

## INVITED PAPER

### NANOCOMPOSITE SURFACES – A REVIEW

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The development of nanocomposite surfaces offers significant improvements in mechanical properties over conventional microstructured surfaces. However, to develop nanostructured surfaces for abrasive wear resistant applications still remains a challenge. This paper gives an overview of some of the more successful spraying techniques such as High Velocity Oxy-Fuel (HVOF) spraying that have been used to deposit thick nanostructured WC-Co based coatings. The retention of the nanostructure developed in the feedstock powders through control of spraying parameters has some limited success in preventing decarburization of the WC nano-sized dispersion in the Co matrix. The use of a novel duplex Co-coated powder has the effect of eliminating decarburization and this is reflected in a noticeable increase in mechanical and wear resistant properties of the final coating. Cold gas dynamic spraying techniques have also been used to control the final composition and grain structure of WC-Co based coatings and the corresponding properties changes are compared and discussed.

**Keywords:** Nanostructure, WC-Co, Coatings, HVOF spraying, CGDS spraying, Wear resistance.

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#### 1. Introduction

The engineering of surfaces to achieve a desired property is used throughout the industrial world as a cost effective method of producing tools and components from materials with lower mechanical properties. For most applications the engineering environment is a challenging one and requires a surface with a low coefficient of friction, good wear and corrosion resistance. This combination of properties suggests that at least two or more combinations of materials are needed if the goal is to be achieved. Therefore, a composite surface is what is required. Furthermore, we may want isotropic properties in order to resist crack propagation from different directions such as the surface, coat/substrate interface or intrinsically within the coating.

The science of materials tells us that as the microstructure becomes finer the size of inherent defects is also reduced. Furthermore, the micro-mechanism of plastic deformation based on dislocation creation and movement changes. The number of interfaces present in a nanostructured material in the form of grain boundaries and triple junctions becomes very large compared to

conventional materials. This has the effect of changing the mechanical properties of a nanostructured material by increasing the toughness and strength of the material [1]. Therefore, the development of a sub-micron structured matrix containing nanometer sized particles as dispersion will lead to an engineered surface with excellent properties. However, the ultimate challenge is how to make such a nanocomposite and deliver it to a material surface. Although there are numerous techniques available such as physical and chemical vapor phase deposition, sol-gel processing, laser alloying and thermal spraying methods, this paper focuses on the development of thick nanocomposite coatings for abrasive/erosive wear resistant applications. The WC-Co cemented carbide system in the form of coatings and sintered components has been found to give good wear resistance in a variety of applications ranging from cutting tool bits for machining through to mineral processing and oil sands environments [2]. The use of thermal spraying methods particularly High Velocity Oxy-Fuel Spraying (HVOF) has been used extensively to deposit WC-Co feedstock powders [3, 4]. However, recently researchers have shown that the

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hardness and toughness can be increased with the use of a nano-sized WC dispersion in the Co metal matrix [5, 6].

This paper provides an overview of the recent work on the use of spraying techniques that have been used to create nanocomposite surfaces. Particular focus is given to the challenges and successes achieved with respect to microstructure and mechanical property changes within these novel coatings.

## 2. Thermal Spraying

A variety of thermal spraying methods are available for the deposition of thick cermet coatings such flame spraying, detonation gun, plasma spraying and HVOF spraying. The HVOF technique has preferred over the other processes because it offers lower flame temperatures (~2500°C) and much greater impact velocities (see Table 1). Both the latter parameters are important because they influence the degree of oxide content and porosity

within the deposited coating. The spraying of nanostructured coatings possesses challenges because the nano-sized powder cannot be directly sprayed using the spray gun. The nanostructured powder must be agglomerated to produce a size large enough (typically between 10-50 μm) to spray. The method of powder preparation is described in earlier work [7], but it is suffice to note that the process must not influence the size of the nanostructured powder and is normally carried out using mechanical alloying and milling in an inert atmosphere such as Ar, N<sub>2</sub> or H<sub>2</sub> to reduce the effects of oxidation.

The HVOF spraying system consists of a water cooled gun (e.g Sulzer-Metco DJ2700), which allows the mixing of 2 types of fuel gases such as H<sub>2</sub>, O<sub>2</sub> or methane, see Fig. 1. The gun brings together O<sub>2</sub>/air and fuel in a specific ratio and this gaseous mixture is ignited by an arc which produces a supersonic flame. A hopper feeds the powder mixture into the path of the flame via an

Table 1. Comparison of thermal spraying methods.

Spraying technique	Temperature (°C)	Impact velocity (m/s)	Oxide content (%)	Adhesive strength
Flame wire	3000	180	4	D
Electric arc	5500	240	0.5-3	C
Detonation gun	4000	900	0.2	B
Plasma arc	5500	240	0.5-1	C
HVOF	2500	700-1200	0.1	A

Adhesive strength: A = Best; D = Worst

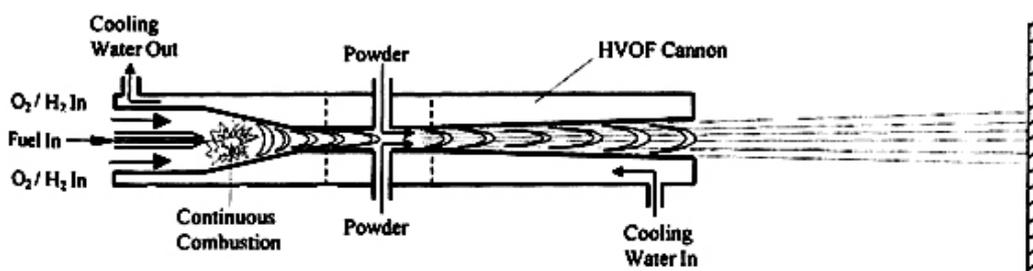


Figure 1. Schematic showing the HVOF spray gun.

inert gas such as  $N_2$ . The powder particles are injected axially into the flame and projected onto the substrate surface.

### 2.1. Powder and Substrate Materials

The HVOF technique has been used to spray a variety of WC-Co systems (e.g WC-12Co, WC-17Co, WC-18Co and WC-10Co-4Cr) onto C-Mn steel substrates such as AISI 1118 (0.18C, 1.4Mn) and AISI 1018 (0.18C, 0.16Si, 0.65Mn).

The WC-Co powder system has been sprayed using various fuel to  $O_2$  ratios where the fuel used has been  $H_2$ , propane or methane and the typical spraying parameters used to deposit 300-550  $\mu\text{m}$  thick coatings is shown in Table 2.

Table 2. Parameters used in the HVOF spraying processing.

Spraying parameters	Parametric value
Shroud gas (air), slpm*	1742
Oxygen, slpm	1346
Methane, slpm	918
Carrier gas (nitrogen), slpm	60
Spray distance, cm	23
Spray rate, g/min	38

\*standard liter per minute.

The characterization of the microstructured and nanostructured powders before spraying showed the powders to be similar in morphology. The microstructured powder particle size has a range from 15 to 35  $\mu\text{m}$  with a WC size of 1 to 3  $\mu\text{m}$ . In comparison the nanostructured WC-Co powder used by Stewart et al. [8] shows the WC with a size between 70 to 250 nm with a median powder particle size of 60  $\mu\text{m}$ .

### 2.2. Nanostructure and Decarburization

Intensive research has been performed to compare the effect of HVOF spraying parameters on the ability to deposit both conventional microstructured and nanostructured coatings from their respective feedstock powders [9, 10]. This research showed that both types of coatings suffer from decarburization of the WC particles in the powder as it is sprayed and a harder  $W_2C$  phase

forms as a reaction product in the deposited coatings. The break down of WC to form  $W_2C$  phase was directly affected by the temperature of the flame and type of fuel used. The work by Marple et al [9] showed that the hardness of coatings deposited using  $H_2$  as a fuel was greater than when propylene was used and this difference was attributed to the greater decarburization of WC to form  $W_2C$ . Interestingly, when WC-Co composites are compacted and sintered, the final product has a higher hardness and wear resistance than similar microstructured WC-Co composites produced in the same manner [10]. However, when nanostructured powders are used to produce coatings by the HVOF process disappointing abrasive wear test results have been reported [5, 11]. The poor wear resistant behaviour of the nanostructured coatings was attributed to the greater decarburization of the nano-sized WC in the Co matrix due to greater surface area to volume ratio. More recent work by Chen et al. [12] compared the wear behaviour of an ultra fine powder containing a WC size of 600  $\mu\text{m}$  with that of a nanostructured WC having a size range between 50 to 500 nm. The wear test was performed using a GCr15 steel counter part at a temperature of 600°C. Their work suggested that decarburization was observed in both types of coatings, but the wear resistance of the nanostructured coatings was greater than that of the ultra fine powder, at 600°C [12].

### 2.3. Duplex Co-Coated Powders

It is evident from published work that the decarburization of WC to form a brittle  $W_2C$  plays a critical role in determining the abrasive wear resistance and failure of the coatings produced by HVOF spraying. Therefore, the powders used for spraying must either be substituted with more inert constituents, for instance replacing the WC with  $Al_2O_3$  or  $Y_2O_3$  or enhance the feedstock powders to resist decarburization effects. The work by Khan et al. [13] has used an engineered powder particle as shown in Fig. 2. The schematic compares the difference between a normal commercially used spray dried WC-17Co powder particle and an enhanced powder. This "engineered particle" contains a Co core into which near-nanostructured WC particles are dispersed and the particle has an outer Co coat which provides a protective barrier during the spraying process. Furthermore, the deliberate use of a near nano-sized WC (427 nm)

particle rather than a nano-sized particle helps to reduce the decarburization of the WC particle.

The HVOF spraying of the novel duplex Co-coated WC-17Co powders was carried out on C-

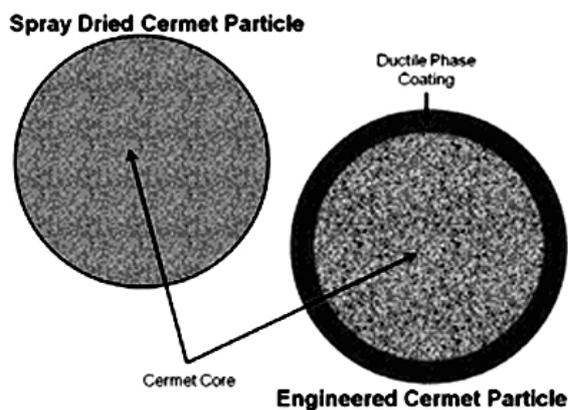


Figure 2. Schematic showing a comparison between the conventional spray dried powder particle and the novel "engineered" duplex Co-coated powder.

Mn substrates to a thickness of 529  $\mu\text{m}$ . A comparison in Vickers hardness values between the duplex coated and commercially used microstructured WC-10Co-4Cr coatings gave 1440 VHN and 1048 VHN respectively [14]. The wear resistance of the coatings using a two-body abrasive wear test on a pin-on-disc wear tester using 120 grit SiC (abrasive particle hardness is 2500 VHN) showed that the WC-17Co coating had superior wear resistance compared with the microstructured coating (see Fig. 3).

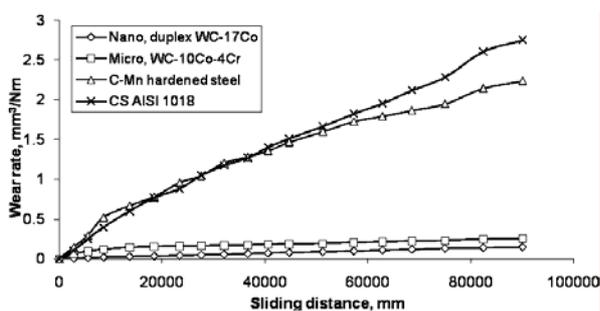
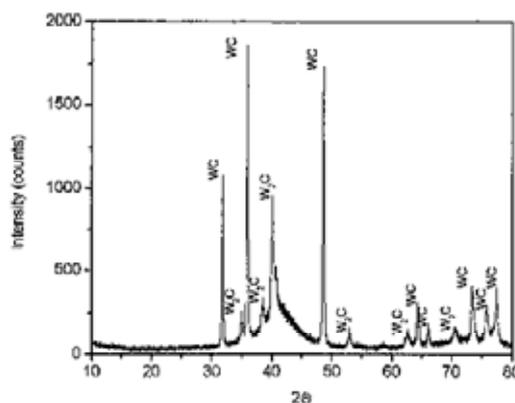


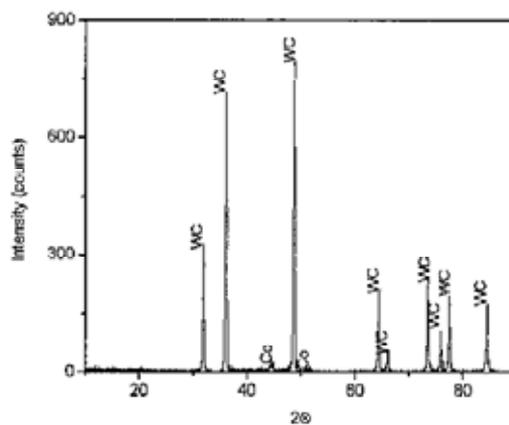
Figure 3. Wear rate as a function of sliding distance for coated and uncoated steel substrates.

Microstructural and compositional characterization of the coatings showed that the duplex Co layer was effective in preventing decarburization of the WC as shown by the X-ray diffraction analysis in Fig. 4. Peaks for  $\text{W}_2\text{C}$  formation were absent from the XRD spectrum taken from the

nanostructured coatings produced using the duplex Co coated powders. Furthermore, the coatings were denser and showed better compositional homogeneity compared with the microstructured coatings [14]. The greater homogeneity of the nanostructured coatings provided better corrosion resistance in a 3.5% NaCl solution and the Nyquist diagrams obtained from the use of Electro-Impedance Spectroscopy (EIS) can be seen in Fig. 5. The size and shape of the capacitive semi-circles clearly showed that the best corrosion resistance was possessed by the near nanostructured coating followed by the microstructured coatings and then the uncoated AISI 1080 steel [15].



(a)



(b)

Figure 4. XRD analysis taken from HVOF sprayed coatings: Microstructured WC-10Co-4Cr coating; (b) Nano-structured WC-17Co coating.

### 3. Cold Gas Dynamic Spraying Process (CGDS).

The CGDS is a relatively new process compared to thermal spraying techniques and was developed in the mid-80's at the Institute of Theoretical and Applied Mechanics in Russia and introduced to North America in the 1990's [16, 17].

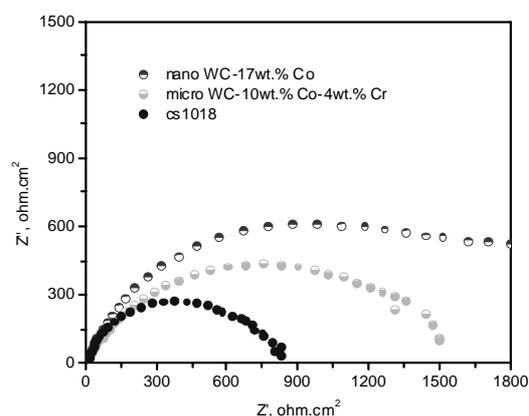


Figure 5. Nyquist diagrams comparing the corrosion resistance of AISI 1018 steel with nanostructured WC-17Co and microstructured WC-10Co-4Cr coatings produced using HVOF spraying.

Unlike thermal spraying where significant heat is generated to melt the powdered particles fed into the spray, the CGDS process uses a low temperature ( $\sim 700^{\circ}\text{C}$ ) supersonic gas jet to project the powder onto the substrate surface. The

advantage of this process is that changes in the microstructure and composition of the starting powders can be minimized. The CGDS method has been applied to iron, copper, nickel and aluminium based alloys [18-21].

The application of CGDS to WC-Co cermet powders offers a potential avenue for depositing coatings without the decarburization effects. Researchers have used this spraying technique to deposit both micro and nanostructured WC-Co coatings from both agglomerated and sintered feedstock powders [22]. The feedstock powders are injected into the supersonic gas flow and accelerated towards the substrate. The particles do not experience temperatures high enough to soften or melt them so that a coating is deposited through a solid-state process. The particles deform plastically and bond to the surface after disrupting thin surface oxides. In principle, the chemical composition and microstructure of the feedstock powder are preserved [19]. The research results from the application of this technique to micro and nanostructured WC-Co powders have shown the technique to be versatile in producing thick coatings with low porosity [24]. However, metallographic analysis has shown that microcracks could still be observed in all the coatings produced by the CGDS process. These microcracks were especially noticeable at regions near to the coat/substrate interface [21] (see Fig. 6). In

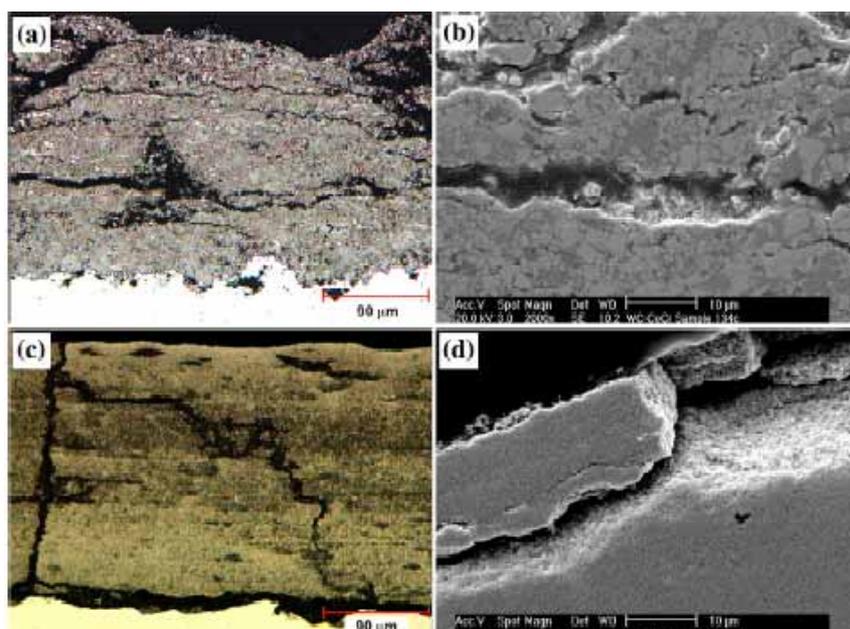


Figure 6. Light and SEM micrographs showing the morphology of conventional (WC-10Co-4Cr) and nanostructured WC-15Co coatings deposited by the CGDS process [22].

order to improve on the CGDS process, researchers have developed the Pulsed Gas Dynamic Spraying (PGDS) process at the University of Ottawa, Canada [23, 24]. As in the CGDS process the powder particles are accelerated to high impact velocities, but this time

process, and no lamellar or banded structures were obtained, which is typically seen in thermal sprayed coatings, see Fig. 7. The hardness for the PGDS coatings (900 VHN) was found to be higher than coatings produced using CGDS (450 VHN).

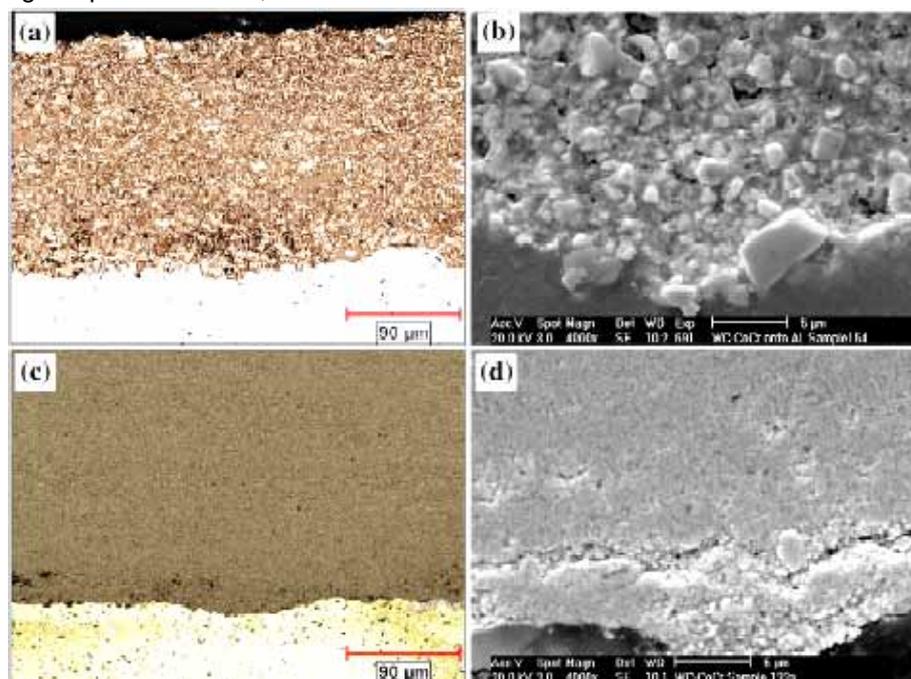


Figure 7. Light and SEM micrographs showing the morphology of conventional (WC-10Co-4Cr) and nanostructured WC-15Co coatings deposited by the PGDS process [22].

the particles experience higher temperatures because the propellant gas does not experience the rapid drop in temperature as found during gas expansion in the CGDS process [24]. Furthermore, pre-heating of the feedstock powders to 400°C was employed as a method of increasing the ductility of the material thereby increasing the ability of the coating to produce denser coatings and increase coat adhesion to the substrate.

Experimental studies using the PGDS process to spray WC-Co powders has shown that denser coatings can be produced with less micro-cracking compared to the CGDS method. The lower temperatures employed eliminate decarburization of the WC which was observed in HVOF spraying techniques. A comparison in the hardness values of the micro and nanostructured coatings when various spraying techniques are used is summarized in Table 3. Microstructural characterization of the coatings also showed that the PGDS coatings were more homogeneous compared to those produced by the CGDS

Table 3. Comparison of Vickers hardness values as a function of deposition process.

Deposition Process	Vickers Hardness /VHN
Nano WC-12Co/HVOF	1048
Micro WC-10Co-4Cr/HVOF	850
“Duplex” Nano WC-17Co/HVOF	1440
Micro WC-10Co-4Cr/CGDS	350
Nano WC-12Co/CGDS	450
Nano WC-12Co/PGDS	900

CGDS-Cold Gas Dynamic Spraying Process

PGDS-Pulsed Gas Dynamic Spraying Process

HVOF-High Velocity Oxy-Fuel Spraying

However, these values are both lower than that recorded for thermal sprayed coatings because decarburization of WC results in a harder  $W_2C$  phase forming in the coating. The greatest hardness value was recorded for the duplex Co-coated powders and this was attributed to less porosity formation in the coatings associated with the formation of  $CO_2$  during the decarburization reaction [14].

#### 4. Conclusions

A review of the spraying methods used to produce thick nanostructured coatings shows that both HVOF spraying and the Cold Spraying techniques can be used to deposit nanostructured coatings onto steel substrates from nanostructured feedstock powders.

The challenge of eliminating the decarburization of WC to form  $W_2C$  has been attempted by careful control of spraying parameters such as the type of fuel or fuel stoichiometry in the HVOF process. However, the use of "engineered powders" which have an outer Co layer to protect the WC particles has shown considerable potential in maintaining the nanostructure of the final WC-Co coatings. The hardness, wear and corrosion resistance of the nanostructured coatings is significantly better than that of similar microstructured coatings. The CGDS and PGDS methods also offer potential in retaining the original composition and microstructure of the feedstock powders used to develop the coatings. However, the inherent low temperatures of the process results in intrinsic defects such as micro-cracking which compromise the final mechanical properties of the coatings.

Further research is necessary to exploit the use of duplex Co-coated powders to other more inert systems compared to the WC-Co composition. For instance, the use of nanostructured Ni and  $Al_2O_3$  or Ni and  $Y_2O_3$  offer greater wear and corrosion resistance in erosive-corrosive environments.

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