A Study of High Velocity Combustion Wire Molybdenum Coatings

S. C. Modi & Eklavya Calla

In this paper coatings manufactured using the high velocity combustion wire spray process (HVCW) have been studied. Molybdenum coatings were prepared in this study and wavelength dispersion spectrometer (WDS) investigations were carried out to ascertain the oxygen content of the coating and its distribution. The XRD analysis of the coating was also carried out to determine the phases present in the coating. Based on the above data, the authors explain the HVCW sprayed molybdenum coating microstructure and properties. These coatings were also sprayed using a modified aircap design. The parameters varied for the molybdenum coatings by HVCW were (1) Distance of the substrate from the spray gun (2) The wire feed rate of the gun. Wear test and coefficient of friction measurements were also carried out for the coatings. Air plasma spraying of Mo-25%NiCrBSi coatings was carried out and these coatings were further checked for wear and friction properties.

1. Introduction

High velocity oxy-fuel (HVOF) coatings are being increasingly used in the industrial environment. HVOF coatings offer a qualitative advantage over Air Plasma Sprayed (APS) coatings. However, most of the HVOF coatings are applied using powders as the feed stock. The high velocity combustion wire (HVCW) spray system uses wire as the feed stock. As well the operating cost of HVCW is lower than most other thermal spray systems.

Molybdenum Coatings were prepared with a HVCW system under different set of parameters and the coatings thus prepared were characterized using the SEM, WDS & XRD phase analysis. Wear test of the coatings was also carried out.

Oxidation in the coating alters the microhardness and the wear performance of the coating. The mechanism of oxide formation in the coatings is discussed and it is co-related to the observed oxygen content of the coatings. The mechanical properties such as wear and friction were also studied by the pin on disk wear test. A Mo-NiCrBSi coating by APS was prepared and characterized for its wear and friction properties. This enabled a comparison of the HVCW wire & APS coatings.

2. The Mechanism of in-flight reactions in the HVCW Coating

There are differences in the mechanisms of in-flight reactions between the powder HVOF and the HVCW spray systems. The heat imparted to the powder particles in the HVOF powder system is expected to be less than the heat transfer to the wire droplets in HVCW. This arises because in most modern HVOF powder guns, the powder is injected in the barrel of the gun where the gas jet is in the expanded condition[6]. The conditions prevailing here are of low temperature but high velocity. The powder injected in the low temperature and low-pressure region of the HVOF torch attains very high velocities but it is at relatively low temperatures[6]. The HVOF powder coating is formed due to the high impact velocity of the powder particles, which leads to impact fusion of the hot powder particles[1, 6].

In the HVCW spray process, the wire droplet must be completely molten when it is being atomized [2]. Moreover the wire droplet is being melted and atomized in the nozzle aircap region, which is a high-pressure and high temperature region [1]. This leads to higher temperature of the atomized droplet. The liquid wire droplet does not attain the velocity from the gases until it is atomized &

entrained in the high velocity gases[7]. It is also possible that the metal is melted and atomized directly from the wire, in this case also the atomized droplets will attain the velocity after they are entrained the high velocity gases[2]. This causes the liquid wire droplet to remain entrained in the high temperature oxidizing jet of the gun flame for substantially longer duration as compared to the powder HVOF Systems[2].

As a result of above discussion it is apparent that

1. powder particles in the powder HVOF systems have lower dwell time in the flame due to higher particle velocity; and
2. temperatures at the point of wire melting & atomization are high in the HVCW spraying system

Due to the higher temperature during melting and atomization, it is expected that in the HVCW spray reactions take place prior to impact upon the substrate and at the site of wire droplet melting. The wire droplet-melting environment is one of turbulent mixing of the liquid droplet, the combustion gases and their reaction products[3,5,7]. The molten droplet when it is formed diffuses the gases of combustion[3, 5]. The rate of diffusion at or near the melting temperature is quite high. The oxidizing conditions that prevail during wire melting and atomization oxidize the wire droplets. Initially the surface of the droplet is oxidized and thereafter further oxidation of the molten droplet depends upon the diffusion of oxygen through the oxide layer to the metallic surface[3, 5].

The high velocity gas flow is turbulent in nature and it imparts turbulence to the liquid metal droplet. The oxides and metallic phases intermingle due to this turbulence. The intermingling of the oxides and the metal in the liquid droplet creates regions of low surface energy within the droplet (where oxides are present). These areas of low surface energy create further sites for atomization of the droplet [3, 5]. The choice of fuel gas also affects the oxidation in the coating during HVOF spraying. Coatings sprayed using acetylene as fuel have lower oxygen content as compared to coatings sprayed using propane as fuel[4].

Usually the density of the oxide layer is less than that of the metal, hence it tends to get blown away to that side of the droplet which is facing the substrate. The relative movement of the oxide and metallic phase occurs because the oxide and metal phase have different densities[5]. Whether the droplet actually gets blown away will depend upon the surface tension between the metallic droplet & the oxide layer[4, 5]. If the oxide layer can overcome the surface tension force of the metallic droplet then the oxide layer forms a discrete splat in the microstructure, otherwise it will be seen on the bottom of the splat. This phenomenon can occur in two ways ;

1. the velocity imparted by the gases is sufficiently high to overcome the surface tension forces between the metallic droplet and the oxide layer;
2. the oxide layer becomes progressively thicker due to further oxidation of the metallic droplet, wherein a stage reaches where the depleted metallic droplet does not have the surface energy in it to hold the enlarged oxide layer.

This process is repeated till the droplet is deposited on the substrate.

Most metallic oxides have a higher melting point than their corresponding metals hence the oxide layer would have solidified immediately on formation hence further oxidation of metal due to diffusion from the oxide layer is minimum[5]. The solidified oxide layer becomes part of a composite coating wherein the oxide particles are evenly distributed in a metallic matrix.

The presence of this oxide layer in the molten droplet or splat may also lead to porosity in the coating microstructure, as the oxide layer which is already solid when it hits the substrate may rebound from the substrate surface thus leaving a gap between the already deposited splat and the incoming splat[5]. Moreover the oxide layer thus deposited may come out during subsequent processing of the coating.

3. Experimental Procedure

The wire HVOF gun used for the experiments in this case was developed by the R&D unit of Metallizing Equipment Company, Jodhpur (India). It is commercially know as HIJET™-9600. Molybdenum wire 3.17mm diameter 99.9% purity was used for preparing the coated samples. The HVCW system works on oxygen - propane / LPG Flame. The present experiments were carried out using an oxygen-LPG flame (propane is not available in India). The composition of LPG gas is as under :

Ethane	00.90% by weight
Propane	28.40% by weight
ISO-Butane	30.20% by weight
N-Butane	40.50% by weight

The parameters of spraying by HIJET™-9600 are shown in Table 1

	Pressure	Flowmeter Reading
Oxygen	6.0 Kg/Cm^2	90
LPG	6.0 Kg/Cm^2	55
Air	5.0 Kg/Cm^2	----

Table – 1 (Parameters for spraying molybdenum)

Thickness of coating for microstructure evaluation and wear testing was 250 microns. The samples were prepared by abrasive grit blasting using the suction type blasting machine using 20 mesh aluminium oxide as the abrasive. The samples were subsequently cleaned in the ultrasonic cleaner, after blasting.

The samples were prepared for (1) Metallography evaluation of molybdenum coatings (2) Wear and friction test of the coatings (3) Tensile bond strength of coatings (as per ASTM C633-79 method).

The parameters of spraying were varied as per Table 2

	Round 1		Round 4		Round 3	
Wire Feed Rate	Cm / min	Gm / min	Cm / min	Gm / min	Cm / min	Gm / min
	11.0	10.00	25.0	22.0	25.0	22.0
Gun to substrate distance	15.00		15.00		08.00	

Table : 2 – Molybdenum Spray Parameters

The wear testing and the measurement of the coefficient of friction of the molybdenum coatings was done by the pin on disc wear test apparatus. The test was carried out as per ASTM G99. The test conditions were maintained as per Table 3

Load (Normal)	3 Kg. (30 N)
Time	17 Minutes
RPM (Disk)	1200 ±40
Wear Track (∅)	80 mm
Total Linear Distance	5.13 Kms.

Linear Velocity	5.02 M / Sec.

Table : 3 – Pin & Disk Wear Test Conditions

The formula used for calculating the coefficient of friction (μ) is :
$$\mu = \textbf{Fictional Force / Normal Load}$$

Apart from the above, trials were also conducted for the molybdenum coating using a modified air cap for the HIJET™-9600 Gun. In this aircap, the distance between the nozzle and the aircap in the gun was increased (i.e. the length of the air cap was increased). Air plasma spraying of the following powder blend was also carried out.

Mo 75% + 25% NiCrBSi, the NiCrBSi powder that was used had the following composition.

Ni	Cr	Fe	Si	B
83.4	9.0	3.0	3.0	1.6

(all compositions are in wt%)

The plasma spraying was carried using the SG-100 Gun of Miller Thermal (now Praxair) and the APS System was operated at a 18 kW power level.

4. Results & Discussion

The coatings were evaluated for microhardness, tensile bond strength & roughness. Results are given in table 4. The bond failure for all the coatings was by cohesive failure. The values reported are the average of the readings taken.

Round	#Tensile Bond Strength (MPa)	Micro Hardness 300 gm load (HV)	Surface Roughness as sprayed (µm)
Round 1	27.9 (2)	891.3 (3)	Ra 3.0 (7)
Round 2	19.7 (2)	982.1 (3)	Ra 3.7 (8)
Round 3	22.6 (2)	811.8 (3)	Ra 5.0 (8)
Molybdenum*	18.6	700.0	Ra 11.6

(Values in parenthesis are the number of tests done)

Table - 4 (Physical properties of Molybdenum Coating by HIJET™-9600)

The SEM photomicrograph of the molybdenum coating for all the three rounds are shown in Fig. 1 (a, b & c) & the X-ray diffraction curve for round 1 is shown in Fig. 2. The photomicrographs show that

oxides are present at the splat boundaries as well as in the form of small spheres. Molybdenum metal oxidizes catastrophically above 400°C Temp. in the spray plume of the HVCW torch are much higher than 400°C hence it is quite possible that mechanisms like shear o the liquid droplet due to intermingling of oxides and breakage of the oxide from the liquid metal droplet also occur but due to catastrophic oxidation of the liquid droplets the metal surface re-oxidizes and when it strikes the substrate an oxide layer is present on the surface.

The lower values of surface roughness of the coatings also indicate a more pronounced atomisation in the droplets of HVCW spray as compared to the oxy-acetylene flame sprayed molybdenum. This supports the hypothesis that atomisation in HVCW spraying is more pronouncedly affected by the oxidation of the droplet as compared to other factors.

The round 2 coating shows higher oxidation as compared to round while the oxidation in round 3 coatings is intermediate between round 1 and round 2. The round 3 coating shows some segregation of the oxide and metal phases this may be due to less torch to substrate distance which restricts oxidation of some of the droplets. The oxygen in the oxy-acetylene flame sprayed molybdenum is of the order 7 – 9 as cited in ref. ………… Some small size porosity also seen in the coating. The larger size pores, particularly in round 1 coating are pullouts during polishing of the coated samples.

The wear test of the coatings was carried out and the coefficient of friction of the coatings was determined. These results are shown in Fig. 3 & Table 5 (wear trend), Fig. 4 & Table 6 (friction force) & Table 7 (friction coefficient).

	Round 1	Round 2	Round 3	Mild Steel
1	3.00e-4	0.01	1.20e-3	0.04
2	3.50e-3	2.00e-4	3.00e-4	
3	1.00e-4	9.00e-4	5.00e-4	
4	0.01	4.00e-4	6.00e-4	

Table - 5 (HIJET™-9600 Molybdenum Coating Wear Data, (Wt. Loss in gms)

The lowest wear was observed for the round 3 coating. This corresponds well with the low values of coefficient of friction observed for the round 3

coatings. In fact for the round 3 coatings the average value of coefficient of friction is 0.35 and some values are as low as 0.25. If the initial values of friction load are discarded as running in period then the average value of μ will be much below the value of 0.35 and closer to value of 0.3. These values of μ are comparable to the values obtained by the powder HVOF system and lower than the values of APS sprayed molybdenum cited in ref. 7. The reason for such low value of μ may be the higher cohesive strength of the coating, as is seen in the table 4 coupled with the higher oxygen content of the coating, see table 5.

The WDS analysis of the coatings was carried out to find out the amount of different constituents in the coating, the results are presented in Fig. 5, Table 8. Table 4 shows that highest adhesive bond strength of coating is obtained for round 1, this is expected because the WDS analysis shows the lowest oxygen content for these coatings.

The coatings for all the three rounds shows higher values of micro hardness than the conventional flame sprayed molybdenum coating. The value of which is given for comparison. The distribution of oxides is very fine in the high velocity processes and hence it results in higher hardness of the high velocity wire sprayed molybdenum coatings as compared to the conventional wire flame spray molybdenum coating.

The low values of as sprayed surface roughness of the HVCW coatings are also as a result of high pressure in the nozzle which results in higher temperature in the nozzle which causes the wire and the wire droplet to heat up. The high temperature of the molten droplet causes a fall in the viscosity of the droplet, which results in greater atomization of the droplet. The high pressure & velocity of the gases is also responsible for finer atomization of droplet.

Apart from the greater atomization of the liquid droplet, another factor for the low values of roughness could be the greater amount of oxidation of the molybdenum particles, leading to more fragmentation of the liquid droplet which causes very fine atomization of the liquid droplet and thus resulting in lower values of roughness. The higher values of roughness observed for the coatings in round 3 may be due to the reason that sufficient time is not available for the fragmentation of the oxide particles at such low gun to substrate distance.

The microhardness of the coating follows the trend expected, i.e. at lower wire feed rate the hardness of coating is lower, except for round 3, where the microhardness value is less than that for round 1. This seems to indicate that there are factors other than fine atomization and oxidation of the coating which contribute to the microhardness of molybdenum coatings. This may be due to the stress relieving occurring in the coating due to the small spray distance, which causes the coating to take up heat from the flame and initiate stress relieving mechanisms. Another reason may be the higher particle velocity prevalent at such low distance which leads to the formation of coatings with low tensile stress.

The microstructures of the coating for all the three rounds show splat structure and some porosity. The coating structure seems to be otherwise homogeneous. The porosity is observed between two splats and some spherical porosity is also seen. The presence of spherical porosity supports the hypothesis of the oxide particle solidifying during flight and then rebounding from surface or getting removed subsequently during polishing due to its poor cohesive bond with the surrounding particles. The coating microstructures for the round 2 and round 3 show less intersplat porosity than round 1. This shows better coating integrity for round 2 and round 3 coatings. This may be due to the superheating of the atomized particle during spraying, which is more for the higher feed rate in the round 2 & round 3. In fact during spraying the brightness of the flame for round 2 and round 3 was more than for round 1.

As can be seen by the results of the WDS analysis in Table 8, oxygen content of the coating is highest for the coatings prepared in round 2. The round 2 coating parameters had higher feed rate of 25 cm / min. as compared to the round 1, where the feed rate was kept 11 cm / min. This shows that higher wire feed rate increases the amount of oxidation of the coating. As the wire feed rate is increased the wire tip advances more into the flame and a longer length of the wire tip gets heated up to red hot condition before melting and atomizing. The diffusion of oxygen through the red-hot wire tip is quite rapid. The oxidizing condition of the flame causes rapid oxidation of the wire tip.

The round 3 coating was carried out at high wire feed rate but less substrate to gun distance. The coating here shows oxygen content much above the value of oxygen content for round 1 but slightly

less the value for round 2. These results indicate that for the HVCW spraying the spray gun to substrate distance parameter does not influence the oxidation of the coating species as much as the wire feed rate parameter. Increasing the wire feed rate increases the oxidation of the wire. While spraying it was observed that increasing wire feed rate increases the red hot length of wire. The oxidation of the coating species occurs mainly in the red hot tip and the liquid droplet before it is pulled away from the tip and accelerated towards the substrate.

Oxidation of the coating species during flight i.e. after leaving the wire tip and before deposition on the substrate is negligible, this is apparent when the oxygen content of the coating for round 2 and round 3 are compared, wherein decreasing the spray distance from 15 Cms to 8 Cms reduced the oxygen content of the coating only negligibly (wire feed rate was 25 cm / min. for both the rounds) Fig. 2 shows the XRD curve taken for round 1 of molybdenum coating. This shows various phases that can form in the coating.

Round 1

Element	Line	Wt %	Cnts/s	Atomic%
O	Ka	15.12	16.09	51.65
Mo	La	84.88	440.12	48.35
	Total	100.00		

Round 2

Element	Line	Wt %	Cnts/s	Atomic%
O	Ka	18.17	18.67	57.11
Mo	La	81.83	395.31	42.89
	Total	100.00		

Round 3

Element	Line	Wt %	Cnts/s	Atomic%
O	Ka	18.04	14.97	56.90
Mo	La	81.96	320.14	43.10
	Total	100.00		

Table 8 (WDS Results)

Wear testing results are shown in the Fig. 3 and Table 3, this shows that coating in round 3 has got the lowest wear rate of all the three rounds. This seems to indicate that higher particle velocities prevalent at the lower distances leads to a lower tensile stressed coating and consequently higher cohesive and adhesive bonding.

The improved wear resistance of the coating sprayed at lower spray distance is result of the high cohesive bonding of the coating. Measurement of

particle velocity at different distances from the gun air cap will throw some light on this phenomenon.

The results of tests for measuring the coefficient of friction of the coating also shows that the coating for round 3 has the lowest coefficient of friction.

A modified air cap was prepared for the HIJET Gun wherein the length of the air cap was increased. The modified air cap was 38 mm long while the conventional air cap for the HIJET is 33 mm long. The wire feed rate of the gun with modified air cap increased to 75 cm / min. from the standard wire feed rate of 25 cm / min.. This large increase in the wire consumption results from the increase in the length of the combustion chamber where the heating & melting of the wire tip is taking place. This is consistent with the results cited in ref. ……….. Although the increase in the size of combustion chamber did cause some heating up of the air cap but it was not high enough to warrant water cooling of the air cap.

The pin on disc wear test results obtained for the air plasma sprayed Mo-NiCrBSi coatings are shown in Fig. 6 and the results of coefficient of friction measurement are shown in Fig. 7. The following conditions were maintained while conducting the test,

Test Standard	ASTMG99
Sliding Velocity	6.28 m / sec.
Test Time	15 minutes
Total Linear Distance Traveled	5.65 Km
Applied Stress	0.876 N / mm^2
Disc Material	EN31,in hardened condition

Four samples were prepared for the purpose of wear and friction test. The results of all the four samples show that the coefficient of friction for the APS sprayed coatings is consistently higher than the coefficient of friction of the HIJET sprayed molybdenum coatings as seen in the table No. 5. The weight loss of the plasma coated specimens is higher than the HIJET molybdenum coated specimens, this can be seen from the results shown in table 3 and figure 6.

6.   Conclusion

This paper studies the influence of parameters on the molybdenum coating produced by the HVCW spray system. The HVCW molybdenum coatings were compared with the plasma sprayed molybdenum-NiCrBSi coatings for wear performance.

Conventionally the wire flame sprayed molybdenum coating is used for piston ring coatings application. The plasma sprayed Mo-NiCrBSi coatings are applied where higher wear resistance, low coefficient of friction and tougher coatings are required. The HVCW molybdenum coatings have lower wear rate and coefficient of friction than the plasma sprayed Mo-NiCrBSi coatings. HVCW system coatings give harder and more wear resistant coatings than the conventional flame sprayed coatings.

The oxygen content of the coating plays a very important role in determining the properties of the HVCW coatings, however, the test results also show that the effect of parameters such as gun to substrate distance also affect the coating properties despite having nearly the same oxygen content. This may be due to the stress relieving in the coating occurring at the small gun to substrate distance and also due to the higher particle velocities expected.

Further studies to study these parameters are required. The wire HVOF spraying differs fundamentally from the powder HVOF spraying with respect to the melting and atomization behaviour of the sprayed particles. The HVCW spray system is capable of producing coating microstructures which are non-conventional with properties that are different from the powder HVOF and wire flame spray system.

Applications of the HVCW system will have to be developed, considering, the coating microstructure and properties attained, for e.g. in the case of molybdenum coating the low coefficient of friction and the high hardness make this coating a good candidate for antiscuff coating on piston rings.

7.   Acknowledgements

8.   Reference

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