A COMPARATIVE STUDY ON WEAR AND CORROSION BEHAVIOUR OF TUNGSTEN CARBIDE-NICKEL AND TUNGSTEN CARBIDE-COBALT HIGH VELOCITY OXY-FUEL (HVOF) FOR CARBON STEEL BLADE

NOOR AQILAH BINTI AHMAD

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

A COMPARATIVE STUDY ON WEAR AND CORROSION BEHAVIOUR OF TUNGSTEN CARBIDE-NICKEL (WC-Ni) AND TUNGSTEN CARBIDE-COBALT (WC-Co) HIGH VELOCITY OXY-FUEL (HVOF) FOR CARBON STEEL BLADE

NOOR AQILAH BINTI AHMAD

The report submitted as partial fulfilment of the requirement for the award of the Degree of Master of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

AUGUST 2017

Dedicated to my beloved parents, sisters, brothers and for those who have contributed to me in order for my completion of this thesis.

Thank you for the support and encouragement.

ACKNOWLEDGMENT

I would like to express my deepest appreciation to my project supervisor, Dr Zakiah Binti Kamdi, who has guided me with care. She has shown the attitude and the substance of a genius: excitement in regard to guidance and invested her full effort in guiding me to achieve the goal. Without her supervision and constant help this project would have not been possible.

Furthermore, a word acknowledges also goes to my co-supervisor, Dr Abdul Latif Bin Mohd Tobi for allowed me to experience master project under his supervision, which encouraging my research and for allowing me to grow as a research scientist. Your advice on both research as well as on my career have been priceless. Thank you for the ideas, encouragement, and understanding on my research project from Material Laboratory's assistant engineer (FKMP), Mr. Anuar and Mr Termizi. All instruction and guidance were much appreciated, which was allowing me to move forward.

I would also like to show my gratitude to the Tioxide (Malaysia) Sdn Bhd for sharing their knowledge and pearls of wisdom with us during the course of this research. This research was financially supported by Knowledge Transfer Programmed (KTP) project under grant no 1483.

Not to forget our parents, my families and friends to give their spirit and encouragement to me finish this final project until the end. Especially, to them given all the energy will be remembered forever.

ABSTRACT

Nowadays, the demand of high wear and corrosion resistance of the components in various industry is increasing from time to time. Therefore, high velocity oxy-fuel (HVOF) thermal spray was introduced to protect machine components from wear and corrosion, to restore worn components and to improve the durability of the components. HVOF is one of the process of depositing a material layer over a base metal or substrate with characteristics of high flame velocity and moderate temperature. The main purpose of this present study is to characterize the structure of the tungsten carbide 10 wt.% nickel (WC-10Ni) and tungsten carbide 12 wt.% w cobalt (WC-12Co) coating deposited by means of HVOF thermal spray onto a continuous digester (CD) blade that made up from carbon steel. The morphology and chemical composition of the coating were characterized by scanning electron microscope (SEM), electron dispersive spectrometer (EDS), and x-ray diffraction (XRD). The hardness test was carried out by using Vickers micro-hardness tester with load of 490.3 mN (0.05 HV). The wear and corrosion behavior and mechanism for both coatings was compared. Three body wear test was carried out in term of weight loss and electrochemical test was performed in acidic media (mixture of sulfuric acid, H_2SO_4 and ilmenite) to obtain the corrosion rate of the coating. From the result, it shows that WC-12Co coating has finer grain size that is around 2.3 µm. WC-12Co has higher wear resistance due to high volume friction, low mean free path, high hardness and lower porosity distribution compared to WC-10Ni. Besides, the formation of secondary phase, W_2C also affected the hardness of both coating, where this phase is harder than WC phase. For corrosion test, WC-12Co shows good corrosion resistance with small differences of corrison rate with WC-10Ni, that is only 0.7016 mm/y. As a conclusion, WC-12Co HVOF coating shows high potential on replacement of CD blade.

ABSTRAK

Pada masa kini, permintaan yang tinggi terhadap komponen yang memiliki rintangan haus dan kakisan dalam pelbagai industri semakin meningkat dari semasa ke semasa. Oleh itu, bahan bakar oksigen berhalaju tinggi (HVOF) diperkenalkan untuk melindungi komponen mesin dari haus dan kakisan, untuk memulihkan komponen yang rosak dan memperbaiki ketahanan komponen. HVOF adalah salah satu proses pengenapan saduran bahan ke atas logam asas atau substrat dengan ciri-ciri halaju nyalaan tinggi dan suhu sederhana. Tujuan utama kajian ini adalah untuk mencirikan struktur tungsten karbida 10 wt.% nikel (WC-10Ni) dan tungsten karbida 12 wt.% kobalt (WC-12Co) saduran yang diendap melalui semburan haba HVOF ke atas bilah cernaan berterusan (CD) yang diperbuat daripada keluli karbon. Morfologi dan komposisi kimia saduran dicirikan oleh mikroskop pengimbas elektron (SEM), spektrometer penyebaran elektron (EDS), dan pembelauan sinar x-ray (XRD). Ujian kekerasan dilakukan dengan menggunakan penguji kekerasan mikro Vickers dengan beban 490.3 mN (0.05 HV). Tingkah laku dan mekanisme haus dan kakisan telah dibandingkan bagi kedua-dua saduran. Haus tiga jasad telah dijalankan dalam bentuk kehilangan berat dan ujian elektrokimia dilakukan dalam media berasid (campuran asid sulfurik, H_2SO_4 dan ilmenit) untuk mendapatkan kadar kakisan saduran. Dari hasilnya, ia menunjukkan bahawa lapisan WC-12Co mempunyai saiz butir yang lebih halus iaitu sekitar 2.3 µm. WC-12Co didapati menghasilkan rintangan haus yang lebih tinggi disebabkan oleh isipadu geseran yang tinggi, laluan bebas purata yang rendah, kekerasan yang tinggi dan pengagihan keliangan yang lebih rendah berbanding dengan WC-10Ni. Selain itu, pembentukan fasa sekunder, W_2C menjejaskan kekerasan kedua-dua saduran, di mana fasa ini lebih keras daripada fasa WC. Untuk ujian kakisan, WC-12Co menunjukkan rintangan kakisan yang baik dengan perbezaan kadar kakisan yang rendah dengan WC-10Ni, iaitu hanya 0.7016 mm/y. Sebagai kesimpulan, saduran WC-12Co HVOF menunjukkan potensi tinggi sebagai penggantian bilah CD.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

WC-10Ni	-	Tungsten carbide- 10 wt.% nickel
WC-12Co	-	Tungsten carbide- 12 wt.% cobalt
HVOF	-	High velocity oxy-fuel
CD	-	Continuous digester
SEM	-	Scanning electron microscope
EDS	-	Electron dispersive spectrometer
XRD	-	X-ray diffraction
WC	-	Tungsten carbide
Ni	-	Nickel
Co	-	Cobalt
SMAW	-	Shielded metal arc welding
EDM	-	Electrical discharge machining
W_2C	-	Tungsten dicarbide
W	-	Tungsten
SiC	-	Silicon carbide

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Nowadays, weld hardfacing had been evolved rapidly and are applied in various industries including nuclear, steam power plants, agriculture and railways, and even in aerospace components (Kirchgaßner *et al.,* 2008). These process not only capable to reduce the cost but also hold promise in improving the life service of machine parts by fabricating or rebuilding (Pradeep *et al.*, 2013). However, this hardfacing techniques also brings along together some crucial problems such as wear, erosion and corrosion which relating to the some application of hardfacing material and its composition of the chemical for a certain application (Shibe & Chawla, 2013). Wear and corrosion are worth investigating due to its problems represent a large portion of the costs, for example in oil and gas producing companies. Garcia *et al*. (2010) reported that the economic costs linked to the corrosion of natural gas sweetening (CO_2 corrosion) and oil refining plants range between 10% and 3% of the maintenance budget. While, in Canada alone, wear is estimated to cost $ 2.5 billion a year (Borle *et al.*, 2015). Engineering components such as in petrochemical, power and aerospace suffer surface degradation primarily due to wear. Both wear and corrosion problems are usually connected with operating problems and equipment maintenance, which leading to recurrent partial and even total process shutdown, resulting in severe economic losses.

Tioxide (Malaysia) is one of the Hunstman's pigments division that are the leading global producer of specialist titanium dioxide (TiO_2) pigments. This pigments primarily deliver whiteness, brightness and opacity to a vast range of products; form coatings and polymers to cosmetics and food. They also help to increase the longevity of products. However, during the TiO_2 manufacturing process, continuous digester (CD) blade that used to mixture sulphuric acid (H_2SO_4) and ilmenite exposed to wear and corrosion. CD blade was made up from medium carbon steel and coated with hard weld deposit (tungsten carbide, WC) based materials. The problem is due to the very corrosive (acid), erosive (ilmenite) environment and also operate at high temperature due to exothermic reaction. Thus, the blade use for the current setup can only last for about six months. Figure 1.1 shows the blade that wear and corrode after three months of operation. Therefore, the components need replacement which costs money and downtime of the equipment. Researchers have identified that by replacing the component frequently, it caused the working parameters of facility disorganize, productivity decreased and the energy consumption increased (Arsic *et. al.*, 2015). Moreover, wear and corrosion often combine to cause aggressive damage in a number of industries (Davis, 2014).

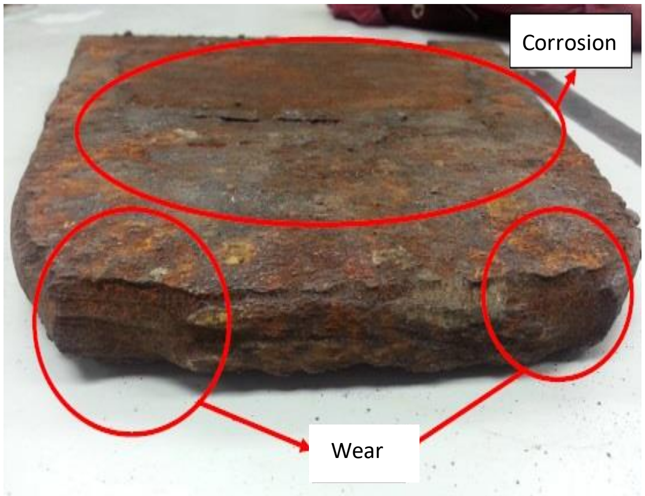

Figure 1.1: Wear and corrosion area of the blade after three months' operation

So, as modern method is quite effective in enhance the corrosion and wear resistance, the option is to change the hardfacing techniques from hard weld to thermal spraying process with WC-based materials. This technique is totally different from hard welding where the heated/melted materials are sprayed onto the surface at high velocity. The thermal sprayed cermet coatings (WC-based) are widely used to restrain the components from corrosion and wear in most industries such as aerospace, petroleum and steel metallurgy (Oksa *et al*., 2011).

High Velocity Oxy Fuel (HVOF) is widely used in groups of thermal spraying and have been extensively used for WC feedstock powder in order to obtain good bond strength, higher density and less decarburization. This is due to the lower temperature (3000 ℃) and higher velocities (400 m/s -1000 m/s) experienced by the powder particles (Lopez & Rams, 2015) compare to other thermal spray technique like vacuum/low pressure plasma (VPS/LPPS) and atmospheric plasma (APS). In order to achieve better wear and corrosion rate, adhesion and porosity of the coating are important properties. Thus, HVOF method are preferred for producing coating with high adhesion and low pores. The main feature of the HVOF method is it is able to produce dense coatings with small amount of degradation, oxidation of materials, and transformations of the phase due to short dwell time of the particles in a relatively cold flame (Oksa *et al*., 2011).

Apart from that, as a based material, WC has been thought of as one of a key factor in controlling wear and corrosion resistance. Content, size and distribution of the WC particles take decisive influence on the wear characteristics. Woezel *et al.* (2003) has reported the wear resistance increases with rising of WC content and reducing the carbide particle size of the powder. Over the years, WC have also proven their superiority in great number of other tooling and engineering applications due to their properties including high hardness, great abrasion or wear resistance, high modulus of elasticity, high compressive strength and low thermal expansion compared to other carbide (Woezel *et al.*, 2003).

Nowadays, cemented tungsten carbide has been introduced to improve the performance of the WC, where it consists of the hard carbide phase embedded in a ductile metallic matrix, referred to the binder phase such as cobalt (Co) and nickel (Ni). For this carbide, components properties are superimposed where the carbide phase produce high hardness and wear resistance. Meanwhile, the binder with ductile feature contributes to toughness and strength. It is often referred as hard metals for excellent combination of hardness and toughness (Su *et al*., 2015). WC-Co based materials are preferred due to their superior abrasive and erosive wear resistance. Besides, their remarkable mechanical properties such as high hardness, excellent high temperature strength, good corrosion resistance and chemical and thermal stability during high temperature operations made them commercially very attractive (Saheb *et al*., 2014). It has been reported that, these mechanical properties are depending on the development microstructure in the sintered parts which is governed by several factors like binder phase content, distribution of the carbide particle size, hardness and volume fraction of the carbide. Thus, nanostructure materials in the form of coatings have been popular to impart wear resistance of various industrial components (Zafar & Sharma, 2016). Other than that, with high corrosion resistance, nickel has received the most attention as an alternative binder to cobalt due to its similarity in structure and properties (Tarragó *et al*., 2015). There are several reason choose nickel as cement for carbides, for example it has high melting point, no structural defects, high resistance to corosion and oxidation, high hardness and strength (Miranda, 2004). Due to these superior mechanical properties, WC-Ni is effective in applications requiring a highs resistance to corrosion.

As many coating enhancements have been reported by researchers, more understanding on the characteristics, wear and behaviour of the HVOF thermal spraying is needed, so that this technique could be commercialized for various industrial applications in the near future. In this research, the application of HVOF process coated with WC based material on the CD blade that was made up from carbon steel was analysed as a potential method.

1.2 Problem Statement

Many industries faced the common problems which is the surface of components were exposed to deterioration, wear and corrosion. For example, in automotive industry, a substantial proportion of the disk brake rotors that is fabricated from gray cast iron with its relatively low cost and desirable properties such as low melting point and good fluidity.

However, due to their poor resistance to wear and corrosion under severe operating conditions, gray cast irons are unlikely to be satisfactory rotor materials without a different alloy system or a coating as potential material for friction system (Samur & Demir, 2012).

As in Hunstman Tioxide industry, an issue of wear and corrosion is also unavoidable. During manufacturing TiO_2 pigment process, there are two shafts with blades that are counter rotating to stir the mixture of ilminite and H_2SO_4 inside the continuous digester in order to produce raw TiO_2 pigment. The blade was fabricated from cast iron carbon steel and coated with hard weld deposit WC exposed to wear and corrosion. This problems is due to the environment during TiO_2 manufacturing process, where it is very corrosive (acid), erosive (ilmenite) and also it operated at high temperature due to the exothermic reaction (operating temperature around 135℃-150℃). Therefore, the lifetimes of the blades are short where the mean time between failure (MTBF) is only six months. The Hunstman spent so much expense to build and refurbishment the blades every time. Moreover, this industry is single line production base plant, where this industry forced to delay the production rate due to the downtime of the components.

Although, the surface of blade implemented by using hard facing (welding) method, the wear and corrosion is inevitable. Therefore, this study was designed to investigate the most favorable coatings material to increase wear and corrosion resistance, hence improve the performance of the blade by using another appropriate method, that is HVOF thermal spraying. This technique has been chosen due to its properties such as high density (low porosity) due to greater particle impact velocities, good bond strength and less decarburization, which leads to enhancement of wear and corrosion resistance. Other than method, based material is also important key in controlling wear and corrosion. With excellent combination of high hardness, high wear and corrosion resistance and high toughness, WC-Co and WC-Ni has good opportunity for replacement materials for the blade.

1.3 Objectives

The present study focuses on the influence of HVOF coating with cemented WC based material on the CD Blade. Therefore, the objectives of the research are:

I. To characterise different HVOF coating (WC-12Co and WC-10Ni) on potential replacement coating for continuous digester blade.
II. To compare the wear and corrosion on behaviour and mechanism for both WC-12Co and WC-10Ni coatings on continuous digester blade.

1.4 Scope of Study

a) Preparation of HVOF cermet WC based coatings:

I. CD blade (medium carbon steel) used as the samples. (CD blade from Hunstman).
II. Powders of WC-12Co and WC-10Ni was used as material based coating.
III. Aluminium oxide use to grit blast the sample before thermal spray.
IV. Diamond jet (sulzer metco) was used to spray the powder to the sample
V. Wire cut 0.20 mm needed for cutting the sample using electrical discharge machining (EDM) wire cut machine.

b) Samples characterisation:

I. Cross section and surface morphology of samples observed by using optical microscope (OM) and scanning electron microscope (SEM).
II. Elemental composition of the coating determined by energy dispersive spectrometer (EDS).
III. The phase of the coating identified by using x-ray diffraction (XRD) and analysed by EVA software.

c) Microhardness, wear and corrosion test:

I. Micro hardness of the coating and substrate tested by Vickers microhardness equipped with diamond pyramid indenter with loads of HV 0.05 (490.3 mN).

II. The wear of coating tested using weight loss method by modified grinder machine with SiC slurry.

III. Wear test carried out with load of 20N/mm in four different sliding distance that is 1000 m, 2000 m, 3000 m and 4000 m.

IV. Electrochemical test was used to test the corrosion behaviour using AC potensiostat/ galvanostat by ACM instruments in mixture of sulphuric acid (H_2SO_4) and ilmenite solutions.

V. Electrode that were used in electrochemical test are platinum (Pt) wire gauze as counter electrode, reference electrode by using silver/ silver chloride (Ag/AgCl) and working electrode (sample).

1.5 Significant of Study

The main purpose of this study are to enhance the wear and corrosion resistant of the CD blade, other than to increase the performance and production rate of the industry. The problem of wear and corrosion are caused by abrasion of blade and the reaction between the material and its surrounding. The environment in continuous digester is one of the factor of the blade to wear and corrode, where it stirs the mixture of sulfuric acid (corrosive) and ilmenite (erosive). Thus, the hardfacing HVOF coating used to improve the quality and performance of blade. At the end of the study, the result will benefit present needs of industry and significantly for further study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Coatings has been evolved nowadays to protect the components against corrosion and wear from physical and chemical interaction with its environment. Wear and corrosion problems are relevance in a wide range of applications in industrial as they resulting in the degradation and eventually failure for both components and systems (Fauchais & Vardelle, 2012). Various technologies such as hardfacing used to deposit the appropriate surface protection that can resist under specific conditions, where it normally distinguished by coating thickness. As Shipway & Hutchings (1995) stated in their paper, the problem of coating damage generally relied on the coating material and its thickness, the interface properties, the material of the substrate and the test conditions.

The use of thermal sprayed coatings of wear and corrosion resistant to protect an underlying substrate has received much interest over the years. This is due to the expectation that very low porosity coatings can be prepared using the HVOF spraying process. This is a consequence of the higher particle velocities with the relatively lower particle temperatures obtained with HVOF compared to the other thermal spraying processes (Oksa *et al*., 2011).

HVOF spray is particularly suited to the deposition of cermet materials such as WC-Ni and WC-Co to solve wear and corrosion problem. Cobalt has been the dominating in metal-ceramic composites known as hard metals since 1923, which is the emergence of the first WC-Co cemented carbide (Ettmayer *et al.*, 2014). This is because, the chemical bonding between WC and cobalt resulting to the nearly perfect wetting, very low interfacial energy and have a very great adhesion in solid state (Tarragó *et al*., 2015). However, the high price cobalt metal together with the need for improving the performance of this carbides under severe working condition such as corrosion, alternative binder, nickel have been promoted. From the previous research on HVOF WC based coatings revealed high hardness, low porosity and high adhesion strength, which comply with the requirement for low wear and corrosion rate (Milanti *et al*., 2014).

In this study, the focusses are on two basics information, where the main problem of this study that are wear and corrosion, and the solution for this problem which is hardfacing technique coated with WC-10Ni and WC-12Co was determined based on previous research. The outcomes of the study are very significant in order to identify whether the result successful or otherwise. Thus, the results need to be compared and discussed with previous research.

2.2 Hardfacing Technique

Hardfacing or also known as hardsurfacing, is a process of depositing a material layer over a base metal or substrate to prevent from wear by abrasion, corrosion and high temperature impact. Material loss due to the wear is significantly high in most industries. Therefore, to prevent costly downtimes and to reduce the cost of expensive parts, component that exposed to heavy wear require efficient protection for the surface. Nowadays, hardfacing method have been developed rapidly and are applied in various industries such as nuclear and aerospace components. From previous research done by Pradeep *et al*. (2012), they identified the harfacing technique extend the equipment's lifetime efficiently by increasing the life service of its parts. This process has been proved in improving the properties of the surface of the base metal.

In hardfacing method, it relies on the selective application of hardfacing material and its composition of chemical for a particular application (Shibe & Chawla, 2013). For example, previous researches revealed the carbon and chromium are the dominant elements that used in hardfacing alloys. Corrosion and wear resistance can be enhanced by varying the percentage of carbon and chromium. For the purpose of improving high stress abrasion and wear, the hardfacing materials that commonly used are iron (Fe), chromium and nickel alloys (Sexton, 2009). Table 2.1 shows the common materials and its purpose for hardfacing.

Table 2.1: Materials and its purpose in hardfacing (Sexton, 2009)

Material Alloys	**Purpose**
Co-base (Cobalt)	Corrosion and wear resistance
Cu-base (Copper)	Rebuilding worn parts of machinery
FcCr (Iron Chromium)	High stress abrasion
Mg (Manganese Steel)	Wear resistance
Ni-base (Nickel)	Metal-to-metal wear resistance
Tool steel	Tooling, wear application
WC (Tungsten carbide)	High stress abrasion

Hardfacing can be applied by number of processes which are welding, cladding and thermal spraying. Selection of most suitable process will rely on a number of factors like nature of work to be hardfaced, accessibility of equipment, the component and the state of repair of worn components (Digambar & Choudhary, 2014). They have been grouped in the following ways (Table 2.2).

Table 2.2: Various processes for hardfacing technique (Digambar & Choudhary 2014)

Category	**Process**
Welding	• Arc Welding -Shielded metal arc welding (SMAW) -Flux cored arc welding -Submerged arc welding • Gas Welding -Deposition by Oxy-Acetylene gas welding • Combination -Tungsten inert gas welding (TIG), Gas of Arc & metal arc welding (MIG) Gas welding
Cladding	• Laser cladding
Thermal Spraying	• High Velocity Oxy-Fuel (HVOF) • Flame spraying • Plasma transferred arc welding • Electric arc spraying

2.2.1 Welding

Welding hardfacing is a preferred method for application that require relatively dense coating with great bond strength. It usually applied on the substrate that can withstand high temperature (commonly 790 ℃). Usually, this process uses the coating material in rod or wire form, where the materials are easily cast in rods or drawn into wires are commonly deposited. Part from that, Shibe & Chawla (2013) also stated that the welding hardfacing are mostly used to deposit various alloys and metals on metallic substrates.

Hardfacing components can applied by a number of welding processes. However, the suitable welding process selection was depending upon various factors, for example size and shape of the components, base metal composition, accessibility of weld equipment, components function, work nature which the component to be hard-faced is subjected to, number of similar items to be hard-faced and the replacement of the part's cost (Pradeep *et al.*, 2013).

2.2.2 Laser clading

Laser cladding technology (LCT) is a method that use high powered laser beam to melted the material of coating and a thin layer of the substrate to form a pore- and crack-free coating with lower dilution, where it perfectly bonded to the metal substrate. The wide range of materials and its suitability for treating small areas make laser cladding particularly appropriate and it open up a new perspective for surface engineering technology (Vilar *et al*., 2009).

This process is used for applications which required surfaces with bulk like properties. However, parts that have extremely large sizes and complex shapes is difficult to clad (Shibe & Chawla, 2013). LCT was found relatively use for the materials protection against corrosion, oxidation and wear for the deposition of self-lubricating coatings and thermal barriers.

2.2.3 Thermal spraying

Thermal spray is a coating method in which molten, semi-molten or solid particles are deposited on a substrate (Pawlowski, 2008). It is a famous method of deposited coatings that has been used to increase the lifetimes of the product under severe environmental, temperature and wear conditions. This process is preferred for applications which required thin and hard coatings that applied with minimum thermal distortion of the component (Shibe & Chawla, 2013).

Thermal spraying process can be classified into three major categories which are plasma arc spray, electric arc spray, flame and cold spray (Figure 2.1). These energy sources are used to heat the coating material such as in powder, wire or rod form to a molten or semi-molten state (Davis, 2014).

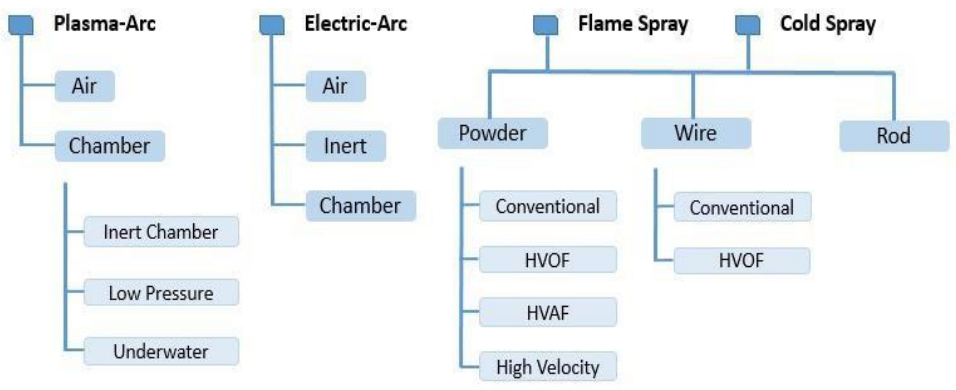

Figure 2.1: Categories of thermal spraying (Davis, 2014)

The advantages of this processes are its ability to be used for a large variety of coating materials and the coating can be applied to the substrates without significant heat input. Materials with high melting point like WC, can be apply to finely machined and parts which is fully heat treated without excessive thermal distortion and properties changing. It also able to strip off and recoat worn or damaged coatings without changing the properties or dimensions of the part. However, this processes have limitations of parts size where it is impossible to coat small and deep cavities into which a torch or gun not fitted (Berndt, 2016).

2.3 High velocity oxy-fuel (HVOF)

The progressive coatings become an alternative for application in various industry because of their flexibility, high quality combined with durability in real and highly demanding conditions. HVOF is one of the technology, which formed coatings with high flame velocity and moderate temperature. It is widely used to deposit carbide-based cermets, metals and alloys coatings such as WC-Co, nickel and stainless steel material (Sun *et al.*, 2014). In HVOF process, fuel (e.g kerosene) and oxygen are injected into the combustion chamber with spray powder. Figure 2.2 shows the HVOF coating device.

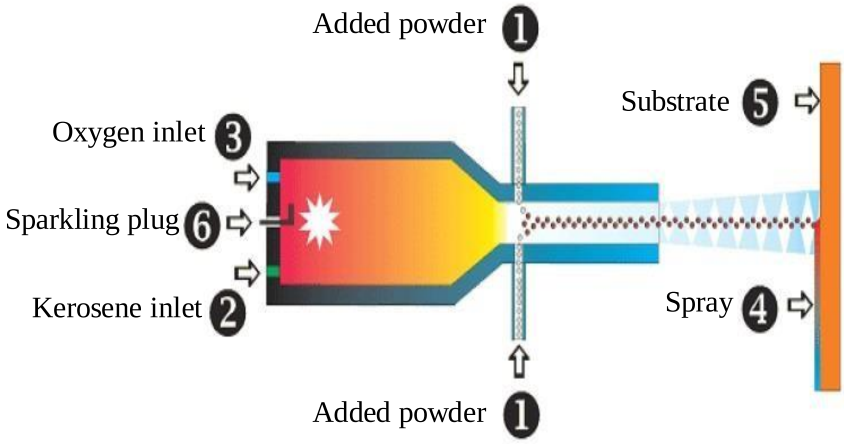

Figure 2.2: HVOF coating device (Rayes *et al.*, 2013)

The combustion of the gases produces high pressure and temperature, that resulting the supersonic flow of the gases through the nozzle. Particles of the powder melt or partially melt in the combustion chamber through nozzle. Oksa *et al.*, (2011) observe that the particles completely melt or only partially relies on material melting point, the flame temperature, thermal conductivity and particles dwell time.

Since coating is built from flattened, fast solidified droplets the velocity plays an important role to obtained the density of the coating structured. The flame temperature also has a huge effect on the appropriate materials to be sprayed. For example, ceramic coatings are mostly sprayed by using atmospheric plasma spray (APS). Meanwhile, materials that has sensitive temperature such as cermet are more preferably manufactured by lower flame temperature method. Figure 2.3 shows the common flame temperature with particle velocity for most thermal spray system.

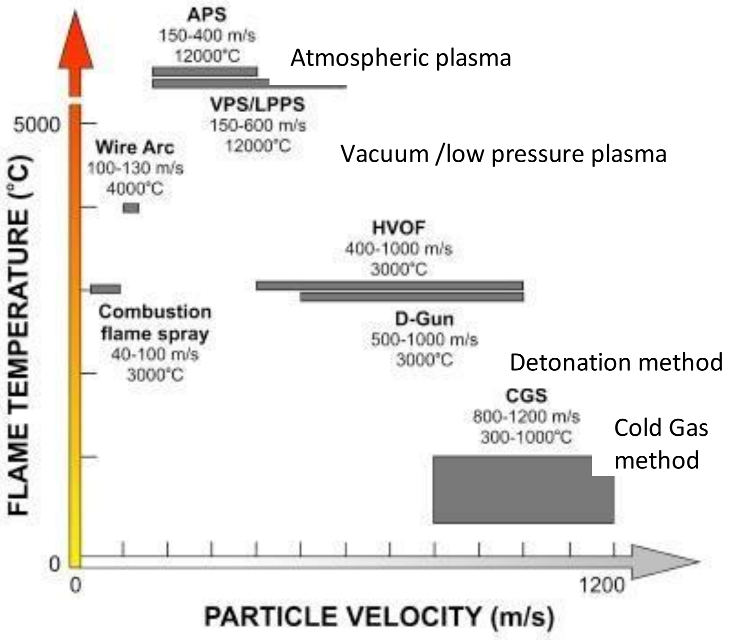

Figure 2.3: Common temperature with particle velocity for various thermal spraying method (Oksa *et al.*, 2011)

Compared to other spray processes, HVOF has special features of higher particle velocity and lower particle temperature, which give it ability in producing denser, better wear and corrosion resistance of coatings. According to Oksa *et al.* (2011), high particle velocities and low particle temperature in HVOF method have a big influence on the coating microstructure, which is the lower the amount of oxidation in the lamella boundary, the flattening rate increased and this is lead to the improving of the coating density.

The combination of high particle velocities and low flame temperature also leads to adherent coatings with low pores, less extent decarburization and low wear rate. A big number of researchers has noted that the decarburization of WC coating resulting the formation of dicarbide (W_2C) and metallic tungsten (W) during coating process. Decarburization was found to have an important role in the coatings microstructure and its properties. It has a detrimental effect not only on hardness, but also on wear properties. However, the drawback of decarburization can be prevented by the cold spray method, a recently emerging technique that operate at temperatures much lower than the melting point of spray materials (Wang *et al.*, 2013). Part from that, spraying parameter optimization is also crucial (Guilemany *et al.*, 2005). It has been proven that the parameters change in spraying process does cause a significant difference in the phase constitution of the coating.

Meanwhile, porosity is also important in coating feature, where it influences the properties of coating. It produces coating with poor cohesion and allows high corrosion and wear rates. It is related with high number of un-melted or partially-melted particles which become trapped in the coating (Art & Brody, 2006). It has been proven by previous research that good adhesion strength and low porosity are desired coating properties in order to achieve better corrosion and wear resistance.

2.4 Tungsten carbide (WC)

Nowadays, tungsten carbide-based powders are used widely in HVOF spray to create dense coating with high hardness and excellent wear resistance. Mechanical properties and wear resistance are influenced by many factors such as content, size and distribution of WC particles. Usually, wear resistance increases, while yield strength decreases with rising of WC content. However, depending on wear mechanism, wear resistance and yield strength can be increased by using powders with small carbide particle size (Watanabe *et al*., 2006).

In order to increase wear and corrosion resistance, WC were reinforced by the binders such as cobalt and nickel. From previous study done by Van Acker *et al.* (2005), the maximal WC contents that can be reinforced with nickel based matrix was 45 vol%. While, it is only 35 vol% for the cobalt based matrix. The microstructure of WC cracks, large pores and poor bonding occurred as the percentage of binder's content increase. Due to large pores, WC coating faced the abrasion and erosion behaviour, where it causes in increasing of wear rate. Table 2.3 shows the WC properties.

Table 2.3: WC Properties (Ulrich, 2005)

Properties	Value
Atomic volume (m^3/kmol)	0.0064
Melting Point (K)	3193
Density (Mg/m^3)	15.88
Compressive strength (MPa)	6833
Hardness (MPa)	36000
Crystal Structure	Hexagon

2.4.1 Cemented carbide

Cemented carbides, or known as hardmetals or cermets are subgroup of composite materials that composed of hard particles of carbide such as WC, bound together by a soft metal binder like nickel and cobalt. Cermets coatings can be attached to less hard and though metal substrates by thermal spray to increase the hardness, resistance to corrosion and wear, lower friction and impact resistance (Venter *et al*., 2013). The most frequently applied HVOF cermet coating are WC-Co coatings due to their great resistance of wear.

Corrosive environments are involved in many applications of cermet coatings. HVOF coatings are expected to exhibit complicated behavior of corrosion. This is because their complex microstructure that involves various corrosion cell induces such as splat interfaces, interlayer boundaries, oxide inclusions, pores and non-uniform carbide dissolution into the metal matrix (Lekatou *et al.*, 2015).

Thermal spray WC based composite powders are produced by various methods such as fusing or sintering and crushing or by spray drying (agglomeration) and sintering. The production of powder process influences the chemical and phase composition of the powder as well as morphology. Generally, crushed powders have irregular shape, where it shows the poorer flow ability than the spherical spray dried powders (Wielage *et al*., 2006).

2.4.1.1 Tungsten carbide-cobalt (WC-Co)

Cobalt is a silver-white element that is brittle, lustrous and hard ferromagnetic. Cobalt is primarily used as the metal in the preparation of magnetic, wear resistance and high strength alloys. Part from that, cobalt metal possesses high melting and boiling points. At standard temperature and pressure, cobalt is not readily oxidized. It means that it does not easily lose electrons from its surface. Nonetheless, if the metal is heated in the air, a cobalt-oxide material forms quite easily (Davis, 2017). Table 2.4 shows the cobalt metal properties.

Table 2.4: Cobalt properties (Kaye & Laby, 1995)

Properties	Value
Melting Point (°C)	1495
Boiling Point (°C)	2927
Density (g/cm^{-3})	8.9
Hardness (N/mm^2)	140-160

One of the most common applications for cobalt is it used as an alloy. Cobalt can be added to the other elements like tungsten, nickel and samarium to forms superalloys. Superalloys are those alloys that possess multiple unusual properties and characteristics. Most of these cobalt superalloys are highly corrosion resistance, incredibly durable and magnetic (Losertová, 2014).

Meanwhile, WC-Co hold a successful past as a good adhesion strength, low porosity and less decarburization in various industry for their excellent combination of high hardness and great fracture toughness as well as comparatively extraordinary wear resistance (Kumar *et al.*, 2016). WC-Co coatings are revealed to exhibit high performances in sliding and abrasive wear, where it shows high hardness. It has been proven that the increasing metallic cobalt binder contents indicated to high ductility and high fracture toughness of WC-Co coatings resulting fewer cracking during rolling contact test (Niemi & Barbezat, 1997).

Generally, the cobalt content, size and quality of the starting powder may affect the chemical composition and microstructure of the coating. As the particles size of WC phase decrease, it allows in obtaining interesting results associated to increasing hardness, wear and abrasion resistance. Grzegorz *et al.* (2013) reported that WC-Co intended for HVOF spraying of wear resistance coatings are usually characterized by size of particle in the range of 30-50µm. Part from that, the powders morphology, their porosity and properties determined the flow of temperature and the velocity of the particles, which in turn influences its porosity, the decarburization and adhesion of the coating to the substrate.

In research done by (Sudaprasert, 2002), great adhesion revealed between the WC-12Co coating layer and the substrate. As shown in Figure 2.4, sprayed coating layers showing lamellar splat structure with a low porosity and bigger WC due to the accumulation of the high speed molten or non-molten particles. The semi molten particles can be observed on the surface of the coating layers. High impact velocity of semi molten coating materials on the substrate accompanies with severe plastic deformation and rapid solidification. Thus, thermal spray coating layers are likely to possess inevitable microcracks and pores.

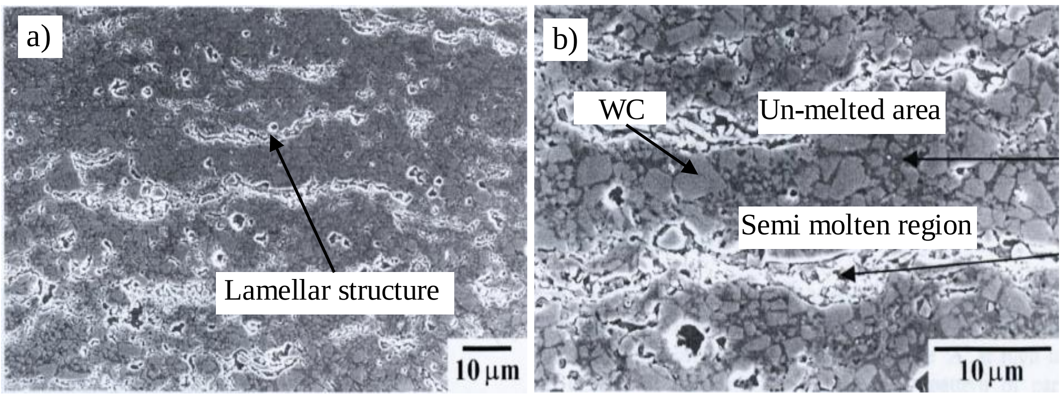

Figure 2.4: Cross sectional SEM microstructure WC-12Co coating layers a) low magnification. b) high magnification (Sudaprasert, 2002)

2.4.1.2 Tungsten carbide-nickel (WC-Ni)

Nickel is a silvery white metal, hard, ductile, malleable and ferromagnetic. This metal is a good conductor of heat and electricity. Nickel has become a very valuable metal. It mostly used in the production of stainless steel, a strong material that does not rust easily. Nickel is one of the metal that resists corrosion and it is used to plate other metals to protect them. It also used in the manufacture of many other alloys (Losertová, 2014). Table 2.5 shows the nickel properties.

Table 2.5: Properties of nickel (Kaye & Laby, 1995)

Properties	**Value**
Melting point (ºC)	1453 ºC
Boiling point (ºC)	2913 ºC
Density (g/cm^3)	8.9 $g.cm^{-3}$
Atomic Number	28

Nickel is a material that most frequently used as a binder alternative to cobalt due to its lower price with similar properties. This carbide has many advantages, for example it increases the coating ductility and improve corrosion resistance due to the high stability of the chemical (Farahmand & Kovacevic, 2015). The principal difference between cobalt and nickel is the higher stacking fault energy of nickel that resulting in lower hardness rates. Therefore, hardness and strength of WC-Co tend to be superior than WC-Ni (Tarragó *et al.*, 2015). However, by adding other elements such as Chromium and Silicon (Correa *et al.*, 2010), an increasing of the hardening rates and fracture strength levels for nickel cemented carbides may achieve as compared to those exhibited by WC-Co grades.

There are several advantages of nickel cemented carbide such as high melting point, low structural defects (pores, etc), good surface roughness showing a mirror surface, high corrosion and oxidation resistance, besides high hardness and strength (Miranda *et al.*, 2004.) Due to these excellent mechanical properties, this cemented carbide is effective in applications requiring high resistance to the corrosion.

2.5 Corrosion

Corrosion is a natural phenomenon, where it defined as the deterioration of a material by its reaction with the surroundings. The corrosion occurs based on the combination of the type of materials, its environments and the service conditions. Zaki (2006) stated the rate of corrosion is different at different places. Besides, corrosion adversely affects the properties that are to be preserved (Sharma *et al.*, 2011).

Corrosion behaviour of HVOF coatings is complex due to their particular multiphase microstructure, splats interfaces, porosity and oxide inclusions. In case of the cermet coatings, carbides and region of total or partial carbide dissolution into the metal matrix. Picas *et al.* (2009) state that this features of microstructural are deeply affect the mechanism of corrosion.

It has been noted by Picas *et al.* (2009), the particles of carbide cause galvanic corrosion in the matrix, or the crevise corrosion take place at the carbide-matrix interface, especially when the metal matrix has passivation capabilities. Part from that, if the coating deposited poorly, it may possess some porosity interconnected, which the substrate exposed to corrosion. Corrosion resistance of thermal spraying is primarily determined by the corrosion behaviour of metallic binders which provide toughness and adhesion to the coatings. In WC cermet coatings, the addition of chromium as binder materials improving the corrosion rate against saline and acidic environment (Voorwald *et al.*, 2010). Moreover, it shows that the decrease the cobalt content in WC-Co or increasing the tungsten content which is dissolved in cobalt binder has a favoring effect on the corrosion resistance of bulk WC-Co. WC-Co have a limited corrosion resistance compared to WC-Co-Cr or WC-Ni due to the electrochemical properties of the cobalt itself. WC-Ni coating has more corrosion resistance and tougher, but it has lower hardness compared to WC-Co.

Another important factors that affect the corrosion rate of cermet coatings are the parameters of spraying and the stress relaxation processes. It has been proved by Picas *et al*. (2013), where the HVOF spraying parameter affect the microstructure of the coating such as the oxygen to fuel ratio, flame temperature, jet velocity and the stand-off distance from the gun. Thus, it is reasonable to suspect that changes can occur in the chemical and electrochemical response of the coating (Picas *et al*., 2013).

2.5.1 Type of corrosion

Nowadays, corrosion of metallic materials remains a major economic challenge, where the lifespan of this components is limited by the corrosion of the metallic parts. Therefore, it is important to study the reaction that occur between metallic materials with the environment to overcome this problem. There are various types of corrosion such as uniform, erosion, galvanic, crevice and pitting corrosion.

2.5.1.1 Galvanic corrosion

Galvanic corrosion or known as bimetallic corrosion occurs when two metals with different potentials are in contact while immersed in a corrosive solution. This is due to every metals have different natural potentials in the liquid. Current will flow from the more electronegative metal (anode) to the more electropositive metal (cathode), which the corrosion on the anode increased (Francis, 2000). Figure 2.5 shows the method of galvanic corrosion.

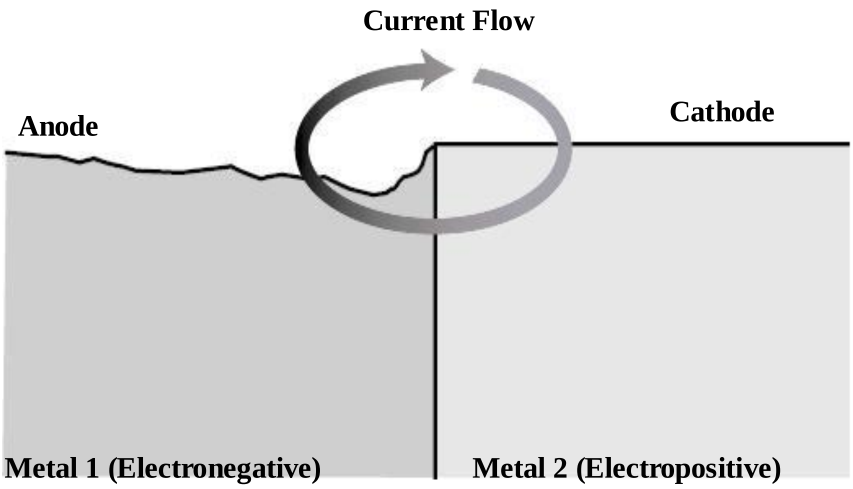

Figure 2.5: Galvanic Corrosion method (Francis, 2000)

Galvanic couple forms when one of the metals becomes the anode and corrodes faster than it would all by itself. While the other metal becomes the cathode and corrode slower than it would (Stephen, 1999). The effect of coupling two metals together increasing the corrosion rate of the anode, then reduces or even suppresses corrosion of the cathode. Thus, to prevent the corrosion, the principle of cathodic protection can applied, where coupling a component to sacrificial anode.

There have two main factors affecting the severity of galvanic corrosion which are the size of the exposed area of cathodic metal relative to that of the anodic metal and the voltage difference between the two metals. Stephen (1999) reported that the anodic metal corrodes faster as the voltage difference increase and as the area of cathode increases relative to area of anode.

2.5.1.2 Pitting corrosion

Pitting corrosion is the most damaging forms and considered to be more dangerous compared to uniform corrosion. This is due to its difficult to detect, predict and design against. Pitting corrosion is the localized corrosion of a metal surface limited to a small area that takes the forms of holes or cavities. A small pit with minimum metal loss can lead to the failure of an entire engineering system.

Usually, pitting found on passive metals such as aluminium and stainless alloys when the ultra-thin passive film (oxide film) is either chemically or mechanically damaged. This leads to resulting pit becomes broad, shallow and deep which can rapidly perforate thickness of the wall metal. There are various factor that caused pitting such as chloride, pH and oxygen.

Oksa *et al*. (2014) study about HVOF iron based coating that exposed to biomass boiler for two years detected several pits with hundred micrometers deep which partly detached oxide layers on the surface. Smaller pits detected below the oxide layer which contained potassium, copper, chlorine and sodium. Stronger pitting can be seen (Figure 2.6), where almost 2 mm wide and 1 mm deep pit with a porous multilayered oxide scale is presented.

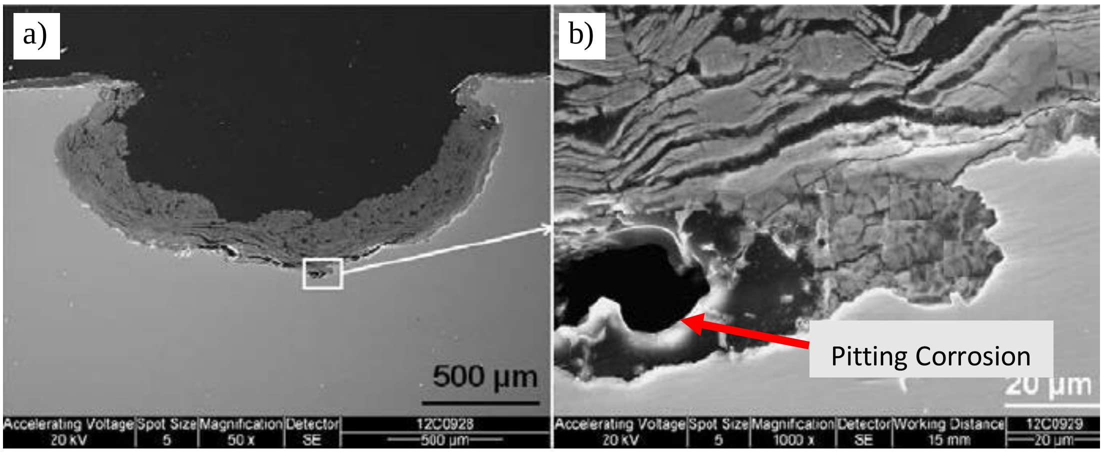

Figure 2.6: Pitting corrosion mechanism on carbon steel; a) low magnification of pit b) high magnification of pit (Oksa et al. 2014)

2.5.2 Electrochemical test

Most metallic corrosion occurs in electrochemical reactions at the interface the metal in electrolyte solution. For example, in the bridges wet concrete is the electrolyte for reinforcing rod corrosion. Normally, rate of corrosion determined by an equilibrium between opposing electrochemical reaction. When corrosion takes place, electrons are released into the metal (oxidation) and known as anodic reaction. The other reaction is cathodic, where the elements (often O_2 or H^+) of the solution is decreased, electrons removed from the metal. When these two reaction are in equilibrium, the electron flow

REFFERENCE

Al-bashir, A., Jawwad, K. A., and Abu, K. (2009). Evaluating the effects of high velocity oxy-fuel (HVOF) process parameters on wear resistance of steel-shaft materials, *Int. Conference On Tribology*, 3(2), pp.157–160.

Alotaibi, J., Yousif, B. and Yusaf, T. (2014). Wear behaviour and mechanism of different metals sliding against stainless steel counterface. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* 228, pp.692–704.

Art, D., and Brody, B. (2006). How to characterize a thermal spray coating using electron microscop. In: Doug Puerta. *Thermal Spray & Surface Engineering. Advance Materials & Processess: Thermal Spray Society*. pp.58.

ASTM E562-01. (2015). Standard test method for determining volume fraction by systematic manual point. , (Eq 3), pp.1–7.

ASTM E1382-97. (2015). Standard test methods for determining average grain size using semiautomatic and automatic image analysis 1. , 97, pp.1–24.

ASTM E2109-01 (2012). Standard test methods for determining area percentage porosity in thermal sprayed coatings, pp.1–8.

Basak, K., Celis, J. P., Ponthiaux, P., Wenger, F., Vardavoulias, M., and Matteazzi, P. (2012). Effect of nanostructuring and Al alloying on corrosion behaviour of thermal sprayed WC-Co coatings. *Materials Science and Engineering A*, 558(16), pp.377–385.

Basak, K., Matteazzi, P., Vardavoulias, M., and Celis, J. P., (2006). Corrosion–wear behaviour of thermal sprayed nanostructured FeCu/WC–Co coatings. *Wear, 261*(9), pp.1042–1050.

Barbera-sosa, J.G. L., Santana, Y., and Staia, M., (2008). Microstructural and mechanical characterization of Ni-base thermal spray coatings deposited by HVOF. *Surface & Coating Technology*, 202, pp.4552–4559.

Berger, L. Saaro, S. and Naumann, T. (2008). Microstructure and properties of HVOFsprayed chromium alloyed WC – Co and WC – Ni coatings. *Surface & Coating Technology*, 202, pp.4417–4421.

Berndt, C., (2016). Thermal spray. *ASM international-India*, pp.1-4.

Borle, S. D., Le Gal, I., and Mendez, P.F., (2015). Primary chromium carbide fraction control with variable polarity SAW., *Supplement to the Welding Journal*,pp.1-7.

Brezinová, J., Guzanova, A., and Draganovska, D., (2013). Assessment tribological properties of coatings applied by HVOF technology. *Acta Mechanica et Automatica*, 7(3), pp.135–139.

Bolelli, G., Lusvarghi, L. and Barletta, M., (2009). HVOF-sprayed WC – CoCr coatings on Al alloy: Effect of the coating thickness on the tribological properties. *Wear*, 267, pp.944–953.

Carlos, A., Giuseppe, A. and Umbelino, U., (2005). Analysis of the structure of a hard metal: A simple method of relating properties to stereological structures. *Materials Research*, 8(2), pp.131–134.

Chang, S., and Chen, S., (2014). Characterization and properties of sintered WC – Co and WC – Ni – Fe hard metal alloys. *Journal of Alloys and Compounds*, 585, pp.407–413.

Chivavibul, P., Watanabe, M. and Kuroda, S., (2007). Effects of carbide size and Co content on the microstructure and mechanical properties of HVOF-sprayed WC – Co coatings. *Surface & Coating Technology*, 202, pp.509–521.

Cho, J.E., Hwang, S.Y. and Kim, K.Y., (2006). Corrosion behavior of thermal sprayed WC cermet coatings having various metallic binders in strong acidic environment., *Surface & Coating Technology*, 200, pp.2653–2662.

Chun, H. G., Cho, T. Y., Yoon, J. H., and Lee, G. H. (2015). Improvement of Surface Properties of Inconel718 by HVOF coating with WC-Metal powder and by laser heat treatment of the coating, *Advances in Materials Science and Engineering*, 2015, pp.1–8.

Correa, E.O., Santos, J.N. and Klein, A.N., (2010). Microstructure and mechanical properties of WC Ni–Si based cemented carbides developed by powder metallurgy. *Int. Journal of Refractory Metals and Hard Materials*.28(5), pp.572– 575.

Cotell, C.M., Sprague, J.A. and Smidt, F.A. (1994). Thermal Spray Coatings. *ASM Handbook*, 5, pp.497–509.

Davim, J. P. (2012). *Materials and Surface Engineering: Research and Development*. 2nd ed. Woodhead Publishing Reviews, Mechanical Engineering Series. pp128-150.

Davis, J.R., (2014). Introduction to thermal spray processing. *Handbook of Thermal Spray Technology*, pp.3–13.

Davis, M. (2017). *The properties of cobalt Resources* on January 5, 2017 from http://study.com/academy/lesson/what-is-cobalt-uses-facts-properties.html.

Digambar, B. and Choudhary, D., (2014). A review paper on hardfacing processes, materials, objectives and applications. *Int. Journal of Science and Research*, 3(6), pp.2012–2014.

Espallargas, N., Berget, J., Guilemany, J. M., Benedetti, a. V., and Suegama, P. H. (2008). Cr_3C_2-NiCr and WC-Ni thermal spray coatings as alternatives to hard chromium for erosion-corrosion resistance. *Surface & Coatings Technology*, 202, pp.1405–1417.

Ettmayer P, Kolaska H, and Ortner H. M., (2014). History of hardmetals. In: Sarin VK, Mari D, Llanes L, editors. *Comprehensive Hard Materials*,1, pp.3–27(1.01).

Farahmand, P. and Kovacevic, R., (2015). Corrosion and wear behavior of laser cladded Ni – WC coatings. *Surface & Coatings Technology*, 276, pp.121–123.

Fauchais, P. and Vardelle, A., (2012). Thermal sprayed used against corrosion and corrosive. *Wear*, pp.3–39.

Francis, R., (2000). Bimetallic corrosion.In: Weir materials and foundries. *The National Corrosion Service*. pp. 1-14.

Garcia-arriaga, V. Alvarez-ramirez, J, Amaya, M., and Sosa, E., (2010). H_2S and O_2 influence on the corrosion of carbon steel immersed in a solution containing 3 M diethanolamine. *Corrosion Science*, 52(7), pp.2268–2279.

Grzegorz, M., Krzysztof, S., Agnieszka, T., and Hanna, M. (2013). Microstructure characterization of superfine WC-Co powders. *Solid State Phenomena*, 204, pp.351–354.

Gu, L., Huang, J., Tang, Y., Xie, C., and Gao, S. (2015). Influence of different post treatments on microstructure and properties of WC-Co cemented carbides. Journal of Alloys and Compounds. *Journals of Alloys and Compounds* 620, pp.116–119.

Guilemany, J., Dosta, S., Nin, J., and Miguel, J.R. (2005). High-velocity oxy-fuel Cr_3C_2 NiCr replacing hard chromium coatings. *Journal of Thermal Spray Technology*, 14, pp.335–341.

Hulka, I., Utu, D., Serban, V.A., Dan, M.L., Matikainen, V., and Vuoristo, P., (2015). Corrosion behavior of WC-Ni coatings deposited by different thermal spraying methods. *Series of Chemistry and Environmental Engineering*, 60(74), pp.60-65.

Hutching, I. M. (1998). Abrasive and erosive wear tests for thin coatings: A unified approach. *Tribology International*, 233-235, pp 623-634.

Ismail, A. and Abd, N., (2014). Corrosion behavior of WC-Co and WC-Ni in 3.5 % NaCl at increasing temperature. *Applied Mechanics and Materials*, 660, pp.135– 139.

Jankauskas, V., Antonov, M., Varnauskas, V., Skirkus, R., and Goljandin, D. (2015). Effect of WC grain size and content on low stress abrasive wear of manual arc welded hardfacings with low-carbon or stainless steel matrix. *Wear*, 328–329, pp.378–390.

Josephson, M., Larsen, A.H. and Larsson, F., (2005). Nanostructured WC-Co Coating. *Introduction to Nanotechnology*. pp.1-11.

Junior, G. S., Voorwald, H. J. C., Vieira, L. F. S., Cioffi, M. O. H., and Bonora, R. G. (2010). Evaluation of WC-10Ni thermal spray coating with shot peening on the fatigue strength of AISI 4340 steel. *Procedia Engineering*, *2*(1), pp.649–656.

Kalish, H. S., (2009). Corrosion of cemented carbides, *ASM Handbooks on-line*, Vol.13B.

Kamdi, Z., Shipway, P. H., Voisey, K. T., and Sturgeon, A. J., (2011). Abrasive wear behaviour of conventional and large-particle tungsten carbide-based cermet coatings as a function of abrasive size and type. *Wear*, 271(9–10), pp.1264–1272.

Kaye, G. W. C. and Laby, T. H., (1995). Tables of physical and chemical constants. 16th Edition, Longman

Kellner, F. J. J., Hildebrand, H., and Virtanen, S. (2009). Effect of WC grain size on the corrosion behavior of WC-Co based hardmetals in alkaline solutions. *Int. Journal of Refractory Metals and Hard Materials*, *27*(4), pp.806–812.

Kirchgaßner, M., Badisch, E. and Franek, F., (2008). Behaviour of iron-based hardfacing alloys under abrasion and impact. *Wear*, 265(5–6), pp.772–779.

Kumar, P., Singh, P., Singh, R., and Kumar, A. (2016). Modes of failure of cemented tungsten carbide tool bits (WC / Co): A study of wear parts. *Int. Journal of Refractory Metals and Hard Materials*, 54, pp.27–38.

Larry, D. and Hanke, P. E., (2014). Electrochemical corrosion Testing. *Handbook of Analytical Methods for Materials Materials Evaluation and Engineering*. pp.1315.

Lee, C. W., Han, J. H., Yoon, J., Shin, M. C., and Kwun, S. I., (2010). A study on powder mixing for high fracture toughness and wear resistance of WC-Co-Cr coatings sprayed by HVOF. *Surface & Coatings Technology*, 204(14), 2223–2229.

Lekatou, A., Regoutas, E. and Karantzalis, A. E., (2008), Corrosion behaviour of cermet based coatings with a bond coat in 0.5 M H_2SO_4. *Corrosion Science*, 50, pp.3389-3400.

López, A. J., and Rams, J. (2015). Protection of carbon steel against molten aluminum attack and high temperature corrosion using high velocity oxygen-fuel WC–Co coatings. *Surface & Coatings Technology*, *262*, pp.123–133.

Losertová, M., (2014). *Advanced materials texbook.* Technical Univesity of Ostrava. pp 1-208.

Lyphout, C., (2013). Tungsten carbide deposition processes for hard chrome alternative: Preliminary study of HVAF vs. HVOF thermal spray processes. *Proceeding of the Int. Thermal Spray Conference*, pp.506–511.

Mahmud, T.A.B., Saha, G.C. & Khan, T.I., (2014). Mechanical property changes in HVOF sprayed nano-structured WC-17wt.% Ni (80/20) Cr coating with varying substrate roughness. *13th Int. Symposium on Advanced Materials, ISAM 2013*, 60(1), pp.1-8.

Maiti, A. K., Mukhopadhyay, N., and Raman, R. (2007). Effect of adding WC powder to the feedstock of WC–Co–Cr based HVOF coating and its impact on erosion and abrasion resistance. *Surface & Coatings Technology, 201*(18), pp.7781–7788.

Magnani, M., Suegama, P., and Espallargas, N., (2008). Influence of HVOF parameters on the corrosion and wear resistance of WC-Co coatings sprayed on AA7050 T7. *Surface & Coatings Technology*, 202, pp.4746–4757.

Marple, B. R., Hyland, M. M., Lau, Y.C., Li, C. H., Lima, R.S., and Montavon, G. (2007). Thermal spray 2007: Global coating solutions. *Proceedings of the 2007 Int. Thermal Spray Conference*. pp.491-494.

Matikainen, V., Niemi, K., Koivuluoto, H., and Vuoristo, P. (2014). Abrasion, erosion and cavitation erosion wear properties of thermally sprayed alumina based coatings. *Coatings*, *4*(1), pp.18–36.

Melendez, N. M., Narulkar, V. V, Fisher, G. A. and Mcdonald, A. G., (2017). Effect of reinforcing particles on the wear rate of low-pressure cold-sprayed WC-based MMC coatings. *Wear* 306, 185–195.

Melnyk, C., Gansert, R., Lajun, D., Weinstein, B., Grant, D., and Watson, M. (2011). Investigation of Mechanical Properties of Coatings and Bulk Components of Various Grain Sized Tungsten-Carbide-Cobalt Based Materials, *Proceedings of the Int. Thermal Spray Conference*. pp.1-5.

Metco, S., (2006). Thermal Spray Materials Guide.4/52.pp.1-176

Milanti, A., Koivuluoto, H., Vuoristo, P., Bolelli, G., Bozza, F., and Lusvarghi, L. (2014). Microstructural characteristics and tribological behavior of HVOF-sprayed novel Fe-based alloy coatings. *Coatings*, pp.98–120.

Miranda, F. (2004). Nickel in Hardmetals. *International Journal of Refractory Metals and Hard Materials* 11(3), pp.137–149.

Monticelli, C., Frignani, A., and Zucchi, F., (2004). Investigation on the corrosion process of carbon steel coated by HVOF WC/Co cermets in neutral solution. *Corrosion Science*, 46(5), pp.1225–1237.

Murugan, K., Ragupathy, a., Balasubramanian, V., and Sridhar, K. (2014). Optimizing HVOF spray process parameters to attain minimum porosity and maximum hardness in WC–10Co–4Cr coatings. *Surface & Coatings Technology,* 247, pp.90– 102.

Nahvi, S. M. and Jafari, M., (2016). Microstructural and mechanical properties of advanced HVOF-sprayed WC-based cermet coatings. *Surface & Coatings Technology*. 286, pp.95–102.

Nahvi, S.M., (2011). *Abrasive wear behaviour of steels and advanced HVOF-sprayed WC-M coatings*. The University of Nottingham: Ph.D. Thesis.

Niemi, K. and Barbezat, G., (1997). Rolling contact fatigue failure mechanisms in plasma and HVOF sprayed WC-Co coatings. *Wear*, 212, pp.66–77.

Oksa, M., Turunen, E., and Suhonen, T. (2011). Optimization and characterization of high velocity oxy-fuel sprayed coatings: techniques, materials, and applications. *Coatings,* 1(2), pp.17–52.

Oksa, M., Varis, T. and Ruusuvuori, K., (2014). Performance testing of iron based thermally sprayed HVOF coatings in a biomass-fired fluidised bed boiler. *Surface & Coatings Technology*, pp. 1-10.

Oladijo, O. P., Obadele, B. A., Venter, A. M. and Cornish, L. A. (2016). Investigating the effect of porosity on corrosion resistance and hardness of WC-Co coatings on metal substrates. *Advances in Materials Science and Engineering,* 2**,** pp.37-45.

Ozbek, Y.Y., Canikoglu, N., and Ipek, M., (2016). The mechanical properties and wear resistance of HVOF sprayed WC – Co coatings. *Acta Physica Polonica Series*, 129(4), pp.600–603.

Pawlowski, L., (2008). Methods of coatings characteization. *Science and Engineering of Thermal Spray Coatings*: British Library Cataloguing. pp.291-588.

Picas, J.A., Xiong, Y., Punset, M., Ajdelsztajn, L., Forn, A., and Schoenung, J.M. (2009). Microstructure and wear resistance of WC-Co by three consolidation processing techniques. I*nt. Journal of Refractory Metals and Hard Materials*, 27(2), pp.344–349.

Picas, J. A., Rupérez, E., Punset, M., and Forn, A., (2013). Influence of HVOF spraying parameters on the corrosion resistance of WC-CoCr coatings in strong acidic environment. *Surface & Coatings Technology*, 225, pp.47–57.

Popović, O., Cvetkovic, R. P., Sedmak, A., Grabulov, V., Burzic, Z., and Rakin, M., (2010). Characterisation of high-carbon steel surface welded layer. *Strojniski Vestnik/Journal of Mechanical Engineering*, 56(5), pp.295–300.

Pradeep, G.R.C., Ramesh, A. and Prasad, B.D., (2012). Comparative study of hardfacing of AISI 1020 Steel by gas welding and TIG welding processes. *IOSR Journal of Engineering*, 2(9), pp.18–22.

Rayes, M.M. El, Abdo, H.S. and Khalil, K. A., (2013). Erosion - corrosion of cermet coating. *Int. Journal Electrochemical Science,* 8, pp.1117–1137.

Rodil, T.A., (2006). Edge effect on abrasive wear mechanisms and wear resistance in WC-6wt % Co hardmetals. *Int. Journal of Refractory Metals and Hard Materials*, pp.1–40.

Saheb, N., Laoui, T. and Mohammad, K., (2014). The synthesis of nanostructured WC-based hardmetals using mechanical alloying and their direct consolidation. *Journal of Nanomaterials*, pp.1-16.

Sahraoui, T., Fenineche, N., Montavon, G., and Coddet, C. (2003). Structure and wear behaviour of HVOF sprayed Cr_3C_2–NiCr and WC–Co coatings. *Materials and Design*, 24(3), pp.309–313.

Sahraoui, T., Feraoun, H. I., Fenineche, N., Montavon, G., Aourag, H., and Coddet, C., (2004). HVOF-sprayed tribaloy-400: Microstructure and first principle calculations. *Materials. Letters.* 58, pp.2433–2436.

Samur, P. and Demir, A., (2012). Wear and corrosion performances of new friction materials for automotive industry. *Metalurgica* 51(1), pp.94–96.

Sankaran, R., Rajamani, D., Natarajan, S., and Thirugnanasambantham, K. G., (2015). Sliding wear behaviour and its mechanisms of carbonitrided AISI 8620 steel at 100°C under unlubricated conditions. *Surface Engineering*.1, pp 1-7.

Scrivani, A., Lanelli, S., Rossi, A., Groppetti, R., Casadei, F., and Rizzi, G. (2001). A contribution to the surface analysis and characterisation of HVOF coatings for petrochemical application. *Wear*, 250, pp.107–113.

Shabana, Sarcar, M. M. M., Suman, K. N. S., and Kamaluddin, S. (2015). Tribological and corrosion behavior of HVOF Sprayed WC-Co, NiCrBSi and Cr3C2-NiCr coatings and analysis using design of experiments. *Materials Today: Proceedings*, *2*(4-5), pp.2654–2665.

Sharma, K., Chatha, S., and Singh, H. (2011). Heat Treatment of Thermal Spray Coatings: A Review. *Int. Journal of Materials Science and Engineering*, 2(1-2), pp.147-152.

Shi, K., Zhou, K., Li, Z., Zhang, D., and Zan, X. (2015). Microstructure and formation process of Ni-pool defect in WC−8Ni cemented carbides. *Transactions of Nonferrous Metals Society of China*, *25*(3), pp.873–878.

Shibe, V. and Chawla, V., (2013). Enhancement in wear resistance by hardfacing: A Review. *Mechanica Confab*, 2(3), pp.111–122.

Stephen, C. D., (1999). Galvanic corrosion. *Applied Science and Marine Biology*, (302) 645-4261, pp.2–3.

Shipway, P.H. and Hutchings, I.M., (1995). Measurement of coating durability by solid particle erosion. *Surface & Coatings Technology*, 71, pp.1–8.

Sexton, C.L., (2009). Hardfacing: Traditional Versus Laser. 38.pp 1-7.

Souza, R. C., Voorwald, H. J. C., and Cioffi, M. O. H., (2008). Fatigue strength of HVOF sprayed Cr3C2–25NiCr and WC-10Ni on AISI 4340 steel. *Surface & Coatings Technology*, 203(3-4), pp.191–198.

Su, W., Sun, Y., Liu, J., Feng, J., and Ruan, J., (2015). Effects of Ni on the Microstructures and Properties of WC–6Co Cemented Carbides Fabricated by WC–6(Co,Ni) Composite Powders. *Ceramics International*, 41(2), pp.3169–3177.

Sudaprasert, T., (2002). An investigation of microstructure sliding wear and thermally sprayed WC-Co coatings. MEng Thesis submitted to the University of Nottingham.

Sun, B., Fukanuma, H., and Saitama, J., (2014). Study on stainless steel 316L coatings sprayed by high pressure HVOF.*Surface & Coating Technology*, 9, pp, 58-65.

Tarragó, J.M., Ferrari, C., Reig, B., Coureaux, D., Schneider, L., and Llanes, L. (2015). Mechanics and mechanisms of fatigue in a WC–Ni hardmetal and a comparative study with respect to WC–Co hardmetals. *Int. Journal of Fatigue*, 70, pp.252– 257.

Trpcevska, J., Ganev, N., Żorawski, W., Jakubeczyová, D., and Briancin, J., (2009). Effect of powder particle size on the structure of HVOF WC-Co sprayed coatings. , *Powder Metalurgy Progress*, 9(1), pp.42–48.

Van Acker, K., Vanhoyweghen, D., Persoons, R. and Vangrunderbeek, J. (2005). Influence of tungsten carbide particle size and distribution on the wear resistance of laser clad WC/Ni coatings. *Wear, 258*(1-4), pp.194–202.

Vanessa, L. (2016). *Tungsten, Cobalt, and more on Mohs Scale of Mineral Hardness. General Hardness Resources* on December 1, 2016 from https://www.larsonjewelers.com/Tungsten-Cobalt-and-More-on-Mohs-Scale-of-Mineral-Hardness.aspx.

Venter, A.M., Oladijo, O.P., Luzin, V., Cornish, L.A., and Sacks, N. (2013). Performance characterization of metallic substrates coated by HVOF WC – Co. *Thin Solid Films*, 549, pp.330–339.

Verdon, C., Karimi, A. and Martin, J.-L., (1998). A study of high velocity oxy-fuel thermally sprayed tungsten carbide based coatings. Part 1: microstructures. *Materials Science and Engineering A246*, 246, pp.11–24.

Vilar R., and Lino, C., (2009). Laser powder deposition. *Rapid Prototyping Journal*, 15 Iss: 4, pp.264 – 279

Voorwald, H.J.C., Vieira, L.F.S. and Cioffi, M.O.H., (2010). Evaluation of WC-10Ni thermal spraying coating by HVOF on the fatigue and corrosion AISI 4340 steel. *Procedia Engineering*, 2(1), pp.331–340.

Wang, Y.Y., Li, C.-J., Kusumoto, K. and Yang, G.-J., (2006). Deposition Behaviors of Solid Phases in Liquid-Solid Two-Phase Particles in High Velocity Oxy-Fuel Spraying. *Materials Transaction,* 47, pp.1684–1689.

Wang, B.Q. and Shui, Z.R., (2002). The hot erosion behavior of HVOF chromium carbide-metal cermet coatings sprayed with different powders. *Wear*, 253, pp.550–557.

Wang, Q., Zhang, S., Cheng, Y., Xiang, J., Zhao, X., and Yang, G. (2013). Wear and corrosion performance of WC-10Co4Cr coatings deposited by different HVOF and HVAF spraying processes. *Surface & Coatings Technology*, 218(1), pp.127– 136.

Wank, A., Weilage, B., Reisel, G., Grund, T., and Friesen, E., (2004). Performance of thermal spray coatings under dry abrasive wear conditions. *Int. Conference The Coatings,* 4. pp 1-9.

Ward, L.P., Hinton, B., Gerrad, D., and Short, K., (2011). Corrosion behaviour of modified HVOF sprayed WC based cermet coatings on stainless steel. *Journal of Minerals & Materials Characterization & Engineering*, 10(11), pp.989–1005.

Watanabe, M., Owada, A., Kuroda, S., and Gotoh, Y. (2006). Effect of WC size on interface fracture toughness of WC-Co HVOF sprayed coatings. *Surface & Coatings Technology*, 201(3–4), pp.619–627.

Wielage. B,Wank A, Pokhmurska. H, Grund.T, Rupprecht.C, Reisel.G, and Friesen.E, (2006). Development and trends in HVOF spraying technology. *Surface & Coating Technology,* 201, pp.2032–2037

Williams, J. A., (1996) Wear modelling: analytical, computational and mapping: a continuum mechanics approach. *Wear,* 225, pp.1–17.

Woezel, M., Pokhmurska, H., Wank, A., Reisel, G., and Steinhaeuser, S. (2003). Influence of Thermal Spraying Method on the Properties of Tungsten Carbide Coatings. *Conference on Modern wear and corrosion resistant coatings obtained by thermal spraying*. pp.39-48

Ulrich, S., (2005). *Tungsten carbide*. SIDS Assessment Report for SIAM 21. UNEP Publications. pp.1-97

Xie, M., Zhang, S. and Li, M., (2013). Comparative investigation on HVOF sprayed carbide-based coatings. *Applied Surface Science*, 273, pp.799–805.

Yuan, J., Ma, C., Yang, S., Yu, Z., and Li, H. (2015). Improving the wear resistance of HVOF sprayed WC-Co coatings by adding submicron-sized WC particles at the splats' interfaces. *Surface & Coatings Technology,* 285, pp.17-23.

Zafar, S. and Sharma, A.K. (2016). Abrasive and erosive wear behaviour of nanometric WC-12Co microwave clads. *Wear*, 346–347, pp.29–45.

Zaki, A. (2006). Principles of corrosion engineering and corrosion control. *Butterwoth- Heinemann/ICheme Series.* pp.382-483

Zavareh, M.A., Sarhan, A.A.D., Bushroa, A.R., and Basirun, W.J. (2015). The tribological and electrochemical behavior of HVOF-sprayed Cr3C2–NiCr ceramic coating on carbon steel The tribological and electrochemical behavior of HVOF-sprayed. *Ceramics International*, 41(4), pp.5387–5396

Zhang, Q., He, Y., Wang, W., Lin, N., Wu, C., and Li, N. (2015). Corrosion behavior of WC-Co hardmetals in the oil-in-water emulsions containing sulfate reducing Citrobacter sp. *Corrosion Science*, 100, pp.322-331.

Zmitrowicz, A., (2006). Wear patterns and laws of wear–a review. *Journal of Theoretical and Applied Mechanics*, 44(2), pp.219–253.