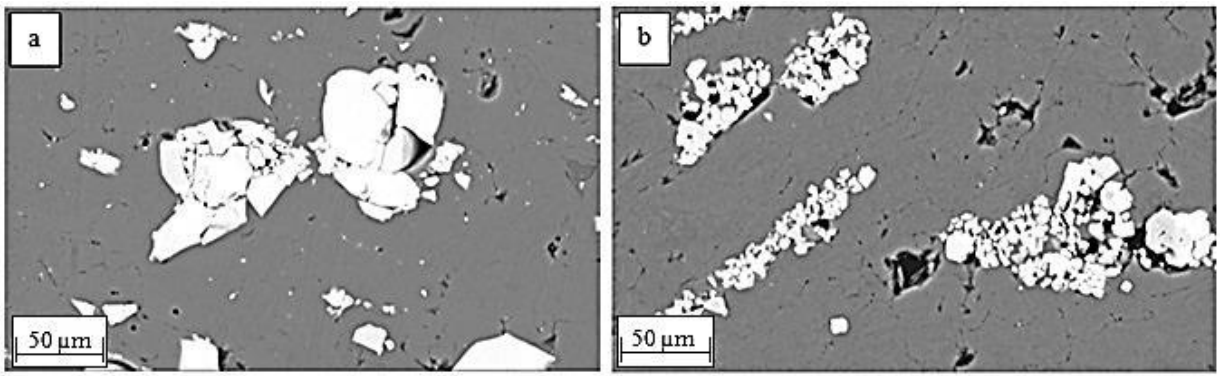


Figure 6 SEM micrographs showing (a) fractured WC particles within the Ni matrix, and (b) elongated and deformed WC-12wt%Co agglomerates within the Ni matrix (Lioma, in press)

3. WEAR PROPERTIES OF COLD SPRAYED WC-BASED COATINGS

Limited studies have been done on the wear properties of cold sprayed WC-based coatings. Couto et al (in press) performed a comparative study between WC-12wt%Co and WC-17wt%Co coatings deposited by HVOF and CGDS. Although the HVOF WC-12wt%Co and WC-17wt%Co coatings possessed higher hardness values of 1536 HV_{300} and 1379 HV_{300} respectively, compared to the CGDS coatings (1419 and 1223 HV_{300}), the cold sprayed coatings had higher abrasive wear resistances, as illustrated in Fig. 7. Similar results were also observed for sliding wear tests conducted by the same authors. The WC-12wt%Co HVOF coatings had a volume loss of 0.00929 mm^3 while the CGDS coatings had a lower volume loss of 0.0038 mm^3. Similarly, the material volume loss of the WC-17wt%Co CGDS coatings was 0.0086 mm^3 compared to the material volume loss of 0.03041 mm^3 observed for the HVOF coatings. The main reason cited for these differences was the detrimental effect of the brittle W_2C phase formed during the high temperature HVOF technique (Stewart, 1999) and (Stewart, 2000).

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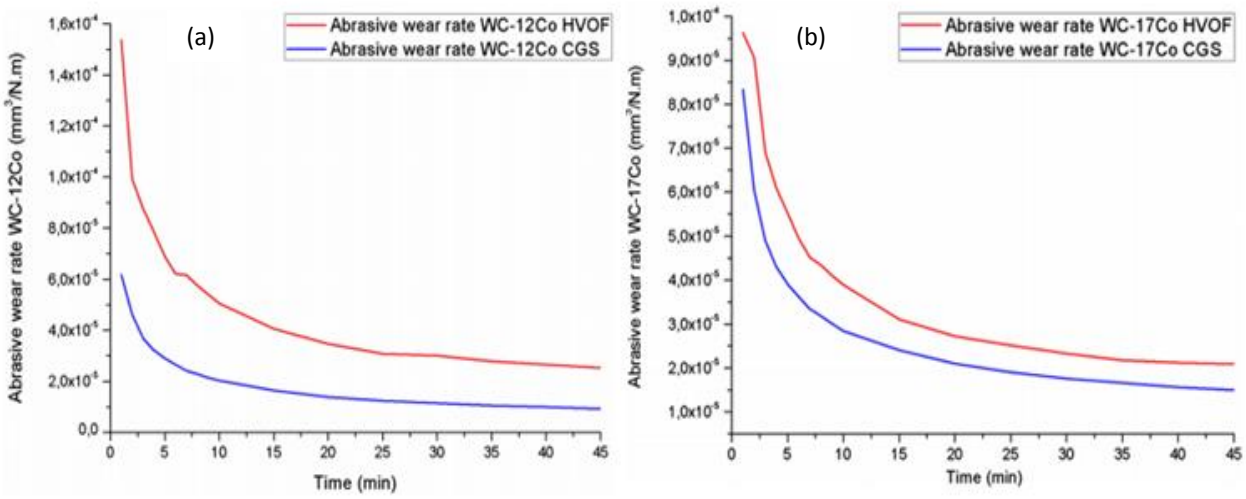


Figure 7 Graphs comparing the abrasive wear rate of (a) WC-12wt%Co and (b) WC-17wt%Co coatings produced using HVOF and CGS (Couto, in press)

Melendez et al (2013b) studied the dry abrasion wear of WC-12wt%Co-Ni coatings deposited onto low carbon steel substrates using a low pressure CGDS system. From the study, it was found that as the hardness and the percentage of WC retained within the coating increased, the wear rate consequently decreased. The relationship between hardness and wear rate for the coatings was relatively linear, suggesting that hardness contributed significantly to the abrasive wear resistance. Although hardness is typically used as a first-order approximation of wear rate for WC-based materials, carbide grain size and binder content have been shown to have an effect on the wear resistance (Luyckx, 2007). The authors also compared the wear rates of the cold sprayed coating with the highest retained WC content of 66 wt% (refer to Fig. 4) to HVOF sprayed WC-Co coatings with 83 wt% retained WC. Once again the same trend observed by previous authors was found here; the CGDS coatings had better wear resistances compared to the HVOF coatings, despite the higher hardness of the HVOF coatings (1100 HV compared to 533 HV). This was attributed to the negative impact of WC decarburization as a result of the high temperature process. The ductility and toughness of the Ni matrix of the cold sprayed carbide coating also contributed to the improved wear resistance. The WC particles reinforced the coating, minimizing the damage to the surface of the coatings. The binder mean free path, which dictates the distance between the reinforcing WC particles within the metallic matrix, may be used to describe the mechanical properties of WC-based coatings. This was done by Melendez et al (2013b) who used the Ni mean free path to explain the changes in the wear rate of the WC-Co-Ni coatings. The authors found that the wear rate of the coatings decreased significantly as the mean free path between the WC-based reinforcing particles decreased, as illustrated in Fig. 8. The main wear mechanism observed was plastic deformation of the soft Ni matrix, while the hard WC particles appeared to remain undamaged (Melendez, 2013b).

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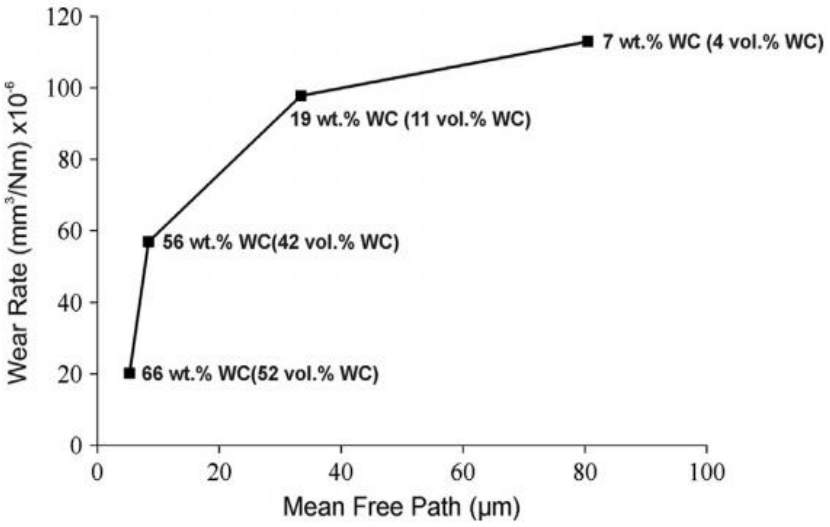


Figure 8 The effect of binder mean free path on the wear rate of cold sprayed WC-12wt%Co-Ni coatings (Melendez, 2013b)

Dosta et al (2013) performed ball-on-disk and dry abrasion tests on WC-25wt%Co coatings deposited onto carbon steel and Al7075-T6 substrates, using a high pressure CGDS system. Low sliding wear rates were observed for both coatings, where the wear mechanism was identified as the non-uniform extraction of WC particles from the matrix. The remaining carbides embedded within the Co matrix maintained their wear resistance function, explaining the low wear rates observed. EDS analysis of the wear debris detected at the edges of the wear track of both coatings, confirmed the presence of oxides, which could be responsible for a lubricating effect. The oxides were formed as a result of the high temperatures reached during sliding. The abrasion tests showed that the uniform WC particle size and the distribution of the carbide particles within the metallic Co matrix resulted in highly abrasion resistant coatings (Dosta, 2013).

4. CONCLUSION

Various authors have demonstrated the feasibility of using high and low pressure CGDS systems to deposit wear resistant WC-based coatings. The deposition parameters used in high pressure systems are sufficient to allow for the adhesion of cemented carbide particles. However, low pressure systems require a ductile metal such as Ni, Al or Cu to co-deposit carbide powders. Spray process parameters and feedstock powder properties influence the coating properties, and subsequently the wear properties. Both high and low pressure systems are able to form WC-based coatings with abrasion and sliding wear resistances comparable to and sometimes higher than coatings produced by high temperature HVOF spray techniques.

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