Coatings Deposited Using a Valve-less Detonation System

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Detonation (D-Gun) Spraying is one of the oldest yet least utilized thermal spray technologies in spite of these coatings being known to be harder and better adhered then those applied via plasma and even HVOF methods. Some of the reasons for the lower popularity of D-Gun spraying are the more cumbersome equipment, lower productivity and higher complexity of interaction between the equipment and powder. Much of this is due to the use of mechanical valving to feed in combustion gases and therefore necessitating the use of intermittent powder flows. In this study we report on a new valve-less detonation spraying device allowing the use of continuous powder feeding and capable of higher detonation frequency than through conventional valved D-Gun systems. Previous valve-less systems were unreliable in terms of firing and safety. Tungsten carbide cobalt chrome (86WC:10Co:4Cr) was used to investigate the process-coating interactions during detonation spraying of tungsten carbide.

1 Introduction

Detonation spraying (D-Gun) is a relatively old but little utilized technology considering its advantages of superior bond, density and hardness when compared against HVOF and plasma techniques, particularly when applying carbides. Other advantages of the D-Gun over HVOF are the lower operating cost and lower heat input into the substrate. Therefore, this technology has the potential of offering superior coatings at lower cost. The traditional D-Gun design consists of a cannon like water cooled tube with mechanical valves for gas metering and a spark plug close to the blind end [1]. A water cooled powder feed tube is usually placed slightly in front of the valves. Combustion mixtures typically of acetylene and oxygen are fed in the tube, ignited via the spark plug and the resulting detonation front carries the powder through the tube and towards the substrate. A nitrogen purge is utilized between firing to prevent backfiring. In contrast, a valve-less D-Gun system eliminates the mechanical valves but retains the spark plug and powder feed tube. Generally, gases are fed through a specially designed path where the gases mix and are fed into a combustion chamber [2]. This design prevents back flow into the gas train, therefore, nitrogen purging can be eliminated. One advantage of such a system is less dangerous propane can be used as the combustion gas rather than acetylene. Additionally, the firing rate and thus productivity can be increased as long as sufficient gas flow can be maintained to sustain ignition. Another key advantage over conventional D-Guns' is that powder can be fed continuously using standard high pressure powder feeders. An important differentiation between the two powder feed methods are that in the valve-less system air is used as the carrier gas not nitrogen. This becomes important in spraying of oxides and carbides. D-Gun systems can be viewed as a high velocity intermittent thermal spray technique. This paper reports on work conducted using a valve-less system.

Tungsten carbides are an industrially important and widely studied thermal spray coating material with abundant literature describing process-material-properties effects [3,4]. Tungsten carbide cobalt chrome, WC-CoCr, (86:10:4) is widely used in aerospace and petroleum industry, therefore, this study concentrated on characterizing this composition using the valve-less detonation gun process.

All tungsten carbide-cobalt based thermal sprayed coatings are very sensitive to process conditions. In particular, oxidation can have a profound effect on the phase composition and thus the hardness and brittleness of the coating. Since the reaction

$$2C + O_2 = 2CO$$

is more thermodynamically favorable then oxidation of cobalt or tungsten [5], brittle phases such as W_2C and $Co_xW_yC_z$ (eta phase) are promoted. Furthermore, as the cobalt binder melts (MP = 1495ºC), WC can rapidly dissolve in it. The solubility of tungsten in cobalt is inversely related to the carbon content. Therefore, decarburization promotes the dissolution of tungsten in cobalt. Fernandes and Senos describe the phase transformations in cemented carbide systems in their review paper for the interested reader [6]. Decarburization and dissolution reactions lead to lower WC containing coatings resulting in reduced hardness and fracture toughness. Since valve-less D-Guns' have extended barrels (up to approximately 1500 mm) with oxygen rich environments, such reactions can be intensified. Decarburization and dissolution reactions are temperature dependent, therefore, the choice of fuel gas is of great importance. Acetylene and propane oxygen flame temperatures are 3480°C and 2526°C respectively, suggesting that valve-less systems may have an advantage in the spraying of tungsten carbides. In fact, patent US4902539 granted to Union Carbide Corporation attempts to solve this problem for the valved system by diluting acetylene with propylene to lower the combustion temperature while maintaining peak pressures [7]. Diluting with argon or nitrogen lowered the peak pressures faster than peak temperature thus lowering particle velocities while still maintaining high temperatures. This work reports the effects of oxygen, propane ratios, flow rates and combustion (shot) frequency on the hardness and microstructure of WC-CoCr coatings. Coating quality was determined on the basis of existing industrial specifications. AMS 2448 is usually the governing specification for HVOF tungsten carbides while Detonation Gun specifications are not widely found, MIL-HDBK-1886(AT) provides some guidelines as to the expected hardness and microstructure. AMS 2448 list minimum hardness of 950 DPH while MIL-HDBK-1886 requirements are 1000-1150 DPH. Both standards require porosity of less than 1% [8,9]. In consideration of the above, in our case the acceptable microhardness was set at 1200 DPH_{300} with porosity less than 1% to demonstrate that industrial and military requirements can be met or exceeded using the current valve-less detonation system.

2 Experimental

All spray experiments were conducted using a robotically mounted system with a simple raster program to minimize process variations. Gas flows were controlled using mass flow meters. All aspects of the process sequence were controlled via a PLC. A cast and crushed powder sized from -44+15 microns was used. The powder characteristics are shown below, **Fig. 1**.

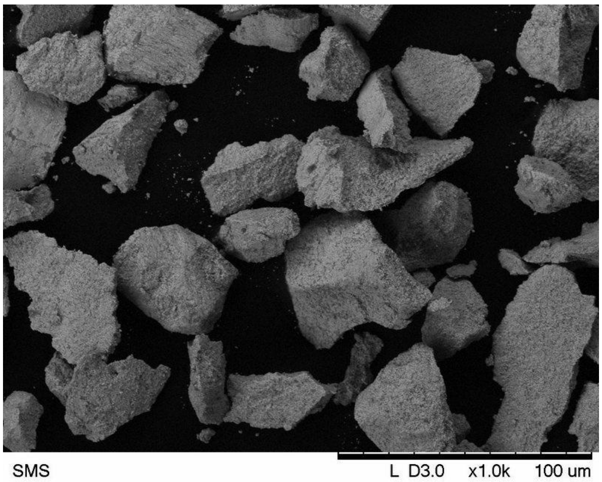

Fig. 1. WC-CoCr Cast and Crushed Powder

Coating characteristics were determined via optical and scanning electron microscopy. Porosity was determined using Paxit image analysis [10]. Hardness testing was conducted using a Phase II 900-392 Vickers Microhardness tester. The built in software is capable of statistical analysis. **Table 1** list the process conditions and sample designations for the experiments. The feed rate was kept constant. X-Ray Diffraction (XRD) analysis was conducted on the samples prepared in Table 1. The X-Ray Diffractometer was model, Lab XRD-6000, Shimadzu (Japan). The XRD diffraction patterns were analyzed with International Centre for Diffraction Data (ICDD), Release 2012.

Table 1 Experimental Conditions

Sample #	Distance (mm)	Oxygen/Propane (slm)	Oxygen/Propane ratio	Shot Frequency
1	300	72/12	6:1	2
2	250	48/12	4:1	2
3	250	64/16	4:1	4
4	250	60/18	3.3:1	2
5	250	63/18	3.5:1	2
6	250	70/20	3.5:1	2
7	250	77/22	3.5:1	2
8	200	82/23	3.5:1	8
9	250	82/23	3.5:1	8
10	300	82/23	3.5:1	8

3 Results

In the valve-less system the powder feed rate is constant and the shot frequency merely distributes the powder in larger or smaller increments per unit time depending on the respective frequency. In **Fig. 2** is a bar chart of microhardness (DPH_{300}) plotted as a function of test conditions. Samples 8-10 were generated at higher shot frequencies.

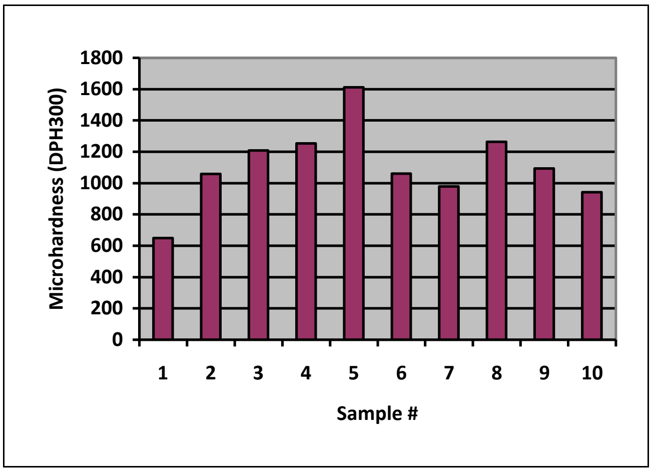

Fig. 2. Microhardness as a Function of Test Conditions

At the higher frequency, the 63/18 oxygen to propane flow rate could not sustain the flame adequately. Therefore, the flow rates were increased to 82/23 while maintaining the fuel-oxygen ratio. **Fig. 3** illustrates the relative deposition efficiency at stand-off distances from 200 to 300 mm. The deposition efficiency is observed with an increase in coating thickness with a change in stand-off distance. All tests were conducted at 8 shots/second.

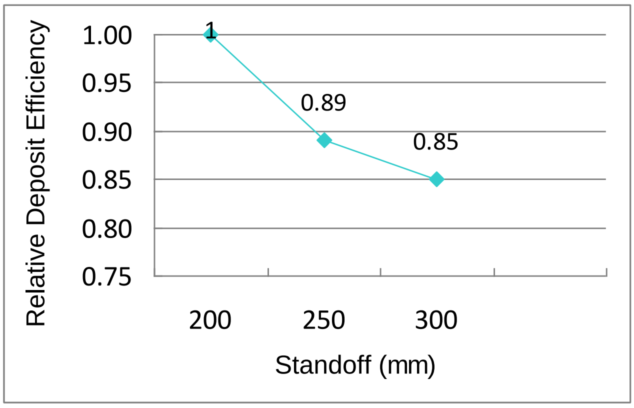

Fig. 3. Relative Deposit Efficiency as a function of Stand-off Distance

Additional samples were prepared to compare efficiencies at 4, 6 and 8 shots per second at the optimized ratio of 3.5:1 oxygen-to-propane (**Fig.4**). The flame stability could be maintained at a ratio of 63:18 oxygen-to-propane and for flow rates of 4 and 6 shots per second, but not at 8 shots/second. As mentioned above, at 8 shots/sec flame stability required flow rates of 82:23 slm oxygen-to-fuel for 8 shots per second.

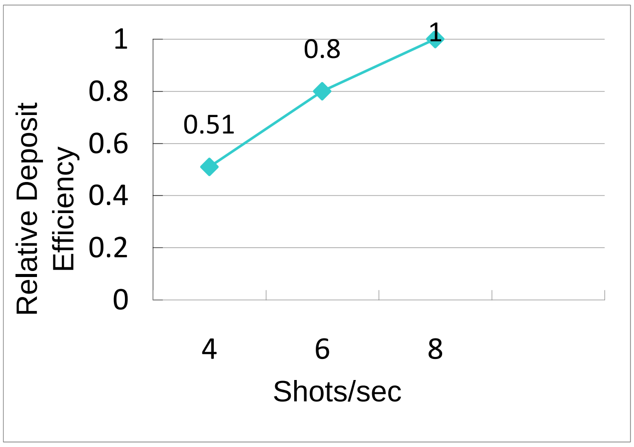

Fig. 4. Relative Deposit Efficiency as a function of Shot Frequency

While coating density is exceptionally high (e.g., +99%) in all cases, there exists microstructural differences (e.g., degree of decarburization) between the coatings as a function of the changes in detonation parameters. Scanning electron microscopy was conducted on all the test samples. **Figs. 5a** and **5b** show the back scattered images of the softest and hardest coatings, respectively.

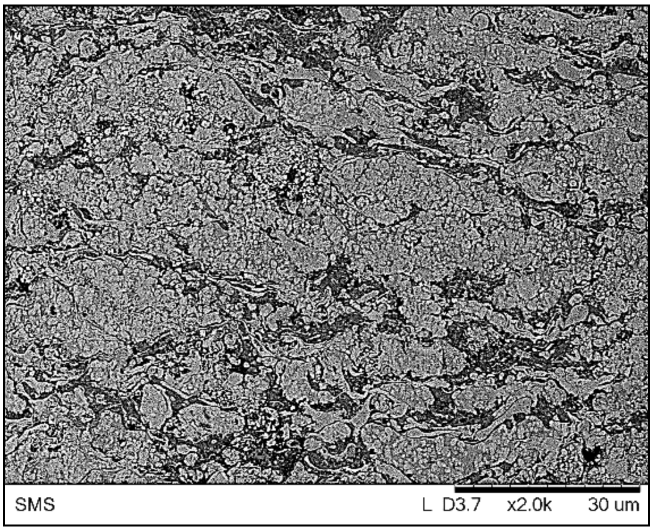

Fig. 5a. SEM Back Scatter Image, Test Sample #1, Cross-Section

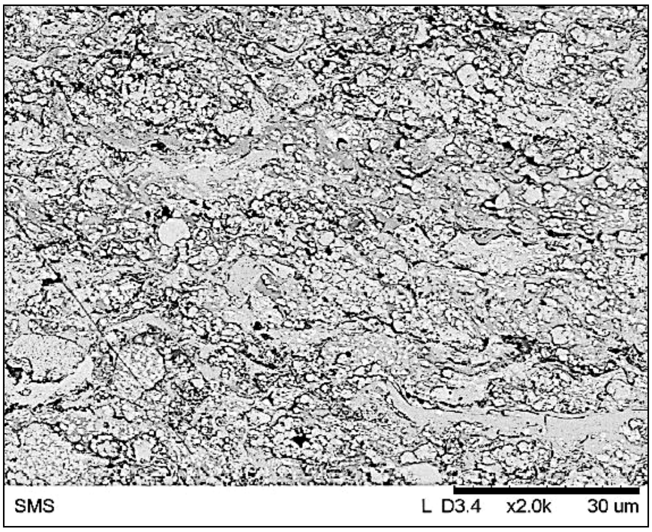

Fig. 5b. SEM Back Scatter Image, Test Sample #5, Cross-Section

X-Ray Diffraction (XRD) analysis was conducted on the samples prepared in Table 1, using a Shimadzu, model XRD-6000, diffractometer. The XRD diffraction patterns that were generated from these samples were analyzed with International Centre for Diffraction Data (ICDD). JCPDS were entered into the data base for the various tungsten carbide cobalt variants that could potentially be formed as a result of the detonation processes. **Fig. 6** provides the XRD patterns for detonation processes conducted at oxygen-to-fuel gas ratios 72:12, and 82:23. The various phases are identified in the two patterns.

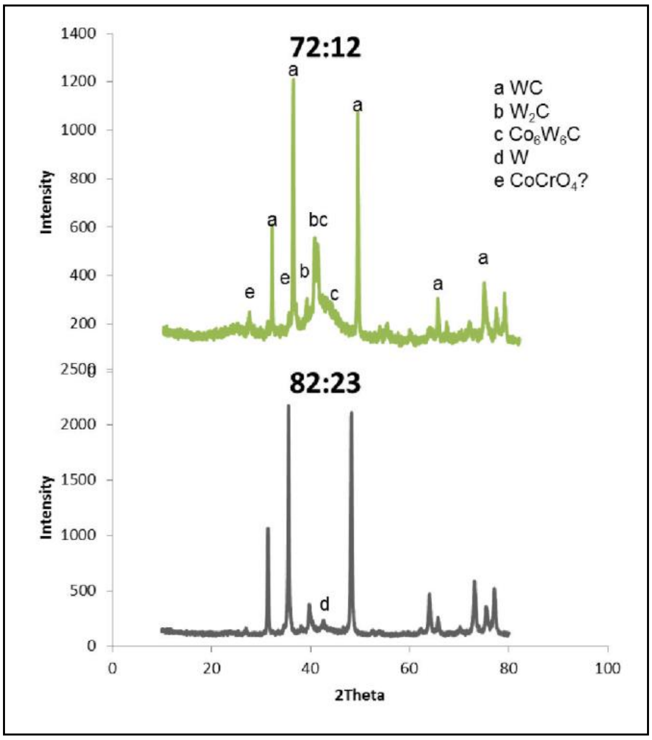

Fig. 6. X-Ray Diffraction Patterns, with Phases Identified for Detonation Process Conditions

4 Discussion

An investigation into valve-less detonation gun spraying of WC-CoCr was conducted. A variety of propane-oxygen flows and ratios were evaluated with the intent to form coatings with at least 1200 DPH which is industrially considered a higher hardness coating without being too brittle. MIL-HDBK-1886 "Tungsten Carbide Coating Detonation Process" lists required hardness as 1000-1150 DPH_{300} with porosity less than 1%. Reference 3 measured microhardness of WC-CoCr coatings applied using two HVOF systems DJ 2700 and JP 5000 and recorded hardness of 1231 DPH. In our case at high oxygen-propane ratios substantial oxidation occurs resulting in lower hardness. Interestingly, all coating microstructure showed less than 1% porosity regardless of gas flow and distance variation from 200-300 mm indicating that coating properties are determined by decarburization and dissolution reactions, except for samples 9 and 10 where porosity increases to 1.5% at 300 mm spray distance. A stoichiometric mix for combustion of propane requires 5:1 oxygen to propane ratio, therefore, at 6:1 ratio an excess of oxygen is created in a high temperature environment where decarburization and dissolution occur. Back scattered electron images of coating cross-sections sprayed at 6:1 oxygen-propane ratios also shows oxidation of the matrix (**Fig. 5a**) as well as the formation of $CoCrO_4$ (**Fig. 6**). This matrix oxidation is not observed in coatings sprayed under reducing conditions (**Fig. 5b**). The $CoCrO_4$ phase has been reported and formed at 600ºC and 2000 bar in a reactor using an oxygen compressor [11]. At slightly reducing conditions of 4:1 oxygen-propane ratio the hardness increases with flow rate and shot frequency. At even more reducing parameters the hardness further increases, however, flame instability was observed at 3.3:1 ratios. A hardness of 1610 DPH was obtained at 3.5:1 ratio and at flow rates of 63:18 slm oxygen to fuel. Further increases in flow rates at this ratio decreased hardness. The most plausible explanation is that the temperature increases with flow rates thereby increasing dissolution resulting in the lower hardness observed. **Fig. 6** illustrates the effects of flow rates and oxygen-fuel ratio on the phase composition of coatings. Oxidizing combustion mixtures (72:12) show an increased amount of W_2C and eta phase Co_6W_6C than reducing mixtures (82:23). A broad mound can be seen in the case of the 72:12 flow rates in the region of 40-46 degrees. This can be attributed to the combination of peaks from eta and free tungsten phases. The eta phase could not be detected in the spectra for 82:23 flow rate, however, free tungsten could. An oxidation product $CoCrO_4$ could be indexed in both coatings with a reduced amount in 82:23 flow rate specimens. A literature search on XRD of sprayed WC-CoCr coatings has not revealed this phase before, however, the two major peaks match quite well. In the WC-Co system, decarburization leads to formation of W_2C and free tungsten. According to the ternary phase diagram the carbon loss leads to carbon content in a region where the eta phase is favored. Thermodynamically, the implication is that WC phase will now dissolve in cobalt to form the ternary eta phase.

The 3.5:1 ratio was considered to be the optimum based on microstructure and hardness at lower shot counts. In order to increase productivity shot rate was increased to 8 while increasing flow rates and maintaining 3.5:1 oxygen to propane ratio. **Figure 3** showed the hardness values as a function of temperature. Acceptable hardness of 1263 could be achieved at 200 mm. More importantly, the efficiency doubled from 4 shots at 63:18 flow rates to 8 shots/sec at 82:23 oxygen-propane flow rate (**Fig. 4**). It was noticed, microstructurally, at low shot frequency, that increased coating erosion could be seen from impingement of carbide particles. It is expected as the shot frequency is increased per flow rate reduction in particle temperatures and velocity will occur therefore less erosion of the coating will be observed. It was estimated from past experiments with DJ 2700 that that time to prepare similar samples thickness was improved by 30%. Since the samples are small not much can be inferred about industrial applications where workpieces are larger and heat effects are not as pronounced.

5 Conclusions

The use of propane as a fuel in a valve-less detonation system proved beneficial when applying tungsten carbide cobalt chrome coatings. Propane-oxygen flow rates, ratios and shot frequency could be changed to obtain coatings with hardness as high as 1600 DPH_{300}. A further advantage of this system is that dense coatings could be produced regardless of variations in process variations with the exception of distance. The most important parameters in controlling the amount of the WC phase were the oxygen-to-fuel ratio, flow rate and shot frequency.

6 References

[1] http://www.praxair-gmbh.de, PST Super D-Gun™.

[2] US 5542606 "Gas Detonation Spraying Apparatus" Kadyrov E. June 17, 1994

[3] Schwetzke R., and Kreye H., Microstructure and Properties of Tungsten Carbide Coatings Sprayed with Various High Velocity Oxygen Fuel Spray Systems, Journal of Thermal Spray Technology, Vol 8(3) Sept. 1999, pp 433-439.

[4]http://www.asetsdefense.org/documents/Workshops/24thCadmiumPlatingMeeting/15.%20Nicoll%20hcat%20july%2021%201.pdf.

[5] Darken, L.S. and Curry R.W., Physical Chemistry of Metal, McGraw-Hill, N.Y. 1953.

[6] Fernandes C.M., and Senos A.M.R., "Cemented Carbides Phase Diagrams; A Review", Int. Journal of Refractory Metals and Hard Materials, vol 29 (4), 2011, pp 405-418.

[7] US 4902539 "Fuel-oxidant Mixture for Detonation Gun Flame Plating" Jackson, J.E., Feb 20, 1990.

[8] AMS 2448A "Application of Tungsten Carbide Coatings on Ultra High Strength Steels, High Velocity Oxygen/Fuel Process" 2008-06-04, SAE International

[9] Mil-HDBK-1886(AT) Dept. of Defense Handbook "Tungsten Carbide-Cobalt, Detonation Process For Dept. of Defense", 27 march 1998.

[10] http://www.paxit.com/.

[11] Kume S., et.al "Generation of High Pressure Oxygen and Synthesis of $CoCrO_4$ with $CrVO_4$ Type Structure", Rev. Sci. Instrum.. 42, 1856 (1971)