Assessment of thermal spray coatings for wear and abrasion resistance applications

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Abstract of the Thesis

Assessment of thermal spray coatings for wear and abrasion resistance applications

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Thermal spray cermet and metallic coatings are extensively used for wear, abrasion and corrosion control in a variety of industries. The first part of the thesis focuses mainly on testing of sand erosion resistance of thermal spray coatings on carbon composites used in the manufacture of helicopter rotor blades. The test set-up employed is a sand blasting machine and is an effort to duplicate the in-flight conditions especially those encountered in hot arid conditions. The technique adopted follows the Department of Defence test method standard. Carbon Composites have excellent stiffness, strength and low weight/density. The strength to weight ratio is high. Hence, these are used in aerospace applications to a large extent. However, the biggest problem encountered with carbon composites is its low abrasion resistance as its surface is very weak. Hence, thermal spray coatings are used to improve the surface properties of CFRP. Zinc bond coats and WC-Co coatings were tested. However, high amount of thermal stresses were developed between the substrate and the coating due to large differences in the CTE's of the both, leading to high mass losses within two minutes and just 130 grams of sand sprayed on to the coatings with the sand blasting machine built; and hence the coatings with CC as a substrate could not qualify for the application.

The second part of the thesis focuses on the assessment of different thermal spray coatings used for manufacture of mechanical seals in pumps and analyze the best coating material for the wear resistance application through detail quantification of material loss by block-on-ring test set-up. A machine based on Block-on-ring test set-up following ASTM G77 (Measurement of Adhesive wear resistance of thermal spray coatings) standards was built to duplicate the pump conditions. Thermally sprayed coated materials were tested in different conditions (Load, time, abrasive). WC-Co had the highest wear resistance (lower volume losses) and proved to be the best coating amongst all the other ones followed by Cr_2O_3 and Al_2O_3 in deionized water. In the presence of abrasive alumina slurry WC-Co offered the highest abrasive resistance with the lowest volume losses followed by Al_2O_3 and Cr_2O_3. In both the testing conditions B_4C coating showed lower wear/abrasion resistance giving the highest volume losses.

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List of Abbreviations

CFRP- Carbon Fiber Reinforced Composite

CC- Carbon Composites

PMC- Polymer Matrix Composites

FGM- Functionally Graded Materials

DC- Direct current

CVD- Chemical Vapor Deposition

PVD- Physical Vapor Deposition

DOD- Department of Defense

NASA- National Aeronautical Space Administration

ASTM- American Society for Testing and Materials

CTE- Coefficient of Thermal Expansion

WC-Co- Tungsten carbide-cobalt

B_4C- Boron Carbide

Cr_2O_3- Chromium Oxide

Al_2O_3- Aluminum oxide

APS- Atmospheric Plasma Spraying

HVOF- High Velocity Oxy-Fuel

VPS- Vacuum Plasma Spraying

D gun- Detonation gun

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Chapter 1

1.1 Introduction

Protective ceramic coatings are used for wear and abrasion resistance and due to their superior thermal and corrosion properties, they are used in high temperature applications as well. However, the production methods for such materials are very unconventional and usually are not straightforward because of many difficulties encountered due to high melting points of the materials, poor thermal and electrical conductivity and high brittleness. Hence, ceramic coatings cannot be deposited as easily as metallic coatings. The techniques that are generally used for depositing metallic coatings are combustion spraying or electric arc process and vapor deposition techniques like chemical and physical vapor deposition. These cannot be successfully employed for ceramic coatings.

The arrival of plasma gun has overcome the difficulties that are encountered in conventional techniques. The plasma gun has much higher temperature capability and uses the raw material in powder form. Any material that does not decompose on heating can be sprayed by the plasma arc process. The advent of plasma gun has expanded the capability of coating wide range of materials and has contributed to a rapid advance in protective ceramic coatings technology. A schematic diagram of plasma spraying process is shown in figure 1 below.

Most of the coatings deposited does not exhibit properties that are similar at the time when they are in powder form. Plasma sprayed coatings behave in similar fashion. There are three types of thermally sprayed coatings:

1) Flame spraying: These are commonly metallic coatings deposited from the wire form using a combustion flame of oxyacetylene.
2) Thermo spraying: These fall into category of metallic or ceramic coatings that are generally sprayed from a powder form using a combustion flame.
3) Plasma spraying: Ceramics and metals sprayed in a plasma arc.

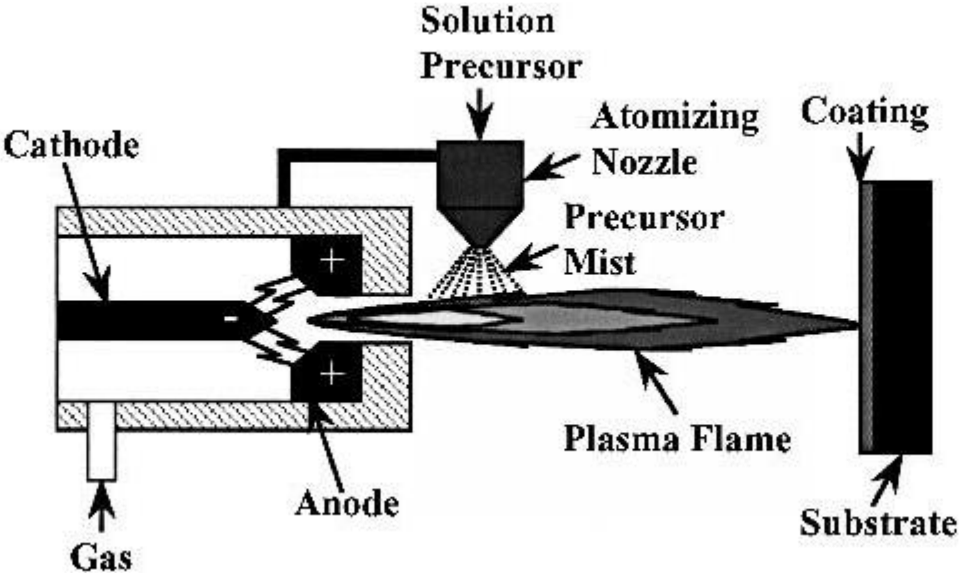

Figure-1 Schematic diagram of Plasma Spraying process (1)

Thermally sprayed coatings generally possess higher strength than that of bulk forms because they these coatings have interlocking microstructure. The extent of directional strength properties, anisotropic microstructure are some of its characteristics that distinguish them from bulk forms.

The adhesion of the coatings with the substrate has to be given prime importance because otherwise the strength of the coating would be compromised. This is of prime consideration in the application that demand large differences in temperature of substrate and coatings, i.e. the conditions which are prone to huge thermal gradient and thermal shock. However, there is very little information available on thermally sprayed coatings for comparison. Properties such as thermal expansion, thermal conductivity etc. related to high temperature ceramic coatings require special attention as these control up to a great extent the quality of coating. This is in turn controlled by the microstructure of the coating. The microstructure of the coating depends upon the type of spraying process used and the parameters employed to operate it. Thermal spraying of coatings introduces residual stresses within the coating especially at the coating substrate interface due to rapid cooling and differences in the expansivity of the phases. These give rise to micro cracks and sometimes peels off the coating pretty easily. Difference in thermal expansion of coating material with respect to the substrate creates lot of stresses and affects life of coatings considerably. This is motivation of many researchers to develop functionally graded materials (FGM) that compromise the large difference in thermal expansion coefficient of substrate and coating and also increase the compatibility of the coating with the substrate.

A comparison between the coatings and its counterparts in the bulk state would be an interesting feature as it would determine the cause for the difference in the coefficient of thermal expansion between the coating and the same material in the bulk state. This might be of great assistance in designing different coating materials for highly specific and customized applications.

1.2 Thermal Spraying process:

This is the process where a material in powder, rod or wire form is continuously fed into a flame, or plasma depending upon the method used for spraying and the molten particles are propelled toward the substrate with the aid of high velocity gas. The different types of thermal spraying techniques are described elsewhere.(2)

The process that uses combustion of fuel gases to bring about the heating effect to melt the material produces temperature around 3000˚C.(3) Hence, this method is not used for the materials that have high melting points. Almost all ceramics cannot be melted at this temperature, hence it is not used for ceramics but is used for coating low melting points materials. The electric arc process produces higher temperature than the combustion of fuel gases but is limited to conductive metals and alloy materials.(3) The schematic diagram of thermal spray process is shown below in figure 2.

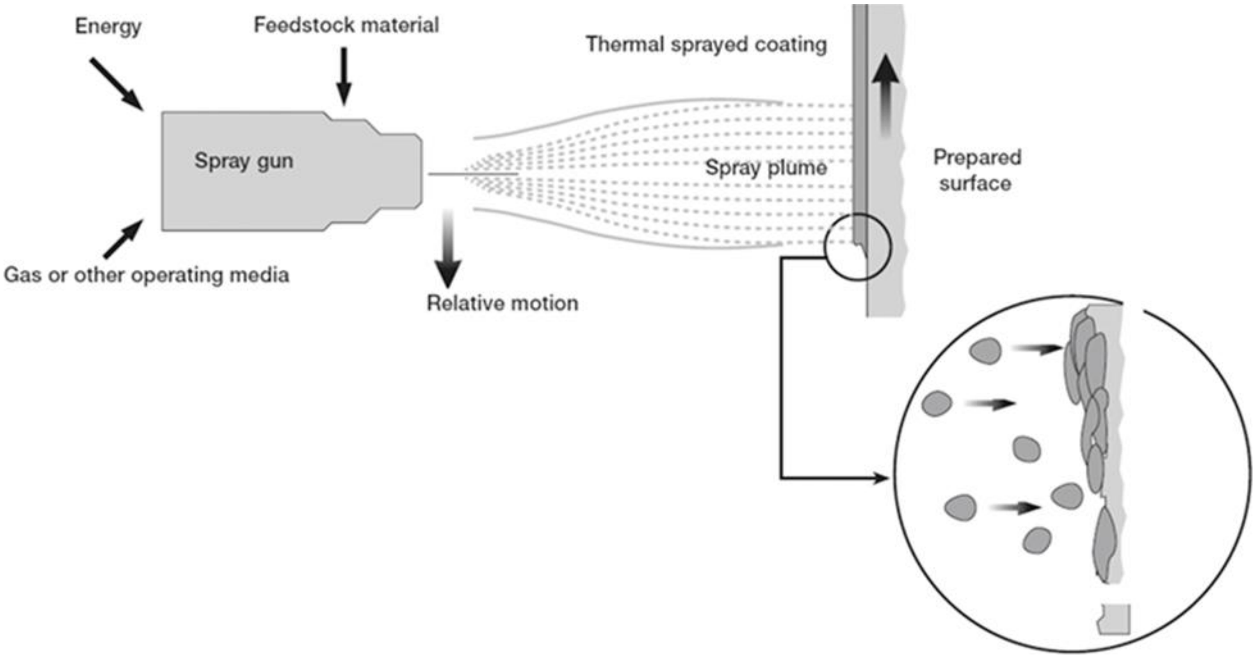

Figure-2 Schematic of thermal spray process(4)

Plasma arc spraying, produces the highest temperature of all the processes. This is done without damaging the specimen. Plasma is formed in the gas stabilized medium where plasma forms from a gas typically argon or helium or their mixtures. A non-transferred DC electric arc between a thoriated tungsten acting as cathode and an internally water cooled copper nozzle which acts as anode.(5) The plasma produces temperatures in the range of 7000-10000˚C. The coating material in powder form (generally) is fed into plasma with the help of an injector and plasma gas (argon, helium) carries the particles while plasma melts it. This is shown in figure 1. The molten particles as they are incident on the substrate start to solidify rapidly due to large temperature differences between the molten particles and the substrate. There is a considerable amount of mechanical interlocking between the substrate and the coating material.

As the temperatures produced by plasma are very high, there might be a problem of oxidation of the coating material (molten particles), hence the process is carried out in controlled atmosphere (low pressure or vacuum) which decrease the oxidation and also produce thick and denser coatings. Below shown is the graph of temperatures achieved by different thermal spray processes versus their particle velocities. The graph shows that plasma spraying process (APS) known to be Atmospheric Plasma Spraying achieves the highest temperature of all processes.

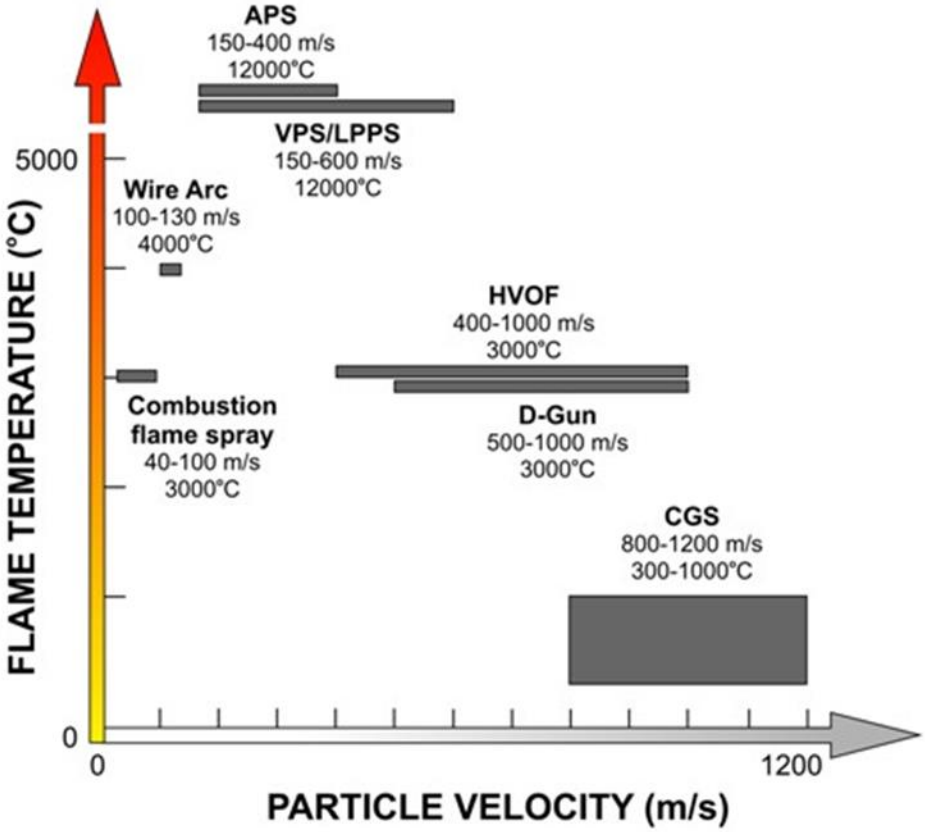

Figure-3 Temperature versus particle velocity for different thermal spray processes(6)

1.3 Plasma spraying parameters:

The parameters that one must maintain while thermal spraying are very critical as these control the nature of coating deposited on the substrate. The deposition efficiency that is determined by the fraction of powder injected into the plasma that is properly melted and deposited on the surface. Below is the list of thermal spray parameters:

a) Spraying distance

b) Powder (feed material) particle size

c) Gas flow rate

d) Powder injection rate

e) Entry position of powder in plasma

These are few critical factors that must be worked closely to improve the quality of coating. For example: Spraying distance i.e. the distance between the spray gun and the specimen is of prime importance; if spraying distance is high then the molten particles would solidify before reaching the substrate specimen or if spraying distance is low then the particles would stay partially molten even though contacted by the substrate surface. These two phenomenon must be avoided and a balance must be struck to get the optimum distance.

Powder (feed material) morphology and particle size is also very important consideration in thermal spray parameters as it will determine the final coating's property. Ideally 5-50 microns particle size is used for oxides and 50-100 for metal powders. In externally fed plasma system, there is a great difficulty in feeding very fine particles because of pinch effect.

The gas flow rate controls the enthalpy of the flame which eventually increase the heat inside the chamber due to rise in the temperature.

1.4 Plasma Sprayed coatings:

When molten particles are propelled from the plasma gun toward the surface of specimen which is at relatively very low temperature compared to plasma, they under rapid solidification and get flattened. The velocity with which the molten particles impact the substrate is also very important. The particles which impact the substrate at high velocities tend to solidify with the surface geometry of the surface on which it is deposited. They have superior bonding strength with the substrate and provide excellent wear/abrasion resistance. The best example for such coatings is Tungsten Carbide with Cobalt binder (WC-Co). While other particles tend to solidify creating porosity at the coating-substrate interface.

More problems arise when arriving molten particles deposit on previously deposited coating which reduces the surface geometry effects on the solidifying layers of the coating. Oxide ceramic coatings are generally prone to this problem due to their insulating nature. This develops a thickness limitation and coatings deposited beyond a certain thickness are prone to develop surface delamination. This develops lamellar cracks in the coating and in the oxide coatings due to rapid solidification there is a possibility of shrinkage. Oxide coatings generally have higher specific heat and hence require longer dwell time in flame to get in molten state. This is sole reason behind adopting smaller particle size for oxide coatings and ceramic coatings as well. Hence, denser coatings are generally resulted with a smooth surface finish compared with metallic coatings.(7)

1.5 Problem of porosity:

The first particles that impinge the substrate surface have cooling rates as high as 10^4-10^6°C/sec for oxides.(8) This creates thermal expansion mismatch between coating and substrate. This high solidification rates gives rise to spherical voids. Now when another layer of subsequent particles are being deposited, they do not undergo solidification rates as high as listed above as this batch of particles is deposited on the insulating surfaces which are at higher temperatures. As a result temperature gradient develops giving rise to stresses. These along with thermal expansion mismatch gives rise to interconnected pores. Also, when non uniform particles are being sprayed, it gives rise to interconnected pores. Finer powders as stated earlier produce much denser coatings and increased cohesive strength. Porosity changes with changing spray parameters and powder size distribution as well.

Pores and cracks due to shrinkage are more prevalent in oxides due to their brittle nature compared to metallic coatings. However, interconnected pores are less common in oxides because of small particle size, higher heat capacity and lower cooling rates during solidification. Due to higher melting rates of ceramic oxides control of porosity by varying spray parameters is difficult. Compositional changes if done may improve the performance of the coating by decreasing the porosity.

1.6 Bonding mechanism:

The bond strength is one of most important parameters which determines the coating’s strength. Coating might be hard and wear resistant but if the bonding between the coating and substrate and between particles of the coating is not strong then the coating deposited will delaminate and will get ripped off or fall off as loose powder. Hence, bonding mechanism in the bulk of the coating and the interface between coating and substrate is an important aspect which has to be given prime importance. It is very difficult to explain and quantify the bonding mechanism in general because of the complexities of microstructure of the sprayed coatings and difficulty in producing precisely uniform conditions in the bulk of the coating. Also, the testing methods used to determine the bond strength and its mechanism are inadequate and less precise.

Hence, considering all these facts, one must adopt surface treatments of the substrate in order to increase the compatibility of the coating with the substrate. (To increase the bonding). Surface treatments would minimize the differences between the properties of coatings and substrates over which they are coated. This would reduce the residual stresses as well. Surface treatments such as grit blasting is done to increase the surface roughness. Surface roughness brings about mechanical interlocking with the deposited coating that increase the bond strength between the two. Grit blasting is generally adopted just before the application of coating. Application of bond coats also helps in increasing the compatibility of coating with the substrate. Such techniques minimize the residual as well as externally applied stresses and are helpful especially when coating materials for high temperature applications.

The bond that is responsible for having such a high is mechanical. The adherence of a coating to the substrate might be due physical, chemical factors apart from mechanical. The physical bonding is due to secondary and van der Waal's forces. However, as this bonding is very weak, it is easily destroyed and its contribution toward the bond strength is negligible as preheating and pre-roughening of the surface is essential as stated in above paragraph to increase the compatibility through mechanical interlocking. If the surface of the substrate is very smooth and shiny, the coating will not form a strong mechanical bond with it as coating needs some kind of grooves or roughness to get interlocked with. Hence, surface preparation is an important process for strong adherence of the coating. While, many methods are undertaken for the surface preparation but, grit blasting with alumina, Silicon carbide is most economical and simplistic way to roughen the surface. The main aim of the surface preparation treatment is to expose the bare metal and remove some oxide layer from the surface. Through blasting, surface becomes rough and anchors the coating to the substrate which results in strong mechanical bond.

Vadivasov (9) links mechanical interlocking to the shape of the surface micro-irregularities generated by grit blasting which promotes the wedging of the particles being deposited. The effect of surface roughness on shear bond strength on alumina was evaluated by Grisaffe. (10)

Bond strength increases with increase in surface roughness but up to a certain limit. It decreases again for highly rough surfaces.

Apart from physical, chemical and mechanical bonds, metallurgical bonds also contribute toward the bond strength of the coating. This had led to the development of “exothermic coatings” which by the heat of fusion of the constituents adhere to the substrate and form strong metallurgical bond. Hence, it can be said that higher substrate temperatures usually result in improve bonding as diffusion and metallurgical reactions are favored at higher temperatures resulting in more cohesive bond. But of all the bonds stated, mechanical bonding contributes the most in the strong bonding of the coating with the substrate. The cohesive bonding of the particles must also be considered and depends upon the spray parameters. Variation in spray parameters control the properties of the molten particles before impinging on the substrate. Viscosity of the molten particle at the time of impact must also be considered. There is a critical velocity of the impact of the particles that must be maintained, if otherwise exceeded the result will be excessive fragmentation of the particles and will eventually reduce the mechanical strength of the coating.(11)

Some of the hard and wear resistant materials which when coated result in poor coating because the particle-particle bonding is very poor. Particle-particle bonding has been given very less importance compared with coating-substrate adhesion phenomenon. However most ceramic oxides are believed to have higher bond strength due to mechanical interlocking, but certain ceramic mixtures such as alumina with 5-25% of fine titania particles bonded to their surface are claimed to produce chemically reacted interfacial layers which when flame sprayed produce much denser coatings. (11)

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(Part-1)

Chapter II

2.1 Introduction

Polymer matrix composites (PMCs) are very competitive materials for aerospace applications, because of their high strength to weight ratio compared to metals. High reliability is a fundamental requirement for aerospace applications, and this makes it somewhat difficult for making more use of PMCs. Strength, stiffness, fatigue strength and corrosion resistance of PMCs can meet the requirement, but the key factor that restrict PMCs from being more widely used are their heat resistance and erosion resistance. The surface properties of the polymer matrix composites are very weak, i.e. they get easily abraded and wear down upon impact of solid particles (for example: sand) in air. Especially in the southeastern areas (hot and arid) where sand concentration in the air is very high and the flow with which sand flows in the air is high as well.

Most of the aerospace applications demand high strength and lower weight materials hence, carbon composites popularly known as carbon fiber reinforced plastics/composites are used extensively in the manufacture of aircraft, helicopters, etc.

Carbon Composites are the materials that are composed of carbon fibers as reinforcement (dispersed phase) and a polymer as a matrix phase. The reinforcing dispersed phase may be in form of either continuous or discontinuous carbon fibers of diameter about 0.0004” commonly woven into a cloth.

Polymer resin serving the purpose of the matrix phase can be of various types: Thermoset resin such as an epoxy or thermoplastic material such as nylon, polyester or vinyl ester etc. Also, the carbon fibers can be of various types categorized according to their types, method of manufacturing and applications.

The properties of the final CFRP product can also be affected by the type of additives introduced to the binding matrix (the resin). The most frequent additive is silica, but other additives such as rubber and carbon nanotubes can be used. In CFRP the reinforcement is carbon fiber, which provides the strength. The matrix is usually a polymer resin, such as epoxy, to bind the reinforcements together. Because CFRP consists of two distinct elements, the material properties depend on these two elements.

Unlike metals, alloys and other conventional materials, CFRP has properties that are dependent on the direction/orientation of the reinforcement phase (carbon fiber in our case) i.e. it is an anisotropic material. Also the properties depend upon the proportion of the carbon fibers relative to the polymer matrix phase.

Generally the carbon fibers (reinforcing phase) provides strength and rigidity while the polymer matrix phase that binds the carbon fibers provides the toughness to absorb the energy/shock acted on the composite material. The strength and stiffness is usually measured by stress and modulus of elasticity

There are many applications of Carbon Fibers reinforced composite materials including Aerospace, automotive, medical, civil structures, etc. The thesis focuses on the testing of different thermal spray coatings on carbon composites for their use in helicopter blades. Hence, the advantages and disadvantages mentioned below are limited to aerospace applications.

Advantages: [2]

1) **Lighter:**

   As measured by density, steel is 4.4 times heavier, aluminum is 1.6 times heavier and titanium is 2.5 times heavier than carbon fiber composites.

2) **Stiffer:**

   Carbon fiber composites are 33% less resistant to deformation than steel but are 88% and 29% more resistant to deformation than aluminum and titanium respectively.

3) **Stronger**:

Carbon fiber composites are 3.8 times stronger than steel, 4.5 times stronger than aluminum alloys and 7.4 times stronger than titanium.

4) **Fatigue Resistance**:

Carbon fiber composites are inherently much more resistant to fatigue than traditional metals. Fatigue is caused by the propagation of micro cracks due to cyclic loading. In traditional metals those micro cracks tend to propagate at a much faster rate than in carbon fiber composites. The reason being is that carbon fiber composites are made of millions of individual strands of carbon fiber and micro cracks tend to stay isolated at the individual strands and not propagate like they do in metals.

5) **Corrosion Resistance**:

Moisture in the air will over time react with iron to create an iron oxide otherwise known as rust. Given sufficient time, oxygen, and water, any iron mass will eventually convert entirely to rust and disintegrate. Carbon fiber composites don't contain any iron and therefore do not rust.

Disadvantages:

1) **Low wear/abrasion resistance of surface:**

Though very strong and hard in itself, but the surface properties of carbon composite are very poor. It can be easily abraded when impacted by sand particles or other solid medium in air.

2) **Low working temperature:**

Carbon Composite cannot be used at very high temperatures. Here, the carbon is not the problem but the matrix which is made of some polymeric resin degrades at high temperature. Due to this, the bonding between the carbon fibers weakens and eventually the composite fails.

2.1.1 Surface protection of Carbon Composites:

As a surface modification technology, thermal spray has gained great success in the protection of metal parts. Several attempts have been made to use these technologies to produce protective coatings for PMCs. The method by which the surface of carbon composites can be protected is through application of coatings.

Surfaces of the solid substances degrade with time as they are in constant contact with the environment. Environmental degradation of the surface phase over time can be caused by wear, corrosion, fatigue and creep. Surfaces can be engineered to enhance their performance either mechanically or physically through various processes. They are as follows:

1) Molten process: Thermal Spraying and welding
2) Gaseous process: Chemical Vapor Deposition and Physical Vapor Deposition
3) Solution process: Electro-less or electrolytic plating, resin bonding
4) Solid process: Friction stir welding, roll cladding etc.

Out of these methods thermal spraying technique is the best suited because of the following advantages:(12)

- Variety of the materials that can be applied is very large in case of thermal spray technique. Cermet, ceramic, metals, alloys, polymer etc. can be applied as a form of coating.
- Virtually any material that does not decompose upon heating can be applied as a coating.
- Thermal spraying has the capacity to form barrier and functional coatings on a wide range of substrates.
- Thick coatings can be applied at considerably high deposition rates compared to any other coating
- Coating does not need to fuse with the substrate and hence, the technique applies coatings on the substrate without much heat input. Hence, high melting point metals can also be applied pretty easily.

Hence, thermal spray coatings were applied on carbon composite substrates to know their validity in harsh sandy environment and sand particle erosion testing of coatings was carried out with sand blasting machine set-up.

American Society of Material's Handbook of thermal spray technology states that, "Thermal Spray coating is a generic term for a group of coating processes used to apply metallic or non-metallic coatings." Various heating sources are used to heat the coating material which is generally in the form of powder, wire or rod to a molten state and is accelerated toward the substrate with high velocity so that it creates a strong bond between the semi-molten or molten coating and the substrate surface. The quality of the bond depends on various process parameters and conditions.

2.1.2 Materials used for thermal spray process(13)

1) Single phase materials:

- **Metals & Alloys**

Most pure metals have been used extensively for thermal spray processes. Metals such as Tungsten, Molybdenum, Nickel based super alloys, Cobalt based stellites, various trialloys, NiCrBSi based self-fluxing alloys, etc. have been utilized for various applications. These provide many advantages such as high strength, wear and corrosion resistance, and also their fatigue resistance. These have excellent bonding characteristics with the base substrate and form mechanically strong bond which have advantages of its own.

- **Intermetallics**

Almost all intermetallics are prone to oxidation at high temperatures and also reactive at that temperature; hence, inert atmosphere must be maintained in order to get the maximum resource efficiency out of the process. Inter-metallics such as TiAl, Ti_3Al, NiAl, Ni_3Al, etc. have been used for thermal spraying.

- **Polymers**

Thermoplastic and thermosetting polymers can be thermally sprayed provided they are available in particulate form. Polymers such as Polyurethanes, Polytetrafluoroethylene (PTFE), Polymethylmethacryalte (PMMA), polycarbonate, etc. are thermal sprayed depending upon the applications.

- **Ceramics**

Wide range of ceramics can be thermally sprayed to get wear and abrasion resistance. Ceramics are very hard in nature, provide thermal insulation/thermal barrier, conductivity, corrosion resistance etc. Ceramics include metal oxides such as Alumina (Al_2O_3), Zirconia (ZrO_2), Chromium Oxide (Cr_2O_3), Magnesium Oxide (MgO), etc. Various carbides include Tungsten Carbide (WC), Silicon Carbide (SiC), Titanium Carbide (TiC), etc. These are generally sprayed by plasma spray that has high energy capable of melting such high melting point materials.

2) Composite materials:

Composite materials are used in the applications where one requires the synergetic effect of ductile/tough metal matrix phase and hard/strong reinforcing phase. The ductile phase acts as a binder which holds the hard reinforcing particles. Wear resistant cermet coatings such as WC/Co, Cr_3C_2/NiCr, TiC/NiCr, etc. are been extensively used in wide areas of applications.

3) Layered or graded materials:

These are generally known as functionally graded materials (FGM).These are useful in the production of thermal barrier coatings where one needs to minimize the intensity of thermal stresses developed due to the large difference in coefficient of thermal expansion between the substrate and the coatings. It has following advantages:(14)

- FGM increases the bond strength between two incompatible materials
- FGM interface layer if applied, it reduces the residual stresses and thermal stresses as well
- Reduces the crack propagation through the interface

It is generally used for the production process of:

- Materials used in the application process where they are subjected to a large thermal gradient.
- Low cost cladded materials for corrosion and wear resistance applications.
- Energy conversion applications

2.2 Literature review

Limited work has been done till now in surface protection of Carbon composites using thermal spray technology. These are very attractive option for their use in aerospace applications because of their high strength to weight ratio.

Miyoshi et al conducted an experiment to investigate the erosion behavior of uncoated and coated Polymer Matrix Composite (PMC) specimens subjected to solid particle impingement. Bond coats were applied prior to applying the main coating of WC-Co to improve the adhesion of the coating and the substrate. Erosion were conducted using Arizona road dust equipment at impingement angles of 20˚-90˚ on both uncoated and two layer coated PMC at an air flow velocity of 220 m/s and at a temperature of 366K. (15)

The results obtained in the investigation carried out by Miyoshi et al. indicated that two layer (WC/Co top coat and metal bond coat) on PMC's remarkably reduced the erosion volume loss by a factor of approximately 10.

Vasquez et al studied the effect of surface modification on adhesion of metal bond coat polyimide composites. This study examined the effect Silica layer has on the adhesion of the proprietary metal bond coat to PMR-15 and PMR-II-50 composite surfaces. The surfaces of PMR-15 and PMR-II-50 composite were modified by following methods: Grit blasting, RF oxygen plasma etch, PECVD of silica, ultra violet ozone etch, UVCVD of Silica. Pull off adhesion test were carried out and fracture surfaces were examined using optical microscope and electron microscopy. (16)

PMR-15 samples with PECVD silica showed a significant increase in adhesion when compared with both UVCVD silica and grit blasting only. PMR-II-50 showed no significant difference in the adhesion strength for any surface modification method. The poor surface quality of PMR-II-50 composites is believed to have a major effect on bond coat adhesion strength.

Rezzoug et al investigated the effect of metallic coating for carbon fiber reinforced polymer matrix composite substrate. In this experiment they used copper and steel powder known as filler powders that will reduce the impact of thermal spray particles which eventually protect the carbon fibers from getting ruptured by thermal spray particles. Further, they showed through microstructure analysis that zinc coating will improve the erosion resistance of the PMC's and also has a good compatibility with the substrate. (17)

Aiguo Liu et al conducted an experiment where they used arc spray to form an erosion-resistant coating for PMC. A cored wire composed of steel skin and Ni–Cr–B–Si as filler material was used as the coating material. Influence of the pretreatment on the shear bond strength, thermal fatigue resistance, and erosion resistance of the coatings were also investigated. They showed that thin Zinc layer as a bond coat could improve the thermal fatigue resistance of the coating.

They proved that the mass loss of the coated PMC in erosion testing was half of that of the uncoated one, and the arc-sprayed coatings could provide good protection of the PMC from erosion.(18)

Drexel University, supported by NASA Glenn Research Center, investigated high velocity oxy-fuel (HVOF) sprayed functionally graded coatings for polymeric substrates (19), in order to solve the problem of thermal expansion coefficient mismatch between the substrate and the protection coating.

The functionally graded coating structures were based on a polyimide matrix filled with varying volume fractions of WC–Co. They found that the pre-heat temperature of the substrate had a great influence on the bond strength of the coating. Anyway, the bond strength was not very high, 5–6 MPa only. The commonly used pre-treatment, grit blasting, would cause substrate damage, and resulted in low bond strength.

2.3 Motivation of work: (Part-I)

The main focus was on to improve the low erosion resistance of the surface of carbon composites as that is the primary reason which limits its use in the applications of the aerospace where the component is subjected to hot arid sandy conditions. Sand easily abrades the surface of carbon composites.

This was the motivation of the thesis where we could protect the surface of the carbon composite components through various hard carbide coatings. This would enhance its use in aerospace manufacturing especially in the manufacture of helicopter blades that is operated in hot and arid environment where the sand concentration in air is very high. Finally, sand particle erosion testing of specimen was carried out to check the validity of the coating.

2.4 Experimental

2.4.1 Set-up:

The purpose of this test was to measure the sand erosion resistance of thermal spray coatings on carbon composite as substrate used in the manufacture of the helicopter rotor blades.

This test can quantify the amount of coating eroded from the substrate through mass loss. Although this test can quote the sand erosion resistance of coatings, but it alone cannot qualify the material for the rotor blade application.

Hence, other characterizations viz. adhesion test, porosity, thermal shock, corrosion test etc. are needed in order to make a decision as to which coating would be best that could serve though not all but many properties during the application. As it would take lot of details for the coating to qualify for the application, mentioning all the processes and parameters is out of scope for the thesis.

The schematic diagram of the set-up is as shown in the figure.

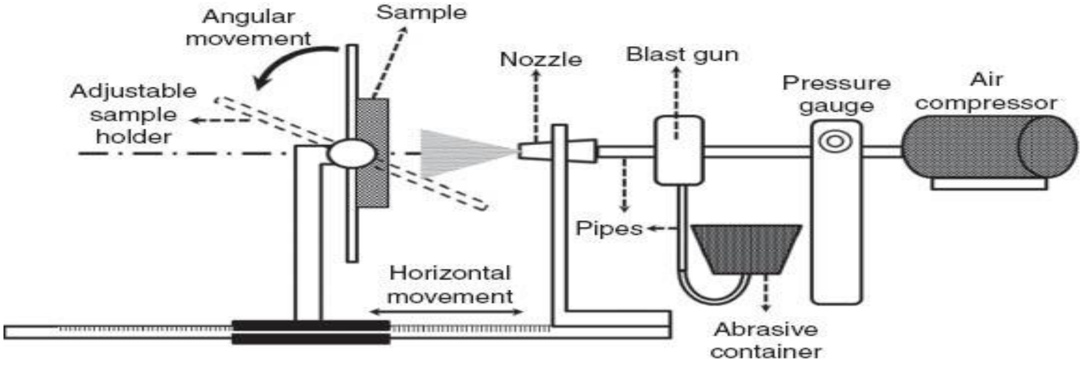


Figure-4 Schematic diagram of the sand blasting machine(20)

2.4.2 Testing apparatus:

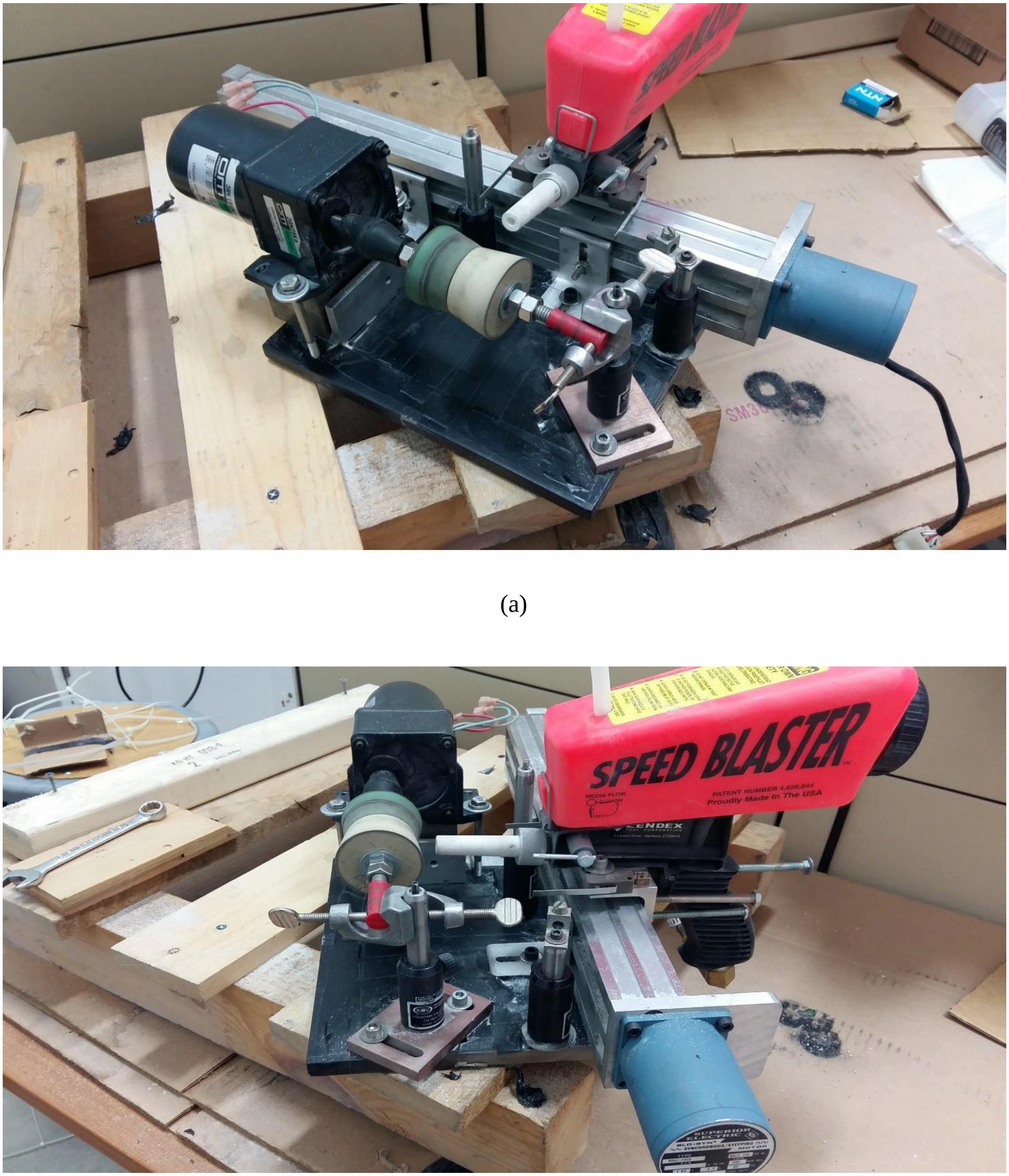
The test apparatus is a sand blasting machine that could simulate the in-service flight conditions. Two motors were used. First one was used for the linear motion of the sand blaster and the second one was employed for the rotation of the sample.

For the sand blaster, linear stage was used in order to convert the rotational motion of the shaft of the motor to linear motion. Sand blaster was placed above the linear stage as shown in the figure. The linear motion of the sand blaster was restricted beyond a certain point on both sides by limit switches as shown in the figure.

Sand blaster was loaded by the silica sand from the top through small diameter hose pipe and high pressure air jet was introduced in the blaster from the rear side through a hose connected to a pressure gauge that could regulate the pressure as needed. Pressure gauge was connected directly to the compressor hose pipe.

The shaft of the motor which run the sample was equipped with coupler to transfer the rotational motion of the shaft to the sample. The free end of the shaft of the sample was being rested on the stand in order to prevent its wobble during the operation. In order to prevent the side motion of the sample and to fix it properly on the rotating shaft it was backed up by the rubber stoppers as shown in the figure.

Sand particles are accelerated through a small diameter nozzle and directed towards the test specimen as shown in the figure. Since, the diameter of the nozzle is smaller than the test specimen area, the test specimen is rotated continuously past the jet while the jet (sand blaster) is oscillated over the linear stage. This mechanism facilitates uniform deposition of the sand particles throughout the surface area of the test specimen.



(a)

(b)

Figure-5 (a) and (b) Actual Set-up of the sand blasting machine

2.4.3 Standard Test Conditions:

1) Erodent:

The erodent/abrasive used was Pro-Angle White Bunker Hydrosand popularly known as golf sand. The source for this sand was R.W. Sidley Inc. located in Painesville, Ohio.

The sand here used had its grains angular in shape. The main reason behind using angular grain shape sand was that the angular shaped grains has more pronounced effect on the abrasion that the rounded shaped grains, i.e. angular shaped grains brings about more severe abrasion than the round shaped grains.

The particle size used was in the range of 240-550 microns. Sand particle size below 200 microns was unacceptable according to DOD test method standard as that was the duplication of the real flight conditions where the sand particle size is never less than 200 microns.

Also the reuse of the sand must be avoided as it would further decrease the abrading effect of the sand and we would get improper results.

2) Velocity of the erodent:

The velocity is representative of the helicopter rotor tip speeds during landing and take-off conditions. The velocity of the erodent as measured at a distance of 20 millimeters from the nozzle tip was 730 ft. /sec

3) Sand particle mass load and impingement angle:

The sand particle mass load was between 30-50 grams/cm^2 and the angle of the impingement was in the range of 20-90 degrees.

4) Nozzle diameter:

The diameter of the nozzle used was around 4.9 millimeters. The nozzle was made of ceramic material in order to resist the abrading action of the high speed and high pressure silica sand passing through it.

5) Pressure & Temperature:

The pressure at which the high speed air jet of the sand was passed through was kept around 90 PSI. Such high pressure was kept in order to maintain the flow rate of 251.5 liters/minute. Also, here the sand has no momentum of its own unlike the real condition where in the hot arid regions the sand comes with lot of momentum and hits the rotor blades. Hence, to compromise the effect of self-momentum of the sand, the pressure of the air kept here was pretty high. The temperature at which this test carried out was normal room temperature (75˚F)

6) Rotational speed of the sample:

The rotational speed of the sample was 70 RPM. It is not necessary to rotate the sample if the sample shape is other than round or cylindrical. In this test, we used a hollow tube whose dimensions are given in later sections. The goal was to test for 15 minutes, i.e. deposition time was to be 15 minutes if the sample could last under such conditions for such long. Hence, number of turns per deposition would be equal to 1050.

7) Linear speed of the blaster:

The linear speed of the blaster was kept around 7.9 cm/min. Hence, number of passes per deposition would be around 37.

2.4.4 Test specimen specifications

1) Type of the specimen:

The specimen used was a hollow tube of carbon composite, over which different coatings were done. Diameter of the hollow tube was 50 millimeters

2) Size of the specimen:

Diameter of the specimen used was 50 millimeters. The scanning length (length along which the deposition will take place) was equal to 32 millimeters. The scanning length represents the length covered by the blaster during its oscillation for one pass. Thickness of the substrate without the coating was equal to 2 millimeters.

2.5 Testing:

The coefficient of thermal expansion of carbon fiber is in the range of −0.3×10−6/°C–1×10−6/°C, and the coefficient of thermal expansion of polyimide is approximately 50×10−6/°C. They are very different from that of coating material, which is in the range of 10×10−6/°C–12×10−6/°C. [11], [12]

Thermal stress would be produced if the coated sample was subjected to thermal cycling, due to the great difference of coefficient of thermal expansion. So a soft bond layer was proposed between the erosion-resistant coating and the substrate to minimize the thermal stress.

1) Uncoated Carbon Composite:

First test was carried out on uncoated carbon composite substrate to check the working of the test system and to know if there is considerable amount of mass loss that could be noted in terms of a proper result.

Firstly, the weight and thickness of the sample was noted as the weight and thickness of the sample before the test.

This was followed by loading the sample between the two rubber stoppers and the motor to which it was connected was switched on to make sure the sample is not wobbling due to its own weight and rotational motion. The linear stage motor was switched on to check the motion of sand blaster over the stage is proper or not.

Sand was introduced from the top of the blaster through a small funnel and a hose. A balance was struck between the sand mass deposition and its flow rate.

Lastly, the compressor valve was opened up and through the pressure regulator the pressure was adjusted to 85-90 PSI.

The test was carried out for 15 minutes. After completion of the test, sample was unloaded and properly cleaned to remove all the sand from its surface. This was followed by weighing the sample and measuring the thickness of the specimen. This was to quantify the wear of the material after test. Results were noted in terms of mass loss and are listed in later chapters.

2) Zinc coating (bond coat) on carbon composite:

The testing procedure was the same as used for the uncoated carbon composite. Results were noted in terms of mass loss and are listed in later chapters.

The test for this specimen was carried out for no more 2 minutes. The main reason behind this was that coating got ripped off from the substrate within 2 minutes of the test. Not more than 130 grams sand was used for the test.

3) Tungsten carbide with cobalt matrix:

The same testing method was employed for this coating as used above. Same kind of results were obtained in case of WC-Co coating as observed for Zn bond coat, i.e. the coating got ripped off globally from the substrate within 2 minutes of the test and no more than 130 grams of sand was used to bring about the ripping effect.

2.6 Results

1. Uncoated Carbon Composite:

Results are as listed in the Table 1. It could be clearly inferred from the data that there is considerable mass loss after the sand particle erosion test. Although, the carbon composites are very stiff and strong but their surface is easily abradable which is an obvious decision one could make from the results.

Sample Number	Before Test						After Test		Total mass loss in %
	Diameter (mm)	Length (mm)	Thickness (mm)	Weight (g)	Sand mass (Kg)	Air pressure (PSI)	Weight (g)	Thickness (mm)	
1	50	22	2	9.333	1.46	90	3.92	1	58.0
2	50	22	1.86	9.8	1.46	90	4.86	1.36	50.4

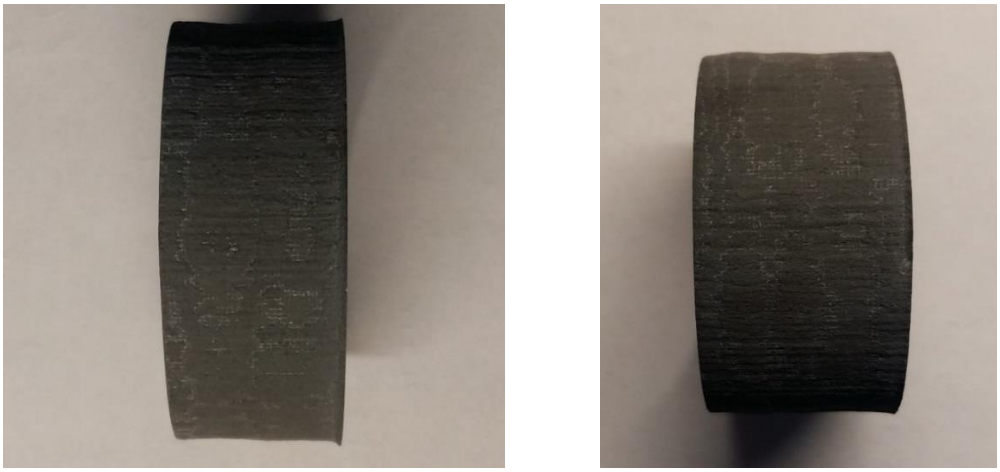
Table-1: Mass loss results for uncoated carbon composite sample

Below shown are the images of the specimen before and after the test and one can clearly see the difference in the surface of the specimen

Before the test

Figure-6 Uncoated carbon composite specimen before the sand particle erosion test

After the test



(a) Sample 1 **(b) Sample 2**

Figure-7 Uncoated CC after sand particle erosion test

1) Zinc coated carbon composite:

Results are as listed in the Table 2. Here the test was carried out for 2 minutes as the coating started to peel off from the substrate within that time. This shows that the adhesion between the substrate and the coating is very poor and hence it could not bond properly with the substrate and got ripped off the surface pretty easily with just 130 grams of sand mass.

Table 2

Sample Number	Before Test						After Test		Total mass loss in %
	Diameter (mm)	Length (mm)	Thickness (mm)	Weight (g)	Sand mass (Kg)	Air pressure (PSI)	Weight (g)	Thickness (mm)	
1	50	22	2.12	11.846	0.13	90	10.799	1.9	8.8

Table-2 Mass loss results for Zinc coated carbon composite sample

Below shown are the images of the Zinc coated carbon composite before and after the test. One can clearly see the condition of the zinc coating on the carbon composite substrate within 2 minutes of the test and using 130 grams of the sand.

Figure-8 Zinc coated sample before the test

Figure-9 Zinc coated sample after the test

2) Tungsten Carbide with Cobalt matrix:

Results are as shown in the Table 3. Here also the same kind of results were observed as in zinc coated carbon composite. Within 2 minutes of test the coating was seen to rip off globally from the substrate so the test had to be terminated. 130 grams of sand was used for the test.

Table 3

Sample Number	Before Test						After Test		Total mass loss in %
	Diameter (mm)	Length (mm)	Thickness (mm)	Weight (g)	Sand mass (Kg)	Air pressure (PSI)	Weight (g)	Thickness (mm)	
1	50	22	2.15	12.797	0.13	90	10.10	1.96	21.1

Table-3 Mass loss results for Tungsten Carbide-Cobalt (WC-Co) coated carbon composite sample

Below shown are the images of the WC-Co coated carbon composite before and after the test. One can clearly see the condition of the WC-Co coating on the carbon composite substrate within 2 minutes of the test and using 130 grams of the sand.

Fig-10 WC-Co coated sample before the test

Fig-11 WC-Co sample after the test

2.7 Discussion

According to the data obtained from the experiments and testing of coatings, it can be said that either the testing equipment used was too intense for such coating material or the coating itself was not bonded properly with the substrate. The reason most likely seems to be with the coating.

Results obtained through the sand particle erosion testing clearly indicated that the coating did not bond properly with the substrate. Coating failed globally instead of failing particle-by-particle. This clearly indicates that coating and the substrate had a thermal mismatch, i.e. there was a large difference in the coefficient of thermal expansion (CTE) between the coating and the substrate. This led to poor bonding between coating and substrate and build-up of thermal stresses. Carbon composites being very stiff and strong, has very low CTE compared to other materials which expand upon heating. This was the sole reason behind the fact that the WC-Co and Zinc coating obtained was locally deformed and cracked long before its effectiveness as a protective erosion barrier could be assessed.

This type of problem must be addressed by employing functionally graded material (FGM) coatings especially where there is large difference in CTE between coating and substrate. In contrast to traditional composites, with a uniform distribution of reinforcing phases, FGM coatings are characterized by a volumetric gradient evolving from one component to another and properties of each component can be utilized effectively without the need to compromise.(21)

According to the work published earlier on thermal spray coatings, the steel substrate best suits as a base for the coatings. Here, we can see the optimum performance of the coatings as the bond between the substrate and the coating is very strong. Hence, the coating does not peel-off from the substrate as in our case where the coating got ripped off globally from the substrate.

2.8 Summary & Conclusion

- The goal of this test was to measure the sand particle erosion resistance of thermal spray coatings on carbon composites relative to uncoated carbon composite specimen for the application of manufacture of helicopter rotor blades.
- The test set-up employed for testing was a machine similar to a sand blasting machine and was an effort to simulate the in-flight or in-service test conditions where the helicopter is subjected to hot-arid environments where the sand concentration in the air is very high.
- Due to large difference in the CTE between carbon composite and coating there was a thermal mismatch that resulted in poor bonding between the two. Hence, the coated specimen obtained was deformed and cracked before it could be assessed for erosion resistance.

- Hence, the results for the erosion test obtained were pretty obvious meaning; the coating (Zn & WC-Co) could not resist the erosion test conditions and got ripped off from the substrate within 2 minutes with 130 grams of sand deposition with considerable mass loss and so the coating did not qualify for the application.

Part-2

Chapter III

3.1 Introduction

Properties of hard materials and methods of their production has been of considerable importance since many years due to their excellent hardness, mechanical properties, wear and corrosion resistance. The best example of such class of hard materials is tungsten carbide-cobalt composite (WC-Co). This comes in the class of Cermet materials. These have excellent hardness and provide superior wear and abrasion resistance. However, there are many other examples of such materials and are listed in later sections. Many different methods are used to produce such class of materials, thermal spray being one of them. Sintered carbides are one of the widely used hard materials for wear and abrasion resistance. In fact, cemented carbides were one of the first examples of successful composite materials in which the beneficial properties of two component materials are retained in the final composite. Hardness and wear resistance is provided by the carbide phase while metallic binder phase contributes strongly to ductility and toughness of the composite.

In the energy generating, aerospace, pulp and paper, automotive and many other industries, thermal spray metallic, ceramic and cermet coatings have been identified as a means to improve the operating performance of engineered surfaces. Many industrial applications such as mechanical seals, bearings, shafts, turbine blades, wear rings, thermal spray coatings are widely used to decrease the surface degradation. Also, in the aircraft and energy generating gas turbine engines, boilers, power plant machinery, thermal spray coatings are being used to mitigate the solid particle erosion and hot corrosion in high temperature components.

This part of the thesis has its objective focused on the assessment of different thermal spray coating materials for wear protection of mechanical seals used in the pump industry.

Mechanical seals are an integral part of pumps that are used for sealing or preventing leakage. It is a device used to seal the interface between a rotating shaft and a stationary housing. These are commonly employed in centrifugal pumps although, quite often used in agitators, turbines, compressors, blowers, etc. The ability of a mechanical seal to meet the requirements depend upon many factors that involves design, operating conditions and support systems and materials of seals as well.(22)

There are various types of mechanical seals depending upon the application. Also, seals can be divided into three categories of components: the seal faces, secondary sealing elements and major metal components.(22)

One of the most important part of a seal is its face as it undergoes wear, corrosion and cavitation damage in service, which reduces pump efficiency and component life and significantly increases the life cycle cost of the pump. All these degradation mechanisms are active on the surfaces of the pump components, and therefore surface coatings could be an effective way of addressing this problem. Wear of materials should be taken into prime consideration as it is one of most important parameters that controls the pump efficiency and durability.

There are types of wear that materials undergo:

a) Adhesive Wear- material pull-off between sliding surfaces

b) Abrasive Wear- loss of clearances

Mechanical seals are subject to abrasion, erosion, cavitation and sliding wear in service. Abrasion and erosion results from abrasive particles in the medium being pumped, but even in the absence of any abrasive particles sliding (or galling) wear can occur due to unintentional contact between rotating and stationery components. Moreover these wear rates in pumps are often unexpectedly high because of the synergistic relationship between wear and corrosion; even a mildly corrosive process media can significantly increase wear rates. This is often increased even more by the high flow velocities that can be found in some high-energy pumps. As the pump components in the flow path wear, efficiency critical sealing clearances increase and vane angles change, resulting in a decrease in pump efficiency over time.

There are numerous strategies to reduce the impact of wear on pump components such as specialized pump design and the use of sophisticated materials (e.g. high-alloy steels, ceramics, rubbers etc.), but surface coatings are some of the most successful and cost-effective tools for managing wear.

3.1.1 A few rules of thumb for mechanical seals [20]

Below listed are the things one must keep in mind before designing a mechanical seal:

- The materials for mechanical seals must be compatible chemically to all the fluids that are being pumped, i.e. all solvents, cleaners or steam that is generally introduced into the system to clean the lines.

- The seal faces must stay together without opening otherwise the seal will leak and penetrate all the solids and eventually damage the faces and lapped surfaces. This would deteriorate a pump's life drastically.
- Any other failure other than the wearing away of the carbon from the face of mechanical seal is considered to be seal failure and is always repairable through different techniques like application of coatings.

3.1.2 Materials used for manufacture of mechanical seals

The best seal face materials should have low friction, high hardness, good corrosion resistance (chemical resistance) and high heat conductivity, adequate wear resistance, etc. Conventionally pump manufacturers used hard martensitic stainless steels maintaining the hardness difference of 50-100 Brinell between stationary and rotary parts of the pump as experience has shown this difference to be adequate enough to prevent galling (23)

Below listed are some conventional coating materials used by the pump manufacturers for making mechanical seals.(22)

1) Carbon:

Being one of the most abundant materials on the earth, it is quite extensively used in the manufacture of faces of mechanical seals. Various forms of carbon are available for use. It takes up amorphous form to graphite and from diamond to fullerene. All forms have their own advantages and applications.

Advantages:

- It is abundant in nature
- Stable, inert, chemical resistant
- Self-lubricating
- Anti-friction properties

Carbon is not used in its original form but it’s generally impregnated with graphite and/or other resin and pitch. Metallic binders may also be added. Manufacturers use their own grades of carbon suitable for the specific application that depends upon factors such as graphite content, binder content etc.

Resin impregnated carbon has its own advantages in a way it provides good frictional resistance and chemical resistance as well. However, these lack wear resistance and hence if one operates such resin impregnated carbon faced mechanical seals in high wear and abrasive conditions it will create lot of material loss. These conditions demand metal impregnated carbon which has superior wear resistance, strength and stiffness and can be employed successfully in high pressure applications for considerable period of time. Although, these lack chemical resistance and also have low friction resistance which brings about lot of seizure or galling on the surface.

One may have to look up for the conditions in which the mechanical seal is being put and then choose the type of carbon for that application. Although there are certain advantages of carbon as a material for mechanical seal face, there is lot of wear that it has to undergo as the surface of carbon faced components is very weak and is prone to abrasion.

2) **Aluminum Oxide (Alumina):**

Alumina is a ceramic material available in different purity levels and its cost increases as the purity level increases. The most pure alumina offers best corrosion resistance but on the contrary its cost increases. Hence, a balance must be struck between the two.

Advantages:

- High stiffness
- Good chemical resistance
- Partially good wear resistance

Other than some strong acids, alumina has excellent resistance against most fluids but due to low heat conductivity it fails/fractures easily by thermal shock. Rapid heating during dry running operations is prevalent which can fracture alumina easily. Hence, alumina as a seal face material for mechanical seal is not recommended in the conditions where temperature changes are prevalent.

3) **Chrome Oxide:**

Chrome oxide is extensively been used for corrosion resistance and against other chemical attack. However, it is eaten by alkaline medium. Also, due to low heat conductivity it fails under thermal shock and its use is limited in the applications where there is a lot of heat gradient within the component. Also, it lacks hardness so cannot be employed under highly abrasive conditions. It has very low elastic modulus hence can fracture easily under high loads.

4) **Silicon Carbide:**

It is one of the best suited material for the faces of mechanical seals that pump manufacturers prefer to use because of following properties:

Advantages:

- Excellent hardness
- Excellent wear resistance
- High thermal conductivity
- Low coefficient of thermal expansion
- Excellent thermal shock resistance
- High endurance limit

There are two forms of silicon carbide that are used for manufacturing of mechanical seals.

Reaction bonded silicon carbide

It has high content of free silicon. Silicon carbide particles and carbon are mixed together with binding agent and pressed into desired shape. Free silicon gets affected by the chemical attack that can weaken the material and result in failure. Strong acids and high pH chemicals easily attack the free silicon hence, these limit its applications. Although, prone to caustics and chemicals, it has higher wear resistance that self-sintered silicon carbide.

Self-Sintered Silicon Carbide

Due to its high hardness, it has low mechanical strength. Unlike reaction bonded silicon carbide, self-sintered silicon carbide does not have free silicon hence, it is chemically more resistant. However, it is more brittle and prone to chipping that reaction bonded silicon carbide.

5) Tungsten Carbide:

Cobalt matrix:

It is one of the most successful seal face material used by the manufacturers and has given promising performance compared to other materials even in aggressive conditions. This material consists of hard tungsten carbide phase in the form of small particles with cobalt used as a metallic binder that acts as matrix phase. In this one can get the synergetic effect of hardness provided by hard carbide phase particles and toughness provided by the softer cobalt matrix phase.

Advantages:

- Superior hardness
- Excellent wear resistance
- Superior Strength
- High thermal conductivity
- Low coefficient of thermal expansion

However, cobalt matrix is prone to chemical attack and is eaten up by strong acids and it fails in chlorine atmosphere as well. It has low friction resistance when it is running under hot water and may cause galling. For the applications where one needs superior corrosion and chemical resistance, nickel as a binder phase instead of cobalt has proved to be far more superior.

Nickel matrix:

Nickel as a binder phase in tungsten carbide is pretty impressive in terms of chemical resistance. Nickel has higher chemical resistance than cobalt in aggressive atmospheres.

Advantages:

- Superior chemical resistance
- High strength and toughness
- Excellent wear resistance

6) Boron Carbide:

Boron carbide is known to be the third hardest material after diamond and cubic boron nitride. It is an unconventional material that is used for coating purpose. The superior mechanical properties of Boron carbide make it very suitable as a wear resistant coating for industrial machinery and components.

Advantages:

- Excellent hardness and strength
- Superior wear resistance
- High resistance to fracture
- High resistance against chemicals (corrosion resistant)
- Anti-galling properties
- Low density
- Excellent resistance to thermal shock

However, there is one major problem associated with this material. During plasma spraying, decomposition of boron carbide powder takes place and results in the formation of BXC phase and an increase of the carbon phase.(24)

3.1.3 Coating Characteristics

In practice coatings are applied for a specific well intended application. Hence, it may possess one of the few properties:(25)

- Wear resistance
- High Hardness
- High melting point
- High corrosion resistance
- High density to protect the gases/liquid to penetrate into the surface

3.1.4 Abrasive Wear Testing

Wear is one of worst failure mechanism of the material as it involves loss of material leading to deterioration of engineering components. It can be defined as “unwanted removal and deformation of material by chemical or mechanical action of the opposite surface”.

Wear can be classified into different categories: Abrasive, fretting, adhesive, erosion, etc. Abrasive wear is predominant in most cases. Mainly the researchers have investigated the problems related to abrasive, impact, erosion and all other types of wear on uncoated specimens as separate problems.

More recently there has been a great deal of research on wear testing of coated components and regarding finding out wear testing mechanisms and standardizing it and calculating its wear resistance. Whether these techniques can be applied to thicker coatings as produced by thermal spraying is still in review. The type of wear occurring under combined impact and sliding wear has hardly been studied according to Swick et al.(26)

Apart from the different categories of wear listed above, there are other types as well that occur especially encountered by the coated surfaces. These are low and high stress abrasion, dry particle erosion, slurry erosion, sliding wear and friction etc.(25) Coatings may experience shear, tensile, or compressive stresses which may lead to deformation.(27)

3.1.5 Variables in wear testing

There are two types of variables in wear testing: One which can be easily controlled and the other one which are difficult to control. Below listed are some of the variables encountered in wear testing.

Variables that are easy to control:

- Running time
- Abrasive feed or rate
- Contact area
- Specimen configuration

Variables that are difficult to control:

- Size of the abrasive
- Shape of abrasive
- Hardness
- Toughness
- Motion of abrasive

Abrasive hardness is the most important variable that has to be considered because it may decide the severity of wear and its rate. Here one must talk about the hardness of the abrasive with respect to the surface of the material being worn.

Generally shape of the abrasive is also considered while designing the test. Because, angular shaped abrasives is more intense that similar size round abrasive. Also, angular soft particles bring about more wear than round hard particles do.

3.1.6 Wear Test Criteria (25)

Below listed factors must be considered before adopting a certain test:

1) Select a suitable test that measures the desirable properties of the material
2) Make sure the test adopted is for bulk material or for coatings
3) Presence of abrasive, its size, shape, and all the specifications must be kept in mind before incorporating that into test.
4) It is advisable to perform a test that will duplicate the actual service conditions so that we can speculate the results beforehand
5) The forces acting on the specimen must be properly calculated along with proper loading conditions.
6) If necessary, test temperature must be so adopted that it simulates the service conditions
7) Test duration is also very important factor that has to be kept in mind, otherwise hardest of the materials also wear down if kept in contact of abrasives for prolonged period.

3.1.7 Wear Testing methods(25)

In this section, some of the currently employed and previously used wear testing methods are briefly reviewed.

1) Pin-on-disc:

The mechanism consists of a stationary "pin" under an applied load in contact with a rotating disc. The pin can be of any shape but is generally taken to be spherical to simplify the contact geometry. The pin on disc test has proved useful in providing a simple wear and friction test for low friction coatings. According to Glaeser and Ruff pin on disc method is most widely used for measuring wear followed by pin on flat.(28) Almond et al. (29) used a pin-on-disc apparatus for testing ceramics and cemented carbides on alumina discs using the pin as the test material. In a two-body abrasion test, a coated pin is pressed against a rotating abrasive paper making a spiral path to avoid overlapping (30), (31). This test process is very common for thin coatings

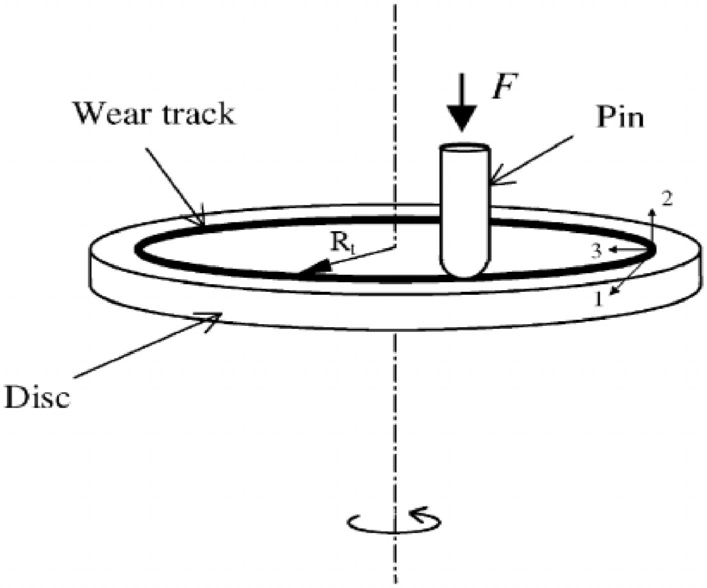


Figure: 12 Schematic of pin-on-disk wear test(32)

2) Pin-on-drum:

In this test, one end of the cylindrical pin is moved over the abrasive sheet of paper with sufficient load to crush the abrasive grains present on the sheet of the paper and in doing so the specimen will also wear down. In this mechanism pin rotates while moving; hence, it can simulate the service conditions that occur during crushing and grinding of ore.

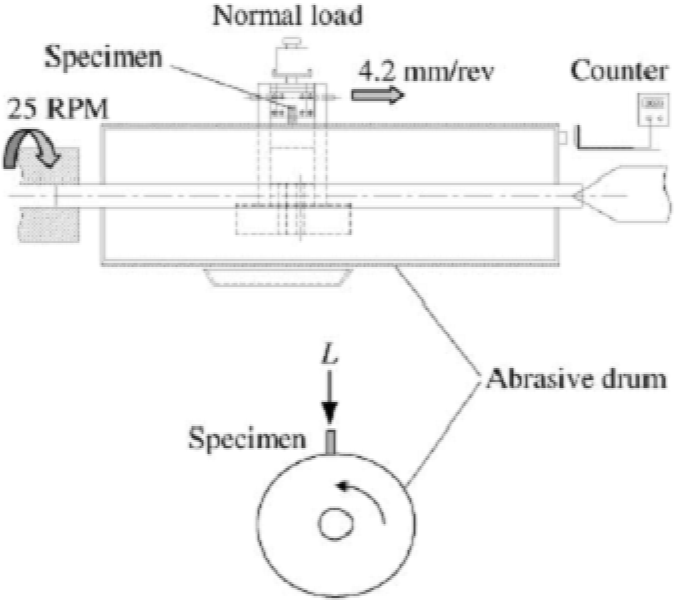


Figure 13: Schematic of pin-on-drum wear test(33)

3) Rubbing test:

This test follows an ASTM (25) standard where one cylinder rubs against other stationary cylinder at right angles. Speed of rotation is equal to 100 RPM. The volume of material loss is calculated through suitable equation. It is used for testing similar and dissimilar metals alloy systems and coatings under unlubricated conditions.

4) Block-on-ring test:

This test works according to ASTM G77-83 standard (25) where a metal ring rotates against a fixed block and makes a line contact with the surface of the block. The advantage of this test is that it allows for variation in materials, test loads, coatings, speeds, and operating atmospheres. Hence, one can tune this test as per his/her requirement.

5) Dry sand rubber wheel test:

This test follows ASTM 65-81 standard and is used to measure the abrasion resistance of materials to silica sand. Here a rubber wheel rubs against a specimen and silica particles are trapped in the rubber wheel and eventually it carries all abrasive particles with it while moving and wears down the specimen.

Cerri et al. (34), using similar equipment, examined the abrasion resistance of carbide powders with several materials and coatings used for applications in abrasive environments.

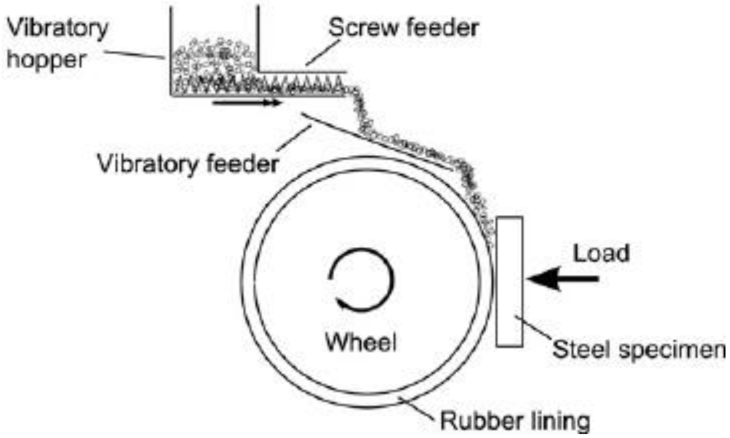


Figure 14: Schematic of dry sand rubber wheel wear test(35)

6) Alumina Slurry test:

This test follows ASTM 611 standard and uses highly abrasive alumina slurry for causing erosive wear. The mechanism incorporates a steel ring that rotates against a flat coated specimen, and the alumina slurry is constantly fed between the interface of the rotating steel ring and the coated specimen. This harsh conditions subjects the sample to a combined impact erosion.

The extent of erosive wear depends upon abrasive size, flow rate, shape of the abrasive, speed of rotation, load acting on the coated specimen, etc.

3.2 Literature Review

Mccaul and Kaufold (23) compared three different types of coatings namely cobalt-chrome, WC (Stellite), and a typical HVOF WC coating. These were sprayed through flame spray, plasma, and HVOF respectively. Coatings performance was evaluated qualitatively on the basis of change in mass and thickness.

The properties of coatings was investigated by testing their abrasive wear resistance, adhesive wear resistance and particle erosion resistance. The results were obtained with microstructure of the final specimen after every test.

Abrasive wear test results showed that tungsten carbide-cobalt coatings show consistently lower losses of both weight and thickness than nickel-chrome- boride and all other coatings. The resistance to abrasion increase as the tungsten content increases.

The results obtained for particle erosion test are consistent with abrasive wear test and showed that tungsten carbide-cobalt sprayed by HVOF method surpassed all other coatings and were more resistant to sliding and abrasive wear conditions.

For adhesive wear test, a proper way to judge a coating's quality is through values of coefficient of sliding friction, scar width, and ring weight loss. All these values must be as small as possible.

Hence, they concluded that tungsten carbide-cobalt appears to be best choice for the mechanical seals with combination of 88 percent tungsten and 12 percent Cobalt. These findings are in full agreement with those of a recently concluded program

While it was not evaluated in this program, there is a published data that states that tungsten carbide-cobalt coatings cannot be used on both mating parts as severe galling and coating failure is likely to occur.

Jari Knuuttila et al.(36) studied the wet abrasion and slurry erosion resistance of alumina and chromia coatings deposited through APS. The effect of Aluminum phosphate ($AlPO_4$) sealing treatment was studied on the wear and corrosion behavior of coatings.

Grit blasting was done prior to coating and no bond coat was used. Quartz sand was used as abrasive for dry rubber wheel abrasion tests while for wet abrasion wear tests, 28 wt% Kaolin or silica was used.

Results of the dry abrasion wear test indicated that Chromia coatings with $AlPO_4$ sealant showed very high wear resistance. However, for wet abrasion wear test, $AlPO_4$ increases the wear for alumina coatings contrary to chromia coatings.

Although, Kaolin is smaller and less hard than silica, still the wear for alumina is high because of chemical affinity between the γ-alumina and kaolin causing tribo-chemical wear.

Rong Liu (37) et al. measured the tribological behavior of Stellite 720 (high carbon Co-Cr- Mo alloy) coating deposited on 304 stainless steel under block-on-ring wear test.

Results of the block-on-ring wear test showed that wear loss increased with contact load but decreased above a certain loads (higher than 900N)

At higher loads, the enhanced friction between the two mating surfaces generates more heat resulting in oxidation of the contact surfaces.

While the oxide films were brittle and weak, they get smashed pretty easily during wear process and gets embedded in specimen surface by high contact load which enhances the hardness which eventually increases the wear resistance.

3.3 Motivation of work

Pump, throughout its lifetime is subjected to various harsh conditions, i.e. it is used in different environment depending upon the type of industry (oil & gas, petrochemical, food, automotive, paper & pulp, etc.). All these industries have different type of conditions at which pump might be subjected to. Conditions vary from highly acidic to highly basic, highly caustic to alkaline or else neutral as well. Hence, the mechanical seals used in such pumps deteriorate and the life of pump decreases drastically.

Keeping in mind the cost saving and to reduce the downtime of the pumps, life of mechanical seals had to be increased to achieve the above objectives. This was the motivation of the work. Thermal sprayed coatings proved to be the best choice for the application due to following advantages offered:

- Coated material can be repaired easily and there is no need to replace the entire part.
- Any hard wear resistant, corrosion resistant and high melting point coating material can be applied which would protect the seal for longer time.
- It considerably reduced cost and downtime with increased life.

Coated specimen had to be tested to know whether it would be able to resist the service conditions or not. Hence, block-on-ring test mechanism was made and was an effort to duplicate the in service conditions of a pump. This test was a measure of coating's wear/abrasion resistance under load and alumina slurry as well to bring about more abrasive conditions similar to a pump when put to service.

3.4 Experimental Procedure:

3.4.1 Test set-up

This test is known as block-on-ring for measuring the wear/abrasion resistance of thermal spray coatings deposited on cold rolled steel substrate. This test can quantify the amount of coating eroded from the substrate through comparison of mass of the specimen before and after the test.

The test set-up was an effort to simulate the in service test conditions of a pump so we can compare the different coatings and could quote the coating that best resists the harsh environments successfully and increase the life of a mechanical seal.

Below shown is a schematic diagram of the test set-up.

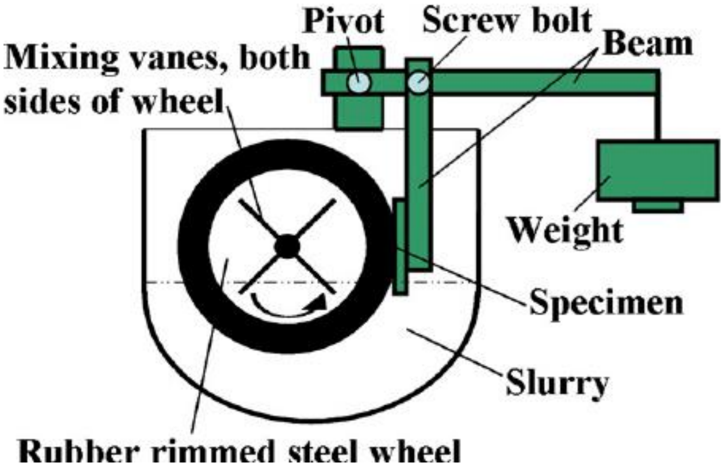


Figure 15: Schematic of test set-up (Earlier) (38)

3.4.2 Testing apparatus:

The figure below shows the actual model of the test set-up known as block-on-ring. The only difference between the actual test set-up and schematic is the way how the slurry is delivered. Earlier we followed the same test set-up as shown in schematics. The actual model of the earlier test set-up is as shown in the figure 17. The slurry delivery mechanism as shown in the schematic diagram above is rotating wheel is dipped into the alumina slurry and it takes the slurry with it to the interface between the ring and the specimen while rotating. The alumina slurry is quite thick and it usually tends to settle down in the container so it needs to be stirred continuously, either with the help of impellor blades as shown in the schematics or by keeping the slurry container over the magnetic stirrer as in our case. (Figure 17).

Unfortunately due to misalignment of the test set-up, especially the slurry delivery mechanism as described above was not giving proper results as the slurry was not mixing well. There was a problem with adjustment of the slurry container over the magnetic stirrer resulting in improper mixing of the slurry giving incorrect results.

The other problem encountered was with the size of the wheel rotating against the coated specimen. The size of the ring was so small that it could not dip properly into the pool of slurry. Hence, the height of the slurry container had to be raised by keeping some wood/plastic plank below it between its base and over the magnetic stirrer. This again reduced the magnetic stirring effect resulting in improper mixing of slurry.

Hence, considering all the problems, the test set-up had to be changed slightly in which just the slurry delivery mechanism was changed as shown in figure 18.

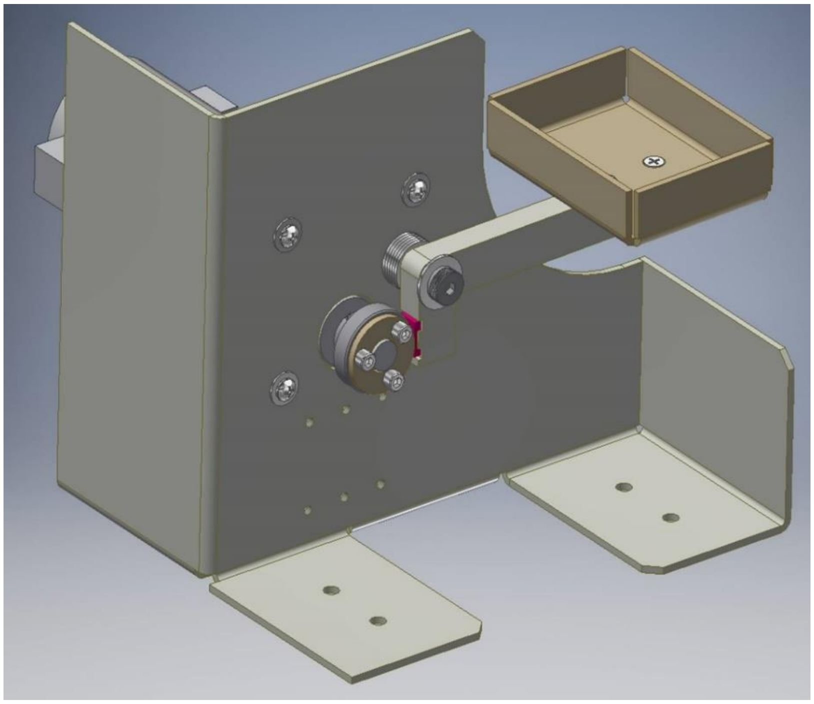


Figure 16: Actual model of the test set-up

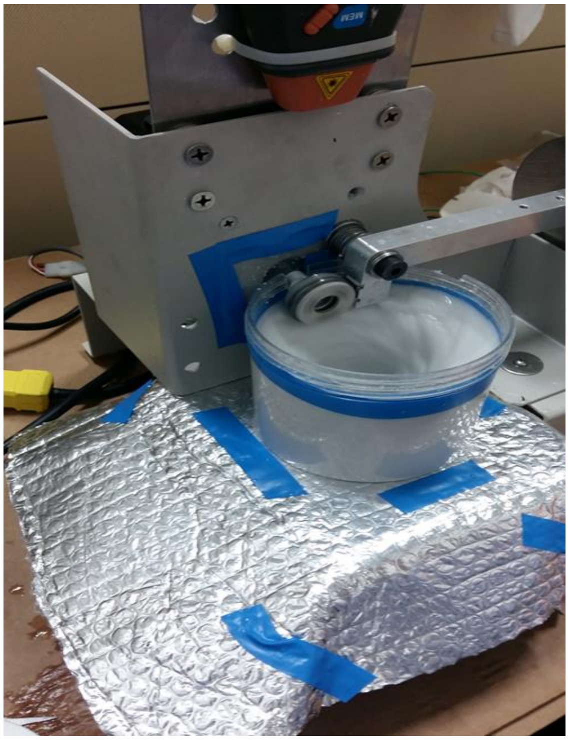


Figure 17: Actual test set-up (Earlier)

As shown in figure 15, slurry is delivered through a small hose pipe onto the interface of rotating wheel and the specimen surface. The hose pipe is attached to the slurry container which is kept over the magnetic stirrer for mixing. The slurry container must be kept exactly in center of the stirrer to get the maximum stirring effect. This is found experimentally. The magnetic stirrer is placed above a box as shown in the figure. This is to give some height to the slurry container with respect to the place where the slurry has to be delivered. This mechanism would make sure that the slurry gets the natural gradient and would flow easily without a need of any pumping mechanism.

A big container is kept below the rotating ring. This container collects the liquid (slurry) that falls from the hose. The slurry container may be refilled at regular intervals from the slurry that falls into the big container.

There is a motor mounted (attached) at the back side which rotates the ring. The ring is a bearing in our case which acts as a steel ring abrading the specimen tangentially. It is fixed against the shaft of the motor with the help of a coupler.

Figure 18: Actual test set-up (modified)

Tachometer was mounted above the shaft of the rotating wheel as shown in the figure 3. This was to measure the RPM of the wheel. Small 12×12 square of reflective adhesive tape was cut and sticked to the shaft of the motor. As the shaft rotated it could successfully measure its rotational speed (RPM) through laser.

The L shaped lever as shown in the figure 3 had a room (slit) made opposite to the rotating wheel to keep the specimen. On the other end of the lever, weights were put in order to load the specimen against the rotating wheel. This would bring about more wear/abrasion to the specimen. Obviously the amount of wear would increase as the load increases. Proper force acting on the specimen was calculated using following formula:

$$\boldsymbol{F = P \times LR}$$

Where $F = force\ acting\ on\ the\ specimen\ due\ to\ load\ applied$

$P = load\ \ (weight)\ applied\ on\ the\ end\ of\ the\ lever$

$LR = Lever\ ratio$

The space through which the shaft of the motor is coming out on the front side is covered by the plastic and taped. This is to protect the motor from getting wet by the liquid (slurry). One must make proper calculations regarding the torque acting on the motor otherwise the motor overheats which might create problems.

3.4.3 Standard Test Conditions:

1) Slurry composition:

Slurry is composed of fine alumina particles with particle size equal to 55-60 microns. 150 grams of alumina slurry is required per test & is mixed in 500 milliliters of distilled water. Hence, the abrasive weight ratio per test would be around 23 %.

2) Ring dimensions:

The rotating wheel is a roller bearing steel and has a slightly tapered geometry. The ring diameter is 35 millimeter and its width is equal to 8.7 millimeters. This rotating steel ring acts as a component that wears down the coated specimen.

3) Rotation speed of ring:

The ring is attached to a motor which rotates at a speed of 400 RPM. This speed was selected between the long ranges of speeds from 250-500 RPM which simulates the service conditions of a pump. The motor was connected to a regulator through which the speed of the motor could be changed.

4) Specimen Size:

Specimen was made of cold rolled steel whose dimensions were equal to 15mm×11mm×1/8inch.

5) Load applied:

The load applied at the end of the lever was equal to 1.45 pounds

6) Force acted on the specimen:

Force acted on the specimen by calculating the lever ratio is equal to 10 pounds. Calculation is as follows:

Here $LR\ (Lever\ ratio) = perpendicular\ distance\ from\ the\ pivot\ point\ to\ applied\ load/$ $Vertical\ distance\ from\ pivot\ to\ specimen$

$$= \frac{\mathbf{147.22}}{\mathbf{21.44}} = \mathbf{6.866}$$

According to equation of force:

$$F = P \times LR$$

$$F = 1.45\ pounds \times 6.866$$

$$\boldsymbol{F = 10\ pounds}$$

7) Torque acting on the motor:

Torque acting on the motor can be calculated by the following formula:

$$\tau = Force\ or\ load\ acting\ \times perpendicular\ distance\ of\ shaft\ from\ the\ specimen$$

$$\tau = 10\ lbs\ \times 17.5mm$$

$$\boldsymbol{\tau = 175\ lbs.mm = \ 6.89\ lbs.in}$$

Generally, motor must be selected keeping in mind the calculations of torque applied when highest weight is applied otherwise problem of overheating might take place.

3.4.4 Materials:

Four different types of coating systems were tested by the block-on-ring test set-up. All the coating systems were deposited on cold rolled steel (15mm × 11mm × 1/8in) and tested according to the test procedure mentioned in later paragraph. The samples were provided by Nevada Thermal Spray Technologies.

- **Tungsten Carbide/Cobalt (WC/Co)**
- **Boron Carbide (B_4C)**
- **Chrome Oxide (Cr_2O_3)**
- **Alumina (Al_2O_3)**

Table 4

Type of coating system	Method of spray	Thickness (Mils)	Density (g/cc)	Porosity (%) Approx
WC/Co (WC-88% & Co-12%)	HVOF	10 to 15	13.97	1
B_4C-200	D-gun	11	2.52	5
B_4C-300	D-gun	10	2.52	5
B_4C-400	D-gun	10	2.52	5
B_4C-500 (Cermet) (B_4C-80% & Co-20%)	D-gun	8 to 9	2.52	4
Cr_2O_3	Plasma spray	10	5.22	2
Al_2O_3	Plasma spray	9 to 11	3.95	2

Table 4 Different thermal spray coating materials with the specifications and properties

3.4.5 Materials Characterization

The microstructure and macrostructure of the coatings, feedstock materials and worn surfaces was analyzed in a light optical microscope. The characterization included measurement of the thickness of the as sprayed/as received coatings. Microstructural and macrostructural images of the worn surfaces of the coatings are shown later. (Fig 31-37) and (Fig 38-44) respectively. The coatings contained different microstructures which can be distinguished through the diversification of microstructural contrast.

3.4.6 Adhesive wear test (block-on-ring) procedure:

First test was carried out on uncoated cold rolled steel substrate to check the working of the test system and to know if there is considerable amount of mass loss that could be noted in terms of a proper result.

Firstly, the weight of the specimen was noted as the weight of the sample before the test. Here ring was getting abraded as well hence, the initial weight of the ring was measured.

The ring was attached to the coupler, and then the combined mechanism was mounted to the shaft of the motor. Proper care had to be taken in the adjustment of the ring over the shaft so that it would rotate smoothly without any wobbling effect. Otherwise it would not render proper results in terms of wear of the specimen. This was made sure by starting the motor and seeing the rotation of the ring without loading the uncoated steel specimen. Once, the rotation of the ring was checked, the specimen was loaded onto the slit made exactly to fit the specimen.

First set of tests were carried out in deionized water at room temperature. After pouring the deionized water into the smaller container, it was kept over the magnetic stirrer to maintain the optimum flow of water. Water was refilled during the test as needed. This was followed by switching on the magnetic stirrer to see its working. The hose pipe connected to the container was adjusted exactly over the interface of steel ring and the specimen as shown in the figure 15. As soon as the hose pipe is tapped down the water starts flowing. The lid of the container was closed in order to prevent the water from spilling out.

Finally the weights were attached to the end of the lever. This made the specimen to be in constant load/force while in contact with the ring. The motor was turned on and the regulator was adjusted so that the speed was maintained at around 400-425 RPM. The speed of the motor was checked at regular intervals during test by tachometer mounted over the rotating shaft as shown in figure 15.

After completion of the test, specimen and the ring was unloaded and properly cleaned with running water to remove all the traces of slurry from its surface. Proper drying of the specimen and the ring was carried out followed by measuring their weight. This was to quantify the wear of the material after test. Results were noted in terms of mass loss and are listed in later chapters.

The same procedure was carried out for all seven coating systems.

This was followed by preparation of slurry. 500 ml of water was poured into a container in which 150 g of alumina powder was added to prepare the slurry solution. It was properly mixed before pouring it into the smaller container through which the slurry was supposed to be delivered instead of deionized water. The wear tests were done in presence of slurry as well because the aim was to duplicate the service conditions of the mechanical seals where they are subjected to abrasive slurries.

The test was carried out for 5, 10, 15, 20 minutes with 10 pounds pressure. The results for the mass loss are shown in the later chapter. Plot of pressure versus time is as shown in figure 16. This was followed by testing at 5 pounds pressure for 20 minutes to measure the effect of prolonged time with lower pressure on mass loss. The tests with alumina slurry were carried out for 10 minutes with 10 lbs pressure. Table 5 shows the testing parameters for adhesive wear tests.

Table 5

Load applied	5 lbs, 10 lbs
Testing time	5,10,15,20 minutes
Motor speed (RPM)	400-425
Temperature	Ambient room temperature
Fluid	Deionized water, alumina(slurry)
Mass loss measurements	Cleaning, drying, measurements after every test

Table 5 Testing parameters for block-on-ring tests

3.5 Results

3.5.1 Microstructure of as-received coatings

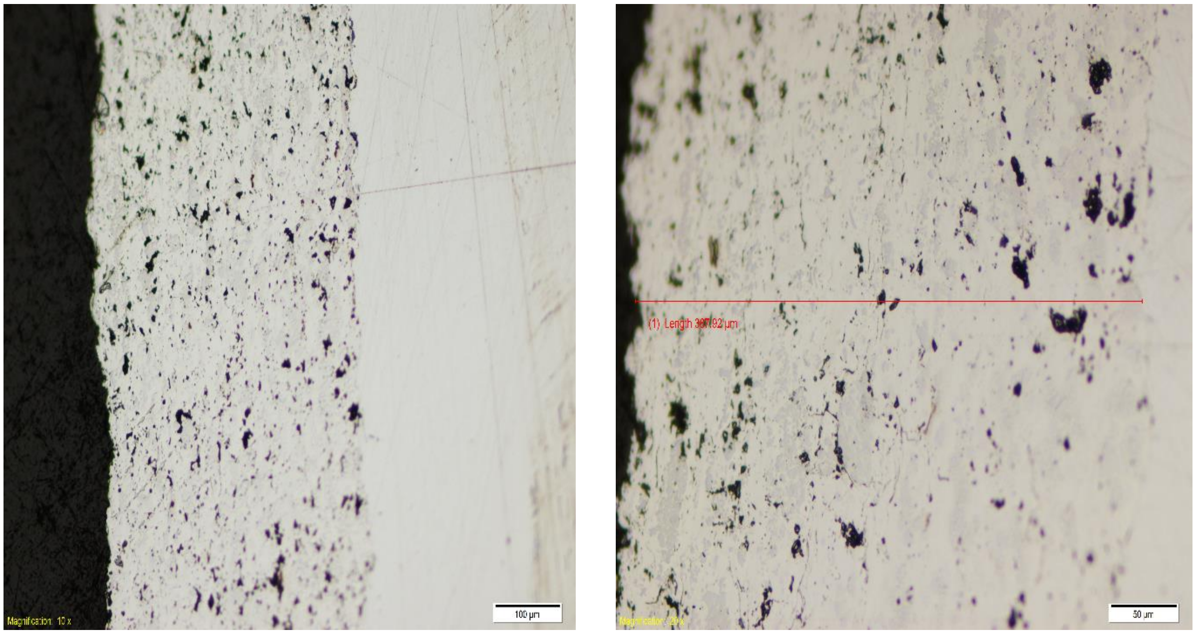


Figure 19: WC-Co Coating

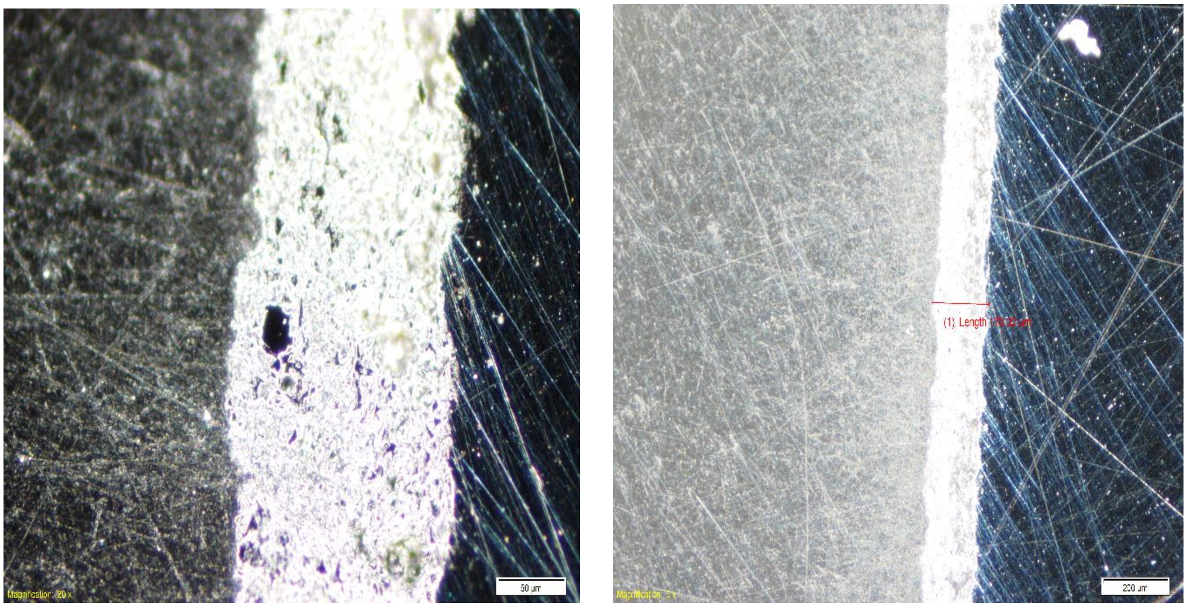


Figure 20: B_4C-200 Coating

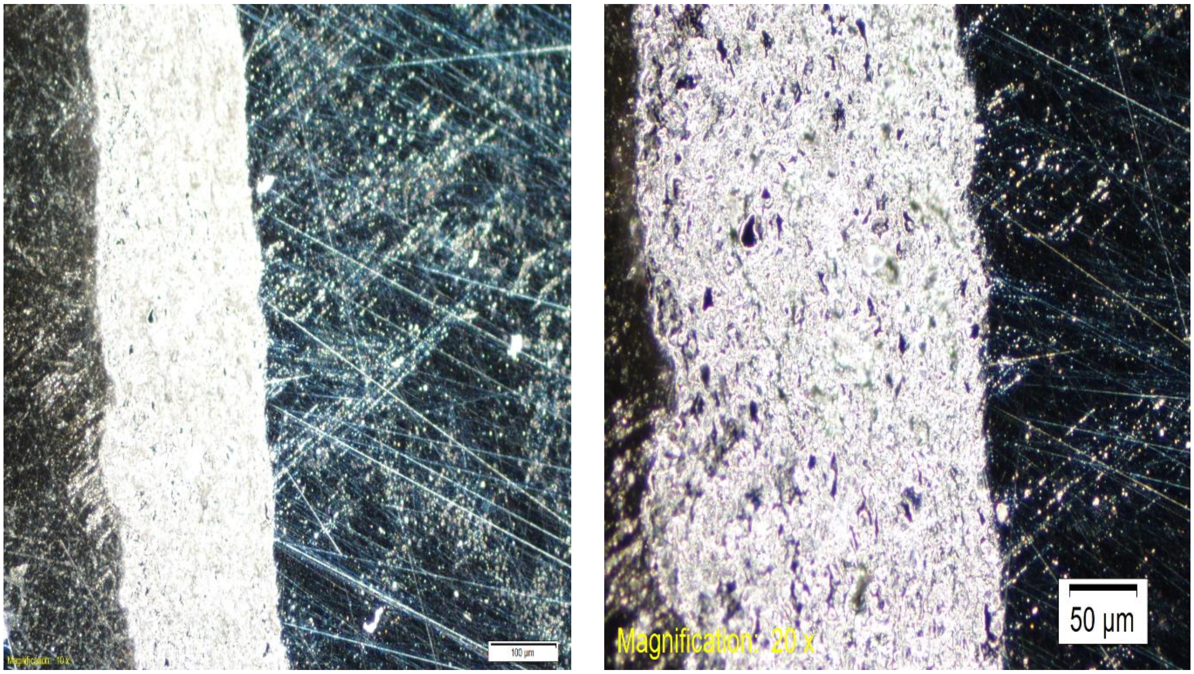


Figure 21: B_4C-300 Coating

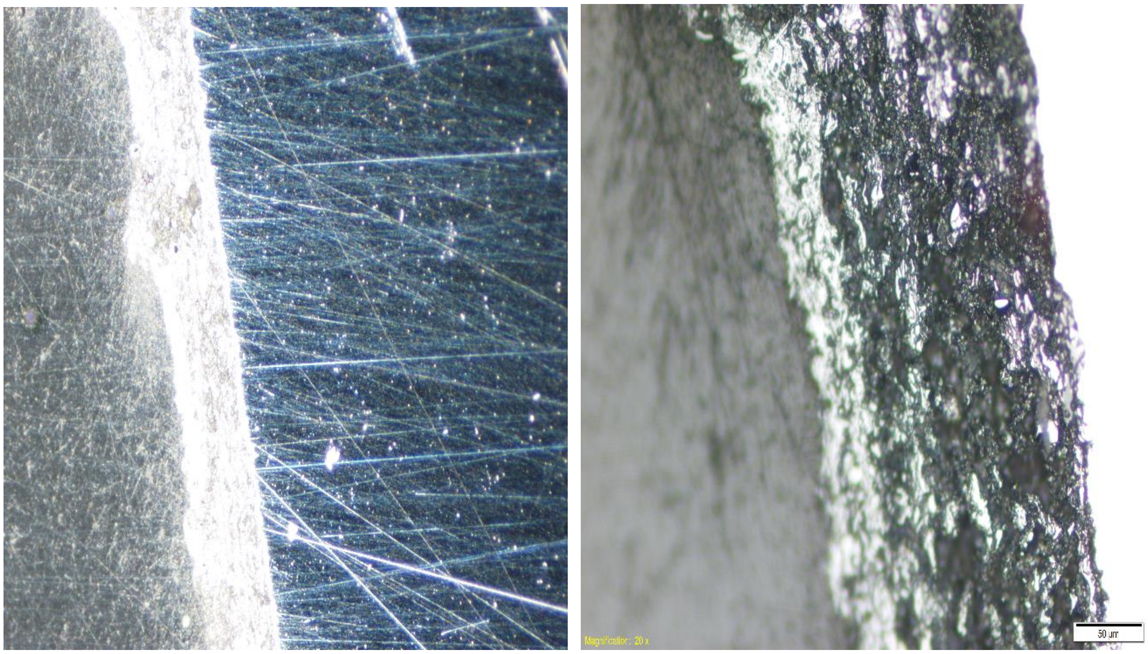


Figure 22: B_4C-400 Coating

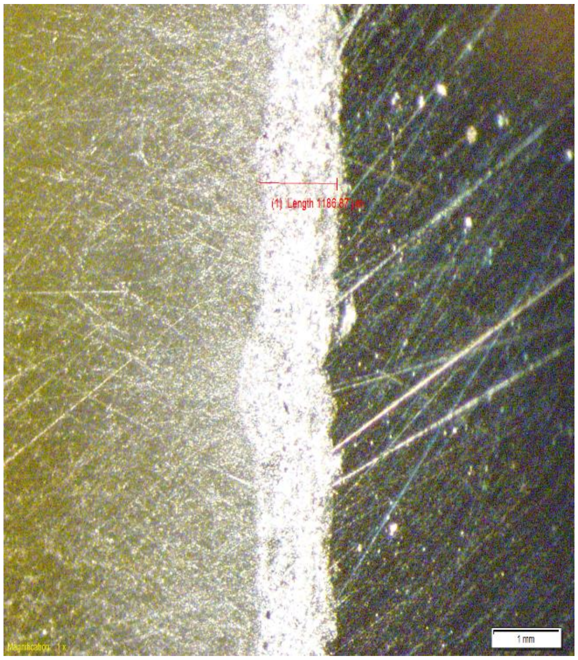


Figure 23: B_4C-500 Coating

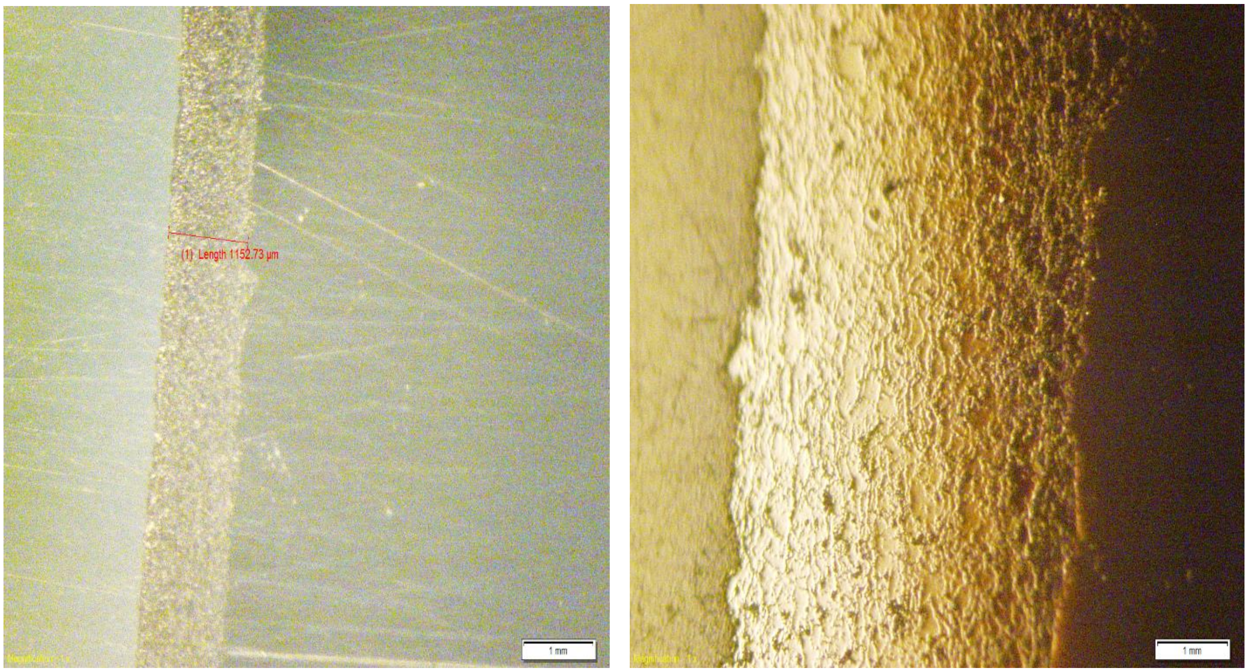


Figure 24: Cr_2O_3 Coating

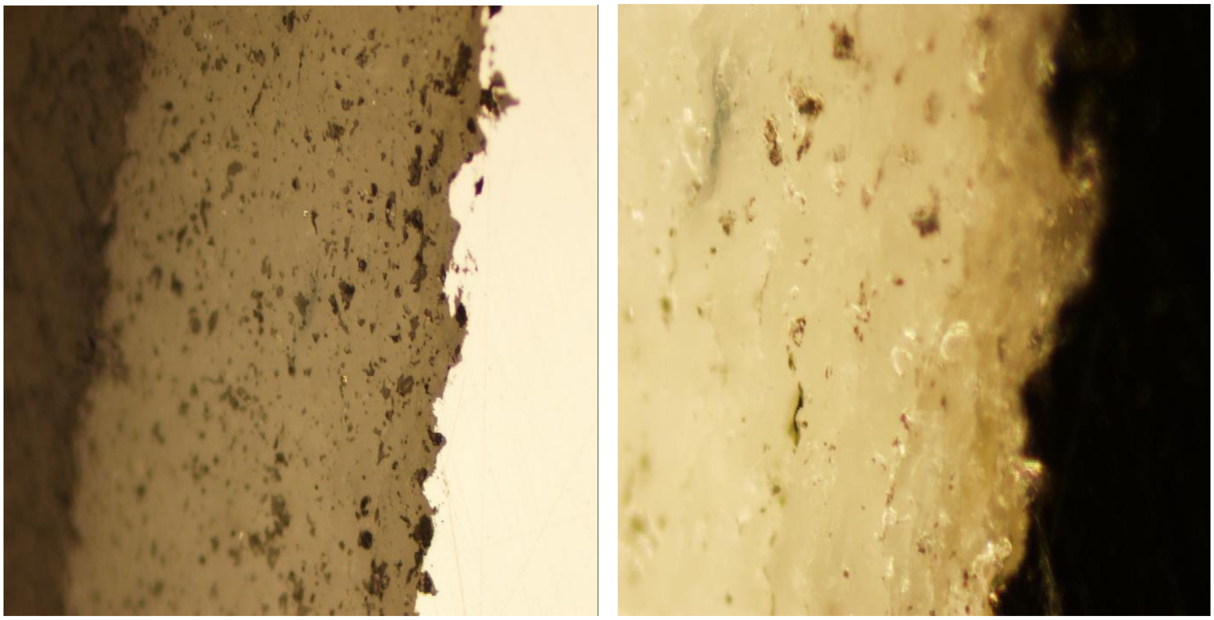


Figure 25: Al_2O_3 Coating

3.5.2 Adhesive wear test with deionized water at room temperature:

Figure 26 below shows the volume losses measured after adhesive wear test in deionized water for 10 minutes under 10 pounds load. Also, table 5 below shows the results of the tests conducted at different times with constant load of 10 pounds. The volume losses follow a linear relation with respect to time in early stages but it roughly follows the polynomial fit of second power following a quadratic approximation (Fig 29). The mass losses were converted to volume losses to get accurate wear loss data. We need to consider the density and porosity of the materials as well. Hence, volume losses would give us more accurate results rather than mass loss.

As it can be seen from the results (fig 26) tungsten carbide-Cobalt (WC-Co), showed the lowest volume loss compared to all thermal spray coatings followed by Chrome oxide (Cr_2O_3) and Alumina (Al_2O_3). B_4C-300 series showed the highest volume loss followed by B_4C-400 series amongst Boron Carbide coatings.

Amongst all the four boron carbide coatings, the one with metal (Cobalt) with 20% volume showed the best results; i.e. lowest volume loss. This may be due to the presence of cobalt metal that acts as a binder that increases the bond strength of B_4C coating.

WC-Co produced the best results. It has thought that superior hardness and wear resistance are brought to the coating by high volume percentage of tungsten carbide, fine grain size of WC, and also the tough matrix phase of cobalt in comparison to other WC coatings.

It greatly depends upon the applied pressure which certainly dominated the wear rates.

For applications demanding adhesive and abrasive wear (Slurry) which is often in case of mechanical pumps, tungsten carbide/cobalt offers best wear resistance in all conditions based on testing conducted in this experiment. The sole aim was to duplicate the service conditions of a mechanical pump. This is 88% WC and 12% Co which offers the best wear resistance and has successfully performed during service according to several reports. It seems that 88-12 WC-Co performs best when run against steel but, cannot be employed if both the mating parts are made of WC-Co. This would cause high galling and coating failure. (39)

Boron Carbide coatings showed the highest volume loss and large scar width as well. Large scar width indicates that this material would deform or wear much quicker than the others. It is more fragile and less dimensionally stable under loading, implying more rapid loss of tolerances between the rotating and stationary rings in a pump.

This may be due to high porosity i.e. low bond strength between particles or very weak particle to particle bonding. According to the definition of thermal spray: “Any material can be thermally sprayed unless it decomposes after heating”. In case of Boron Carbide after heating, carbon phase falls apart from the coating in the form of loose powder. Hence, the overall coating gets too porous giving highest wear loss.

However, a reduction of porosity could probably result in an increase of wear resistance due to high hardness of boron carbide. This is showed and experimentally proven through an experiment in the current program, where the testing of B_4C-500 (Cermet) shows lower volume loss because of the presence of Cobalt metal binder.

Below shown are the results for the first run of the tests with the following parameters:

1) Rotational speed of the ring: 400-425 RPM
2) Time: 10 minutes
3) Pressure: 10 pounds
4) Temperature: Ambient room temperature
5) Slurry: None (Deionized water)

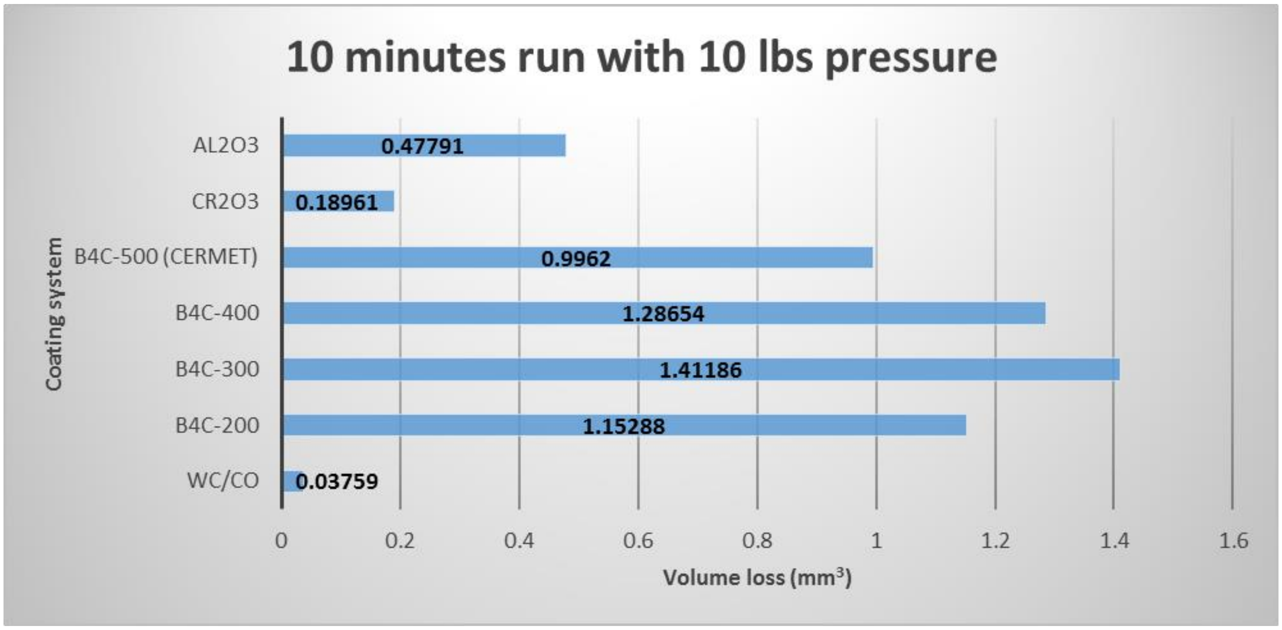


Figure: 26 Volume loss of specimen in cubic millimeter after 10 minutes with 10 pounds load

Below shown are the results for the second run of the tests with the following parameters:

1) Rotational speed of the ring: 400-425 RPM
2) Time: 20 minutes
3) Pressure: 5 pounds
4) Temperature: Ambient room temperature
5) Slurry: None (Deionized water)

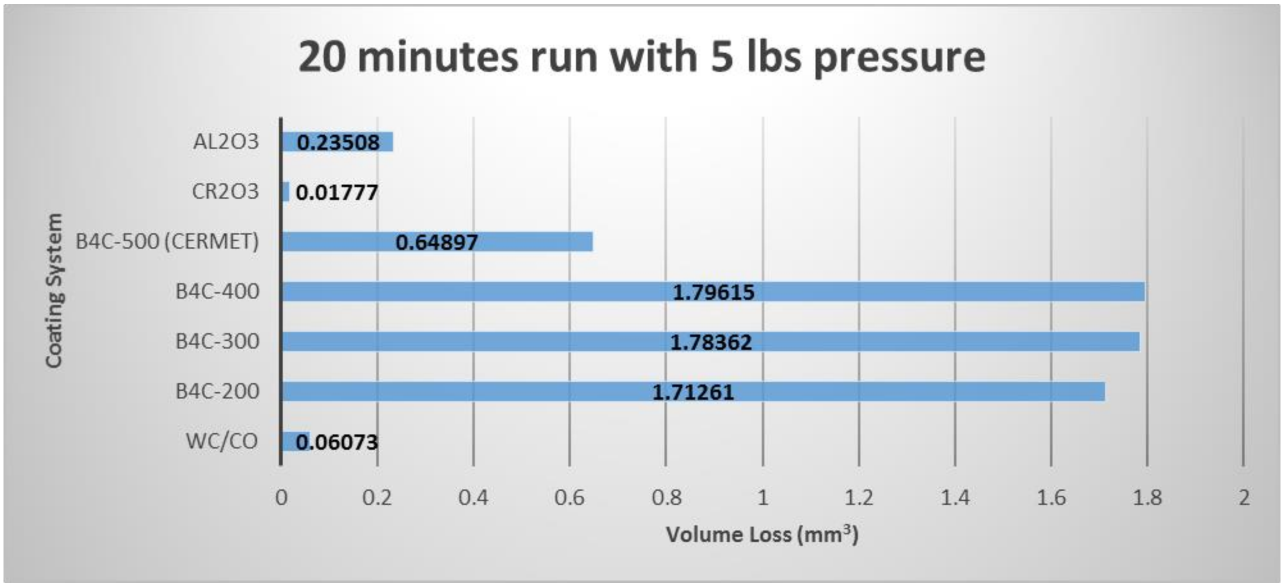


Figure: 27 Volume loss of specimen in grams after 20 minutes with 5 pounds pressure

Below shown are the results for the third run of the tests with the following parameters:

1) Rotational speed of the ring: 400-425 RPM
2) Time: 5 minutes
3) Pressure: 10 pounds

4) Temperature: Ambient room temperature

5) Slurry: None (Deionized water)

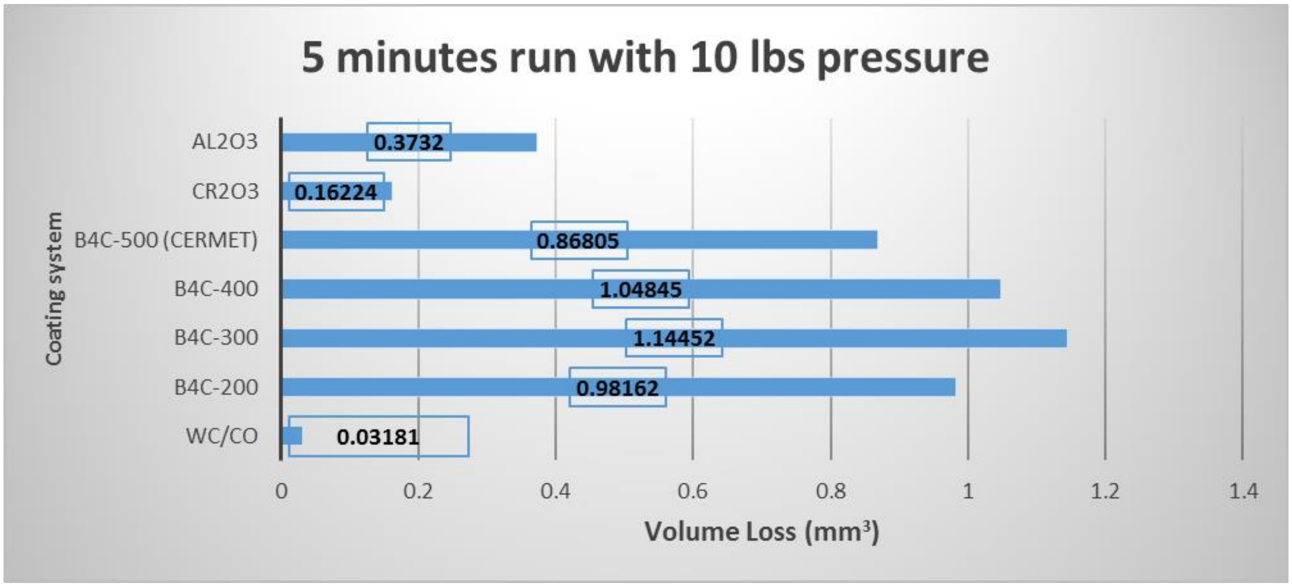


Figure: 28 Volume loss of specimen in grams after 5 minutes with 10 pounds load

Below shown are the results of volume losses over different time intervals at constant load.

Table 6

Time (Minutes)	WC/Co	B_4C- 200	B_4C- 300	B_4C- 400	B_4C- 500 (Cermet)	Cr_2O_3	Al_2O_3
5	0.03181	0.98162	1.14452	1.04845	0.86805	0.16224	0.3732
10	0.03759	1.15288	1.41186	1.28654	0.9962	0.18961	0.47791
15	0.03976	1.4035	1.59983	1.48705	1.20701	0.27367	0.56316
20	0.0535	1.80451	2.03	1.89223	1.57903	0.35968	0.84732

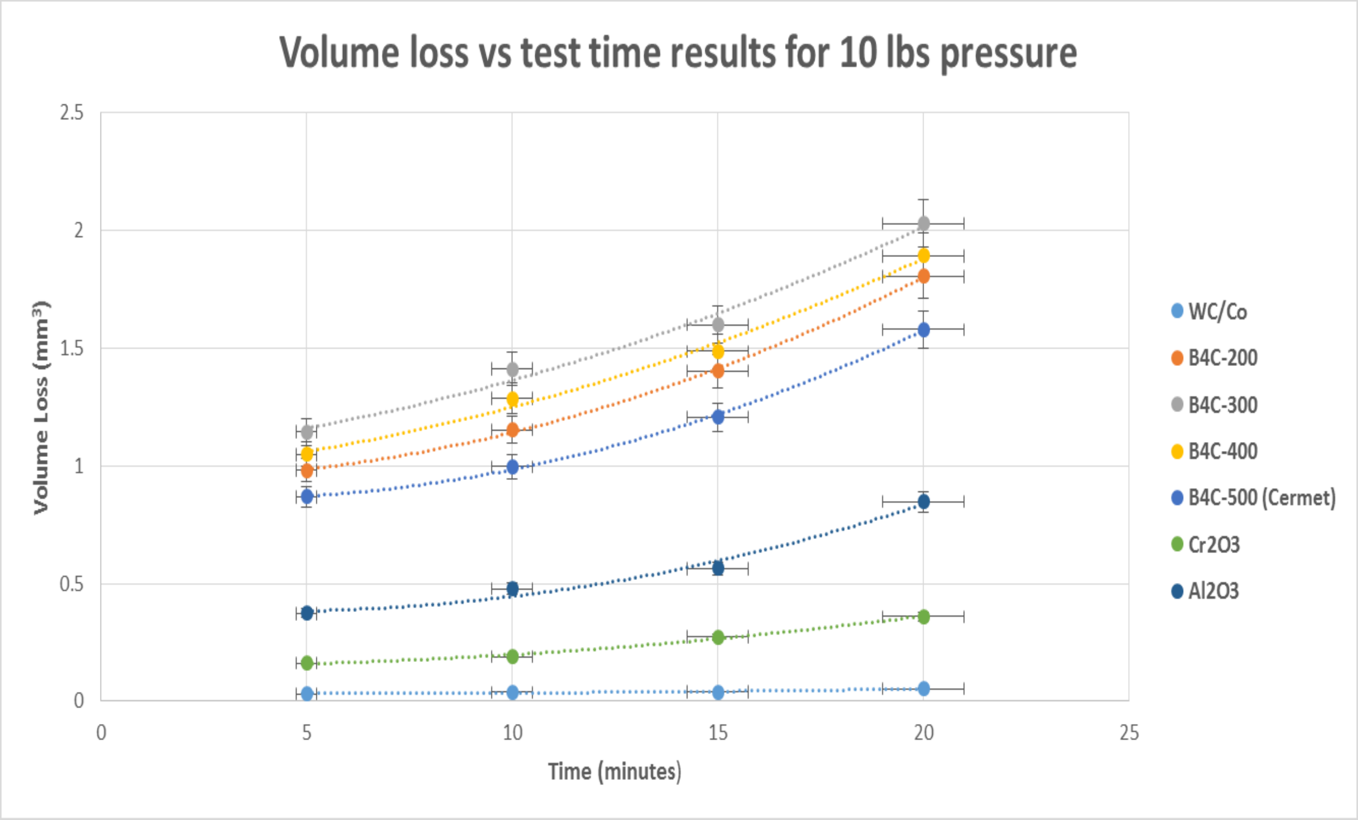


Figure 29 Volume losses in cubic millimeter with constant load (10 lbs) as a function of testing time

3.5.3 Adhesive wear test with alumina slurry at room temperature:

Alumina slurry with particle size 50-55 micron was used as abrasive medium to measure the volume losses of the coatings at 10 lbs load for 10 minutes. The concentration of slurry was 50 grams per every 150 milliliters of deionized water.

Figure 26 shows the volume losses measured after each adhesive wear test in alumina slurry. As expected, the volume losses were much higher compared to in deionized water. This clearly shows that an abrasive medium (alumina slurry) has much more damaging effect in terms of material loss compared to deionized water.

As it can be seen from the results (fig 26) tungsten carbide-Cobalt (WC-Co), showed the lowest volume loss and outperformed all the other thermal spray coatings followed by Alumina (Al_2O_3) and Chrome oxide (Cr_2O_3). Also as expected, boron carbide had the worst results in terms of mass loss/volume loss.

While it is not listed in the results, there has been research done on WC-Ni coatings instead of WC-Co where Nickel metals replaces Cobalt and gives anti-corrosive properties to the coating system. Nickel is much more chemical resistant than cobalt and hence does not get affected by the caustic, high/low pH abrasive slurries. But cobalt being an excellent binder it is extensively used with WC in pumps seals. For anti-corrosion, chemical resistance, chromium and its alloys are generally taken into consideration.

Below shown are the results of fourth run of tests with the following parameters:

1) Rotational speed of the ring: 400-425 RPM
2) Time: 5 minutes
3) Pressure: 10 pounds
4) Temperature: Ambient room temperature
5) Slurry: Alumina (55 micron)

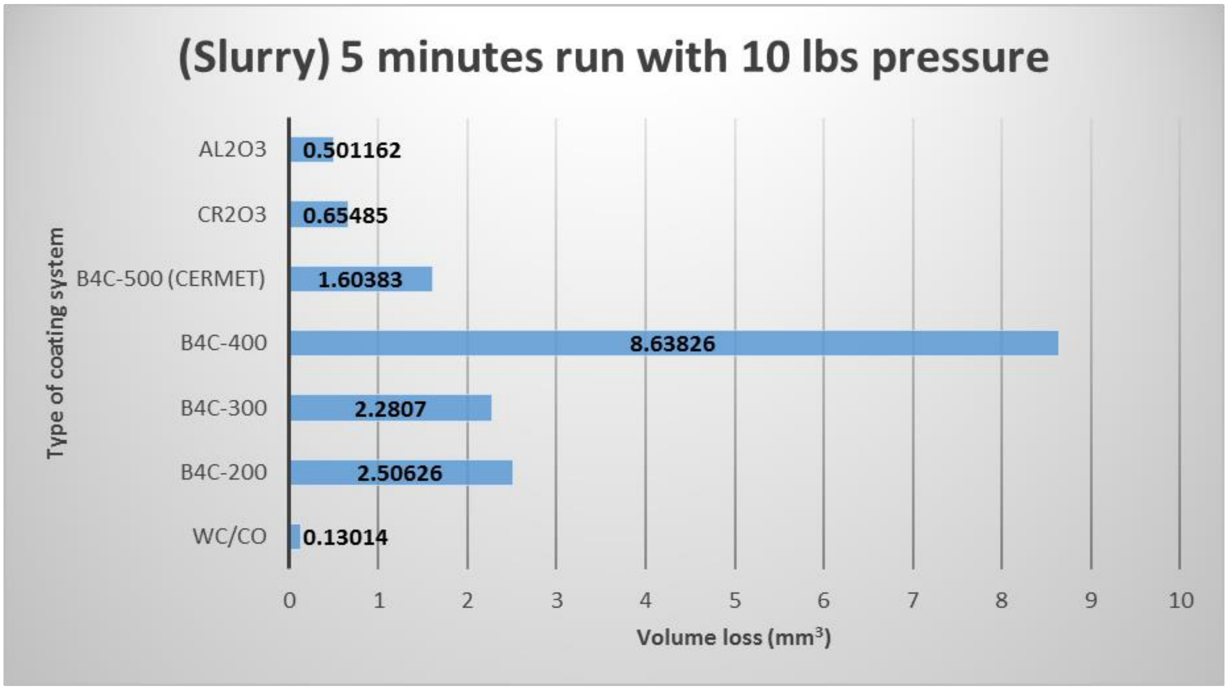


Figure: 30 Volume loss of specimen in cubic millimeter after 5 minutes under 10 pounds loads in presence of alumina slurry

3.5.4 Analysis of worn surfaces and identification of wear mechanisms in adhesive wear test with deionized water at room temperature:

3.5.4.1 Microstructural Images of worn surfaces

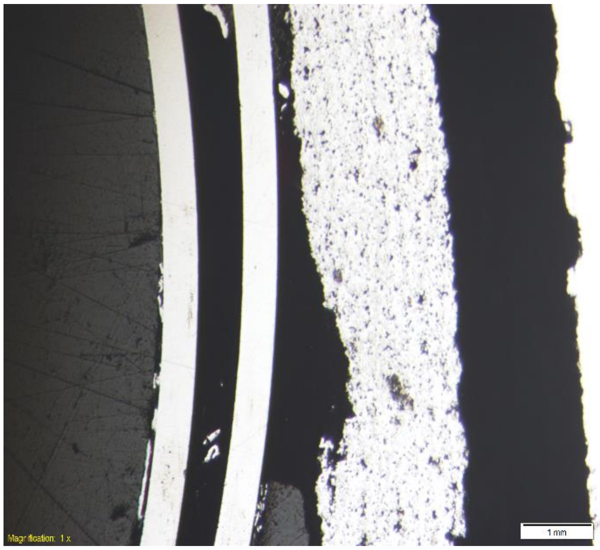


Figure 31 WC-Co Coating

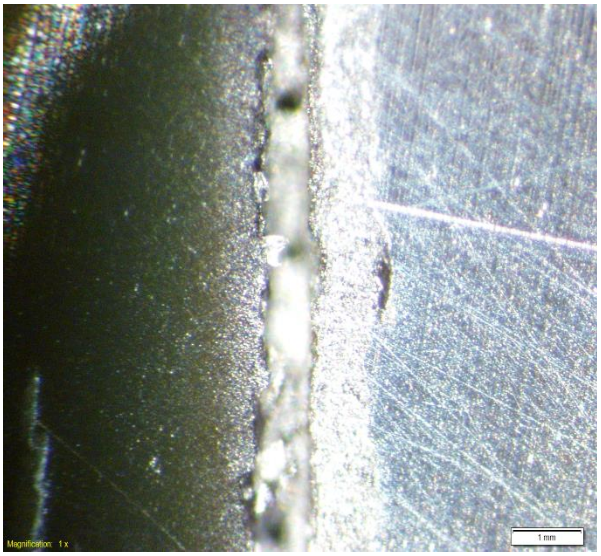


Figure 32 B_4C-200 Coating

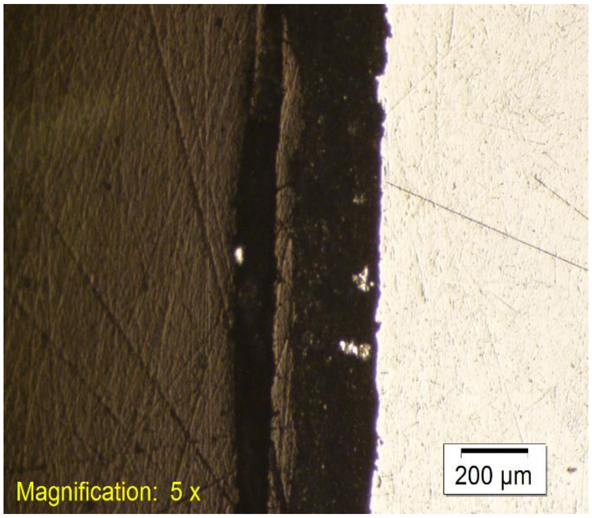


Figure 33 B_4C-300 Coating

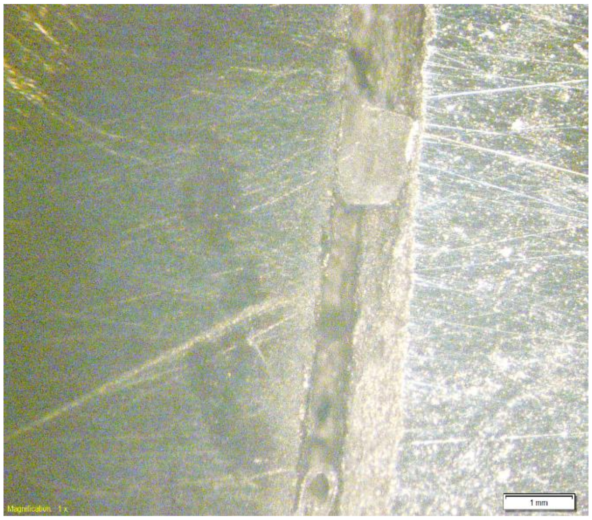


Figure 34 B_4C-400 Coating

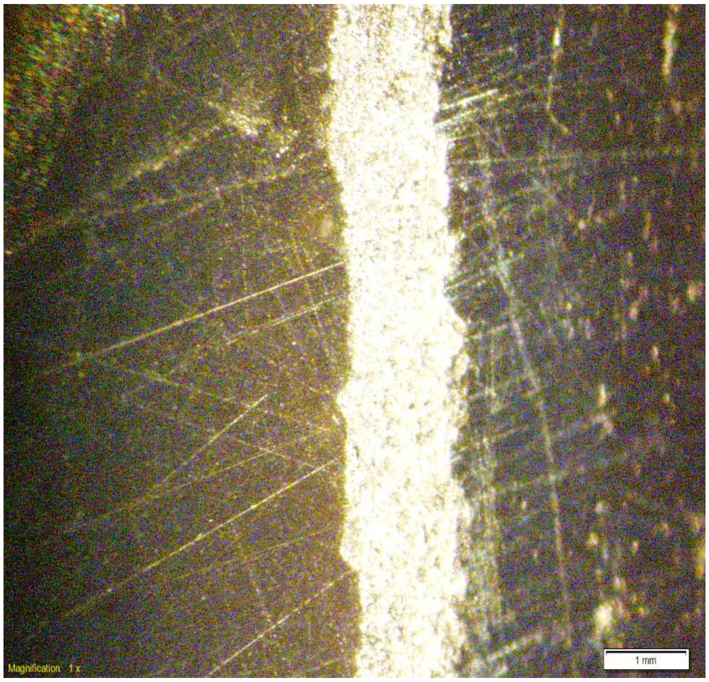


Figure 35 B_4C-500 Coating

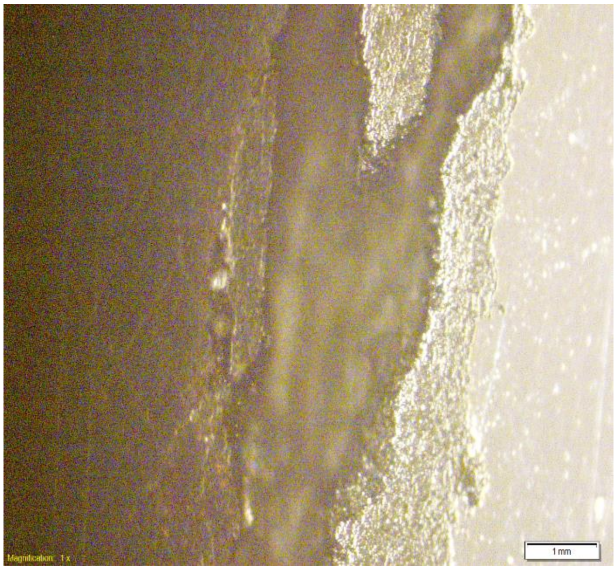


Figure 36 Cr_2O_3 Coating

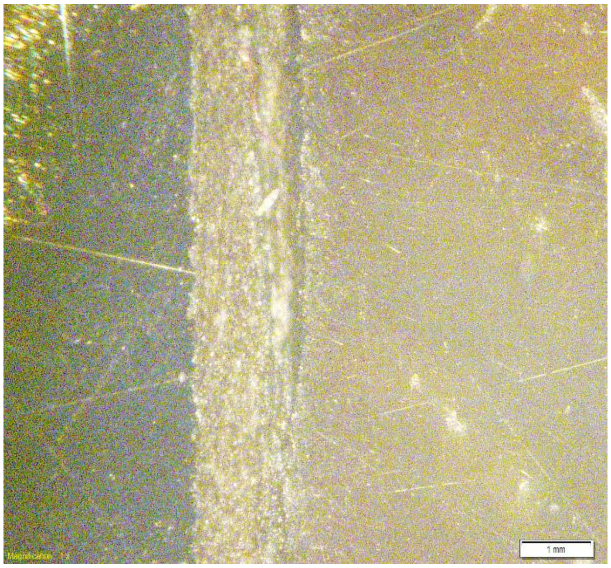


Figure 37 Al_2O_3 Coating

3.5.4.2 Macrostructure images of worn surfaces

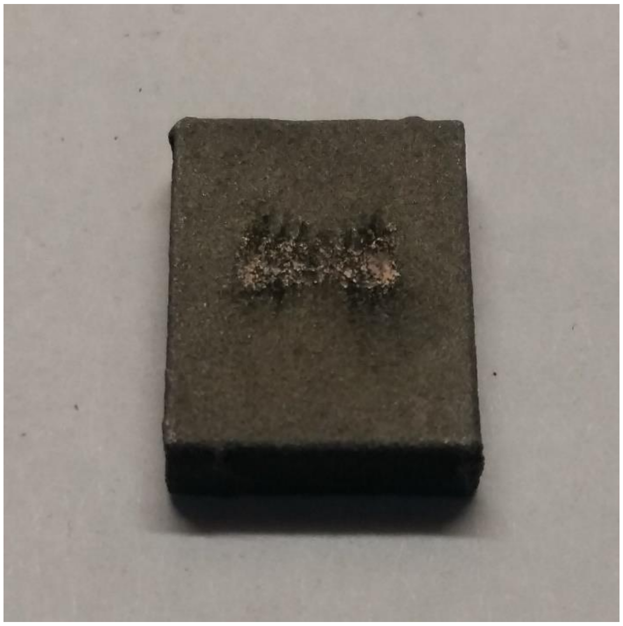


Figure 38 WC-Co Coating

Figure 39 B$_4$C-200 Coating

Figure 40 B$_4$C-300 Coating

Figure 41 B$_4$C-400 Coating

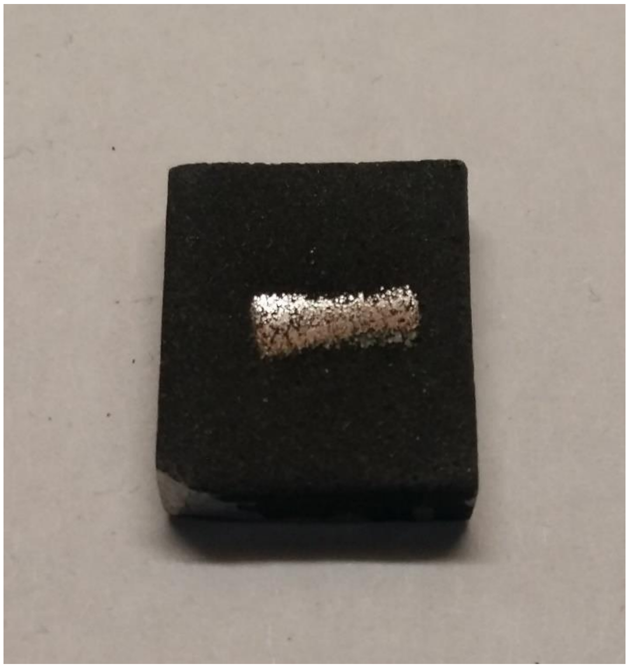


Figure 42 B_4C-500 Coating

Figure 43 Cr_2O_3 Coating

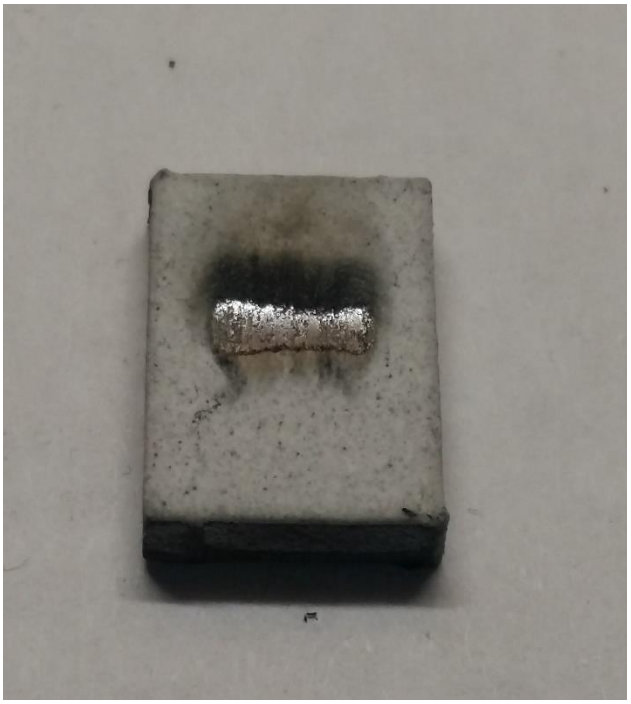


Figure 44 Al_2O_3 Coating

3.6 Discussion

According to the macroscopic test data obtained (Fig 38-44), it can be said that the scar width of the Tungsten Carbide-Cobalt (WC-Co) is smallest amongst all coatings followed by the Chrome Oxide (Cr_2O_3) and Alumina (Al_2O_3) which supports the experimentally found data of volume loss.

Although, by looking at the shiny part on the surface of the specimens (Fig 38-44) it looks like the wear scar has got down to the substrate, but the microscopic images (Fig 31-37) show that the coating has not been entirely chewed up by the wear mechanism and has not got down till the substrate.

The shiny part in the macroscopic images constitutes a very thin microscopic stainless steel layer which has been stuck on the surface of the specimen during the operation. This might be probably due to the heat produced by the friction between the mating surfaces (stainless steel ring and the specimen) during the test. This phenomenon can be seen prominently with boron carbide coatings (Fig 32-34) where one can clearly see two distinct phases in coating after the wear test.

There was a direct correlation observed between the thickness of the coatings and its wear resistance property. As it can be clearly seen from the microstructural images of boron carbide coatings (Fig 32-35), the thickness of B_4C-200 (11 mils) coating was the highest amongst all and it had highest wear resistance compared to B_4C-300 and B_4C-400. Thinner coatings are somewhat more defective, because the flattening of cermet particles impacting onto substrate surface is restrained by the deformation of the surface itself, so that the particles retain small pores. Thicker coatings, are denser because, as a new layer is deposited, the high velocity impact of the particles forces the previously deposited material with high pressure and densifies it. Also (40) new particles can flatten more efficiently, as they impact on a much harder surface (the previously deposited coating layers); therefore, the new coating layers are less defective than the first ones.

Table-5 shows that the volume losses increase linearly with time and follows the polynomial fit of second power with quadratic relation. This shows the amount of load is a prominent factor that determines the measure of volume loss. The results obtained for 5 pounds and 20 minutes (Fig 27) were unexpected and are not very definitive.

The wear test carried out in the presence of an abrasive (Alumina) (Fig 30) shows that volume losses are higher compared to the test carried out in the deionized water with all the other conditions same. Tungsten Carbide- Cobalt (WC-Co) outperforms every other coating followed by Alumina (Al_2O_3) and Chrome Oxide (Cr_2O_3). This data supports the claim that the hardness of alumina (9 on Mohs scale) is higher than Chromium oxide (8-8.5 on Mohs scale) and hence, it wears down Chromium oxide more than that of Alumina, and we get higher volume loss for chromium oxide in the presence of alumina slurry. But, the hardness of Tungsten carbide particles (9-9.5 on Mohs scale) is higher than alumina abrasive particles, hence, the wear loss is much lesser, so we get lowest volume loss for Tungsten Carbide-Cobalt (WC-Co) in presence of alumina slurry.

3.7 Summary and Conclusion

The goal of this test was to measure the abrasion/wear resistance of different systems of thermal spray coatings for the application of mechanical seals used in various pump industries.

This was done by building up a machine according to the ASTM G77 test standards (block-on-ring) test set-up that measures the adhesive/sliding wear resistance of thermal spray coatings with and without the presence of abrasive slurry (alumina in current program). This machine was built in order to duplicate the pump's service condition so we could get the perspective of the best coating in the required conditions.

The test study shows that Tungsten Carbide-Cobalt (WC-Co) with 88% WC and 12% Co offers the highest abrasive/wear resistance followed by Chrome oxide (Cr_2O_3) and Alumina (Al_2O_3) in deionized water i.e. without the presence of abrasive slurry. This data is supported by the macroscopic images of the specimens which shows that the scar width of Tungsten Carbide-Cobalt (WC-Co) is smallest followed by Chrome oxide (Cr_2O_3) and Alumina (Al_2O_3). Boron Carbide (B_4C-200,300,400) set of thermal spray coatings offers lowest wear/abrasion resistance due to high porosity (poor particle-particle bonding); which had the largest scar width. Amongst boron carbide thermal spray coatings, B_4C-500 (Cermet) comprising of 80% B_4C and 20% Co offers the highest wear resistance. This is due to presence of binder metal (Cobalt) which binds the loose boron carbide particles.

Tungsten Carbide-Cobalt (WC-Co) with 88% WC and 12% Co outperforms every other coating in presence of alumina slurry as well, followed by Alumina and chromium Oxide. Alumina offers higher wear resistance than Chrome oxide as its hardness is almost equal to the slurry and higher than chrome oxide. The volume losses follow a linear relation with respect to time in early stages but it roughly follows the polynomial fit of second power following a quadratic approximation

While, the wear does not reach up to the substrate level, it does reveal some shiny silvery part on the surface of the specimen. The silvery shiny part is revealed by optical microscopy to be a thin layer of stainless steel which is stuck on to the coatings due to heat produced by the friction between the mating surfaces.

Also, it was found through the materials characterization in light optical microscopy that thickness of the coatings has a direct correlation with their wear resistance. As the thickness of the coatings increases, their wear resistance also increase.

Chapter IV

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