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Abrasive wear behaviour of engineering materials and coatings

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More than half of the industrial wear situations are predominantly abrasive in nature. To withstand the extremities of such conditions, considerable strength is required on the surface layers to resist the imposed loads, in combination with suitable bulk hardness and toughness, which is required to prevent bulk failures.

Due to stringent requirements on material surfaces, which is where the interactions with abrasives occur, and the emergence of new challenges in surface engineering, the present work has been undertaken to study the abrasive wear behaviour of selected engineering materials such as monolithic SG irons, stainless steels and high chromium irons (cast and heat treated), ceramics such as zirconia and alumina, and thermally sprayed tungsten carbide-cobalt (WC-Co) coatings applied by the High Velocity Air Fuel (HVAF) process, using powders from two sources.

The effect of low stress and high stress abrasive wear on the monolithic materials and coatings was studied, by using a three body rubber wheel abrasion tester and a two body pin-on-drum tester. The interrelationship between microstructure and abrasive wear was established by microstructural characterization carried out using X-ray diffraction, optical microscopy and scanning electron microscopy. The WC-Co coatings were characterized to study the effect of starting powders on the coating quality. This prompted further investigation towards understanding the WC-Co coating system, and finding ways to improve the coating quality and performance through study of the effect of chamber pressure on the coatings.
The present study showed that the alumina ceramic had the best low stress abrasion resistance followed by zirconia. Chromium irons in the heat treated condition, provided excellent abrasion resistance, due to the precipitation of dispersed secondary M3C carbides, but the heat treatment is expensive. The present study also confirmed that the application of thermally sprayed (WC-Co) coatings on stainless steel using the HVAF process, provided superior abrasion resistance. Among the materials investigated in two body high stress abrasive wear, chromium iron in the heat treated condition provided the best abrasion resistance to abrasives, silicon carbide, alumina and garnet. The WC-Co coating sprayed at 45 psi chamber pressure from both powder sources, was investigated for two body abrasion for silicon carbide abrasive. It was observed that the coatings provided better abrasion resistance than heat treated chromium irons, and one coating designated JK112 was superior to the one designated WOKA.

The HVAF process, is superior to the HVOF process reported in the literature, since the HVOF process results in detrimental phase transformations occurring within the thermal stream, leading to decarburization products being formed within the coating. It was observed that the HVAF process results in minimal decarburization and leads to maximum retention of fine grain tungsten monocarbide in the coating, which is the necessary condition for good abrasion resistance. It was also found that higher chamber pressures lead to higher particle velocity, which subsequently enhances the coating density and results in improved abrasion resistance. Hence, the present work justifies the industrial usage of WC-Co coatings to provide high quality resistance to abrasive wear.
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INTRODUCTION
INTRODUCTION

The phenomenon of wear (which can be defined as the loss of material from two surfaces in relative motion across a common interface) is encountered in many situations ranging from household appliances to industrial machinery. Despite the general acceptance of this definition, the precise nature of the mechanisms governing the wear behaviour of materials is not fully understood. Wear is not a material property; it is a system property effected by a multitude of parameters, both intrinsic and extrinsic, which collectively dictates the behaviour of a particular system.

In modern societies, where mechanisation is indispensable, wear inevitably leads to a huge expenditure on maintenance and replacement of industrial equipment, together with a subsequent loss of production due to down time. In environmentally conscious, developed countries, minimising wear is of paramount importance due to the changing pattern of modern society from a disposable to a more conservationist approach (1).

Wear occurs through complex processes, involving inter-alia, surface chemistry, machine dynamics, time-dependent triaxial state of stress, and plastic flow in a highly localised zone. Due to these complexities, various anomalies are found in wear related failures, which can be gradual or catastrophic (2).

Mechanical abrasive wear is defined as damage to a solid surface by a progressive loss of material. It occurs due to the relative motion between two contacting surfaces. Wear may be divided into various categories, including, adhesion, abrasion, fretting, corrosion and erosion. Adhesive wear occurs when two smooth surfaces slide over each other under pressure, providing intimate contact between asperities. Bowden and Tabor (3) suggested that the asperities become welded together, leading to fracture.
Erosive wear occurs by impingement of particles on the surface, resulting in deformation and material removal. Abrasive wear occurs when hard particles or protuberances are forced against, and move along, a solid surface. Fretting wear occurs due to the oscillatory motion of two mating surfaces under load, manifesting itself as surface damage surrounded by oxidised debris. Corrosive wear occurs due to chemical reactions involving the formation of new substances. These substances are partially distributed on the surface of the material. This material surface (or subsurface) fails during rolling, sliding and repeated impacts. During the application of low stresses, numerous pits or cavities occur on the metal surface. Most industrial wear situations are a combination of those previously mentioned, and are very rarely due to one mechanism (4).

There is a strong economic and environmental incentive to reduce energy consumption and material loss. A high level of research effort is required to reduce wear and it is important to select the right materials to provide an adequate wear life. Research efforts are being focused on improving the surfaces of materials, since they play a major role in determining the wear behaviour in a contact system.

A number of techniques have been applied to counteract the tribological problems of materials. One technique requires the application of hard "wear resistant" coatings on metal substrates. Techniques such as electroplating, flame spraying, plasma spraying, ion implantation, and ion beam mixing are commonplace. The choice of the coating and technique, is usually dictated by matching the application requirements to the physical properties of the coating. The durability of a coating under wearing conditions depends to a large part on its mechanical properties, microstructure, and how well it adheres to the substrate (5).

The primary purpose of this thesis is to study the abrasive wear behaviour of a range of engineering materials which include; monolithic stainless steels, cast irons, high
chromium irons and ceramics such as alumina and zirconia. The work was extended to include cermet coatings deposited by the high velocity air fuel process. A surface modification method has been proposed in this thesis after studying the abrasive wear behaviour of monolithic materials. This method involves the application of a thermally sprayed tungsten carbide/cobalt coating on stainless steels. The application of such a coating greatly improves the abrasion resistance of materials. Various methods are available for spraying tungsten carbide/cobalt. In the present work, thermal spraying was utilised using the high velocity air fuel process, which is presently a state-of-the-art spraying technique. The thesis also discusses the microstructural characterisation and correlates the effects of varying the spraying parameters on the microstructure, mechanical properties and wear resistance of WC-Co coatings.

The abrasion tests carried out in this work are two-body high stress and three-body low stress abrasion. Chapter 2 contains an indepth review on abrasive wear, its classification, and how microstructure of the materials affects abrasive wear behaviour. Section 2.2, provides a review on high chromium (28%) irons, which are usually the most effective abrasion resistant alloys, used by industry. Section 2.3 presents various surface modification methods which are in current use to combat wear. In Section 2.4 thermal spraying is reviewed as an effective surface coating method. Section 2.5 reviews the principles and advantages of the high velocity oxygen fuel process, and Section 2.6 presents a detailed discussion on the tungsten carbide-cobalt system. In Chapter 3 experimental work, conducted during the course of this study, is presented and in Chapter-4 results of the various abrasive wear tests done on monolithic and coated materials are presented. This chapter also contains, results of the characterisation done on tungsten carbide/cobalt starting powders, and the resultant coatings after thermal spraying. Chapter 5 provides a discussion on the wear mechanisms of monolithic materials when subjected to high stress and low stress abrasion (a wearing correlation with the microstructure has been sought). The chapter also highlights the various detrimental phases present in the tungsten carbide coatings,
and underlines the effects of varying the spraying parameters to improve coating quality. Finally, Chapter 6 provides a conclusion on the work carried out so far on the abrasive wear behaviour of the engineering materials and coatings.
CHAPTER-2

LITERATURE REVIEW
LITERATURE REVIEW

2.1 ABRASIVE WEAR AND ITS CLASSIFICATION

Abrasive wear is one of the most critical and costly problems faced by industrialised economies. Abrasive wear costs the industrial nations 1-4% of their Gross National Product. It normally occurs in mining, earthmoving, mineral beneficiation, rock drilling, agriculture, and machines such as, chutes, hydraulic systems with dirt, extruders, rock crushers, dies in powder metallurgy, and so on, in which materials containing an abrasive particle are processed. Abrasive wear is defined as the wear due to the penetration of hard particles or surface asperities of one solid into the surface of a softer solid, during sliding contact. This results in the ploughing or cutting of material from the softer surface (6).

The abrasive wear processes are traditionally divided into two major groups - two body and three body abrasive wear. Two body abrasion is mainly encountered in material removal operations, while three body abrasion is mainly found in agriculture and industrial equipment. In two body abrasive wear, a rough surface or fixed abrasive particles slide across another surface removing material in the process. In three body abrasive wear, loose particles move relative to one another, and possibly rotate, while sliding across the surface and removing material in the process. Wear volume is about one to two orders of magnitude smaller in three body abrasion, than in two body abrasion.
The phenomena of two and three body abrasion is illustrated in Fig. 2.1.

![Diagram showing two body and three body abrasive wear](image)

Fig.2.1. Diagram showing two body and three body abrasive wear (28).

### 2.1.1 TWO BODY ABRASION

Two body abrasion occurs through various mechanisms, and causes damage to the surfaces through processes such as scratching, plastic deformation and cutting. Khruschov and Babichev (7) suggested that the two processes which take place during wear are:

- formation of plastically impressed grooves with no metal removal, and
- formation of microchips due to metal removal.

It is observed that some abrasive grains merely make elastic contact with the surface (8-10). Some researchers (11) found that the inclination of the cutting face and its orientation are critical in determining the chip formation. The critical angle, in turn, depends on the material under wear and is determined by the coefficient of friction between the contacting surfaces, which in turn depends on the particle shape (12).
2.1.1.2 MECHANISMS OF TWO BODY ABRASIVE WEAR

In practical situations the wear of a material under a two body regime is a complex phenomenon. Several types of wear processes appear to be operating simultaneously. The main mechanisms leading to material removal are usually identified as microploughing, microcutting and microcracking as shown in Fig 2.2.

Fig 2.2 Diagram showing interaction between abrasive particles and material surface (28).

2.1.1.3 MICROPLoughING

During microploughing, the material is plastically deformed and displaced to the sides forming ridges along the grooves. The material removal takes place through a low
cycle fatigue, with many abrasive particles acting simultaneously. Microploughing may often accompany the cutting action, or it may be a precursor to microcracking (13).

2.1.1.4 MICROCUTTING

During microcutting the material is removed, in the form of wear debris as microchips. The volume of material removed is equal to the volume of wear groove produced, under the pure microcutting action. This process is similar to mechanical machining, where ribbon like chips are the products of the cutting action. Mulhearn, Samuel and Sedricks et al (14-16) proposed that material detachment takes place during microcutting, only when the attack angle of the hard abrasive particle is greater than a critical angle. This critical angle is a function of the test conditions and the wearing material.

2.1.1.5 MICROCRACKING

During microcracking, highly concentrated stresses are imposed upon the abrasive particles leading to the formation and propagation of cracks. This type of wear is usually accompanied by a large amount of wear debris becoming detached from the surface. The wear volume is generally larger than the groove volume and is strongly influenced by material properties such as fracture toughness, and hard phase distribution. Zum Gahr (28) states that brittle materials such as steels with a martensitic structure undergo microcracking.
The ratio of volume of material removed as wear debris to the volume of wear groove is known as $F_{ab}$ as shown in Fig 2.3.

$$F_{ab} = \frac{A_V - (A_1 + A_2)}{A_V}$$

Where:

$A_V$ = Area of groove volume.

$(A_1 + A_2)$ = Areas of material pushed to the sides by plastic deformation.

For ideal microploughing to take place $F_{ab} = 0$, and for ideal microcutting to occur $F_{ab} = 1$. Microcracking normally occurs in brittle materials for which $F_{ab} > 1$. For most other materials the value of $F_{ab}$ ranges from 0.15 to 1 (17).

It has been observed that microploughing and microcutting are the dominant wear mechanisms in ductile materials. Both these processes are associated with high
deformation and large strains on the worn surface (18-19). Zum Gahr (28) asserts that the transition from microploughing to microcutting depends on the properties of the worn metal and the operating conditions. Bowden and Tabor (20) consider that predominant microploughing changes to predominant microcutting as a result of the increasing hardness of the worn metal. A further increase in hardness results in a transition from microcutting to microcracking; as observed in very brittle materials where the plastic deformation zone exceeds a critical value, resulting in cracking.

2.1.2 THREE BODY ABRASION

Three body abrasion is also known as grinding wear, and it manifests itself in comminuting and grinding industries. In three body abrasive wear, the loose abrasive particles are trapped between two surfaces, and the two surfaces and the abrasive particles form the three bodies. It occurs under the conditions of low load and the wear is governed by the properties of the abrasive and the material against which the particles are rubbing. The hardness ratio of the abrading particles and the surface, is of critical importance during this process. For appreciable wear of the material to occur the abrasive must be harder than the material. The surface hardness is important too, in blunting the sharpness of the cutting points of the abrasive particles. Three body abrasion is again subdivided into "closed" and "open" types.

In a closed three body abrasive wear, loose particles are trapped between two rolling or sliding surfaces, which are close to each other. As a result, the particles indent and settle into a softer surface, subsequently causing abrasive wear. This type of wear situation resembles a two body situation in many ways. An example of closed three body wear is a Jaw Crusher shown in Fig 2.5.
Open three body occurs when two surfaces are far apart, or if only one of the surfaces is actively involved in the wear process. This type of wear occurs in many situations, and can be further subdivided into gouging, high stress and low stress (39).

Gouging occurs when coarse materials such as rocks, cut into a material and remove large amounts of material. It normally occurs in impact type pulverisers and shovels digging into rock piles. Extensive work has been done by the Climax Molybdenum Company by Borik and Diesburg (37). They observed that a small increase in carbon in the range of 0 to 0.8%, considerably improves the abrasion resistance. Beyond 0.8% the abrasion resistance increases slowly with the carbon content. Most austenitic manganese steels and chromium white irons fall in this area. Austenitic manganese steels are principally used for gouging wear conditions, due to their excellent toughness properties and good abrasion resistance.

Fig 2.5. a) open and b) closed three body abrasion (6).
2.1.2.1 High Stress Abrasion

A large tonnage of ferrous materials are consumed under the conditions of high stress, open three body abrasion in various grinding mills. Ball mills, which are normally used for grinding metallic and non-metallic minerals, account for a major portion of consumption. The mining industry has extensively studied the materials for grinding balls, using various testing procedures. For steel grinding balls of varying composition, the surface hardness and the microstructure strongly influence their properties (38). At a given microstructure the wear rate increases constantly with decreasing hardness. However, with different microstructures at the same hardness, there is a marked difference in the wear rates. It has been observed that untempered martensite or martensite tempered below 450°C, has the best wear resistance. Bainitic structures have similar wear resistance as tempered martensite, at the same hardness.

2.1.2.2 Low Stress Abrasion

The most common occurrence for this type of wear is in earthmoving, mining, agriculture and coal hydrogenation process. It is the commonly found abrasive wear in machine parts and is also the least understood. During low stress abrasion the imposed stresses do not exceed the fracture stress of the abrasive. Plastic deformation takes place with very little work hardening and the wear rates are low. In order to simulate industrial situations, a rubber wheel abrasion tester is commonly used to study low stress abrasive wear.

2.1.3 CORRELATION BETWEEN TWO BODY AND THREE BODY ABRASIVE WEAR

The two abrasive wear processes have many aspects in common.
2.1.3.1 Similarities

One of the most significant similarity is the wear resistance and the annealed hardness of the pure metals. For both two body and three body abrasive wear the relationship is linear. Another common factor is that in both the processes, an increase in hardness of the material by work hardening does not increase its abrasion resistance. It is also observed that the hardness of the abrasive has the same effect on both two and three body abrasion. If \( H \) is the hardness of the material and \( H_a \) is the hardness of the abrasive, wear rate is constant if \( H/H_a < 0.8 \), and is very low if \( H/H_a > 1.2 \).

2.1.3.2 Dissimilarities

For the two body abrasion the weight loss is generally found to be proportional to applied load, whereas for three body wear the weight loss first increases non-linearly with load and then increases linearly. During two body abrasive wear the wear rate is independent of the distance travelled and no incubation period is observed, whereas in three body abrasion there is an initial incubation period after which a steady wear rate is observed.

2.1.4 PROPERTIES INFLUENCING ABRASIVE WEAR

Wear behaviour of the materials is dependent on physical properties such as hardness, ductility, work hardening, mechanical instability, fracture toughness and on the microstructure of the materials.

2.1.4.1 INFLUENCE OF HARDNESS

Tabor (21) states that hardness is the most important mechanical property of a wear resistant metal. Even though the surfaces of some materials may be covered by hard
oxide layers, hard abrasive particles have a tendency to penetrate oxide layers. One such commonly found hard abrasive in many tribosystems is quartz sand. It has a hardness between 900HV to 1300HV, and it can abrade the hardest steels.

An abrasive is considered to be "Hard" if its hardness is 20% more than the hardness of the stressed material in the worn condition, and 50% more in the unworn condition. Work carried out by many researchers (22-25) proves that the wear resistance to hard abrasives substantially depends upon the hardness of the wearing material. However, hardness is only an indicator of abrasion resistance and materials with the same hardness have differences in their abrasion resistance. An increase in abrasion resistance with increasing hardness is greater for pure metals than for heat treated steels. At the same hardness, steels with higher carbon content will have a higher abrasion resistance.

Moore and Swanson (26) pointed out that the wear resistance of a material is more sensitive to the hardness of the worn surface than to the hardness of the unworn surface. This is due to work hardening which takes place during the plastic deformation which occurs during wear. As a result, the hardness of the bulk material sometimes fails to be a true indicator of abrasion resistance. Hardness can predict the wear resistance of a material if the ratio between microcutting to microploughing, ie the $F_{ab}$ value, is constant. Pure metals have a relatively good abrasion resistance due to their low $F_{ab}$ values. However, predeformation of materials to improve the abrasion resistance is not useful because deformation capability decreases with predeformation, resulting in an increase in $F_{ab}$ value. It is observed that work hardening occurs independently, with or without predeformation.

It is hence evident that abrasive wear resistance is not a simple linear function of the hardness of deformed and undeformed metals, but it depends on various other factors as well.
2.1.4.2 INFLUENCE OF WORK HARDENING & DUCTILITY

Many researchers agree that the hardness of the undeformed material cannot be used to predict abrasion resistance. Zum Gahr (28) agrees that materials showing low work hardening exhibit a low abrasive wear resistance, relative to their bulk hardness. Richardson (27) observed that the hardness ratio between the worn surface and the unworn surface is a measure of the work hardening due to abrasion. It is observed that work hardening influences both the width of the wear groove and the ratio between microcutting to microploughing. The groove width and the $F_{ab}$ value are found to decrease, with increasing work hardening during abrasive wear, for a given yield stress or bulk hardness.

Ductility which is defined as capability of deformation during abrasive wear, strongly affects the ratio between microcutting and microploughing. This ratio decreases with increasing ductility during cold rolling, tensile testing and during abrasion. Ductility is a very important factor in the abrasive wear of harder and more brittle materials (28).

2.1.4.3 INFLUENCE OF MECHANICAL INSTABILITY

Mechanical instability occurs due to structural changes which take place during mechanical action. Normally, austenitic steels are known for becoming thermally unstable and undergo stress or strain induced instability. Precipitation-hardened alloys in the underaged structure soften due to plastic deformation during abrasion. Hadfield manganese steels, which are well known for their high toughness and good abrasion resistance, also undergo a strain induced transformation from austenite to martensite during abrasion. Studies on manganese steels have showed that abrasive wear resistance increases strongly with volume fraction of unstable austenite. It occurs mainly due to the increased work hardening and high capability of plastic deformation.
during phase transformation, and also because of effects due to compressive residual stresses (28).

### 2.1.4.4 MICROSTRUCTURE AND WEAR INTERDEPENDENCE

Microstructures of engineering materials depend on various parameters during their processing history, such as composition, thermal, and mechanical treatments. A wide range of chemical compositions can [normally] be obtained by suitable alloying. The microstructure of materials is of significant importance and features such as inclusions during melting, second phases for hardening, matrix, crystal defects, and microstructural anisotropy, greatly influence their abrasive wear.

### 2.1.4.5 EFFECT OF INCLUSIONS

Most inclusions in metallic materials are compounds such as oxides, silicates, aluminates or sulphides and are usually present as idiomorphic or irregularly shaped regions. Elongated hard inclusions act as stress raisers in brittle materials. Studies carried out by Zum Gahr (28) on 0.94% carbon steel, to investigate the influence of alumina on abrasive wear revealed that with increasing alumina content, the abrasive wear also increases. Samples with larger alumina particles (70-200μm) in size, exhibit lower wear losses than smaller (<10μm) alumina particles. Evidently the presence of alumina is harmful, but the presence of larger alumina particles is less harmful than smaller particles.

### 2.1.4.6 INFLUENCE OF SECOND PHASES FOR HARDENING

Second phases such as precipitates in intermetallic compounds, or carbides in dispersion hardened alloys, are important for strengthening of materials, but are only moderately successful in improving the wear resistance. Studies done by Wilman and
Lin (29) showed that intermetallic precipitation leads to insignificant improvements in wear resistance, compared to transformation hardening.

2.1.4.7 INFLUENCE OF CARBIDES

Most wear resistant components contain carbides of different type, shape and volume. Usually 18 volume % carbides are present in tool steels, and about 45\% in chromium alloyed white cast iron. The indentation hardness of carbides is generally 3-4 times more than the matrix. The size, shape and bonding of carbides to the matrix is of a significant importance to abrasive wear. A matrix is normally considered soft when its hardness is much lower than that of the carbides. It is found that carbides embedded in a soft matrix substantially reduce the abrasive wear loss (30-32).

High Cr-Mo white cast irons are well known for their low wear loss. They are commonly used in slurry pumps, mill liners, liner plates and other parts of the mining and earthmoving equipment's. Their high wear resistance is mainly due to the large primary or eutectic carbides of the \((\text{Fe, Cr})_7\text{C}_3\) type, which is usually present in a predominantly austenitic or martensitic matrix. An increase in the volume of massive carbides results in an increase in the hardness of the irons.

Zum Gahr et al (33) studied the effect of carbide volume and matrix structure of Cr-Mo white cast irons, on the resistance to abrasive wear. They observed that at lower carbide content, austenitic white irons show lower wear loss than martensitic irons. The martensitic structure is favourable for irons containing large carbide volumes. They also observed that the austenitic structures result in lower wear losses, when the structure is susceptible to work hardening, and partially transforms to martensite during abrasion. Hence, a metallurgically metastable matrix is preferred for reducing wear.
Investigations by Zum Gahr (28), on the effects of type of abrasive on wear loss showed interesting findings. Wear loss caused by softer abrasives such as 80 mesh flint and 80 mesh alumina, decreased with increasing carbide content in the steel. Conversely, wear loss was found to increase with increasing carbide volume, when hard SiC particles were used. Zum Gahr explained that this phenomenon was due to the change in wear mechanism from microploughing and microcutting, to microcracking, with increasing hardness of the abrasive. It was observed that when the hardness of the abrasive exceeded the hardness of the massive carbides by 20%, spalling of the carbides took place.

Fig 2.4. Diagram showing abrasive wear volume loss and hardness of white cast irons as a function of volume of massive carbides (28).

A wet rubber wheel test conducted by Borik (34) on white cast irons, Fig 2.4, showed that the wear loss of austenitic and martensitic irons decreased to a minimum with increasing carbide volume upto 10%. Beyond this amount, the abrasive wear loss increased, due to microcracking and spalling of the massive carbides. For the same
carbide volume, grooving was found to be deeper for austenitic than for the martensitic structure. At 10% carbide volume a deep groove was observed, at 30% it was shallower, and at 41% carbide volume, pits were formed due to pull out of the massive carbides.

2.1.4.8 INFLUENCE OF MATRIX.

The abrasive wear resistance of a multiphase structure usually depends on the properties of the matrix, the properties of the constituents embedded in the matrix, and the interaction between all the phases involved.

The stacking fault energy is particularly significant for abrasion resistance. Materials with a low stacking fault energy favour inhomogeneous slip, consequently leading to microcutting becoming the dominant wear mechanism. Nickel has a high stacking fault energy and it shows a substantially higher abrasion resistance.

With increasing carbon content there is a tendency towards decreasing abrasive wear loss. Studies done by Diesburg and Borik (32) showed that abrasive wear loss is strongly dependent on carbon content in the range of 0 to 0.8%. Moore (25) suggested that a slight increase in carbon content substantially decreases the abrasive wear loss. However above 0.8%, the abrasive wear decreases slowly with increasing carbon content. It is thus observed that the abrasive wear loss does not linearly depend on the carbon content, but it is the microstructure that determines the wear resistance.

Spheroidal carbide, resulting from the tempering of martensite has a better ductility than the spheroidized ferrite-pearlite structure, due to the uniform distribution of carbide in its structure (35). Larsen Badse and Mathew (36) revealed that work hardening increases in the sequence ferrite, to spheroidized pearlite, to lamellar pearlite,
and abrasive wear resistance of lamellar pearlitic steels is higher than that of spheroidized pearlitic steels.

At a given hardness, the bainitic structure shows a lower wear loss compared to the tempered martensitic structure. This is because tempering of martensite results in a decrease in the matrix hardness, subsequently leading to an increase in the wear loss. The better wear resistance in bainitic steels is also due to the high volume fraction (upto 20%) of retained austenite, compared to (6%) in tempered martensite. However, retained austenite is harmful, if abrasive wear is accompanied by impact or fatigue.

It has been largely observed that abrasive wear resistance increases in the sequence: martensite > martensite + cementite > pearlite > pearlite (lamellar) + ferrite > spheroidal cementite + ferrite > ferrite. At a given hardness, austenite exhibits better wear resistance than ferrite-pearlite, and bainite exhibits better wear resistance than martensite-cementite. It is observed that wear resistance of martensite increases with increasing hardness and is further enhanced by alloying, or by carbides such as M7C3, M3C and MC. Metastable austenite is also very effective in reducing abrasive wear, if it is able to transform to martensite during abrasion.

2.2 HIGH CHROMIUM IRONS

High chromium irons have a distinct advantage in abrasive wear applications (39). Their composition is adjusted so that they contain moderate amounts of chromium, and yet, solidify to produce massive chromium rich carbides, in an austenitic matrix with a reasonably good hardenability. They are transformed into martensite with simple heat treatments.

Chromium bearing white irons are extensively used on an ever increasing scale, and complicated heat treatments need to be carried out to provide the structure with first
rate abrasion resistant qualities. Studies of the structure in the as cast condition is therefore particularly important, since the as cast structure defines the heat cycle necessary to be responsive to heat treatments (40).

The three major advantages of chromium in cast irons is, a) formation of carbides, b) to impart corrosion resistance, and c) to stabilise the structure for high temperature application. Chromium < 10% stabilises the pearlite in the grey iron and influences the fineness and hardness of the eutectic carbides. When chromium is greater than 10%, eutectic carbides of type M7C3 are formed, and there is a significant change in the solidification pattern. The M7C3 carbides are surrounded by an austenitic matrix or its transformation products (41).

Avery (42) points out that the wear resistance of high chromium white irons is due to M7C3 chromium rich carbides. These carbides although have a high level of hardness, are brittle, and the degree to which they are supported by the matrix determines their cracking ability during abrasion (43).

The carbide volume fraction plays a significant role in determining the abrasion resistance. Fulcher (44) studied the wear resistance of hypo and hypereutectic cast irons using two different abrasives, quartz and alumina. Alumina which has a hardness of approximately 2000kgf/mm², is comparable to the hardness of the M7C3 carbides in white irons. Quartz on the other hand has a hardness of 1000 kgf/mm², and is softer than the carbide. It was observed that with increasing carbide volume fraction in the hypoeutectic alloys, there was an increase in the wear resistance, for both the abrasives. The retained austenite matrix in the hypoeutectic alloy was preferentially removed during wear testing, and the hard eutectic M7C3 carbides stood out in relief. The wear resistance of hypoeutectic alloys was found to increase with chromium and carbon additions.
For hypereutectic alloys, a trend of decreasing wear resistance with increasing carbide volume fraction was observed, due to cracking of the massed primary carbides. Diesburg and Borik (45), also found that fine eutectic carbide structure induced by the high solidification rate, decreased the wear resistance of white irons, proving that carbide morphology is also important along with the carbide volume fraction, for wear resistance.

Karl Zum Gahr (46), studied the influence of matrix structure on the abrasive wear of 28% chromium iron. He mainly studied the austenite and martensite matrix structure. The austenitic condition was achieved by stress relieving the as cast structure at 200°C for 2 hours, and the martensitic condition was achieved by heat treating the as cast irons at 900°C for 5 hours, followed by forced air cooling to room temperature. This was followed by a refrigeration operation twice to -78°C, and a stress relief operation at 200°C for 2 hours.

The abrasive wear loss was found to be greater for the austenitic matrix, than for the martensitic matrix. It was also found that the abrasive wear loss decreased to a minimum upto 30% carbide volume, and beyond 30% carbide volume the abrasive wear loss increased. It was also observed that grooves on the worn surface were deeper in the austenitic structures than in the martensitic structure. Also, shallow grooving pits were observed in both austenitic and martensitic structures, which were essentially due to the carbide pullout.

Gundlach and Parks (47), investigated the influence of abrasive hardness on the abrasive wear resistance of high chromium irons. Their results indicated that the hardness and type of abrasive, were significant factors influencing the abrasion resistance. The pearlitic 20% chromium iron had the lowest wear resistance, regardless of the abrasive used. They found another interesting phenomenon, that the order of resistance to abrasion for as cast austenite and heat treated martensitic irons changes
with the type of abrasive, particularly the hardness of the abrasive. When abraded by garnet, the martensitic irons showed greater resistance to abrasion than the austenitic irons. It was also seen that for abrasives softer than the primary carbides, austenitic irons had the greatest abrasion resistance. This is presumed due to the high degree of strain hardening or strain induced transformation of the austenitic matrix.

Studies done by X.H Fan et al (48), on the three body abrasion resistance of high chromium martensitic irons showed that lower the carbon content of the martensitic matrix, better is its impact fatigue resistance. Some of the interesting features of the austenite matrix are a) it exhibits a higher toughness against single blow impact, b) it has a higher dynamic fracture toughness, and c) it has a better static fracture toughness. The plasticity of austenite provides a good resistance to crack propagation. The binding force at the carbide-austenite interface is larger than the carbide-martensite interface, which consequently reduces crack propagation. Some of the ill effects of austenite, though, are the lower hardness of retained austenite which results in spalling.

Norman (49) points out that when high chromium irons are used as balls in ball mills, the repeated impact and the resultant work hardening causes the retained austenite at the surface to transform into martensite. Due to this transformation, compressive stresses are induced on the surface and the transformed austenite is restrained from expanding. Due to these compressive stresses, triaxial tensile stresses are developed on the subsurface, causing severe spalling during service. Some of the common problems of the grinding balls, which are normally made of high chromium cast irons, are the dangers of impact loading and spalling. This leads to high rates of material loss.

Cox (50) states that a full martensite matrix, free of retained austenite is desired to avoid spalling under repeated loading. It has been proved that the impact fatigue resistance is increased with decreasing carbon content in the martensite matrix, and with decreasing retained austenite. In a low carbon martensite the substructures are
mainly of dislocation types, with lath like morphology. In high carbon martensite, the substructures are normally needles and have many microcracks at their junctions. During repeated impact loading, these microcracks join together to form macrocracks. This phenomenon does not take place in a low carbon martensite owing to its dislocation substructure, which leads to a higher plasticity. The presence of retained austenite however reduces the hardness of the matrix. This leads to a higher spalling tendency owing to its work hardening ability.

Quindre Zhou (51) and other researchers found that 28% chromium irons, which are the most widely used materials, in slurry pumps, fail prematurely due to corrosive-abrasive wear. However, in specified media with appropriate pH values, they can exhibit corrosion-abrasion resistance. Boron addition is found to considerably improve their abrasion corrosion resistance. The addition of boron increases the hardness of the carbides in 17% Cr white cast irons, upto 2000-2700HV, and martensite appears in the as cast condition.

2.3 SURFACE ENGINEERING

The interaction of materials with the environments begins at the surfaces, and much attention is being paid since the last decade to develop, modify, and improve the surface properties of the materials (5). Surface engineering encompasses a wide range of generic technologies, the common factor of which is to improve wear, corrosion, fatigue and biocompatibility of the surface.

The chief aim of surface hardening is to improve the wear resistance of parts without affecting the soft and tough interiors. Surface hardening of steels has an advantage over through hardening, since it is less expensive, and also, problems such as distortion and cracking associated with through hardening of thick sections, can be effectively minimised.
There are mainly two distinctive methods of surface hardening.

a) Methods involving intentional buildups or layer additions.

b) Methods involving surface modification without any buildup or changes in part dimensions.

Some of the methods are given in Table 2.1.

<table>
<thead>
<tr>
<th>Layer Additions</th>
<th>Substrate Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hardening</strong></td>
<td><strong>Diffusion Methods</strong></td>
</tr>
<tr>
<td>Fusion Hardfacing</td>
<td>Carburising, Nitriding,</td>
</tr>
<tr>
<td>Thermal Spray</td>
<td>Boriding, Nitrocarburizing,</td>
</tr>
<tr>
<td>Coatings</td>
<td>Bonding, Nitrocarburizing,</td>
</tr>
<tr>
<td>Electrochemical Plating</td>
<td>Toyota Diffusion Process.</td>
</tr>
<tr>
<td>Chemical Vapour Deposition</td>
<td><strong>Selective Hardening Methods</strong></td>
</tr>
<tr>
<td>(Electroless Plating)</td>
<td>Flame Hardening, Induction</td>
</tr>
<tr>
<td>Thin Films (PVD, Sputtering,</td>
<td>Hardening, Laser Hardening,</td>
</tr>
<tr>
<td>Ion Plating)</td>
<td>Ion Implantation, Electron</td>
</tr>
<tr>
<td></td>
<td>Beam Hardening.</td>
</tr>
</tbody>
</table>

Coatings and overlays are less cost effective with increasing quantities of production, especially when entire surfaces of workpieces are to be hardened. Overlays are normally useful when selective areas are to be hardened.

During diffusion hardening entire surfaces of the parts are effectively hardened. This process is normally used when large number of parts are to be surface hardened. Selective hardening, in contrast, involves transformation hardening, like heating and
quenching, and various other methods such as selective nitriding, ion beam mixing, and ion implantation, which are solely based on compositional modification.

During diffusion hardening, the hardening species such as carbon, nitrogen, or boron are transported to the part surface, in the form of ions, gases or liquids. These variations in the species produce different case depths and hardness (52).

Some of these principal processes by which a hard surface is produced by the diffusion of these elements is explained briefly.

**Carburising** involves addition of carbon to low carbon steels, at a temperature of 850-950°C. At this temperature austenite with its high carbon solubility is the stable structure. Hardening occurs when the high carbon surface structure is quenched to form a martensitic case. This case has good wear and fatigue properties. Some of the significant methods by which carburising is achieved include gas carburising, plasma carburising, vacuum carburising, pack carburising and salt bath carburising. Among these, gas carburising is widely used for large scale production, due to the accurate control achieved by this process which minimises special handling.

**Nitriding** involves introducing nitrogen into steel in the ferritic region, at temperatures of 500-550°C. Nitrogen has a partial solubility in ferrite, and it forms a solid solution with ferrite, at nitrogen contents upto 6%. At 6% N a compound called $Y'$ (gamma prime) Fe$_4$N is formed, which has a cubic structure. This layer is also known as the "white layer" and it has good wear and corrosion resistance properties, at thicknesses between 0.0002-0.0004 in. Beyond this thickness it is brittle, and has a tendency to spall. At nitrogen contents above 8%, a compound called $\epsilon$ Fe$_3$N is formed which is also a hard phase. Various methods are available for nitriding which include gas, liquid and plasma (ion) nitriding. The advantages of plasma nitriding is the shorter nitriding time and cleaner surfaces (53).
**Boriding** (54) is the process in which boron is diffused onto the surface of a plain carbon steel and low alloy steels at temperatures of 950°C. It leads to the formation of iron borides (thickness 100μm) having a hardness ranging from 1800-2100HV.

**SURFACE COATING/LAYER ADDITION**

The various methods available to produce surface coatings is described next.

**Electrochemical Coatings**: These coatings are produced by electrolysis of an aqueous salt solution of the metal coating, with the component to be coated being the cathode. Chromium coatings are most widely produced by this technique and these coatings have an excellent wear resistance. The hardness value of chromium coatings is high (upto 1000HV), combined with corrosion resistance and low frictional values against steels. Coating thickness is however limited to 0.5mm due to internal stresses.

**Chemical Coatings**: These type of coatings are produced by immersing the component in a salt solution without any impressed currents. Coatings of nickel phosphorous and nickel boron alloys are produced by this method. The process involves reduction of nickel salts by sodium hypophosphite or sodium borohydride respectively. Coatings have a high hardness upto 1000HV, and they also posses good adhesive wear resistance after heat treatment.

**Chemical Vapour deposition**: This is a process by which compounds are dissociated in a gas phase to form dense layers on a coated surface. The most widely deposited material by this process is titanium carbide and titanium nitride. These coatings have a good wear resistance but the coating thickness is limited to 10μm due to interfacial stresses. Substrate choice is also limited due to thermal distortions and chemical reactions which take place in the temperature range of 800-1000°C, which is the
deposition temperature for producing these type of coatings. However, compared to PVD (physical vapour deposition), the CVD has a better throwing power and the ability to coat complex components with a uniform thickness.

**Physical Vapour Depositions**: This process is performed at subatmospheric pressure, and the coating atmosphere is generated by thermal evaporation or electric sputtering of a source material. Titanium nitride is the most widely used wear resistant material deposited by this process, and it has a coating rate of a few micron per hour and a thickness ranging from 1-10μm. The substrate temperature is maintained below 500°C and the coatings formed are dense and adhere well to the substrate.

**Spraying Processes**: A large number of spraying processes have evolved in recent years, in which particles of material are heated to a molten or plastic state and projected onto a relatively cold substrate. The coating density and bond strength increases with increasing projected velocity. The mechanical bonding between the coating and the substrate results in a lower bond strength compared to other coating processes.
Table 2.2 List of principal wear resistant material and their properties (54).

<table>
<thead>
<tr>
<th>Wear Resistant Material</th>
<th>Hardness HV</th>
<th>Max Service Temp °C.</th>
<th>Coating Application Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Metals hardened by Dispersed Oxide</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>390</td>
<td>250</td>
<td>Flame Spraying</td>
</tr>
<tr>
<td>13% Cr Steel</td>
<td>330</td>
<td>600</td>
<td>Flame Spraying</td>
</tr>
<tr>
<td><em>Intermetallics</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiAl</td>
<td>250-350</td>
<td>850</td>
<td>Flame and Plasma</td>
</tr>
<tr>
<td>CoCrMo (Lave Phase)</td>
<td>1100</td>
<td>1000</td>
<td>Flame and Plasma</td>
</tr>
<tr>
<td><em>Hardened Steel</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12%Mn Steel</td>
<td>150-400</td>
<td>150-200</td>
<td>Welding</td>
</tr>
<tr>
<td>Martensitic Steel</td>
<td>300-850</td>
<td>150-200</td>
<td>Thermochemical</td>
</tr>
<tr>
<td>Nitrided Steel</td>
<td>800-1200</td>
<td>500</td>
<td>Thermochemical</td>
</tr>
<tr>
<td><em>Cast Iron</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Martensitic Iron</td>
<td>400-600</td>
<td>200-250</td>
<td>Welding</td>
</tr>
<tr>
<td>High Chromium Iron</td>
<td>400-600</td>
<td>1000</td>
<td>Welding</td>
</tr>
<tr>
<td>Wear Resistant Material</td>
<td>Hardness HV</td>
<td>Max Service Temp °C.</td>
<td>Coating Application Method</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------</td>
<td>----------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td><strong>Nitrides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiN</td>
<td>2000</td>
<td>1000</td>
<td>CVD, PVD</td>
</tr>
<tr>
<td><strong>Borides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeB</td>
<td>1650</td>
<td>200</td>
<td>Thermochemical</td>
</tr>
<tr>
<td>CrB</td>
<td>3500-4000</td>
<td>800</td>
<td>Fusion of Powders</td>
</tr>
</tbody>
</table>

![Diagram of coating thicknesses and application methods](image.png)

Fig 2.6 Typical Coating Thicknesses of materials after surface treatments. (54)
2.4 THERMAL SPRAYING

Thermal spraying is a generic term used to denote a group of commonly used processes for depositing metallic and non-metallic coatings (55). During thermal spraying, coatings of high performance materials, such as metals, alloys, ceramics, and cermets are applied to relatively easy to work, and economical base metals (56). There are two basic types of thermal spraying processes. The first type is known as the combustion process. It chiefly relies on the combustion of a hydrocarbon fuel (acetylene, propane, hydrogen kerosene etc.), and oxygen or air, to provide the enthalpy and kinetic energy needed to plasticise and propel the powder particles onto the substrate. In the second process, electric power (wire arc or thermal plasma gas stream) is the source of energy used to melt and spray the powder particles. Various techniques such as flame spraying, arc plasma spraying, electric arc spraying, harmonic electric spraying, detonation gun spraying and HVOF spraying, are included within the above mentioned categories.

One of the significant features of thermal spraying is its diverse applicability. This is mainly because the material composition is unlimited, and it can be tailored to specific applications. Secondly, the temperature of the part can be kept low to minimise distortion, oxidation and phase transformations. The thermal spraying process and the coating combination can be tailormade to provide resistance to heat, corrosion, wear or erosion, and unique surface characteristics can be generated.
2.4.1 PROCESS DESCRIPTION

Thermal spraying is a process in which finely divided metallic or non metallic powders are deposited on a substrate in a molten or semimolten state to form a deposit, Fig 2.7. The heat required for the spraying materials to reach the plastic or molten state is supplied by an oxyfuel gas flame, plasma, or an electric arc, and hot material is propelled onto the substrate from the spray gun in a gaseous stream. After striking the substrate, molten particles flatten and form thin platelets, which confirm to the irregularities of the part geometry and finally cool and solidify. Successive layers are built, and finally a lamellar structure is formed. The bond between the coating and the substrate can be mechanical, metallurgical or chemical, or a combination of these. Bond strength can be usually increased by a post-spray heat treatment. The density of the coating depends on the type of material, the method of deposition and the post spray treatments

Fig 2.7. Thermal Spraying Sequence (84).

2.4.2 SPRAYING PROCESS (57)

There are 5 different commercially available methods for thermal spraying.
**Oxyfuel Wire Spray** is the oldest method and requires the least capital investment. In this process Fig 2.8, the coating material is in the form of a wire, and the heat source is an oxygen-fuel gas flame. The wire is driven into the flame through drive rolls, and is powered by air turbines or electric motors. The wire tip is melted after entering the flame, where it is atomised by compressed air, finally being propelled onto the workpiece. It is normally applied for corrosion protection of large structures such as bridges and storage tanks. This process cannot be used for spraying ceramic or refractory materials, due to the low flame temperatures attained during this process. It is mainly used to spray metals of low melting points.

![Wire Flame Spray Gun](image)

Fig 2.8. Wire Flame Spray Gun (58).

**Electric Arc Wire Spraying** uses metals in wire form and also ceramic materials in the form of rods, Fig 2.9. Two electrically charged wires are fed through the arc gun to make a contact at the gun tip. The arc that is created has a temperature of about 5500°C. The molten metal is atomised by compressed air and is projected onto the
metal surface. Some of its significant applications include, surfaces which have a large area that needs to be sprayed and which require a heavy coating buildup.

**Fig 2.9 Electric Arc Wire Spraying Gun (58).**

*Plasma Arc Powder* is one of the more sophisticated thermal spraying methods. Temperatures upto 11000°C can be achieved by the plasma equipment, Fig 2.10. Material decomposition is minimised due to the extremely high gas velocities generated by the plasma, which results in lowering of the particle residence time in the thermal stream. "Plasma" is generated when the energy state of the gas is raised after being passed through an electric arc. When the gas returns to its ground state, energy is released, resulting in exceedingly high temperatures. The plasma gas first dissociates,
which is followed by ionisation, and finally free electrons are released. These electrons recombine with the ionised species outside the electric arc releasing heat and light. Powdered ceramic materials, when suspended in such a gas, get melted, and are propelled at a high velocity onto the workpiece. The coatings thus produced have superior mechanical and metallurgical properties. The most significant applications of plasma spraying include, zirconium oxide for turbine engines combustors, and chromium oxide for printing rolls.

Fig 2.10 Plasma Arc Spraying System (58).

*High Velocity OxyFuel Powder Spray* is discussed in greater detail in section 2.6. It represents the state-of-the-art thermal spraying process for metallic and cermet
coatings. The process depends on high kinetic energy and controlled thermal energy supplied to powders to produce coatings having low porosities, combined with good bond strengths and low residual stresses.

2.4.2.1 GENERAL CONSIDERATIONS RELEVANT TO ALL SPRAY COATINGS

Some of the significant factors that need to be considered while selecting the thermal spraying method are:

a) surface preparation,
b) rate of deposition,
c) adhesion to the substrate,
d) thickness limitation of the coating, and
e) coating finish.

Surface Preparation chiefly relies on the mechanical interlocking of the sprayed coating to the substrate metal. Most coating failures are due to poor surface preparation. The parts to be coated are initially cleaned to remove any organic contamination. This is done by vapour degreasing, or by washing the parts with hot detergent solutions. The cleaned parts are grit blasted uniformly using either aluminium oxide or chilled angular iron steel grit, to achieve a white metal condition. This causes substrate roughening, which leads to the creation of minute asperities on the surface. These asperities provide an effective surface area, for effective coating adhesion and bond strength.

The Deposition Rate of a coating is limited by the method of application and the melting point of the coating material. The efficiency of deposition is measured by the ratio of the quantity of material deposited to the quantity of material sprayed. This factor influences the cost.
**Thickness Limitations** in coatings arise mainly due to internal stresses, which are developed during the shrinkage and solidification of the molten particles. The amount of shrinkage varies for different materials and spraying methods. During contraction, tensile stresses are set up in the deposit, and shear stresses are set up across the bond between the deposit and the substrate. These stresses are generally higher for harder coating materials, such as carbides, or ceramics. When these internal stresses exceed the adhesive strength of the coating, delamination of the coating from the substrate occurs. Also, porous coatings exhibit lower stresses than denser coatings. A typical coating cross section illustrating the lamellar structure of oxides and inclusions is shown in Fig 2.11.

![Coating cross section](image)

Fig 2.11. Coating cross section showing inclusions and pores (58).

**Coating Finishing** is normally done either by single point machining or by grinding. Hard surfacing materials such as ceramics and carbides are usually ground finished using diamond wheels. Most of the thermal spray coatings can be machined to 1 to 2 mm $R_a$, and ground to about 0.25 to 0.5 mm $R_a$. 
2.4.3 THERMAL SPRAY APPLICATIONS

The main usage of thermal spray coatings is mainly divided into three major industries, a) aerospace, b) land base turbine engines for power generation, and c) chemical processing plants. Some of the other usages include oil industry, paper and steel mills etc (53). Table 2.3 gives more details

Table-2.3 Various industries using thermally sprayed wear resistant coatings (55).

<table>
<thead>
<tr>
<th>Flight Gas Turbines</th>
<th>Land Base Turbines</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Path Seals</td>
<td>Piston rings (IC Engines).</td>
<td>Shaft Sleeves.</td>
</tr>
<tr>
<td>Mid-Span Stiffeners</td>
<td>Hydroelectric Valves</td>
<td>Gate Valves, Seats.</td>
</tr>
<tr>
<td>Z- Notch tip shroud</td>
<td>Boiler tubes</td>
<td>Rolling Element bearings.</td>
</tr>
<tr>
<td>Combustor and Nozzle Assemblies</td>
<td>Wear rings, Gas path seals.</td>
<td>Dies and Moulds, Diesel Engine Cylinder.</td>
</tr>
<tr>
<td>Blade Dovetails</td>
<td>Impellor Shafts.</td>
<td>Hip joint prosthesis.</td>
</tr>
<tr>
<td>Flap and Slat tracks</td>
<td>Impellor pump and Housing.</td>
<td>Hydraulic Press sleeves.</td>
</tr>
<tr>
<td>Compressor stators</td>
<td></td>
<td>Grinding Hammers, Agricultural knives, Biological Implants.</td>
</tr>
</tbody>
</table>

These applications are for some of the common industrial parts. As better understanding of the coating develops, the applications are bound to increase.
Table 2.4 is a compilation of various wear processes to which most machine parts are subjected to, and where thermal spray coatings are applied to counteract the damage. A large number of coatings are available for various applications and careful evaluation of the coatings needs to be made for each application. This is because component wear occurs due to various mechanical and chemical wear mechanisms.

**Table-2.4** Wear Processes and thermally sprayed coatings used to counteract the damage (55).

<table>
<thead>
<tr>
<th>Wear Process</th>
<th>Typical thermal spray coatings used.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion</td>
<td>Al$_2$O$_3$, ZrO$_2$, Cr$_2$O$_3$, WC-Co, TiC-Ni, Cr$_3$C$_2$-NiCr</td>
</tr>
<tr>
<td>Cavitation Erosion</td>
<td>NiTi, Cu-Ni, 316SS</td>
</tr>
<tr>
<td>Liquid Impingement Erosion</td>
<td>Stellite, Al$_2$O$_3$, WC-Ni</td>
</tr>
<tr>
<td>Fretting (Low Amplitude)</td>
<td>Cu-Ni, Cu-Ni-In.</td>
</tr>
<tr>
<td>(High Amplitude)</td>
<td>CoMoCrSi, Mo-NiCrBSi, T-800</td>
</tr>
<tr>
<td>Abradable</td>
<td>Ni Graphite, CoNiCrAlY,</td>
</tr>
<tr>
<td>Impact and Sliding</td>
<td>WC-Co, T-800, Cr$_3$C$_2$-NiCr</td>
</tr>
<tr>
<td>Galling</td>
<td>Cr$_3$C$_2$-NiCr, T-800</td>
</tr>
<tr>
<td>Solid Particle Erosion</td>
<td>WC-Co, Cr$_3$C$_2$-NiCr, Cr$_3$C$_2$-MCrAlY, T-800.</td>
</tr>
<tr>
<td>Adhesive</td>
<td>Al Bronze, Al$_2$O$_3$+TiO$_2$, WC-Co</td>
</tr>
<tr>
<td>Scuffing</td>
<td>Mo, Mo-NiCrBSi.</td>
</tr>
<tr>
<td>Dry Sliding</td>
<td>WC-Co, Cr$_2$O$_3$, Cr$_3$C$_2$-NiCr.</td>
</tr>
<tr>
<td>Biological Implants.</td>
<td>TiO$_2$, ZrO$_2$, Hydroxylapatite, Fluorapatite.</td>
</tr>
</tbody>
</table>
2.4.4 THERMAL SPRAY CHALLENGES

There is plenty of scope to make substantial improvements in the thermal spray technology. One of the major drawbacks of the thermal spray industry, however, is the lack of proper standards for spray guns and coating materials. Edward Oswecki (59), believes that thermal spraying involves at least 200 variables in the application of coatings, and recognition and control of these variables is particularly important to achieve coating predictability. Specific standards are also necessary for characterising the coatings to avoid variations in laboratory tests. Due to the lack of standardisation in metallographic polishing methods, porosities and oxide content in the coatings are interpreted differently. Since the coatings are not generic, they lack reproducibility in their quality. The coating integrity is important, because any failure would limit the overall coating substrate usefulness (60). Another important factor that plagues the thermal spray industry is the high equipment costs.

2.5 HIGH VELOCITY OXYGEN FUEL PROCESS

The high velocity oxygen fuel (HVOF) process is the most sought after coating process, and is the most significant achievement after plasma spray (61). It has achieved an enormous growth and has generated considerable interest in surface coating technology in recent years. The original HVOF process was known as the D-Gun, and was developed by Union Carbide. But it was only after Browning Engineering Corporation introduced the Jet Kote HVOF, that a broad base development and utilisation of HVOF took place. The HVOF coating service industry is estimated to be $160 million world wide.
The HVOF offers a safer, cleaner, better quality at lower costs, compared to some of the other thermal spray processes such as plasma, low velocity combustion and electric arc (62)

2.5.1 PRINCIPLE

The HVOF uses an internal combustion (rocket jet) to generate hypersonic gas velocities, of speeds greater than 5 times the speed of sound in air. Ceramic powders are fed into the rocket jet, and the exhaust gases are constricted into the nozzle. The fuels used are normally gaseous hydrocarbons, such as propylene, acetylene, propane and hydrogen. These fuels when burned with oxygen, produce temperatures well above 2760°C. The flow rate of the gases is controlled by a flow meter and the feed rate is automatically monitored. The pilot flame is manually ignited.

Thorpe and Richter (63) believe that the thermodynamic principles of the HVOF process have not yet been fully understood. It has been established that particle velocity, which is the speed at which the particles of the coating materials travel during their flight from the spray gun to the part being coated, is a critical factor in all the thermal spray processes. The HVOF guns that are currently available can produce very high particle velocities. Some of the distinctive advantages that the HVOF process provides are:

a) a favourable environment,

b) a very short exposure time during particle flight,

c) reduced mixing with the ambient atmosphere, after the jet and the particles leave the gun,

d) lower particle temperatures compared to plasma or arc guns, and

e) a very high particle kinetic energy upon impact against the substrate.
Due to all these factors, the HVOF yields better coatings than plasma in terms of hardness, bond strength, and density of the coatings. The higher adhesive strength and cleaner microstructures improves the wear resistance of the coating (58).

Some of the principal high velocity guns that are industrially used include, D-Gun, Jet Kote, UTP Top Gun and METCO Diamond Jet gun. The salient features of these guns are described below (58).

**D-Gun** : The detonation gun process is solely operated by the Union Carbide Corporation in most of the industrialised countries. The D-Gun, shown in Fig 2.12, consists of a water cooled steel tube closed at one end. It uses an energy of explosions of oxygen acetylene mixtures, to blast powder particles onto a metal substrate. The oxyacetylene mixture is ignited using an electric spark, at either 4.3 or 8.6 times per second. This creates a series of detonation waves which accelerate and heat the powder particles as they move along the barrel. The particle velocity during the operation is about 800m/sec and the flame temperature is about 3000°K. Low porosities and good bond strengths can be obtained by this process. The process produces better coatings than the plasma process, but the principal disadvantages are high equipment costs and high noise levels, upto 150dB, which occur during the functioning of the gun.
Jet Kote: This is the first commercially available high velocity gun developed by Browning Corporation. In this process, Fig 2.13, a mixture of oxygen and acetylene is burned under a pressure of 0.4-0.6 N/mm$^2$. The exhaust gases from the combustion chamber pass through 4 converging channels into a nozzle, generating gas velocities upto 1400 m/sec, and particle velocities ranging from 900-1100 m/sec during operation. Temperatures upto 2100°C are easily achieved by this process and noise levels are much lower than plasma. Coatings with good adherence and high hardness are achieved, due to higher particle velocities obtained during the process. The gun is light and can be hand held.
Fig 2.13  Diagram showing the Jet Kote Spray Gun (58).

Fig 2.14  Diagram showing the UTP Top Gun (58).
**UTP Top Gun**: The HVOF Top gun, Fig 2.14, has an internal combustion chamber connected to a water cooled accelerator nozzle. The ignition is electronically carried out and the ignition flame produced gets rapidly converted into a combustion flame. This conversion takes place on running the gun at full operation pressures of fuel gas and oxygen. The system can use any type of fuel such as propane, propylene, hydrogen, acetylene, or natural gas, or a combinations of these. Particle velocities upto 700m/sec can be reached during this process and high flame temperatures upto $3100^\circ$C can be achieved using acetylene fuel.

The deposition rate of the Top gun is twice that of Plasma and this process can spray all types of powders. The gases are inexpensive and the deposition efficiency is greater than 75%. However, the only problem encountered is the powder buildup within the combustion chamber/nozzle, which is a function of powder feed rate and carrier gas flow. A proper control of these two parameters is essential for successful operation of this process.

![Fig 2.15. METCO Diamond jet spraying gun (64).](image-url)

Kaufold and Rotcolio (64) studied the new *Metco Diamond Jet HVOF* gun shown in Fig 2.15. A significant feature of this gun is that it involves a continuous internal
combustion of oxygen and a fuel gas within an air cooled chamber. After combustion, the hot gases are discharged and the powder is fed axially and centrally into the exhaust gas stream. The flame velocity generated by this gun is in the order of 4000-4500ft/sec, and the accompanying particle velocity is approximately 2500-3000ft/sec, depending on the powder material.

The basic objective of the thermal spray process is to transfer kinetic and thermal energy to the powder particles, with a high degree of efficiency. The kinetic component of the particles supplies a mechanical force upon collision with the workpiece. The collision generates heat, and helps the particles to bond with the previously deposited mass. The high velocity causes the particles to deform and fill the irregularities of the surface.

Another significant advantage of this process is the relatively low temperatures associated with the HVOF system. The feed particles tend to become extremely plastic by a method of convective heat transfer, thus preventing superheating and vaporisation. Upon impact with the substrate, the high kinetic energy is transformed into thermal energy and this energy is uniformly absorbed by the substrate, resulting in a rapidly solidified dense coating having low residual stresses.

2.5.2 GAS DYNAMICS OF THE HVOF PROCESS.

Hackett and Settles (65), raised the question concerning the influence of gas dynamics of the HVOF process on the coating quality. Thorpe and Thorpe (66), reiterated that HVOF coatings cannot be considered to be generic, because they are totally dependent on gun designs, type of fuel, operating pressures, and the input energy level. The particle velocities in most HVOF processes reaches 20-25% of the gas velocities and 80% of the particle impact velocity is generated by the time the particles reach the exit
of the torch, which means that higher barrel velocities yield higher particle velocities. Hence, it is important to maximise the particle velocity within the barrel.

Particle velocity also depends on the density and size of the powders. For a 10 micron tungsten carbide particle, the particle velocity is 53% of the gas velocity, whereas it is only 26% for a 50 micron tungsten carbide. This shows that lighter particles obtain higher velocities.

The internal gas dynamics also, has an influence on the external gas flow. The gas flow in the nozzle is non-adiabatic, due to the cool water circulation. The combustion products are accelerated to Mach 1 at the nozzle throat, and are then expanded to Mach 2 at the juncture of the nozzle and the barrel. Gases that leaves the nozzle are supersonic with a static pressure greater than 1 atmosphere, and the gases which leave the barrel are underexpanded, and form an axisymmetric supersonic freejet.

The most notable feature of the HVOF is the presence of "shock diamonds" in the initial part of the jet. These diamonds are naturally visible, due to the optical emission property of the hot gas. The characteristic diamond shape occurs due to repeated reflections of the oblique waves within the supersonic core of the jet, during the expansion and contraction cycle of the waves, along with simultaneous interaction with the surrounding atmosphere. As the flow expands, the static temperature is lowered, and the visible emission ceases. Subsequent compression again raises the temperature, and makes it visible. This pattern of compression and rarefaction continues until the supersonic core of the jet is eventually dissipated by atmospheric mixing.

The length of the visible shock diamond plume indicates the longitudinal distance of the supersonic core of the jet. It has been observed, that an increase in chamber pressure increases the supersonic core. This takes place due to an increase in static
pressure at the barrel exit. The length of the barrel however, does not have a strong influence on the supersonic core of the HVOF exhaust.

Atmospheric mixing with the hot exhaust HVOF jet however, causes the supersonic core to dissipate after a distance of 20cm from the barrel exit. The HVOF plume that actually impacts the target undergoes sufficient atmospheric mixing and becomes subsonic. The chief factor which affects the mixing is the temperature of the jet, or more specifically, the density ratio between the jet and the surrounding atmosphere (65).

Mixing of the HVOF jet with the oxidising atmosphere is detrimental to the coating quality, possibly due to oxidation prior to the coating. Further research needs to be aimed at decreasing the mixing of the HVOF jet with the atmosphere. Jet noise is another troublesome area in HVOF spraying, although it is not related to coating quality. It occurs due to the interaction of the vortical structures of the turbulent mixing layer with the shock diamonds. Even though jet noise is of a secondary consequence in HVOF spraying, research needs to be focused in this area because it is hard to ignore.

2.5.3 HVOF CHALLENGES

A considerable amount of energy is generated by the HVOF. The process has a tendency to impart more heat into the part, necessitating cooling techniques and interruption of the spray process. McPherson (67) observed that spraying of higher melting point materials, such as alumina, zirconia and chromia is a problem using the HVOF, since HVOF temperatures are much lower compared to plasma. A further limitation is the reduced residence time of the particles in the flame, caused by higher particle velocities. Higher temperatures can, however, be achieved by using fine size powders (-15 +5 microns), but this causes additional problems in powder handling and feeding.
2.6 HIGH VELOCITY AIR-FUEL (HVAF) THERMAL SPRAY SYSTEM

This is a more recent thermal spray process patented by the Browning Engineering Corporation. It differs from the HVOF in many significant ways. Firstly, it does not use pure oxygen during its operation. Oxygen is only used during ignition and remains for 10 seconds. Instead of oxygen, compressed air is used because it is inexpensive. The compressed air first cools the torch by passing through an internal cooling jacket and then burns in the combustion chamber after mixing with kerosene. Kerosene is the fuel used for this process.

The advantages of the Browning HVAF system is that it yields very consistent higher density coatings, and the process produces one of the best tungsten carbide-cobalt coatings available today. This process enables high deposition rates at lower temperatures and higher velocities.

2.7 TUNGSTEN CARBIDE-COBALT SYSTEM

Cemented carbide cutting tools have been widely researched since the beginning of 1950 due to their excellent mechanical and wear resistant properties. Almost 95% of the cemented carbides cutting tools are tungsten carbide based, and they are essentially aggregates of particles of refractory metal bonded together by an iron group metal. The principal cermet used for high speed cutting tools and drills for mining is composed of tungsten carbide (WC), and 6-20% cobalt. WC is a hard and brittle ceramic with a hexagonal crystal structure, and cobalt is a ductile metal with a closed pack hexagonal structure. The compositional balance of these phases influences the properties and application range of the alloy system.

Tungsten forms two hexagonal carbides, a monocarbide WC and a subcarbide W$_2$C, which is obtained as an intermediate product. The monocarbide is of importance and it
has a simple hexagonal structure with 2 atoms per unit cell, and a c/a ratio of 0.976. The carbon atoms are located either at 1/2, 2/3, 1/2 or all at 2/3, 1/3, 1/2 voids in a simple hexagonal lattice of tungsten atoms.

The exclusive use of cobalt as the binder phase in cemented carbides is due to its outstanding wetting and adhesion properties. The sintering behaviour of the carbide/binder mixture is determined by the wettability of the carbide in the molten binder to form a dense body. Cobalt also enhances the toughness of the material by introducing a ductile component into the microstructure.

The properties of the sintered WC-Co composites largely depend on the final composition and microstructure. During the sintering of WC, carbon control is extremely crucial to obtain strong sintered bodies. If the carbon content is too low, carbon deficient eta phases η phases, Co₃W₃C are precipitated, and if the carbon content is too high graphite is precipitated. Both of these phases are detrimental to the mechanical properties of the sintered materials.

*Fig 2.16* Isothermal section of the WC-Co ternary phase diagram in the sintering temperature range (68).
The ternary diagram of the Co-W-C system, Fig 2.16, at 1400°C which is the common sintering temperature, shows that two types of \( \eta \) phases \( M_{12}C \) (Co\(_6\)W\(_6\)C) and \( M_{6}C \) (Co\(_3\)W\(_3\)C) can be precipitated during sintering or during cooling. Fig 2.16 also shows that WC is in stable equilibrium with liquid cobalt in a narrow compositional range, with its solubility in cobalt decreasing with cooling (68-70).

### 2.7.1 TUNGSTEN CARBIDE-COBALT COATINGS

Thermally sprayed tungsten carbide-cobalt (WC-Co) coatings are used for various applications in the industrial and aerospace markets. A vast majority of aircraft engine manufacturers use hardface WC-Co coatings, for critical engine overhaul and repairs, and also for original engine manufacture. The coatings are principally known to resist severe wear environments, such as abrasion, adhesion, fretting and particle erosion. Similarly, turbine gas industries use tungsten carbide-cobalt coatings to resist heat transfer, and friable abradable coatings to provide gas seal paths (71). Some of the other application of the coatings include, compressor piston rods, pump plungers, shaft sleeves on centrifugal pumps and fans, midspans of compressor blades in turbines etc (72).

To achieve successful optimisation of the coatings, researchers in industries and academia are trying to understand the complex relationship of carbide shape, size and distribution; Matrix hardness and toughness; coating density; particle to particle cohesion; and particle to particle adhesion. Better understanding of the coating properties can be obtained by studying the interrelationships among the spraying processes, spraying parameters such as gas flow, spray rates, spraying distance, and starting powder properties such as (size distribution, carbide size, manufacturing process and chemistry) (73).
2.7.2 STARTING POWDERS

The shape and size of powders significantly influences the end product coating, and hence the powder manufacturing method is particularly important. Different WC-Co powders can have the same grain size but different morphologies, which in turn could affect the coating quality. The powders should possess excellent flow properties to achieve constant feed rates, which in turn is dependent on the grain size and powder morphology (74). Some of the problems associated with powders include gun clogging, poor deposition rates and spalled deposits.

Some of the common techniques by which the WC-Co powders are manufactured are a) fusing and crushing, b) sintering and crushing, and c) agglomerating and sintering. The morphologies of the powders are different for each technique. Various detrimental phases, such as eta phases, which are discussed in greater detail in section 2.6.2, are formed during the powder manufacturing method, and great care needs to be taken while selecting the best method.

As the particle size decreases, the surface to volume ratio becomes larger and greater amount of heat per unit volume is transferred to the particle (75). Similarly spherical particles, usually manufactured by agglomerating and sintering have a low mass to volume ratio and hence, have good flowability.

FABRICATION OF POWDERS BY AGGLOMERATION AND SINTERING

The fabrication of dense WC-Co powders in the 50 to 1000μm range is generally difficult and expensive. However, small WC-Co spheres can be produced by agglomerating WC and Co powder mixtures, followed by cold compaction and sintering. The powders are agglomerated in a rotating tilting cylinder which is placed in a hermetic chamber, which controls the relative humidity. For agglomeration to take
place, 0.75-1.5% paraffin binder dissolved in benzene is added. Prior to agglomeration, the mixtures are ball milled to obtain a homogeneous mix and to crush the large particles. Benzene is then evaporated to produce a solid cake which is crushed with a pestle and screened through a 65 mesh sieve, to remove the large agglomerated masses. The resulting seeds and particles are presintered at 850°C for 1 hour to remove the paraffin binder and for slightly sintering them. They are then dispersed in graphite powder and cold isostatically pressed at 640 Mpa in polyurethane bags to remove density gradients within the granules. Sintering is finally done in a (vacuum) graphite crucible at 1450°C (76).

Even though there is no single optimum powder manufacturing method, a good match needs to be made between powder cost, coating rate and efficiency, and coating characteristics. A good working relationship between the end user and the powder manufacturer is the best tool for a successful coating application. Unfortunately, no systematic work has been carried out to elucidate the exact influence of the powder manufacturing route on the coating characteristics.

### 2.7.2 DECARBURISATION REACTION

Tungsten carbide-cobalt (WC-Co) coatings have been historically known to have excellent wear resistant properties. The properties of the coating are attributed to the complex interrelationship between the carbide size, shape and distribution, matrix hardness and toughness, and the carbon dissolved in the cobalt matrix (77). WC-Co coatings achieve their maximum abrasive wear resistance when a fine distribution and high volume of tungsten monocarbide (WC) particles are present in the matrix. The presence of large amounts of tungsten monocarbide is dependent on minimising the decarburisation of WC, which readily occurs during the high temperatures associated with the thermal spray process.
The mechanism of decarburisation occurs through carbon losses occurring through an oxidation reaction. Many reactions are possible which lead to the formation of various detrimental phases. Some of these reactions are:

\[
\begin{align*}
2WC & \rightarrow W_2C + C \\
W_2C & \rightarrow 2W + C \\
2WC + O_2 & \rightarrow 2W + 2CO \\
4WC + O_2 & \rightarrow 2W_2C + 2CO \\
3Co + 3WC + O_2 & \rightarrow Co_3W_3C + 2CO \\
12Co + 12WC + 5O_2 & \rightarrow 2Co_6W_6C + 10CO (78)
\end{align*}
\]

All these reactions are kinetically controlled and are dependent on time and temperature. The degree of decarburisation is related to the manufacturing method of the starting powders, the flame temperature, and flame velocity. The decarburisation reaction can be effectively minimised by limiting the flame temperature and increasing the particle velocity, but it cannot be totally eliminated. These conditions can be brought about by the high velocity oxy-fuel process. During the spraying process, dilution and diffusion of tungsten carbide into cobalt results in the formation of various cobalt containing subcarbides such as, Co₃W₃C also known as "η" (Eta Phase) and "ε" phase Co₆W₆C. In addition to the eta phase, which is a detrimental brittle phase with a dendritic structure, various other stoichiometric phases such as W₂C, pure W, and pure C are formed due to the complex physical and chemical transformations occurring within the thermal stream (79).

Nerz and Kushner (73) who worked on WC-Co coatings, used a fused and crushed WC-12%Co powder, which is normally used for the aircraft gas turbine industry, and
sprayed it using an HVOF Metco diamond jet system. They found that the HVOF sprayed coating contained larger percentage of tungsten monocarbide which they confirmed using X-ray diffraction analysis. It was presumed that the higher flame velocity and lower flame temperature of the HVOF process led to the retention of WC.

X-ray diffraction of the coatings showed substantial amounts of $W_2C$ and elemental tungsten, but did not reveal any cobalt containing subcarbides. X-ray analysis also showed a broad maxima in the $2\theta$ range of 38 to 46°, characteristic of amorphocity. The cobalt and excessive carbon were present in the coatings in an amorphous state. Bright field transmission electron microscopy analysis revealed the presence of crystalline particles, which mainly consisted of hexagonal $W_2C$ having a c/a ratio of 0.97, and WC having a c/a of 1.57, embedded in a dark grey amorphous cobalt matrix. The WC crystals had a high density of dislocation and a high stacking fault energy, possibly due to impact stresses during spraying. They finally concluded that the broad maxima is an amorphous material created by the diffusion of carbon and tungsten into the cobalt matrix.

Jarosinki and Gruninger (80) who did similar work, used different WC-Co powders fabricated by different manufacturing techniques, and analysed the coatings using both HVOF and the relatively newer HVAF system. It has been understood that the mechanical properties of the coatings are strongly influenced by the amount, size and distribution of the WC phase. The strength and wear resistance of the coatings is found to increase by the presence of larger amounts of small WC grains, distributed uniformly in a binder with a continuous mean free path.

They used five different powders in their work, and the manufacturing method of the powders varied from sintering and crushing, agglomeration, and casting and crushing. All the powders were successful for HVOF spraying, but the cast and crushed powder was unsuitable for HVAF spraying due to lower temperatures achieved by HVAF.
They found that the carbon loss appeared to be highest in the HVOF coatings, while the HVAF sprayed coatings retained a larger percentage of finer carbides. The compressed air feature in the HVAF torches, subjected the powders to much lower temperatures, subsequently reducing carbon losses. The deposition efficiency was found to be the highest and decarburisation was minimum for sintered and crushed powders, because of a more uniform particle heating, softening and melting. The authors demonstrated the importance of manufacturing method, the coating process, and the deposition method for producing good quality coatings.

X-Provot, Richard and Manesse (78) studied the effects of spraying WC-17% Co powders using the HVOF spraying system. They observed that spraying provoked cobalt dilution and diffusion into the tungsten monocarbide to form various subcarbides containing cobalt, such as Co3W3C \("\eta\" phase and \("\varepsilon\" phase Co6W6C, in addition to W2C and pure W. Their presence was detected in the broad maxima observed in the X-Ray diffraction chart between the two main WC peaks. This was confirmed as an amorphous region containing high amounts of Co\(_x\)W\(_y\)C\(_z\) by conducting transmission electron microscopy.

It has thus been observed by researchers that an optimum coating quality with excellent abrasion resistance is obtained when the microstructure contains large volumes of fine tungsten monocarbide grains in a cobalt matrix. This is normally achieved by high particle velocities and low flame temperatures, as found in the HVOF processes, finally resulting in minimum decarburization.
CHAPTER-3

EXPERIMENTAL PROCEDURES
EXPERIMENTAL PROCEDURES

In the present project, experimental work was devised to compare the abrasive wear behaviour of various monolithic materials and thermally sprayed tungsten carbide-cobalt coatings. To study the abrasive wear behaviour of these materials, tribological systems simulating low stress and high stress abrasive wear were set up.

The low stress abrasive wear behaviour of the materials was studied using a rubber wheel abrasion tester described in section 3.3.1. The high stress abrasive wear behaviour was examined using a pin-on-drum two body abrasion tester described in section 3.4.1. In order to gain an insight into the operating wear mechanisms, the wear tracks were examined using a scanning electron microscope. A series of WC-Co coatings were prepared by varying the chamber pressure, using an aero spray high velocity air-fuel (HVAF) system, in order to optimize the processing conditions of the coating.

This chapter discusses the salient features of the various equipments and experimental procedures that were used during the present work.

3.1 EXPERIMENTAL MATERIALS

The materials investigated for low stress abrasive wear are presented in Table 3.1. The test specimens chosen were rectangular in shape, 25 by 76 mm and between 3.2 and 12.7 mm thick. High stress abrasive wear was studied for all the monolithic materials described in Table 3.1, and two WC-Co coatings sprayed using powders from sources JK112 and WOKA, prepared at 45 psi chamber pressure. Materials studied for high stress abrasive wear were pin specimens of 6mm diameter, and had an allowable length of 20-35mm.
Table 3.1  Materials studied in the present work.

<table>
<thead>
<tr>
<th>Monolithic Materials</th>
<th>Ceramic Materials</th>
<th>Coated Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suppliers: Keystone Pacific Ltd.</td>
<td>Suppliers: Keystone Pacific Ltd.</td>
<td>Suppliers: L&amp;R Ashbolt and C-Ramic Australia</td>
</tr>
<tr>
<td>316 stainless steel</td>
<td>Alumina ceramic-R</td>
<td>WC-Co on stainless steel (sprayed using JK112 and WOKA powders at various chamber pressures) Process: HVAF</td>
</tr>
<tr>
<td>Cr-16-18%, Ni-10-14%, Si-0.75%, Mn-2%, C-0.08%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304 stainless steel</td>
<td>Alumina ceramic-1000</td>
<td>WC-Co on Mild Steel (Sprayed using WOKA) Process: HVAF</td>
</tr>
<tr>
<td>Cr-18-20%, Ni-8-10%, Si-0.75%, Mn-2%, C-0.08%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG iron-I (2.5%C)</td>
<td>Nilcra zirconia (Advanced engineering oxide ceramic, magnesia partially stabilized zirconia)</td>
<td>C-9001 (Proprietory)</td>
</tr>
<tr>
<td>SG iron-II (3.5%C)</td>
<td>ALANX-CG 273</td>
<td>C7928 (Proprietory)</td>
</tr>
<tr>
<td>28% Chromium iron (as cast)</td>
<td></td>
<td>C7916 (Proprietory)</td>
</tr>
<tr>
<td>C-2.3-3%, Si-1%, Mn-0.5-1.5%, P-0.1%, S-0.1%, Cr-23-30%, Mo-1.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28% Chromium iron (heat treated)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2 THERMAL SPRAYING OF TUNGSTEN CARBIDE-COBALT POWDERS

Two different WC-Co (88-12%) powders from sources JK112 and WOKA were thermally sprayed at L & R Ashbolt, using a high velocity air-fuel thermal spray system, shown in Fig 3.1. The first set of samples were initially prepared using the parameters described under section 3.2.1, followed by a second set by varying the chamber pressure, described in section 3.2.2.

3.2.1 PROCESS PARAMETERS

The WOKA was a sintered and crushed WC-Co (88-12%) powder, whereas the JK112 was a premium grade sintered powder. The mesh size of the powders was -45 + 10 μm for JK112, and -45 + 5.6 μm for the WOKA.

AIM: To compare the effect of starting powders on the coating characteristics (microstructure and wear).

A first set of test samples was prepared using both the powders JK112 and WOKA on stainless steel, and another set of samples was prepared using WOKA on mild steel. The aim was to characterize the coatings and to also evaluate the suitability of the substrate by performing low stress abrasion tests, on both mild steel and stainless steel substrates, sprayed using WOKA.

Before thermal spraying, the stainless steel substrates were sand blasted using fine aluminum oxide grit, to produce a rough surface, which is essential for better coating adhesion. The spraying parameters during the first set of samples prepared are given in Table 3.2. The specimen was kept stationary whereas the gun was traversed at its maximum speed during the first set of sample preparation.
Table 3.2. HVAF OPERATING PARAMETERS

<table>
<thead>
<tr>
<th></th>
<th>Flame Temperature</th>
<th>2150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Fuel</td>
<td>Kerosene</td>
</tr>
<tr>
<td>3</td>
<td>Nozzle Length</td>
<td>12&quot;</td>
</tr>
<tr>
<td>4</td>
<td>Spray Distance</td>
<td>7&quot;</td>
</tr>
<tr>
<td>5</td>
<td>Oxygen Pressure</td>
<td>110 psi</td>
</tr>
<tr>
<td>6</td>
<td>Chamber Pressure</td>
<td>40 psi</td>
</tr>
<tr>
<td>7</td>
<td>Career Gas (Fuel)</td>
<td>70 psi</td>
</tr>
<tr>
<td></td>
<td>Pressure</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Number of gun passes</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2.2 PREPARATION OF COATINGS BY VARYING THE CHAMBER PRESSURES.

AIM: To study the effect of one process variable on the coating characteristics.

After analyzing the first set of coatings, four specimens were prepared using the WOKA powder at chamber pressures 30psi, 35psi, 40psi and 45psi, and a 5th sample was prepared at 45psi using the JK112 powder. Only one sample was prepared at 45 psi due to shortage in the supply of the WOKA powder. This specimen was meant for making useful comparisons between the two coating types. 316SS of size 25mm x 75mm, was chosen as the substrate material for all the coatings. The coatings were prepared by affixing the substrate to a wheel rotating at 450rpm, with the spray gun kept stationary. This method ensured a better control on the evenness of the coatings. The spraying distance was kept at 10 inches, and a 12 inch nozzle length was chosen for spraying the coatings.
Fig 3.1  a) Diagram showing HVAF system controls, and the thermal spray gun.  
b) Shock diamonds during thermal spraying of tungsten carbide-cobalt.
3.2.3 HIGH VELOCITY AIR-FUEL SYSTEM (HVAF),

The process is also known as the aerospray system and is patented by the Browning Engineering Corporation. The coatings produced by the aerospray system are harder, tougher, and contain less oxides, resulting in lower residual stresses.

The torch is regeneratively cooled by the compressed air that it burns, and does not require any water cooling. This absence of a heat exchanger and water chiller is an additional advantage. An onboard fuel pump is supplied along with the controls and the tremendous thrust generated in the system causes it to be only machine held. The entire system has a rugged stainless steel construction that can last for hundreds of hours, with little or no maintenace. A series of nozzles of varying lengths are available for operation alongwith user friendly pedestally mounted control consoles. Four guages, monitoring pressures and flows are preset for optimum operation.

3.3 LOW STRESS ABRASION

Low stress abrasion is defined as the condition in which the stress imposed on the abrasive particle does not exceed the crushing strength of the abrasive particles. The most common laboratory wear testing machine to evaluate materials for their low stress abrasion is known as the dry sand rubber wheel abrasion tester. This wear tester was constructed, commisioned and standardized in the Department of Materials Engineering, at the University of Wollongong, following the relevant ASTM designation G 65-85 (81).
3.3.1 Dry Sand Rubber Wheel Abrasion Tester (81)

Figure 3.2 shows the commonly used tester which is used to determine the resistance of materials to abrasive wear. The test involves abrading a standard test specimen with a grit of controlled size and composition. The abrasive is introduced between the test specimen and a rotating rubber wheel. The specimen is pressed against the rotating wheel at a specified force, while a controlled sand flow, maintained between the wheel and the specimen, abrades the test surface. The wheel rotates such that the contact face moves in the direction of the sand flow.

The abrasion test results are reported as volume loss in cubic millimeters. There are four recommended procedures for varying degrees of wear resistance.

*Procedure-A* is a severe test used to rank materials with a wide volume loss ranging from low to high abrasion resistance. It is useful when materials with a medium or high abrasion resistance are to be ranked. The duration of this test is 30 minutes, and a 7Kg load is used to produce a 130N force.

*Procedure-B* is a short term variation of procedure A and is used to rank highly abrasive resistant materials, but is particularly useful in ranking medium and low abrasive resistant materials. The duration of this test is 10 minutes and a 7Kg load is used to produce a 130N force.

*Procedure-C* is a short term variation of procedure-A for use on thin coatings. The duration of this test is 30 seconds and a 7Kg load is used to produce a 130N force.

*Procedure-D* is a lighter load variation of procedure -A used for ranking materials of low abrasion resistance and materials of a specific generic type with volume losses
close to rates of procedure-A. The duration of this test is 30 minutes and a 2Kg load is used to produce a 45N force.

**Procedure A** was chosen during all the low stress abrasion tests done in the present work.

### 3.3.2 Table-3.3. **TEST PARAMETERS FOR DIFFERENT PROCEDURES**

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Force against specimen (Newton)</th>
<th>Wheel revolutions</th>
<th>Linear abrasion in meters</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>130</td>
<td>6000</td>
<td>4309</td>
</tr>
<tr>
<td>B</td>
<td>130</td>
<td>2000</td>
<td>1436</td>
</tr>
<tr>
<td>C</td>
<td>130</td>
<td>100</td>
<td>71.8</td>
</tr>
<tr>
<td>D</td>
<td>45</td>
<td>6000</td>
<td>4309</td>
</tr>
</tbody>
</table>

### 3.3.3 MATERIALS AND APPARATUS DESCRIPTION

Many elements are of critical importance to ensure uniformity in test results among laboratories. Some of these are the type of rubber, type of abrasive, its shape, positioning, size opening of the sand nozzle, and the lever system to apply the required force.

**RUBBER WHEEL**: The rubber wheel on the apparatus consists of a steel disc with natural rubber moulded to its periphery. Uncured rubber is bonded to the rim and is
fully cured in a steel mould. The hardness of the wheel is kept to Durometer A-60 and a variation between A-58 to A-62 is acceptable according to the ASTM standards. The hardness of the wheel is measured using a shore A Durometer tester, by taking four hardness readings 90° apart.
Fig 3.2  a) The dry sand rubber wheel abrasion tester. b) Sand flowing between a WC-Co coated specimen and a rubber wheel rotating at 200 rpm, abrasion test being carried out under Procedure-A (Load: 130N, Time: 30mins)
Fig 3.3  Diagram of dry sand rubber wheel abrasion tester.

**ABRASIVE:** The abrasive used was a rounded quartz with a grain size of A 30-60 (Australian Standard No.), which is the same as AFS 50/70 (300-200 mm) (American Foundrymens Specification), as specified by ASTM designation G 65-85 (81). Care was taken to ensure that the moisture content did not exceed 0.5 weight % by baking the sand in an oven for 1 hour. It was observed that the same sand could be
used no more than two successive tests, since the test results were found to be affected with further use.

**SAND FLOW AND CURTAIN**: The sand nozzle is designed in such a way as to produce an accurate sand flow and a proper shape of the sand curtain. The rate of flow is adjusted by grinding the orifice of the nozzle. The recommended sand flow rate is 250-400 gms/min. In all the tests the sand flow was maintained at 390 gms/min. The sand curtain was properly controlled to avoid any turbulent sand flow, since turbulence causes inconsistencies in the test results. A streamlined sand flow was hence passed between the specimen and the wheel, and the nozzle was kept as close as possible between the wheel and the specimen.

**MOTOR DRIVE AND COUNTER**: The wheel is driven by a 0.7 kW (1 hp), DC motor through a 10/1 gear box to ensure maximum torque. The number of revolutions is kept at (200+ 10rpm), which remain constant under load. The machine is equipped with an incremental revolution counter that monitors the number of revolutions of the wheel, and shuts off after the preselected number of revolutions.

**SPECIMEN HOLDER**: A specimen holder is attached to the lever arm, and weights are added to apply a force along the diametric line of the wheel. The actual weights to be added in order to obtain the force was determined by a load cell. A load of 7Kg was found to produce a Force of 130N, for Procedure-A, and a load of 2Kg, produced 45N for Procedure-D.

**TYPICAL SPECIMENS**: The test specimens chosen were rectangular in shape, 25 by 76 mm and between 3.2 and 12.7 mm thick. The test surface is maintained flat within 0.025 mm maximum. It is ensured that the specimens are smooth, flat, free of scale, and free from surface defects such as porosities and roughness. The samples were ground flat to ensure the specifications.
3.3.4 TESTING PRECAUTIONS

* The samples are initially cleaned in alcohol and dried to remove any foreign matter before and after the test.

* A dwell time of 30 minutes is maintained between each test for the rubber wheel to return to room temperature.

* The wear scar was observed after each test and ensured for evenness.

* A new dressed wheel is first used on a soft iron steel using procedure-A, to produce a smooth non-sticky surface. Dressing is done by mounting the wheel on a lathe and machining the surface by using a tool bit specially used for rubber applications.

* The maximum diameter of the rubber wheel is 228.6 mm and the minimum is 215.9 mm. The wheel is relined after it reaches this minimum.

* The mass loss of the specimens is measured using an analytical balance having sensitivity of 0.0001 gms.

* A reference material, 316 SS has been chosen in this work to monitor the apparatus from time to time.

3.3.5 PRESENTATION OF RESULTS

The abrasion test results are presented as volume loss for comparisons between different laboratory tests, and to avoid confusion arising due to differences in densities
between different materials. The mass loss is converted into volume loss as follows:

\[
\text{Volume Loss, (mm}^3\) = \frac{\text{Mass Loss (gms)}}{\text{density (gms/cm}^3\)} \times 1000.
\]

As the rubber wheel wears down in diameter, the abrasion produced is also reduced accordingly. The actual volume loss hence turns out to be inaccurate. The Adjusted Volume Loss (AVL) takes this into account and indicates abrasion produced by a 228.6 mm wheel. The Adjusted Volume Loss is calculated as follows:

\[
\text{AVL} = \frac{\text{Measured Volume Loss} \times 228.6 \text{ mm}}{\text{wheel diameter after use}}.
\]

Three tests were performed on the same day on each of the materials and a consistent reproducibility was maintained within an acceptable narrow range. Statistical analysis of the data showed that the coefficient of variation is less than 7% (the acceptable range), for all the materials that were tested for three body abrasion.

### 3.4 HIGH STRESS ABRASION

To study the high stress abrasive wear behaviour a two body abrasive wear testing system was set up in the laboratory. This model is known as the pin-on-drum machine, and it simulates the practical work conditions.

#### 3.4.1 Pin-on-Drum Machine

The pin-on-drum machine is constituted as shown in the Figure 3.4. The pin specimen is 6 mm in diameter, with an allowable length of 20mm to 35mm. The pin can be adjustable with a screw on the top of the specimen holder, so that it can make full contact with the drum. The rotating drum is 86mm in diameter with a length of 300mm, and is driven by a variable speed electric motor through two gear boxes I and II.
When the drum rotates, the entire surface of the specimen continuously comes in contact with a virgin abrasive paper along a helical path. The wear path for the test is selected as 6m for which the horizontal distance of specimen movement is 181.8mm.

Fig 3.4 Photograph of the pin-on-drum machine.
Fig 3.5  Diagram of the pin-on-drum wear testing machine.
3.4.2 Table-3.4. Design data for pin-on-drum machine

<table>
<thead>
<tr>
<th>Machine Parts</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor</td>
<td>Variable speed 60-200 rpm</td>
</tr>
<tr>
<td>Gear Box-I Motor</td>
<td>Speed reduction ratio $i_1 = 1:10$</td>
</tr>
<tr>
<td>Gear Box-II-Gear-</td>
<td>$Z_1 = 20, Z_2 = 40, Z_3 = 180, Z_4 = 22$</td>
</tr>
<tr>
<td>Speed reduction ratio</td>
<td>$i_2 = Z_1/Z_3 = 1:9, i_3 = Z_3/Z_4 = 90:11$</td>
</tr>
<tr>
<td>Guide screw</td>
<td>$t_s = 1$ mm</td>
</tr>
<tr>
<td>Drum</td>
<td>$D = 86$ mm, $L_D = 300$ mm</td>
</tr>
<tr>
<td>Pin</td>
<td>$d = 6$ mm, $l = 20-35$ mm</td>
</tr>
</tbody>
</table>

Table-3.5 Relationship between sliding speed of specimen and rotating speed of the motor.

<table>
<thead>
<tr>
<th>Motor speed (rpm)</th>
<th>60</th>
<th>200</th>
<th>500</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding speed (mm/s)</td>
<td>3</td>
<td>10</td>
<td>25</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

During wear testing the sliding speed was kept constant at $V = 50$ mm/s.

Table -3.6. Applied load related to added weight (at $V = 50$ mm/s)

<table>
<thead>
<tr>
<th>Added weight</th>
<th>2x50g+25g</th>
<th>5x50g</th>
<th>2Kg+2x50g</th>
<th>2Kg+5x50g</th>
<th>2x50g+4Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied load (N)</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

Load is applied to the specimen by adding weights at the end of the arm connected with the specimen holder.
3.4.3 WEAR TESTING

The wear testing was carried out using the pin-on-drum wear testing machine, with a pin specimen 6mm in diameter and 30mm in length. The specimen was well run-in before the actual test was performed, and tests were performed at varying loads with the wear path and sliding speed kept constant at 6m and 50mm/sec, respectively. The mass loss was determined by weighing the samples before and after the test on an electronic balance sensitive to 0.0001g. The specimen is well cleaned and dried with hot air before weighing. Three tests were performed on each material. The results obtained were meaningful and the variation between each repetition was found to be below 5%.

3.4.4 ABRASIVE PAPERS

Dry abrasive papers of size 230 x 280 mm² were used to cover the drum with one end in a slot located on the drum, and the other end on a double sided adhesive. Commercial silicon carbide, alumina and garnet abrasive papers were selected for wear testing. The abrasive papers from only one manufacturer, Carborundum Abrasives Pty Ltd., Australia, were used in the tests each of a grit size of 180#.

3.5 SPECIMEN PREPARATION FOR MICROSCOPY

Optical and Scanning electron microscopy was done to examine the microstructures of the monolithic materials and the WC/Co powders and coatings. A small section of the monolithic materials was mounted in bakelite and metallographic specimens were made by hot compression. Cross sections of the WC-Co coatings were prepared using a high speed cutting wheel, and mounted using epomet and bakelite (1:1). The powder cross sections were prepared by first mounting very thin layers of the powders in bakelite, and then light polishing on a 1200 grit paper. The monolithic materials were hand
ground using 180, 240, 320, 400, 600, 800 and 1200 grit abrasive papers and then polished on a 6µm and 1µm diamond wheel. For polishing the WC-Co coatings the following procedure was adopted. Grinding and polishing operations were done using an Abramin automatic polishing machine. A 40µm diamond grinding disc was used for 20 minutes. This was followed by polishing on a 6µm diamond polishing pad using a pan-w napless cloth (duration: 27 minutes), followed by polishing on 1µm diamond polishing pad for 5 minutes, and finally using a Metaldi DP Nap cloth for 1/4µm polishing (duration: 2 minutes). A pressure of 200N was applied, and the rpm was maintained at 300, during all the operations.

3.5.1 Table-3.7. ETCHANTS

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>ETCHANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG iron-I and SG iron-II</td>
<td>10 % Nital, swab</td>
</tr>
<tr>
<td>316 SS and 304SS</td>
<td>10% oxalic acid at 0.5 A current and 5V Voltage, 20 secs.</td>
</tr>
<tr>
<td>28% Chromium Iron (As Cast and HT)</td>
<td></td>
</tr>
<tr>
<td>Tungsten carbide-cobalt coatings (88-12%)</td>
<td>Murakami Reagent (10gms K₄FeCN₆+10gms NaOH+10gms H₂O), Swabbed for 2 minutes.</td>
</tr>
</tbody>
</table>

3.6 X-RAY DIFFRACTION

X-ray diffraction of the WC-Co powders and coatings was done at the Research and Technology Center, Sheet and Coil Products Division, BHP, using a Siemens 5000 diffractometer. A full scan was carried out in the angular range of 30-60° at a step size of 0.01°, using a copper Kα radiation, operating under 40KV and 50mA.
3.7 HARDNESS MEASUREMENT

The hardness of the monolithic specimens was measured using a Vickers Hardness Machine at 30Kg load. The hardness values were determined after an average of 5 measurements.
CHAPTER-4

RESULTS
RESULTS

Results are presented in this chapter for:

a) the low stress abrasive wear tests carried out on six monolithic materials, five coated materials and three ceramic materials using the dry sand rubber wheel abrasion tester, described in section 3.1.1.

b) the high stress abrasion tests conducted on six monolithic materials and two coatings using the pin-on-drum machine, described in section 3.4.1.

c) microstructural studies using optical and scanning electron microscopy carried out on the specimen materials to study the worn surface, to understand the prevailing wearing mechanisms, and to study the correlation between the hardness, microstructure and wear rate, and

d) X-ray diffraction to identify the phases present in the WC-Co powders and coatings.

4.1 LOW STRESS ABRASION RESULTS.

The results of the low stress abrasion tests are given in Figs 4.1, 4.2 and 4.3, in which

a) for the six monolithic materials, shown in Fig 4.1, 304SS had the highest adjusted volume loss, while 28% chromium iron (heat treated) iron had the lowest. This indicates that the abrasive wear resistance of 28% chromium (heat treated) iron is the best and the abrasive wear resistance of 304SS is the poorest.

b) for the ceramic materials, shown in Fig 4.2, Al₂O₃-R (alumina) had the highest abrasion resistance, and ALANX-CG273, a ceramic/metal composite, had the lowest.

c) for the coatings, shown in Fig 4.3, the tungsten-carbide-cobalt coating sprayed on stainless steel using JK112 powder had the highest abrasion resistance, and C7928 sprayed on stainless steel had the lowest. The tungsten carbide-cobalt (WOKA) sprayed on stainless steel had a better abrasion resistance than the one sprayed on mild steel.
4.1.1 Relationship between hardness and adjusted volume loss

Vickers hardness (30Kg) was measured for all the monolithic materials. The hardness values are shown in Fig 4.4 as a function of adjusted volume loss, to make comparisons between the hardness and the abrasion resistance of the materials. The results indicate that 28% chromium (heat treated) iron has the highest hardness and 304SS has the lowest hardness, among the materials tested, and that the bulk hardness of the material is only an indicator of its abrasion resistance. For materials of the same class, eg SG iron-I and SG iron-II, 316SS and 304SS, 28% chromium (as cast) iron and 28% chromium (heat treated) iron, the harder the material, the better the abrasion resistance. Comparisons between the hardness and wear resistance of dissimilar materials, eg SG iron and 316SS, cast iron and 304SS, are conflicting, and hardness cannot be used to indicate abrasion resistance.

![Dry Sand Rubber Wheel Abrasion Test Results of Monolithic Materials](image)

Fig 4.1 Low Stress Abrasion Test Results of Monolithic materials.
Adjusted Volume Loss (Avg)

Dry Sand Rubber Wheel Abrasion Test Results of Ceramics.

- Force: 130N, Time: 30mins, (Procedure-A)

Fig 4.2  Low stress abrasion test results of ceramic materials.

Dry Sand Rubber Wheel Abrasion Test Results
of proprietary coatings

- Force: 130N, Time: 30mins, (Procedure-A)

Fig 4.3  Low stress abrasion test results of coated materials.
4.1.2 Microstructure

The microstructures of the monolithic materials are presented from Fig 4.5 to Fig 4.7 to provide comparisons between materials of the same class. Figure 4.5 shows the microstructure of 28% chromium (as cast) iron and 28% chromium (heat treated) iron. The as cast structure, Fig 4.5 (a-b), shows M7C3 eutectic carbides surrounded by a pearlitic matrix. The heat treatment of the as cast iron produced finely dispersed secondary carbides, Fig 4.5 (c-d).
Figure 4.6 (a-d), shows the structures of SG iron-I and SG iron-II. The structure of SG iron-I, 4.6 (a-b), shows large amount of ferrite in the matrix, whereas the matrix of SG iron-II, 4.6 (c-d) was mainly pearlitic. The graphite was spheroidal in both irons.

Figure 4.7 shows the microstructure of 316SS and 304SS. The 304SS has a cast dendritic structure, whereas the 316SS had a banded austenitic structure.

4.1.3. Wear topography after low stress abrasion.

Figure 4.8 a-d) shows wear tracks for five of the monolithic materials. For 316SS, Fig 4.8 a), the wear tracks indicate that plastic flow occurred adjacent to the wear grooves together with some shearing and cutting. For 304SS, Fig 4.8 b), the wear tracks indicate pits inside the grooves with significant amounts of microcutting. The wear track of SG iron-II Fig 4.8 c), shows large amounts of pitting, and the mechanism of wear appears to be microcutting. The 28% chromium iron, Fig 4.8 d), whose abrasion resistance is very high, showed a prow inside the wear track at a very high magnification, indicating that the material was hardly being worn. Figure 4.9 presents the photomicrograph of the WC-Co coating before and after wear. It indicates that the coating did not fail after the low stress abrasion test, and the possible wear mechanism would have been selective removal of the cobalt binder, followed by removal of the carbide grains.

4.2 HIGH STRESS ABRASION

Results of the six monolithic materials and WC-Co coatings (prepared using JK112 and WOKA powders, at 45 psi chamber pressure) studied under two body high stress test condition are presented from Fig 4.9 to Fig 4.11. The applied load was the only variable in all the groups of the test, and the sliding speed and the wear path were kept constant. The standard testing condition was 20N applied load, 50mm/s sliding speed and 6m wear path.
Fig 4.5 Photomicrographs showing the structure of 28% chromium (as cast and heat treated) iron. The heat treated structure clearly indicates the finely dispersed carbides.
Fig 4.6 Photomicrographs showing the structure of SG iron-I and SG iron-II. The difference between the matrix is clearly observed. The SG iron-I indicates large amounts of ferrite in the matrix.
Photomicrographs showing the structure of 304SS and 316SS. The 304SS indicates a cast dendritic structure. a) cast structure showing carbide precipitation (overetched), b) structure showing 100% FCC austenite grains and the bands represent plastic deformation. Black spots are etching artefacts.
Fig 4.8 Photomicrographs showing topography of the worn surface after dry sand rubber wheel abrasion test (Procedure-A). Mag 1.2 KX. a) ductile flow of material representing microploughing, b) microchips observed on the surface representing microcutting, c) detached wear debris showing microcracking, d) displaced prow showing a cutting action.
Mag 800X

Dense WC-Co coating

Fig 4.9 Photomicrograph of wear scar of tungsten carbide-cobalt coating (JK112) after RWAT, and the unworn coating.
4.2.1 Effect of Applied Load.

Relationship between mass loss and applied load from 10N to 50N, 50mm sliding speed and 6m wear path are shown in Fig 4.10, for SiC abrasive, Fig 4.11 for alumina abrasive, and Fig 4.12 for garnet abrasive. Figure 4.10 shows that mass loss increases with load, for all the six monolithic materials. The SG iron-I showed the highest mass loss and 28% chromium (heat treated) iron showed the lowest. Nonlinearity between mass loss and load was observed for all the materials, and at 10N load, the mass loss of SG iron-II was found to be greater than SG iron-I. The WC-Co coating prepared from JK112 source showed a lower mass loss than the coating prepared from WOKA source.

Figure 4.11 shows that the mass loss of SG iron-I is the highest and 28% chromium (heat treated) iron is the lowest, for 120# alumina abrasive, similar to the results obtained using SiC abrasive. The mass loss however was higher for the alumina abrasive than for the SiC abrasive. The notable feature was the lower mass loss of 304SS compared to 28% chromium (as cast) iron.

Fig 4.12 shows that the mass loss of SG iron-II is the highest and 28% chromium (heat treated) iron is the lowest, for garnet abrasives.

The relationship between the mass loss and applied load was however nonlinear, for each of the three abrasives. For the different abrasives it is clear that the 28% chromium (heat treated) iron has the lowest mass loss, among the monolithic materials that were studied.
High Stress Abrasion Test Results.  
Conditions: V=50mm/sec, Path 6m, 180# SiC Abrasive.

![Graph showing mass loss and applied load for Silicon Carbide abrasive.](image)

Fig 4.10  
Diagram showing mass loss and applied load for Silicon Carbide abrasive.

HIGH STRESS ABRASION TEST RESULTS.  
CONDITIONS: V=50mm/sec, wear path=6m, 120# Alumina.

![Graph showing mass loss and applied load for alumina abrasive.](image)

Fig 4.11  
Diagram showing mass loss and applied load for alumina abrasive.
HIGH STRESS ABRASION TEST RESULTS.
CONDITIONS: V=50mm/sec, Wear Path=6m, 180# garnet.

Fig 4.12 Diagram showing mass loss and applied load for garnet abrasive.

4.2.2 Topography of the Worn Surface

The topographical features of the pin specimens under standard test conditions of applied load 20N, wear path 6m and sliding speed 50mm/sec, for 180# SiC abrasive, were observed using scanning electron microscopy. Figure 4.13 a) shows that in the SG Iron-I, cut chips were formed on the worn surface and the predominant wear mechanism appeared to be microcracking, which resulted in large removal of wear debris. Fig. 4.13 b), shows that in the SG iron-II fracture cracking took place causing
significant material removal. Fig.4.13 c) and Fig.4.13 d) shows 316SS and 304SS respectively, and the dominant wear mechanism in both appears to be microcutting followed by fracture.

Figure 4.13 e) and Fig 4.13 f) shows 28% chromium irons, both in the as cast and heat treated conditions. The wearing mechanism is observed to be microploughing, since prongs are seen on the abraded surface, and material removal seems to have taken place due to repeated contact with the abrasive.

4.3 THERMAL SPRAY COATINGS

One of the principal functions of this work was to compare the wear characteristics of thermally sprayed WC-Co coatings with the wear characteristics of other engineering materials. After studying the low stress and high stress behaviour of a range of materials, a special study on WC-Co coatings was undertaken. These coatings are principally known for their excellent abrasion resistance, and in this work the coatings were studied using two variables, a) powder source and b) chamber pressure.

Tungsten carbide-cobalt powders from two sources JK112 and WOKA, were characterised using scanning electron micrography and X-ray diffraction. The WOKA is a sintered and crushed powder, of composition (WC 88%-Co 12%), and mesh size -325/down, whereas the JK112 is a premium grade sintered powder. The JK112 and WOKA powders were sprayed on stainless steel substrates using a high velocity air-fuel thermal spray system.
Fig 4.13 Photomicrographs showing topography of the worn surface after high stress pin abrasion test. Test conditions: V=50mm/sec, load=20N, X=6m, 180# SiC abrasive. (Mag 500X), a) cut chips due to wear debris removal causing microcracking, b) fracture cracking, c & d) microcutting followed by fracture, e & f) microploughing as a precursor to microcracking.
4.3.1 Powder Characterisation

Figure 4.14 (a-d), shows the photomicrographs of the two powders JK112 and WOKA. The WOKA is a round and porous powder with a spherical morphology, whereas the JK112 has an angular morphology. Both powders appear to have tungsten monocarbide and metallic cobalt finely distributed in them.

Figure 4.15 shows the cross sections of the two powders WOKA and JK112. The cross sections reveal that the JK112 particles are less porous than the WOKA particles.

Figure 4.16 shows the results of the X-ray diffraction studies carried out on the two powders. A full scan in the angular region of 30-60°, using a copper Kα radiation operating at 40KV and 50mA, revealed broad low intensity peaks of cobalt (111) at a 2θ range of 42-44°, in both the powders. The observation of the peaks showed that the WOKA powders were pure, with WC as the major phase and cobalt (111) as the minor phase. However, the decarburization product W2C was indicated in the X-ray diffraction chart of the JK112 powder, Fig 4.16.

4.3.2 Coating Characterisation

The JK112 and WOKA powders were thermally sprayed using the High Velocity Air Fuel system, described in section 3.2.3. Table 4.1 presents the maximum thickness of the coatings. Both the WOKA and the JK112 coatings had an uneven thickness when sprayed with a traversing gun with the substrates kept stationary (during first set of sample preparation).
Fig 4.14 Photomicrographs of the two powders used for thermal spraying, showing different morphologies.
Fig 4.15 Photomicrographs showing the cross sections of WOKA and JK112 powder particles. The JK112 particles are clearly less porous than WOKA particles.
Fig 4.16  X-ray diffraction charts of the two powders used for thermal spraying, showing peaks of the various phases.
Table 4.1 Coating Thickness.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>COATING THICKNESS (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WOKA</td>
<td>230mm</td>
</tr>
<tr>
<td>JK112</td>
<td>220mm</td>
</tr>
</tbody>
</table>

Figure 4.17, shows the micrographs of the first set of coatings that were prepared. On observing the WOKA and JK112 coatings, it was found that the WOKA has a lower porosity than the JK112 coating, but this result cannot be considered conclusive due to the unsuitability of Silicon Carbide abrasive for metallography.

Figure 4.18 shows the X-ray diffraction charts of the two coatings. The peaks of the JK112 coating showed the presence of the decarburization product W2C (422), at various regions. The coating sprayed with WOKA powder was however observed to be pure, and it did not show any signs of decarburization or eta phase formation.

Figure 4.19 (a-d) shows the photomicrographs of the coatings. Tungsten monocarbide is present as irregular shaped particles surrounded by the cobalt binder. Porosity is clearly observed in both the JK112 and WOKA coatings. The presence of the W2C phase in the JK112 is considered to be detrimental to the mechanical properties of the coating.
Fig 4.17 Photomicrographs of the two coatings showing varying levels of porosities, when SiC abrasive is used during polishing.
Fig 4.18  X-ray diffraction results of the JK112 and WOKA coatings after thermal spraying. The JK112 coating indicates decarburization peaks.
Fig 4.19 Photomicrographs of the JK112 and the WOKA coating showing porosity.
4.3.3 Effect of Chamber Pressure on the coating

The five coatings prepared by varying the chamber pressures were subjected to low stress abrasive wear using procedure-A. Figure 4.20 shows the results of the abrasion tests conducted on the coatings. The JK112 coating prepared at 45 psi showed excellent abrasion resistance. Among the coatings prepared using the WOKA source, the coating sprayed at 40 psi showed the highest abrasion resistance. The coatings sprayed at 30 and 35 psi had the highest adjusted volume loss, and were severely worn after the test.

Fig 4.20 Low stress abrasion test results of WC-Co coatings sprayed at varying chamber pressures.
4.3.3.1 X-ray diffraction results

Figures 4.21 and 4.22, indicate that the coatings prepared from WOKA powder at various chamber pressures had WC as the major phase, and cobalt as the minor phase, along with some elemental tungsten. There was no evidence of any eta phase nor any other decarburization product in the coating. The X-ray results indicate that no phase transformation occurred with increasing chamber pressure, when WOKA powder was used. The peak intensity of WC, however, decreased with increasing chamber pressure. On the contrary, the coating prepared using the JK112 powder at 45 psi, showed the decarburization product W2C at various regions in the X-ray chart, Fig 4.23, indicating that decarburization occurs on using the JK112 powder.

4.3.3.2 MICROSTRUCTURE OF THE COATINGS

Figure 4.24 shows the optical micrographs of the coatings sprayed at different chamber pressures. All the coatings sprayed with the WOKA powder showed large amounts of cobalt pools in the coatings, whereas the JK112 sprayed coating did not show any.

The Photomicrographs in Fig 4.25 show that the cobalt lakes are not continuous, and they contain voids within them. At lower chamber pressure the voids appear to be more compared to higher chamber pressures.

A dendritic network feature characteristic of a nucleation mechanism was observed within the cobalt pools shown in Fig 4.26. Conclusive statements about these features can however be only made by performing transmission electron microscopy on the coatings.
Fig. 4.21 X-ray diffraction charts of the HVAF sprayed (WC-Co) coatings prepared with the WOKA powder, at 30 and 35 psi chamber pressures.
Fig. 4.22  X-ray diffraction chart of the HVAF sprayed (WC-Co) coatings, prepared using WOKA source at 40 and 45 psi chamber pressures.
Fig. 4.23 X-ray diffraction chart of the HVAF sprayed (WC-Co) coating prepared using JK112 source powder, at 45 psi chamber pressure. The coating indicates the presence of the decarburization product W₂C.
Fig 4.24 Photomicrographs of the coatings sprayed at different chamber pressures showing large cobalt pools in the WOKA coatings (As Polished, Mag 200X).
Fig 4.25 Photomicrographs of the coatings prepared at different chamber pressures, showing cobalt pools and varying porosities.
Fig 4.26 Photomicrographs of the coatings sprayed at 40 psi chamber pressures showing a dendritic nucleation feature within the cobalt pools in the WOKA coatings.
DISCUSSION

CHAPTER 5
DISCUSSION

In the present chapter the results presented in the last chapter have been discussed. In section 5.1, a discussion is presented on the low stress abrasion behaviour of the materials and the factors affecting the abrasion process and the various mechanisms involved. Section 5.2 provides a discussion on the high stress abrasive behaviour of monolithic materials and WC-Co coated materials. Finally, section 5.3 provides an indepth discussion on the HVAF sprayed WC-Co coatings.

5.1 LOW STRESS ABRASION

Six monolithic, three ceramics, 3 proprietary coatings and a series of WC-Co coatings were tested for low stress abrasive wear in order to understand the behaviour of these materials under such a kind of wear. Low stress abrasion occurs commonly in mining, earthmoving and various agricultural and machine parts, and is yet considered to be one of the least understood. The abrasion tests conducted using a rubber wheel abrasion tester gave some useful and interesting information. Among the six monolithic materials that were tested, the 304 stainless steel showed the poorest abrasion resistance, while the 28% chromium iron in heat treated state showed the best, Fig 4.3. The 28% chromium (as cast) iron, which shows the second best abrasion resistance, questions the need for complex and expensive heat treatments to improve the abrasion resistance of high chromium irons. Similar tests conducted on ceramic materials, Fig 4.3, showed that, alumina-R had the best abrasion resistance, whereas ALANX-CG273, a ceramic/metal matrix composite, had the poorest abrasion resistance. The thermally sprayed tungsten carbide-cobalt coatings prepared on stainless steel showed the best abrasion resistance among the coatings tested, whereas C7928 a proprietary coating (chemically bonded ceramic matrix composite) showed very poor abrasion resistance.
The analysis of the quantitative wear data of different materials prompted further investigation into the factors affecting abrasive wear, and correlation between microstructure, bulk hardness and resistance to abrasion was sought.

5.1.1 THE EFFECT OF HARDNESS AND MICROSTRUCTURE ON ABRASIVE WEAR RESISTANCE

Work by previous researchers such as Moore, Prasad and Kulkarni et al (25, 82) has shown that abrasive wear resistance can be explained neither by bulk hardness, nor the morphological characteristics. However, it has been suggested (25) that material microstructure has a greater influence on the wear resistance than bulk hardness.

Figure 4.4 corroborates the work done by most of the previous researchers. A correlation between bulk hardness and wear resistance can be drawn for materials of similar class, and it is observed that the harder the material the more wear resistant it is. However, comparing the 316SS and the SG iron-II it is found that the 316SS, although having a higher hardness than SG iron-II, has a much lower abrasion resistance, which clearly suggests the significance of microstructure when comparing dissimilar materials. A similar disparity occurs on comparing SG iron-I and 316SS. The microstructures of all the monolithic materials studied are different. The SG iron-I and SG iron-II had a characteristic "Bulls Eye" structure, Fig 4.6, with the graphite surrounded by ferrite in a pearlitic matrix. The higher volume loss (220.47) and lower hardness of SG iron-I, when compared to SG iron-II (165.06) is in agreement, due to the higher volume fraction of ferrite in the structure of SG iron-I as indicated in Fig 4.6. In SG iron-II, the matrix consists of a larger amounts of pearlite, and pearlite being a hard constituent explains for the higher hardness and wear resistance of SG iron-II. Comparing the microstructures of 304SS and 316SS, the lower wear resistance of
304SS is due its cast dendritic structure, whereas 316SS which has a banded austenitic structure has a higher hardness and a higher wear resistance.

The 28% chromium irons generated particular interest in this study, because of their historical importance as highly abrasion resistant materials used for slurry pumps, mill liners and liner plates for crushers, and various other earthmoving equipment. The high hardness is the principal reason for the industrial importance of these irons and the high hardness is due to the presence of M7C3 carbides. Studies on abrasion resistance of these irons has indicated that martensitic white irons have superior abrasion resistance to pearlitic or austenitic white irons. The hardness of the abrasive has a marked influence on the abrasion resistance of these alloys. Silica which is the most commonly encountered abrasive in service, is not hard enough to abrade the M7C3 carbides, but it can abrade martensite, pearlite or austenite. The M7C3 carbides thus stand out in relief during the abrasion process. Figure 4.5 (a-d) shows the microstructural features in the as cast and heat treated conditions. The as cast structure shows the M7C3 carbides in the pearlitic matrix. Heat treatment by austenization at 1000°C for 3-4 hours to precipitate dispersed secondary M3C particles followed by air quenching and stress relief tempering at 200-250°C, causes an increased hardness, which leads to enhancement in abrasive wear resistance. This observation is similar to work done by Avery, Fulcher and Zum Gahr (42, 44, 28), who stated that M7C3 eutectic carbides were effective in improving abrasion resistance.

5.1.2 WEAR MECHANISM

Zum Gahr (28) suggested that the removal of material from the surfaces of steels worn by hard abrasives takes place by three principal mechanisms namely, microploughing, microcutting and microcracking. The phenomenon of microploughing involves a ductile flow of material and is clearly shown for 316SS, Fig 4.8 a). Material is lost by repeated contact with the abrasive particles in the form of wear debris. Microcutting
appears to be the possible wear mechanism in 304SS, Fig 4.8 b), and the wear rate is also effectively higher than 316SS. Micropits which are observed within the wear tracks could have been due to the cast dendritic structures of this steel. A transition from microcutting to microcracking, is observed in SG iron-II and cracking is clearly revealed in Fig 4.8 c). A prow which is displaced to the side is revealed in the high chromium irons Fig 4.8 d), suggesting that a cutting mechanism takes place, which is due to the high hardness of these irons. However, the material loss was very low for these irons.

5.2 HIGH STRESS ABRASION

Investigation of the six monolithic and two WC-Co coatings using both (JK112 and WOKA source) prepared at 45psi chamber pressure indicated that 28% chromium (heat treated) iron had the lowest mass loss for each of the three abrasives, SiC, alumina and garnet. The JK112 coating had a better abrasion resistance than the WOKA coating for SiC abrasive.

5.2.1 EFFECT OF APPLIED LOAD

The wear rate in the case of all the materials tested using SiC, alumina and garnet abrasives appeared to increase with increasing load. Increase in mass loss is attributed to the increase in groove depth and number of grooves formed. The results of these tests, from Fig 4.10 to Fig 4.12, clearly indicate that 28% chromium (heat treated) iron has the lowest mass loss under each of the three different types of abrasives. Relationship between the applied load and wear rate is clearly dependent on the microstructure of the material and the abrasive hardness. The 28% chromium iron (as cast) showed a higher mass loss than 304SS for alumina abrasive, which is attributed to the change in wear mechanism, due to similar hardness of alumina and the M7C3
carbides. The heat treated chromium iron due to the M3C dispersed carbides, provides a better relief against the abrasive particles, subsequently leading to lower mass losses.

The WC-Co coating prepared using powder source JK112, and sprayed at 45psi chamber pressure, is very dense with few ductile cobalt pools compared to the coating prepared from WOKA, which explains its lower mass loss.

5.2.2. WEAR MECHANISM

Wear mechanisms were studied under the "standard wear test condition" of applied load: 20N, wear path: 6m, sliding speed: 50mm/sec, 180# SiC. The results presented in Fig 4.13 clearly indicate that wear debris is mainly formed by microcutting or microcracking, with microploughing as the precursor to these mechanisms. The process of microploughing occurs due to plastic deformation and material is removed by a low cycle fatigue on repeated contact with the abrasive. During microcutting ribbon like chips form the wear debris and are known as microchips. Microcracking takes place due to highly concentrated stresses, which leads to crack formation and propagation. Both the SG iron-I and SG iron-II underwent fracture to form wear debris, and microcracking took place after microcutting. The high chromium irons which had the lowest wear rate, had curled prows and also indicated occasional microcutting.

5.3 HVAF SPRAYED WC-Co COATINGS

A wide variety of research activity is taking place worldwide to characterize the tungsten carbide-cobalt coatings. Various processes such as High Velocity Oxygen Fuel (HVOF), High Energy Plasma (HEP) and Plasma spraying are being used to deposit the coatings. The starting powders are being manufactured by different techniques, such as, fusing and crushing, sintering and crushing and agglomeration and
sintering types. Each powder manufactured by a certain technique varies in chemical composition, particle morphology and particle size distribution.

The two powders JK112 and WOKA, which were used in the present work, varied in morphology as shown in Fig 4.14. The sintered and crushed WOKA powder, had a rounded morphology with finely distributed tungsten monocarbide and cobalt. However, the cross sections of the powders shown in Fig 4.15, indicated that WOKA particles were more porous then the JK112 particles. X-ray diffraction results shown in Fig 4.16 shows that WC is the major phase and cobalt is the minor phase, in the WOKA powder. There are no signs of decarburization, nor eta phase formation, suggesting that the starting powders were free from any deleterious phase contamination. On the contrary, the JK112 powder shows the presence of the decarburization product W₂C, as shown in the X-ray chart in Fig 4.16. The occurrence of this phase may be attributed to the powder manufacturing technique. Similar work was done by Ramanathan and Jayaraman (79), who observed that sintered and crushed powders are porous and rounded, and WC and cobalt are finely distributed in them. The study of the two powders indicates the importance of appropriate choice of the powder, and the understanding of the powder manufacturing method to produce these types of coatings.

The choice of substrate is equally important in preparing these type of coatings and Fig 4.3 suggests the suitability of stainless steel over mild steel, due to a higher volume loss observed after abrasion tests, when using mild steel as a substrate. This is possibly due to stronger mechanical bonds formed in stainless steels.

5.3.1 METALLOGRAPHY AND PHASE ANALYSIS OF THE COATINGS

The results of the powder and coating characterisation confirmed observations by previous researchers. Decarburization was observed in the JK112 powder, and the
resultant coating also showed the presence of W\textsubscript{2}C, which is confirmed by X-ray diffraction. Initially the porosity of JK112 coating appeared to be higher than the porosity of the WOKA coating, but it was later confirmed that removal of particles during grinding with SiC abrasive, often led to erroneous and misleading interpretations about the apparent porosities of the coatings. In fact the JK112 coating had a lower porosity than the WOKA coating. This is possible due to more even spreading of the JK112 particles after striking the substrate at very high velocities. The WOKA particles which are essentially more porous than JK112, spread unevenly on striking the surface, leading to porosity in the coating. It can hence be said that porosity in the starting powder can lead to porosity in the coating.

5.3.2 EFFECTS OF CHAMBER PRESSURE VARIATION ON ABRASIVE WEAR AND MICROSTRUCTURE.

The low stress rubber wheel abrasion test conducted on the coatings prepared by varying the chamber pressures provided interesting results. The 30 and 35 psi chamber pressures were inappropriate to produce the WC-Co coatings using the HVAF process. Both the coatings had high adjusted volume losses and both the coatings were worn through to the substrate. It is observed that as the chamber pressure was increased, the apparent porosity in the coatings was lowered. The WC-Co particles are softened and some of them are partially melted in the high temperature flame region, and upon impact with the substrate, tend to spread evenly across the surface. They form successive layers upon repeated impacts and a lamellar structure is obtained. At lower chamber pressures, due to lower particle velocities, the particles do not attain sufficient kinetic energy to spread upon impact. Thus, the porosity tends to be higher in the coatings sprayed at lower chamber pressures. Porosity in the WOKA coating is also higher than the JK112 coating, mainly due to the larger porosity in the WOKA starting powders, Fig 4.15.
The WOKA coatings sprayed at 40 and 45 psi proved to have a good abrasion resistance. Interestingly, L & R Ashbolts have been using 40 psi as the chamber pressure in all their work with WC-Co coatings, which probably justifies its use. The X-ray diffraction data in Fig 4.21 showed no eta phases or W\(_2\)C, but traces of elemental tungsten were detected. All the WOKA sprayed coatings at various chamber pressures showed similar peaks.

The most significant observation which needs much further investigation is the excellent abrasion resistance of the JK112 sprayed coating. The JK112 coating was sprayed at 45 psi, and it had the highest abrasion resistance, even as the coating showed the presence of the decarburizing product W\(_2\)C, as indicated in Fig 4.22. A broad hump was observed in the region 42-44° and the phase could not be clearly ascertained. This broad hump is characteristic of an amorphous region as has been indicated by various other researchers. John Nerz and Burton Kushner (73) who conducted various differential thermal analysis (DTA) tests on similar coatings found that at approximately 860°C, there is an indication of a strong exothermic reaction which recrystallizes the amorphous region into eta phase carbides Co\(_6\)W\(_6\)C and Co\(_2\)W\(_4\)C, and the precipitation of these eta phase carbides markedly improves the wear resistance of the coatings. Similar observations were made by X. Provot and D. Mannesse (78) and they recommended the need for a more thorough characterization of the amorphous phase.

A great deal of investigation needs to be done in this area to conclusively observe the effects of W\(_2\)C and the other cobalt bearing subcarbides on abrasive wear. It is understood that W\(_2\)C with a microhardness value of 3000 Kg/mm\(^2\) is harder than WC, which has a microhardness value of 2400, but is still considered to be undesirable due to poor mechanical properties resulting from its brittleness. However, whether its presence is detrimental to abrasion resistance needs a more careful evaluation, since it does not appear to be the case from the work done in this present work. It is understood
that a good coating essentially has minimal porosity, minimal decarburization, and a large volume fraction of WC with a fine grain size, for optimum mechanical properties.

5.3.3 CRUCIAL OBSERVATIONS

The work done so far on the coatings sprayed at different chamber pressures provided interesting findings, and also assisted to elucidate other aspects that need to be examined more carefully, while investigating these types of coatings. Firstly, the polishing methods have to be appropriately ascertained, and automatic polishing should be essentially done using a diamond lapping for grinding, and diamond slurry for final polishing. This method has shown a marked reduction in the apparent porosity, which otherwise showed large inconsistencies when using Silicon Carbide abrasive for grinding. Similar suggestions have also been made by M.F Smith and D.T Mc Guffin (83). They observed that polishing with SiC leads to edge rounding and significant particle pull outs.

A critical feature that was observed for the second set of coatings, was the presence of large amounts of cobalt pools in the WOKA coatings, when prepared by varying the chamber pressure. The source of these cobalt pools is essentially the starting powders, but cross sections of the starting WOKA powders used during the first set of samples did not show any cobalt pools. While making the second set of coatings, powder samples were not taken again for characterisation, assuming that WOKA powders from the same manufacturer would not vary in composition. But the presence of large cobalt pools in the second set of coatings, questions the reliability of the powders that come from the manufacturer. It seemed obvious that powders from WOKA coming as WC-Co (88-12%) were varying in both chemical and physical composition. Hence it is particularly important to take a sample of the powders from the hopper before making coatings from them, and characterize them each time before a set of coatings are prepared, to make affirmative judgements about the coatings quality and integrity.
CHAPTER 6

CONCLUSION
CONCLUSION

The present research was undertaken to understand and evaluate the abrasion resistance of selected engineering materials which include monolithic, ceramic and thermal spray coatings. The major concentration of the research was to analyze tungsten carbide-cobalt coatings, and to understand the properties of the starting powders and the thermal spray processing parameters, which influence the coating quality and integrity.

The conclusion from the work are as follows.

1. Among the monolithic materials studied under three body low stress abrasion test conditions, the 28% chromium iron in the heat treated condition offered excellent resistance. This is due to the precipitation of dispersed secondary M3C carbide particles during heat treatment, which led to increased hardness and abrasion resistance. The 28% chromium iron (as cast) offered the second best abrasion resistance because M7C3 carbides provided relief against the abrasives, whereas 304SS showed the poorest due to its cast dendritic structure.

2. Among the ceramic materials studied under three body low stress abrasion test conditions, alumina showed the best abrasion resistance, followed by zirconia. Alumina also showed the best resistance to abrasive wear among all the materials investigated for low stress abrasive wear in this present work.

3. Among the WC-Co coatings studied under three body low stress abrasion test conditions:
   a) tungsten carbide-cobalt (WC-Co) coatings prepared by the HVAF process provided higher abrasion resistance than the 28% chromium (heat treated) irons, but they were inferior to both alumina and zirconia,
b) the WC-Co coatings prepared on stainless steel substrate showed better abrasion resistance than the coatings prepared on mild steel substrate,
c) the coatings prepared using the JK112 source powder showed better abrasion resistance than the coatings prepared using the WOKA source powder, and
d) the JK112 coating sprayed at 45 psi provided the best abrasion resistance, among the coatings studied from chamber pressures 30 to 45 psi. This was due to higher coating densities achieved at higher chamber pressures.

4. Under two body high stress abrasion test conditions:
a) For SiC abrasive - tungsten carbide-cobalt coating prepared using JK112 powder at 45 psi chamber pressure showed better abrasion resistance than the coating prepared using WOKA powder. Among the monolithic materials, 28% chromium iron (heat treated) showed the best abrasion resistance, whereas SG iron-I showed the poorest
b) For alumina abrasive - 28% chromium (heat treated) iron showed the best abrasion resistance, whereas SG iron-I showed the poorest
c) For garnet abrasive - 28% chromium (heat treated) iron showed the best abrasion resistance, whereas SG iron-II showed the poorest.

5. The JK112 source starting powders and the coatings produced from them showed the presence of decarburization product W2C, whereas the WOKA source starting powder and the coatings prepared from them did not show its presence.

6. The coatings prepared at higher chamber pressures, had lower porosities and showed better abrasion resistance. This was essentially due to the attainment of higher particle velocities of the starting powders in the thermal stream at higher chamber pressure, which subsequently led to denser coatings. Even though the dwell time of the particles was reduced at higher chamber pressure, causing lesser particles to be melted, the impact due to the high kinetic energy caused the softened particles to spread more evenly across the surface.
REFERENCES
REFERENCES


34. F. Borik, "Rubber Wheel Abrasion Test" *Society of Automation Engineers. Pap. 700687 Sep 1970.*


52. S. Lampman, "Introduction to Surface Hardening of Steels", *ASM International, p259-267.*

54. Comparison of Surface Treatment Processes, "Wear Resistant Surfaces in Engineering". Publ: Her Majesty's Stationary, Dept of trade and industry, ISVM 0115138269


58. Courtesy, : "L &R Ashbolt Pty Ltd. and C-Ramic Australia Pty. Ltd".


70. H. E Exner, "Physical and Chemical nature of Cemented Carbides" International Metals Review, 1979, No 4, p149-172.


