Comparative Study of the Wear Behavior of Thermal Spray HVOF Coating on 304 SS

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Abstract - Coatings have been developed to protect the surface from the physical and chemical reactions with the environment. Thermal spray coatings are one of many methods of coating for modification of part's surface properties. The technology is based on the principle of melting and acceleration of fine particles and their rapid solidification after impact on the substrate. Amongst all the techniques of thermal spray coatings, High Velocity Oxy Fuel process is widely used in various applications. In the present work, the coatings of tungsten carbide and chromium carbide sprayed by HVOF are studied. Both the coatings have same binder with equal percentage. The comparative study of these coating materials sprayed by same method, has not observed in the available literature. The mechanical and structural characterizations were carried out with the help of Scanning Electron Microscope, Image Analyzer, X-ray Diffractometer, Energy Dispersive Spectroscopy and Pin-on disc wear testing machine. The results show that the wear rate of tungsten carbide coating is much lower than that of chromium carbide coating at different loads and room temperature.

Keywords: Thermal spray coating, pin-on-disc, SEM, EDS

I. INTRODUCTION

Corrosion and wear problems are still of great relevance in a wide range of industrial applications and products as they result in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Various technologies can be used to deposit the appropriate surface protection that can resist under specific conditions. There are many thermal spray processes currently available for depositing coatings. Out of these, the HVOF thermal spray process is widely used to produce wear-resistant coatings. . It is the process in which finely divided metallic or nonmetallic materials are deposited in a molten or semi molten condition to form a coating. The coating material may be in the form of powder, ceramic-rod, wire, or molten materials. It is advantageous due to its ability to create a cermet-based coating having a lower level of porosity than other traditionally used thermal spray processes such as arc spraying or conventional plasma spraying [1].

The main materials used in HVOF are tungsten carbide or chromium carbide particles in a metallic alloy matrix consisting of various combinations of Co, Ni or Cr. The two most common carbide coatings are WC-Co and Cr_3C_2-NiCr [1].

Coatings from chromium and tungsten carbides with ductile metal binder, commonly cobalt or nickel are very often used in the industry conditions for protection against the wear and corrosion. The main purpose of application of cermet coatings is to increase coated part's wear and oxidation resistance. Chromium coatings have high wear resistance, corrosion and oxidation resistance which promote many surface engineering applications for components used in critical mechanical components such as valves, landing gears, pistons, rods and hydraulic machine parts. WC–Co cermet has its own applications in machinery industries as wear resistance coating, due to better hardness and wear resistance than CrC–NiCr coatings. Thermal spray technology also works as the alternative to hard chromium plating. One more requirement for tungsten carbide coatings is to have better wear and fatigue properties than hard chromium when applied in aircraft manufacturing, power plants, oil drilling, turning, cutting and milling, where abrasion, erosion and other forms of wear exist.

The present study was undertaken to investigate and compare the sliding wear performance of tungsten carbide and chromium carbide coating compositions applied during HVOF process.

II. EXPERIMENTAL PROCEDURE

Experiments are carried out to examine metallurgical, topological, and wear properties of HVOF coating of Tungsten Carbide and Chromium Carbide.

1.1 Materials

Two different commercially available tungsten carbide and chromium carbide powder composition have been selected. Both powders contain 17% cobalt as a binder material in it. These powders were manufactured using an agglomerating and sintering approach. The substrate to be coated was chosen as 304 ASS, as it is widely used material because of its excellent corrosion and wear resistance in various aggressive environments. But it is having poor tribological properties, so this creates barriers to its broad applications.

Table No: 1 Chemical composition of the WC coating and Cr_3C_2 coating

WC coating		**Cr_3C_2 coating**	
Element	% Wt	Element	%Wt
Tungsten	Balanced	Chromium	74
Cobalt	17	Cobalt	17
Carbide	5-6	Carbide	4-5
Fe	0.3	Fe	0.216
Ferric oxide	0.2	Silicon	0.252
		Aluminum	0.2
		Sulphur	0.01

The mechanical and structural characterization carried out for the observation of the various properties of the specimens. The mechanical characterization includes the microhardness test and surface roughness test. Microhardness testing was carried out using Vicker's microhardness tester following ASTM E384 and surface roughness test was carried out with roughness tester following ASTM B46.1.

The structural characterization of coating was done with the help of Image analyzer and SEM. Thickness of the coating is measured with the help of image analyzer. The samples were prepared by polishing it and then cleaning it by immersing in Nital solution for 30 sec (ASTM E2 109). Energy Dispersive Spectroscopy (EDS) was accommodated for the elemental analysis.

II.I Pin on disc wear test:

The three types of pins used in the pin-on-disc are the WC-17%Co coated sample, Cr_3C_2-17%Co coated sample and a 304 ASS sample. The samples were of cylindrical shape having diameter upto 1-1.2 mm and length from 35-45 mm (ASTM G99). The disc used in the test was of Alumina (Al_2O_3) having hardness in the range of 1800-2000 HV. The wear test was conducted according to the ASTM standard G99. The different loads considered for test were of 4 kg and 6 kg, and the different temperatures were room temperature and 100^0C. The RPM set was 800 and the radius of wear track was 70mm. The cycle time for one reading was of 30 min. The mass loss after every 30 min was recorded.

III. RESULT AND DISCUSSION

The average porosity measured in both the coatings is 0.195 for WC and 0.24 for Cr_3C_2 using the software of image analyzer.

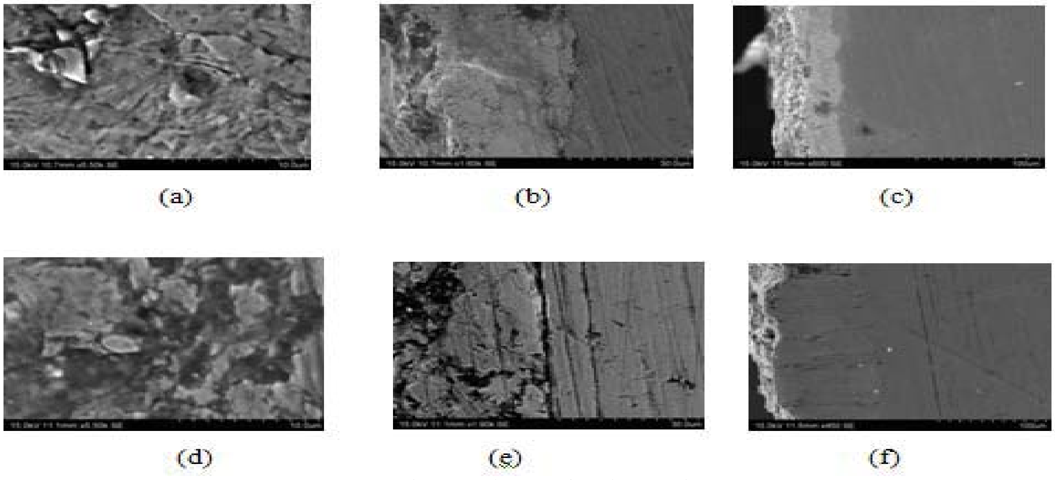


Fig 1 SEM images of coating samples
(a), (b), (c) WC samples; (d), (e), (f) Cr_3C_2 samples

The microhardness of the coatings is measured with the help of Vickers microhardness tester. The readings are as shown below in the fig 2,

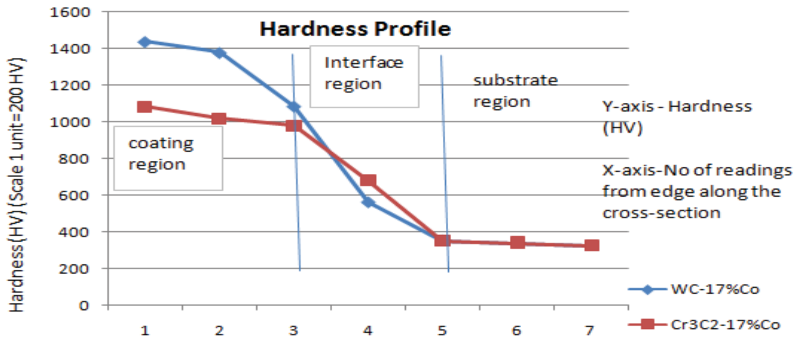


Fig 2 Comparison of hardness of WC and Cr3C2 coatings

Surface roughness of both the coatings was measured using surface roughness tester. The average roughness values for WC coating were found as 0.76Ra and that of for Cr_3C_2 coating is as 1.47Ra.

III.I Pin on disc wear testing

The Archad’s equations were used for further calculations.

III.II Wear test results, graphical representation

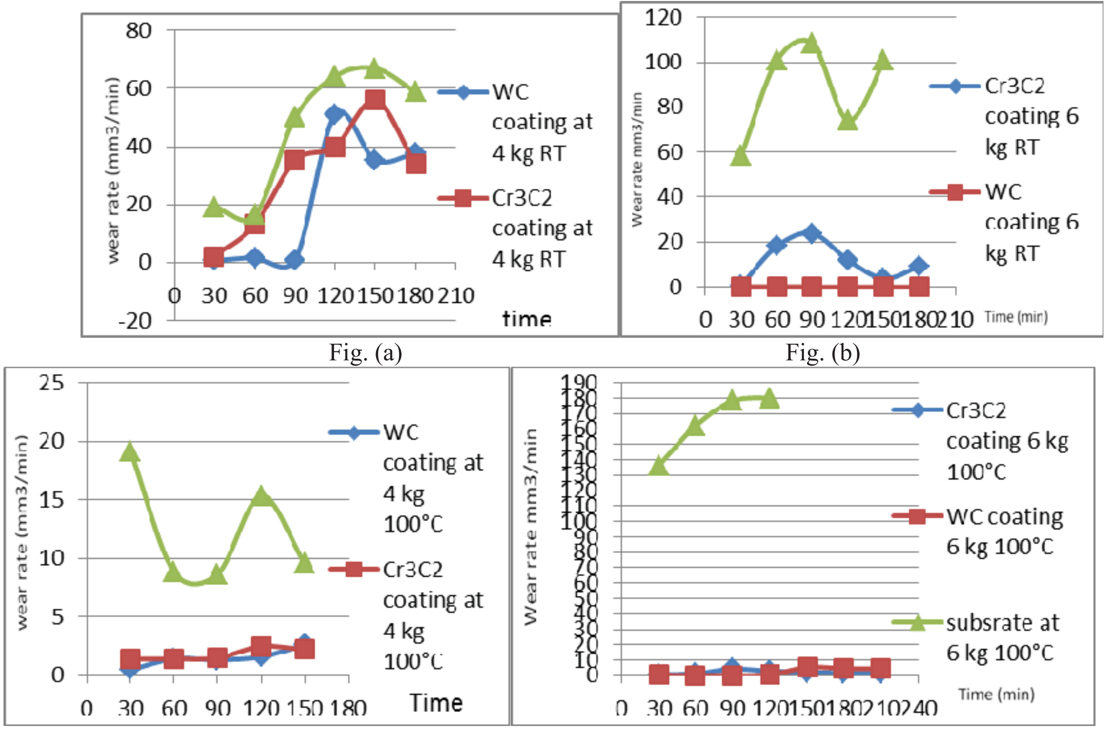


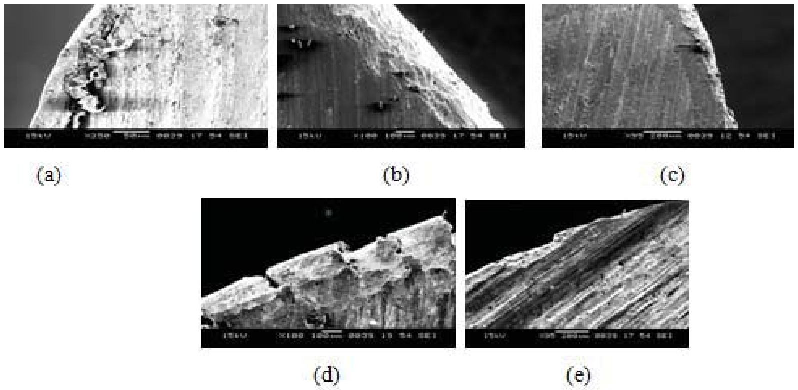
Fig. (a) Fig. (b)

Fig. (c) Fig. (d)

Fig 3 Graphical representations of wear test results
for 4 kg load and room temperature, (b) for 6 kg load and room temperature,
(c) for 4kg load and 1000C, (d) for 6 kg load and 1000C

III.III Scanning Electron microscope

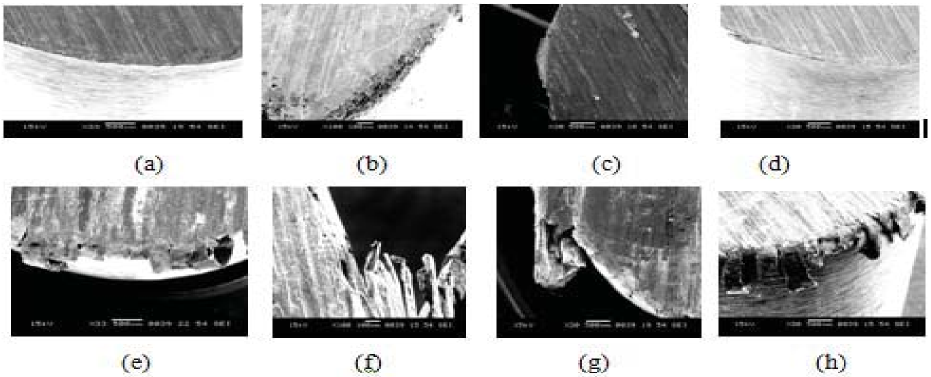
The images got from the SEM support the wear test results. The topography seen in the images clarify the behavior of both the coating materials at different stated conditions.



(a) (b) (c)

(d) (e)

Fig 4 SEM images for worn surface at 4 kg and room temperature
(a), (b), (c) WC coating samples; (d), (e) Cr_3C_2 coatng samples

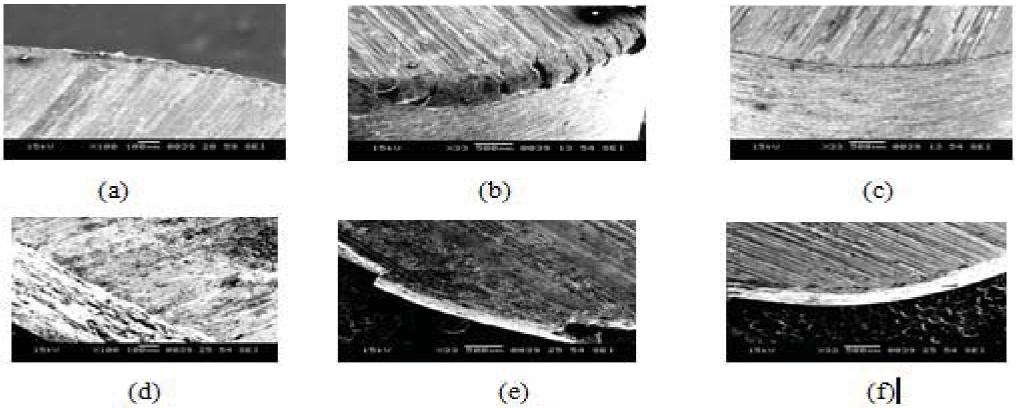


(a) (b) (c) (d)

(e) (f) (g) (h)

Fig 5 SEM images for worn surface at 6 kg and room temperature
(a), (b), (c), (d) WC coating samples; (e), (f), (g), (h) Cr3C2 coatng samples

As on the basis of the wear test results, WC gave the best results for this condition. Whereas Cr3C2 coating gave the worst performance and degraded heavily.



(a) (b) (c)

(d) (e) (f)

Fig 6 SEM images for worn surface at 4 kg and 100°C
(a), (b), (c) WC coating samples; (d), (e), (f) Cr3C2 coatng samples

As observed from the wear test results, it is clear that at elevated temperature, the Cr_3C_2 coating has comparatively less wear rate and sustained for a long time than WC coatings. Both the coatings have degraded a lot after a long cycle of wear test.

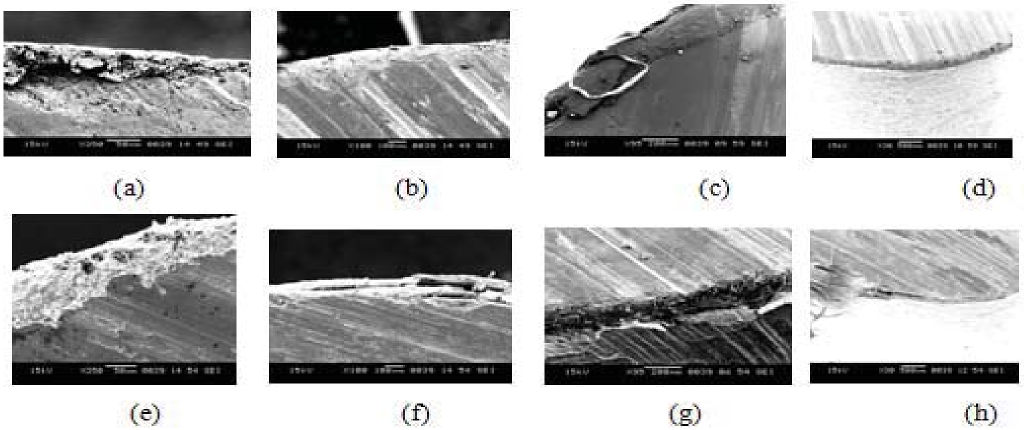

(a) (b) (c) (d)
(e) (f) (g) (h)

Fig 7 SEM images for worn surface at 6 kg and 100°C
(a), (b), (c), (d) WC coating samples; (e), (f), (g), (h) Cr3C2 coatng samples

As from the wear test results, it is observed that the wear rate is somewhat similar in the beginning of the wear test cycle in this condition. Cr_3C_2 coating has slightly more wear rate afterwards.

III.IV Debris investigation

As in all of the above conditions, the lowest wear was seen for WC coating for the condition of 6 kg load and room temperature. The highest wear was for $C_{r3}C_2$ coating for simillar condition. So only these two debris have been considered for further studies. The conclusions have been done on the basis of SEM and EDS.

III.IV.I SEM of debris


(a) (b)

Fig 8 SEM images of debri of coating samples (a) WC sample, (b) Cr3C2 sample

As seen from the above images, the debris show the flaky structure. The average debri size in WC coating is smaller than that of in Cr_3C_2. This directly affects the wear rate of both the coatings.

III.IV.II EDS

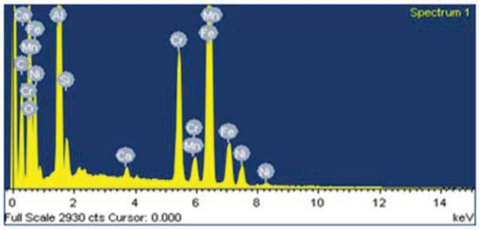


Fig 9 EDS of WC coating sample debris

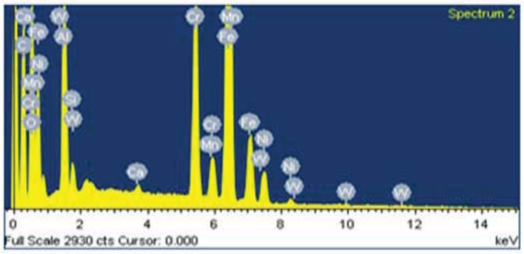


Fig 10 EDS of Cr_3C_2 sample debris

Table 1 Elements present in WC coating debris

Elements	%weight	%Atomic weight
O K	14.65	33.88
Al K	11.65	15.98
Si K	1.07	1.41
Ca K	0.27	0.25
Cr K	14.02	9.97
Mn K	1.55	1.04

Table 2 Elements present in Cr_3C_2 debris

Elements	%weight	%Atomic weight
C K	23.88	23.88
O K	20.10	20.10
Al K	12.96	12.96
Si K	1.09	1.09
Ca K	0.39	0.39
Cr K	8.35	8.35

Fe K	51.53	34.13
Ni K	5.30	3.34
W M	0.04	0.01
Total	100.00	

Mn K	0.83	0.83
Fe K	29.61	29.61
Ni K	2.80	2.80
Total	100.00	100.00

As the coating thickness was very small, the EDS analysis show more percentage of the substrate material. Some oxides are also present on the worn surfaces. Small amount of tungsten and chromium is also seen in the EDS in the fig 9 and 10 respectively.

III.V Characterization of coatings

In the SEM images WC coating shows a denser and more uniform structure than the Cr_3C_2 coating [fig 1 (a) and (d)]. The Cr_3C_2 coating shows more un-melted carbide particles than in the WC coating. The micro cracks seen in the coatings of Cr_3C_2-17%Co are more than that of in WC-17%Co coating. These results can be seen from the images in the fig 1 a, b, c, d, e, f. The various reasons for these observations are discussed below.

III.V.I Microcrack formation-

The cracks in the coatings are formed due to the relaxation of residual tensile stresses formed in coating during its deposition. Residual stresses in the thermal spray coatings could be of a tensile or compressive nature. Compressive residual stresses in the coatings have a beneficial effect on the adhesion and fatigue behavior of the system. Tensile residual stresses are the result of particle contraction during cooling and can cause cracking and promote fatigue failures if their magnitude exceeds the tensile strength of the coating [20]. One more reason is observed here, that is the difference in the thermal expansion coefficients between the coating (α_c) and substrate (α_s). The difference can cause uneven expansion and contraction. This leads to cracking.

III.V.II Porosity-

The powder particles may have less particle melting and dissolution of carbides due to very high velocity of particles. The particles are not of exactly same size. The small particles get melted completely, but bigger particles may not. The wide size range will result in some particles which are greatly overheated, while others will be insufficiently melted. This is a possible reason for increased porosity and reduced hardness. The porosity of the coating is also increase with increased in the carbide size. They also have slightly varying temperature from its centre to boundary. The cooling rate in the air before impact on substrate is lesser than that of a particle after impacting on the substrate. The conduction of heat helps in rapid cooling after impact. The structure of HVOF coating is splat like structure. Splats getting deposited also increase the temperature unevenly. These phenomenons cause the reduced level of particle melting and allow it to decompose.

III.V.III Hardness of the coating samples-

The hardness of the WC coating is greater than that of Cr_3C_2 coating. At the time of deposition, particles come in contact with oxygen and decarburization occurs. This increases the W_2C phase at the surface, which is obviously having greater hardness due to more W particle. For oxidation occurring at the gas and powder particle interface, the oxygen can react directly with carbide particles which are at the free surface of heated powders. The result is that W_2C and W are formed directly from WC particles. Many researcher in their papers shows the phases present in the coating surfaces with the help of XRD analysis. Qiaoqin Yang et al [6] in his research paper stated that WC may decompose to hemicarbide (W_2C), even to metallic tungsten and the decomposition products may dissolve into metallic cobalt to form an amorphous Co–W–C phase or complex carbides such as Co_3W_3C, Co_2W_4C, Co_6W_6C and $Co_3W_9C_4$. These present phases are very much responsible for the behavior of the coating. Commonly seen phases in WC and Cr_3C_2 coatings are W, W_2C, Co_3W_3C and Cr_3C_2, Cr_2O_3, Cr_3C_2Co respectively.

The oxidation in the case of WC coating reduces the superficial hardness and as temperature increases, this tendency increases. In the case of Cr_3C_2 coating, the oxidation increases as temperature increases and it causes the protective layer on the surface, which does not affect the hardness of the coating.

The phases present are responsible for the hardness of the coating. After a limit, W_2C phase becomes brittle and lowers the hardness. The excess amount of Cr_2O_3 phase also reduces hardness after decomposition. In the present study, the maximum hardness recorded on WC coating is 1436HV and that on Cr_3C_2 coating is 1083HV. As the pointer of the Vicker's micro hardness tester's indenter shifted towards the center, the hardness values showed slightly lesser values. These readings clearly show the difference in the hardness values of the coating region, interface region and the substrate region.

The value of surface roughness of both the coatings shows the difference. The roughness of the surface leads to increase in the wear rate against the counterpart. The unevenness of the surface leads to more material loss due to the micro edges coming out of the surface layer.

III.VI Wear behavior of coatings

The wear test cycles were decided to take for a long duration for observing the behavior of the coating for a heavy period of time. During the cycle, the carbide particles are being exposed until they become weak to cause its removal by fracture or complete detachment. According to the graphical representation of the wear rate readings, at 6kg load and room temperature, the WC coating gave the best results. After a long duration, this coating can sustain. For the same condition, Cr_3C_2 coating shows the worst result. It got a heavy damage to the boundary.

The preliminary reasons for this behavior of the coatings are the porosity present and the surface roughness values of the coating surface. The porosity present in the tungsten carbide coatings is lower than that of the chromium carbide coatings. The surface roughness is greater in chromium carbide coatings than that of tungsten carbide. The pours act as the edges for further cutting (wear) of the counterparts. The wear debris also remain in the pours and because of its flaky structure, it increases further wear.

As many researchers commented on the better performance of WC coatings on stainless steel, this study also got the same results. The Cr_3C_2 coatings gave the better performance than SS, but degraded heavily.

At higher temperature, as it is clear from results that the SS get worn out heavily, but both the coatings gave better performance. Although in the starting cycle the wear of WC was less but latter it has shown greater wear than Cr_3C_2 coating at 6 kg and 100^0C. Cr_3C_2 coating has sustained for a long time at higher temperature.

III.VII Wear mechanism

When pin and disc brought into contact with each other, at starting the soft ductile cobalt matrix undergoes deformation. Then after the microcracking and pull out of WC and Cr_3C_2 occurs when the support of matrix are no longer present. It leads to the formation of the wear debris of the WC and Cr_3C_2. Obviously percentage of cobalt would be more in the wear debris. Some of the wear debris is lost from the system, but some is entrapped between the contact surfaces. The entrapped debris particles produce further damage on both surfaces as a third-body abrasive and the debris itself undergoes fragmentation during the sliding, resulting in the formation of very fine debris particles. Since finer particles produce less damage on both surfaces, finer carbide size coatings and their counterparts would show a lower wear rate.

The initial wear of the WC is lesser due to the formation of the soft ductile film of cobalt. This phenomenon can be seen in both the coatings cases. Qiaoqin Yang [6] has stated that the hard phases (WC, W_2C) yield only a small displacement from the normal and tangential stress applied by the abrasive particles. Thus, deformation mainly occurs in the soft and ductile matrix. Then the soft and ductile matrix is forced to protrude outside the surface of the material by the stress of compression of the abrasive particles due to the poor deformability of the hard phases.

When pull out of a single particle is there, less damage will be there. Also the debri consisting finer carbide particles are less effective as third body abrasives. The sliding wear rate decreases with decreasing carbide size of the coatings.

Hathaipat Koiprasert [27] stated that, a reduction in the weight of WC coating at an early stage of testing due to loss of WC particles. Detachment of hard particles is possible due to the oxidation of the coating, forming a brittle product $CoWO_4$. This causes a decrease in ductility around WC particle and hence the particle can detached easily. The W_2C is formed in large number and larger size of unstable pores, which promotes oxygen absorption. This leads to the formation of oxidation products, such as $CoWO_4$ and WO_3, due to wettability and surface energy change, the resultant coating break down.

After some time during the testing of Cr_3C_2 coating, the oxidation starts. Further testing could cause the thickening oxide layer to crack and produce hard oxide debris which will accelerate the wear process.

III.VIII Worn surface and debris investigation

As discussed, worn surface and debris of the best wear resistance condition and that of worst wear resistance condition has been done with the help of SEM, EDS. The average size of the debris of the WC coating is less than that of the Cr_3C_2 coating (fig 9(a) and (b)). The structure of the debris are flaky, it causes the further wear rapidly as three body abrasion wear. The EDS of the WC coating debris shows the presence of W particles in lesser amount, which supports the wear test results. Rests of the elements present are of the substrate (fig 10). The EDS analysis of the Cr_3C_2 coating debris shows the presence of C particles in higher amount; also Cr particles are present in considerable amount, which may be of coating and substrate both (fig: 11). The lower hardness value and higher surface roughness might be the primary reason for the heavy wear in this case. The microstructure, adhesion strength and the residual stresses produced during the coating are also the reasons for the higher wear rate in this case. The debris is embedded in the surface of both the counterparts and causes further rapid wear. The wear rate increases further rapidly.

III.IX Applications for WC and Cr3C2 coatings

On the basis of the result got from the experimentation, these coating can be applied for various applications. Some of the related applications are discussed below in brief,

The nozzle and the nozzle collar used in the turbines face problem due to fretting wear and worn out quickly due to high vibrations and the increased temperature. The WC coating can give the solution for this application. The hard coating provides the protection against the fretting wear and minimizes the degradation of the part. The Cr_3C_2 coating can also help in the high temperature environment.

The compressor shafts faces high wear and so get worn out soon. The WC coating can give the protection due to its hard surface on the contact surface of the shaft.

The rollers used in paper industry face corrosion and wear due to the hydrous working conditions. The Cr_3C_2 coating can provide the protection against both of these problems.

The pins and keys used in various mechanical applications can sustain for a longer period with the help of the coating applied on it.

IV. CONCLUSIONS

From the experiments present in this study, following conclusions can be drawn regarding wear resistance of the tungsten carbide and chromium carbide,

1. In tungsten carbide coatings deposited by HVOF, the morphology of the coating shows lower porosity and surface roughness value than that of chromium carbide coatings. Whereas, the surface hardness of tungsten carbide is greater than that of chromium carbide.
2. EDS analysis of the coatings revealed that the WC coatings consist of significant quantities of W_2C and eta particles. Cr_3C_2 coatings consist of oxides of chromium.
3. Comparison of laboratory wear test according to ASTMG99, WC shows better wear resistance than Cr_3C_2 coatings at room temperature. Whereas, Cr_3C_2 coatings sustain for longer period at higher temperature than WC coatings.

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