EFFECTS OF CORROSION AND WEAR ON CERMET BASED COATINGS

NUR AMIRA BINTI MOHD RABANI

A thesis submitted in 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
“Special dedicated with much love and affection to my beloved father Mohd Rabani Bin Hj Soyam, my beloved mother Junaidah Binti Ismail, all my sisters and brothers, my supervisor Dr Zakiah Binti Kamdi and also to all my fellow friends who always helped and encouraged me to complete my study in Master of Mechanical Engineering.”
ACKNOWLEDGEMENT

In the name of Allah, Most Gracious, Most Merciful

Alhamdulillah, all the praise for Allah S.W.T. the most graceful and merciful; who give me the courage and faith for me along the period to complete this project. Praise be to Allah for, without His will, I would have not able to complete this project. Firstly, I would like to express my deepest gratitude to my supervisor Dr Zakiah Binti Kamdi for her endless support, guidance, supervision, advices, patience, ideas and unlimited encouragement through my research.

Besides that, millions of thank to my beloved parents for keep supporting me physically and mentally. I am also wanted to praise all my friends for their kind support, encouragement and understanding during completion this research. I would like to extend my appreciation to those who indirectly helped me; lecturers, laboratory technical assistants; En Anuar Bin Ismail, Encik Abu Bakar Bin Ahmad, and En Tarmizi Bin Nasir and all the staff in Faculty of Mechanical and Manufacturing Engineering (FKMP), Universiti Tun Hussein Onn Malaysia. This accomplishment would not have been possible without them. With that, I would like to thank them very much. May Allah S.W.T. bless all of you. Ameen.
ABSTRACT

Cermet based coating is a combination of ceramic materials and metal which has an excellent combination of hardness and toughness characteristics. The implementation of coatings has been largely used for application on steel in order to control and minimize the corrosion and wear effect of the materials. This study compares the corrosion and wear resistance of cermet based coatings which consist of tungsten carbide-17cobalt (WC1), tungsten carbide-9nickel (WC2), electrodeposited Ni (N1), and electrodeposited nickel-silicon carbide, (N2) coatings. They were produced by two different methods of high velocity oxygen fuel (HVOF) spraying process and electrodeposition methods onto AISI 1018 carbon steel plates. The microstructures of the coatings were examined by optical microscope (OM), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The hardness was measured by using Vickers microhardness tester. Electrochemical polarization tests were performed in 0.5 M H$_2$SO$_4$ aqueous solution with pH value of 1, and 30% by weight of bentonite solution with pH value of 9 for the corrosion test. There were two types of abrasive wear test covered in this study which was pin-on-disk and three-body wear test with two types of slurries which were silicon carbide slurries and bentonite slurries. Both of HVOF coatings show an average of 10% higher in wear resistance compared to electrodeposited coatings. However, N2 coating and WC2 show the highest corrosion resistance in acidic and bentonite solution respectively compared to other coatings. While the hardness for both HVOF coatings were extremely high which approximately 1500 HV compared to the electrodeposited coatings which only 350 HV in average. The hardness, corrosion and wear resistance of the coatings are depend on the coatings deposition methods, conditions of the environment such as pH value of the solution and the abrasive characteristics, grain size of the particles used, as well as composition of the coatings.
ABSTRAK

Salutan berasaskan logam-seramik terdiri daripada kombinasi bahan seramik dan logam yang mempunyai kombinasi sangat baik dari segi kekerasan dan ketahanan. Pelaksanaan lapisan sebahagian besarnya telah digunakan untuk aplikasi pada keluli untuk mengawal dan mengurangkan kesan karat dan hakisan pada bahan. Kajian ini membandingkan kesan karat dan hakisan lapisan seramik-logam yang terdiri daripada lapisan tungsten carbide-17cobalt (WC1), tungsten carbide-9nickel (WC2), electrodeposited Ni (N1), and electrodeposited nickel-silicon carbide (N2) coatings. Salutan ini telah dihasilkan oleh dua kaedah yang berbeza iaitu bahan api oksigen halaju tinggi (HVOF) semburan proses dan pengelektroenapan kaedah ke atas AISI 1018 plat keluli karbon. Mikrostruktur lapisan telah diperiksa dengan optikal mikroskop (OM), mikroskop imbasan elektron (SEM), tenaga spektroskopi serakan (EDS) dan X-ray pembelauan (XRD). Manakala, kekerasan diukur dengan menggunakan ujian Vickers microhardness. Ujian polarisasi elektrokimia telah dijalankan dalam dua larutan iaitu 0.5 M sulfurik asid (H2SO4) dengan nilai pH 1, dan 30% larutan bentonit dengan nilai pH 9 untuk ujian karat. Terdapat dua jenis ujian hakisan kasar dalam kajian ini iaitu ujian pin-on-disc dan ujian haus tiga badan menggunakan dua jenis bendalir iaitu silikon karbida dan bendalir bentonit. Kedua-dua lapisan HVOF menunjukkan purata 10% lebih tinggi dalam ketahanan hakisan berbanding lapisan electrodeposited. Walau bagaimanapun, N2 dan WC2 menunjukkan ketahanan karat yang paling tinggi dalam larutan berasid dan bentonit masing-masing berbanding dengan lapisan lain. Walaupun kekerasan untuk kedua-dua lapisan HVOF adalah amat tinggi, purata 1500 HV berbanding lapisan electrodeposited yang hanya 350 HV. Kekerasan salutan dan, ketahanan terhadap karat dan hakisan bergantung kepada kaedah salutan pemendapan, keadaan alam sekitar seperti nilai pH larutan dan ciri-ciri bendalir, saiz sebutir partikel yang digunakan, serta komposisi lapisan salutan.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE</td>
<td>i</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS AND ABBREVIATIONS</td>
<td>xx</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xix</td>
</tr>
</tbody>
</table>

## CHAPTER 1 INTRODUCTION

1.1 Background of study 1
1.2 Problem statements 2
1.3 Research objectives 3
1.4 Scopes of study 3
1.5 Significance of study 5

## CHAPTER 2 LITERATURE REVIEW

2.1 Introduction 6
2.2 Coatings 7
    2.2.1 Metal matrix composite coatings 9
    2.2.2 Cermet coatings 9
2.3 Tungsten carbide based materials 11
    2.3.1 Tungsten carbide nickel 13
    2.3.2 Tungsten carbide cobalt 14
2.4 High velocity oxygen fuel (HVOF) 16
2.5 Electrodeposited coatings 18
2.6 Corrosion 20
   2.6.1 Galvanic corrosion 22
   2.6.2 Pitting corrosion 23
   2.6.3 Pourbaix diagram 24
2.7 Electrochemical test 26
   2.7.1 Electrolyte 29
2.8 Wear 30
   2.8.1 Abrasive wear 33
   2.8.2 Pin-on-disk test 34
   2.8.3 Three-body abrasive wear 36
2.9 Hardness 38

CHAPTER 3 METHODOLOGY
3.1 Introduction 39
3.2 Materials used 41
3.3 Sample preparation 41
   3.3.1 Wire cutting 41
   3.3.2 Electrodeposition 41
   3.3.3 Mounting 42
   3.3.4 Grinding and polishing 42
   3.3.5 Etching 43
3.4 Vickers micro hardness 43
3.5 X-ray diffraction (XRD) 44
3.6 Surface morphologies studies 44
3.7 Electrochemical Test 44
   3.7.1 Electrolyte 46
3.8 Wear test 46
   3.8.1 Pin-on-disc wear test 47
   3.8.2 Three-body wear test 48
3.9 Atomic force microscopy (AFM) 48
CHAPTER 4 RESULT AND DISCUSSION

4.1 Introduction 50
4.2 Observation and measurement 50
4.3 Sample characterization 51
  4.3.1 Morphologies and particle distribution of the coatings 52
    4.3.1.1 Electrodeposited coatings 52
    4.3.1.2 HVOF coatings 56
  4.3.2 Phase analysis 57
4.4 Vickers micro hardness 61
4.5 Corrosion test 62
  4.5.1 Sulphuric acid (H_2SO_4) aqueous solution 62
    4.5.1.1 Electrochemical test in H_2SO_4 aqueous solution 62
    4.5.1.2 Morphologies of the coatings in H_2SO_4 aqueous solution 64
  4.5.2 Bentonite solution 67
    4.5.2.1 Electrochemical test in bentonite solution 68
    4.5.2.2 Morphologies of the coatings in bentonite solution 70
4.6 Wear test 73
  4.6.1 Pin-on-disc wear test 74
    4.6.1.1 Morphologies of the coatings after pin-on-disc wear test 76
    4.6.1.2 Surface topography of the coatings after pin-on-disc wear test 79
  4.6.2 Three-body wear test 79
    4.6.2.1 HVOF coatings 79
      4.6.2.1.1 Morphologies of HVOF 82
      4.6.2.1.2 Surface topographies of HVOF coatings 84
LIST OF TABLES

3.1 Composition and parameters of electrodeposited plating bath used 42
3.2 Composition of solution for etching process 43
4.1 Observation of the coatings 51
4.2 Hardness of the coatings 61
4.3 Electrochemical test in 0.5 M of H₂SO₄ solution 63
4.4 Electrochemical test in 30% by weight of bentonite solution 69
4.5 Mass loss in mg in certain distance for pin-on-disk wear test 74
4.6 Mass loss of HVOF coatings in SiC and bentonite slurries 81
4.7 Mass loss of electrodeposited coatings in SiC and bentonite slurries 86
**LIST OF FIGURES**

2.1 The cross-sectional micrographs and the morphology of WC-Co coating 8

2.2 The cross-sectional micrographs and the morphology of WC-Ni coating 8

2.3 SEM micrographs of WC-Co material untreated 10

2.4 XRD patterns of tungsten carbide based coatings and their respective starting powders 12

2.5 Micrograph of HVOF sprayed tungsten carbide based coatings of WC-17Ni with average porosity 2.12% 13

2.6 Micrograph of HVOF sprayed tungsten carbide based coatings WC-17Co with average porosity of 2.21% 14

2.7 Back-scattered SEM images of cross section of WC-17Co HVOF sprayed coating 15

2.8 HVOF spray process 16

2.9 X-Ray diffraction patterns of the powders and corresponding as-sprayed (a) WC-12Co and (b) WC-10Ni of HVOF coatings 17

2.10 SEM image of HVOF WC-Co-Cr surface 18

2.11 SEM image of pure Ni deposit coating 19

2.12 SEM image of Ni-SiC electrodeposited coating 20

2.13 Sketch of the corrosion of binder and hard phase on the thermal spray coatings 21

2.14 Autocatalytic process occurring in a corrosion pit in an aerated sodium chloride (NaCl) solution 23

2.15 Pourbaix diagram for Cobalt – H₂O system 25

2.16 Pourbaix diagrams for the carbon and tungsten terminated surfaces, using the calculated values of charge transfer per
adsorbed hydrogen atom.

2.17 SEM micrographs of the surface of WC-Co WC-Ni after 120 h immersion in the aerated 5 wt. % H$_2$SO$_4$ solution

2.18 Open-circuit potential (Eoc) vs. time of WC-17Ni coating and WC-17Co coating

2.19 Illustration of electrochemical reactions occurring during of metal in air-free hydrochloric acid

2.20 Electrochemical reactions occurring during corrosion of metal in aerated hydrochloric acid

2.21 SEM image shows that WC fine particles

2.22 Schema of cracking of the abrasive particle

2.23 Schematic diagram of two-body abrasion

2.24 Worn surface of WC-17Co HVOF coating under SEM after being test with pin-on-disc wear test

2.25 SEM image of the wear track of electrodeposited Ni-SiC coating

2.26 Schematic diagram of three-body abrasion

3.1 Flowchart of the project methodology

3.2 Schematic diagram of three electrode cell setup which graphite as the counter electrode, silver/silver chloride (Ag/AgCl) as the reference electrode, and sample as the working electrode

3.3 Schematic diagram of pin-on-disc diagram apparatus

3.4 SEM micrograph of bentonite powder

4.1 SEM micrographs of the N1 coatings with (a) $\times$500 and (b) $\times$1500 magnifications

4.2 EDS of N1 coating

4.3 Cross image of N1 coating

4.4 SEM micrographs of the N2 coatings with (a) $\times$500 and (b) $\times$1500 magnifications

4.5 EDS of certain points of N2 coating

4.6 Cross image of electro N2 coating

4.7 Secondary electron of SEM morphology of (a) WC1
and (b) WC2 coating

4.8 Cross images of WC1 and WC2 coatings

4.9 XRD pattern of N1 coating

4.10 XRD pattern of N2 coating

4.11 X-ray diffraction patterns of the corresponding as-sprayed HVOF of WC1 coating

4.12 X-ray diffraction patterns of the corresponding as-sprayed HVOF of WC2 coating

4.13 Potentiodynamic polarization curves of WC1, WC2, N1 and N2 coatings in H₂SO₄ aqueous solution at room temperature

4.14 SEM micrographs of WC1 coating in H₂SO₄ aqueous solution

4.15 SEM micrographs of WC2 coating in H₂SO₄ aqueous solution

4.16 SEM micrographs of N1 coating in H₂SO₄ aqueous solution

4.17 SEM micrographs of N2 coating in H₂SO₄ aqueous solution

4.18 Potentiodynamic polarization curves of WC1, WC2, N1 and N2 coatings in bentonite solution at room temperature

4.19 SEM micrographs of WC1 in bentonite solution

4.20 SEM micrographs of WC2 coating in bentonite solution

4.21 SEM micrographs of electro N1 coating in bentonite solution

4.22 SEM micrographs of electro N2 coating bentonite solution

4.23 Cumulative mass loss of the coatings against distance on pin-on-disk wear test for a fixed force of 10N

4.24 Wear rate of WC1, WC2, N1 and N2 coatings for pin-on-disk wear test

4.25 SEM images of the surface of wear tracks of N1 coating for pin-on-disk wear test

4.26 SEM images of the wear tracks surface of N2 coating for pin-on-disk wear test

4.27 SEM images of the surface of wear tracks of WC1 coating for pin-on-disk wear test

4.28 SEM images of the surface of wear tracks of WC2 coating for pin-on-disk wear test

4.29 Surface topographies of (a) WC1, (b) WC2, (c) N1 and (d) N2
coatings after undergo the pin-on-disk wear test

4.30 Mass loss of HVOF coatings in SiC and bentonite slurries against the distance under force of 20 N

4.31 Wear rate for HVOF coatings of WC1 and WC2 in bentonite and SiC slurries

4.32 SEM images of the wear tracks of WC1 coatings in SiC slurry

4.33 SEM images of the wear tracks of WC2 coating in SiC slurry

4.34 SEM images of the wear tracks of WC1 coatings in bentonite slurry

4.35 SEM images of the wear tracks of WC2 coatings in bentonite slurry

4.36 WC1 coatings in (a) SiC slurry and (b) bentonite slurry

4.37 WC2 coatings in (a) SiC slurry and (b) bentonite slurry

4.38 Mass loss of HVOF coatings in SiC and bentonite slurries against the distance under force of 20 N

4.39 Wear rate for N1 and N2 coatings in bentonite and SiC slurries

4.40 SEM images of the surface of wear tracks of N1 coating in SiC slurries

4.41 SEM images of the surface of wear tracks of N2 coating in SiC slurries

4.42 SEM images of the wear tracks of N1 coating in bentonite slurry

4.43 SEM images of the wear tracks of N2 coating in bentonite slurry

4.44 Surface roughness of the N1 coatings in (a) SiC slurry and (b) bentonite slurry

4.45 Surface roughness of the N2 coatings in (a) SiC slurry and (b) bentonite slurry
### LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>Tungsten carbide</td>
</tr>
<tr>
<td>WC-Co</td>
<td>Tungsten carbide cobalt</td>
</tr>
<tr>
<td>WC1</td>
<td>Tungsten carbide with 17% Cobalt</td>
</tr>
<tr>
<td>WC-CoCr</td>
<td>Tungsten carbide cobalt chromium</td>
</tr>
<tr>
<td>WC-Ni</td>
<td>Tungsten carbide nickel</td>
</tr>
<tr>
<td>WC2</td>
<td>Tungsten carbide with 9% Nickel</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>N1</td>
<td>Nickel electrodeposited coating</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>N2</td>
<td>Ni-SiC electrodeposited coating</td>
</tr>
<tr>
<td>Ni-SiC</td>
<td>Nickel silicon carbide</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>H&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Hardness of abrasive</td>
</tr>
<tr>
<td>H&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Hardness of materials</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega pascal</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>Symbol</td>
<td>SI Unit</td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
</tr>
<tr>
<td>mm</td>
<td>-</td>
</tr>
<tr>
<td>ml</td>
<td>-</td>
</tr>
<tr>
<td>wt.%</td>
<td>-</td>
</tr>
<tr>
<td>°C</td>
<td>-</td>
</tr>
<tr>
<td>g/cm³</td>
<td>-</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Volume of concentrated H₂SO₄</td>
<td>104</td>
</tr>
<tr>
<td>B1</td>
<td>Average and standard deviation for the thickness of coatings</td>
<td>105</td>
</tr>
<tr>
<td>C1</td>
<td>Data of mass loss</td>
<td>107</td>
</tr>
<tr>
<td>D1</td>
<td>Proceeding and Journal papers</td>
<td>108</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of study

Corrosion is defined as a destructive attack of a metal or deterioration of a material by chemical or electrochemical reaction with its environment (Fontana, 2005; Gezawa et al., 2015). It is almost impossible to prevent corrosion as it occurred naturally. In fact, corrosion in oilfields occurs at all stages from down hole to surface equipment and processing facilities (Finšgar & Jackson, 2014). The process can be controlled by understanding the coating microstructure and control of process parameters which technically can improve its corrosion resistance. Therefore, appropriate corrosion control can help avoid many potential disasters that can lead to serious issues including water resource contamination, environmental pollution, and loss of life (Finšgar & Jackson, 2014).

Friction and wear are surface phenomena and are of high concern especially in industrial components resulting in huge economic losses and sometimes lead to catastrophic failure (Ramesh & Seshadri, 2003). Erosion and corrosion of engineering materials are important factors that cause failures during service of engineering components (Juneghani et al., 2013). Thus, these wear properties can be improved by use of hard metal ceramic composite coatings obtained by dispersing refractory oxides, nitrides and carbides in nickel matrix (Ramesh & Seshadri, 2003). As the development of surface engineering design getting wider, the need to evaluate the properties of new raw materials and substrate coating combinations are become more significant.
It is important to understand how materials respond to corrosion and wear depending on the environmental and tribological conditions imposed. This significantly prolongs the lifetime of the equipment and machinery which suffer from severe wear (Petrica et al., 2013) as well as corrosion (Bai et al., 2014). This is then beneficial to the development of new corrosion inhibitors and improve the implementation of coatings on the substrate. Based on a previous journal, the most significant factors giving impact on the corrosion resistance are the chemical composition of metallic binder materials and control of microcracks (Cho et al., 2006). Thus, modern methods and techniques of surface engineering enable the production of different types of composite and complex coatings.

1.2 Problem statement

Corrosion can cause damage to everything from pipelines, bridge, and public building to vehicle, water and wastewater system and even home appliances (Gezawa et al., 2015). In fact, carbon steel that are exposed in oil production techniques are subjected to wear and erosion by the movement of sand grains that exist in the environment (Farrokhzad et al., 2014). Although high cost corrosion resistance alloys were developed to resist internal corrosion, carbon steel is still the most cost effective material used in most of the industry production. Corrosion can affect appearance of equipment especially in automobiles field. Badly corroded and rusted equipment in a plant would leave a poor impression on the observer. In fact, there were cases of plants shut down or a process in a system stopped because of unexpected corrosion failures (Fontana, 2005). Low carbon steel of AISI 1018 is an available carbon steel which had been used widely in industrial field. However, the characteristics of low carbon steel of AISI 1018 against corrosion and wear resistance required further study to find appropriate methods for corrosion and wear control as to protect the steel.
1.3 **Research objectives**

The objectives of this study are:

i. To produce and characterize electrodeposited of Ni and Ni-SiC composite coatings on low carbon steel of AISI 1018

ii. To characterize cermet based coatings of WC-17Co and WC-9Ni deposited by high velocity oxygen fuel (HVOF) sprayed technique

iii. To determine the reactions of corrosion of electrodeposited coatings and high velocity oxygen fuel (HVOF) coatings in acidic and alkali environment

iv. To identify and compare the hardness, corrosion resistance and wear behavior of coatings prepared by electrodeposited method and high velocity oxygen fuel (HVOF) sprayed technique

1.4 **Scopes of study**

The scopes covered in this study include three major parts which are preparation of the electrodeposited coatings, preparation of high velocity oxygen fuel (HVOF) coatings, and the characterization and testing of the samples.

1.4.1 **Preparation of Ni and Ni-SiC electrodeposited coatings**

The details that covered under the preparation of electrodeposited coatings are:

i. Commercial Nickel plate was used as the anode electrode and low carbon steel of AISI 1018 as the cathode

ii. Nickel sulphate (NiSO₄), nickel chloride (NiCl₂), boric acid (H₃BO₃) and distilled water were mixed to form the electrolyte or Watts bath

iii. 3 wt% of silicon carbide (SiC) was used for electrodeposition of cermet coatings

iv. Optimum parameters for electrodeposition process have been set as follows: temperature of 30 ± 0.5 °C, current density of 50 mA/cm² and agitation rate of 250 rpm
1.4.2 Preparation of HVOF cermet based coatings

The sample preparation for HVOF coatings include:

i. Two commercially available WC-17Co and WC-9Ni coatings were supplied by the external vendor

ii. The sample preparation for this coating consists of the process to clean the surface of the coatings by grinding by using standard grit of Silicon carbide paper (SiC) with grit of 240, 320, 600, 800, and 1000, and then polishing

iii. Murakami's etching were prepared by using a mixture of equal quantities of 10wt.% aqueous solution of potassium ferricyanide, K₃Fe(CN)₆ and sodium hydroxide, NaOH with 100ml distilled water

1.4.3 Characterization of samples

All the samples are required to be characterized and the details are as followed:

i. Surface morphology and element composition of particles by using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS)

ii. Phase identification and preferred orientation of the deposited particles on the surface of the coatings by using X-ray diffraction (XRD) with EVA Software analysis

iii. Surface roughness by using profilometer and atomic force microscope (AFM)

iv. Microhardness test of surface coatings by using Vickers microhardness equipped with a diamond pyramid indenter with loads of 490.3 mN (HV 0.05)

v. Corrosion behavior by using electrochemical test by using AC potensiostat / galvanostat by ACM instruments in 0.5 M sulphuric acid (H₂SO₄) aqueous solution and 30%wt bentonite solution at room temperature

vi. Pin-on-disk wear test method (ASTM G99) by using Taber test machine by measuring the weight loss of the samples
vii. Wet wear test with two types of slurries of 3%wt of silicon carbide (SiC) and 3%wt of bentonite solution by using modified grinder machine under weight loss test method

1.5 Significance of study

Corrosion problems associated with the transportation process can exist at every stage of production, from the initial extraction to refining and storage prior to use. The materials used for pipeline and drilling construction play an important role in the petroleum industry as they carry liquids and gases over long distances from their source to the ultimate consumers (Finšgar & Jackson, 2014). Environments those are inherently corrosive in nature required equipment that is strongly protected and high resistance to corrosion and wear. Thus, this research is necessary to investigate the properties in both corrosion and wear resistance in order to optimized the lifetime of the equipment and avoid premature failure. Subsequently to minimize premature failures which lead to loss of production due to total shut downs and severe economic losses because of the inflating maintenance costs (El Rayes et al., 2013). Therefore, full attention should be given to the wear and corrosion resistance to optimize the application of particular equipment or systems. In fact, it has been estimated that about 25—30% of the total losses sustained by the industry due to corrosion damage could be avoided if currently available corrosion technology were efficiently applied (Gezawa et al., 2015). Thus, due to the high hardness and superior wear resistance of WC-based sprayed coatings are typically used for various components exposed to these harsh environments (Thakare et al., 2012). While, electrodeposited coatings of nickel matrix and composite coatings of silicon carbide dispersed in nickel matrix solution were also synthesized. Hard phase such as SiC can be included into the Ni matrix to improve the wear resistance of Ni-based (Benea et al., 2015).
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Corrosion is an electrochemical charge transfer leads to material loss (Souza & Neville, 2005). The charge transfer rate can be accentuated by the increased mass transfer or mechanical impacts as a result of an impinging flow. Corrosion product films should be characterized to determine the corrosion mechanism and is significant in the development of new corrosion protections (Bai et al., 2014). The test should be keep as simple, cost-effective, and reproducible as possible while still providing relevant contact geometry and tribological testing conditions to application of interest (Fildes et al., 2013).

Wear is defined as the progressive loss of material from the surface of a solid body due to mechanical action for example the contact and relative motion of a body against a solid, liquid or gaseous counter-body (Navya et al., 2014). It has been found that the wear mechanism depends on the properties of both hard metals and abrasive and particularly on the hardness ratio between abrasive (H_a) and material (H_m) (Pirso et al., 2011). The demands for productivity and the needs for more reliable manufacturing process growing continuously have driven efforts towards reducing wear of tool and components. These goals are fundamental to improve industrial competitiveness (Bressan et al., 2001).

In general, mechanism of coating damage in this type of test depend on the coating material and its thickness, the properties of the interface, the substrate material and the test conditions (Shipway & Hutchings, 1995). Thermal spray coating is a process in which a mixture of ceramic particles and metallic binder
materials are embarked with high velocity spraying and coated on the metal substrates (Cho et al., 2006). The main role of this WC based coatings is to reduce the mechanical wear processes include cavitation, erosion and abrasive (Souza & Neville, 2005). While the applications of electrodeposited composite coatings are widely used as protective surface coatings of engineering components (Narasimman et al., 2012). This is one of the efforts in order to improve their wear resistance and corrosion-resistant coatings, service life, self-lubricating systems and dispersion-strengthened coatings (Gyftou et al., 2008; Narasimman et al., 2012). In this study, carbon steel is used as the substrate as carbon steel is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions (Noor & Al-Moubaraki, 2008).

2.2 Coatings

Coatings of a wide variety of materials are commonly applied to substrates for many purposes (Shipway & Hutchings, 1995). There are different kind of coatings that can be applied onto metallic materials to increase their corrosion resistance, such as organic silanes, polymer, electroless nickel, nickel chromium plating, ceramic, and metallic-ceramic (cermet) coatings (Magnani et al., 2008). However, the common situations in coating substrate that might occur are the intrinsic defects found in the coatings which act as corrosion attack such as microcracks, porosities and oxide phases (Aw et al., 2008). Thus, in order to prevent erosion and corrosion damaging the components, a proper coating system is used on the surface to protect the materials (Juneghani et al., 2013). In most of the coating, general corrosion such as galvanic corrosion occurred in binder materials between WC particles and metallic binders (Cho et al., 2006).

Most coating experience shear, tensile and compressive stresses which may lead to failure by cracking and spalling. Hard coatings have some disadvantages, which include porosity, insufficient bonding to the substrate, and in some cases it probably have limited thickness (Kennedy & Hashmi, 1998) which might affect the characteristics of the coatings as well (Shipway & Hutchings, 1995). However, there are some coatings that can exhibit good wettability and full dense hardmetals coating without anomalous porosity produced as found by the previous researcher by
combining both cobalt or nickel with tungsten carbide (WC) particles (Tarragó et al., 2015). Figure 2.1 shows the cross sectional micrographs and the morphology of WC-Co and Figure 2.2 shows the cross sectional micrographs and the morphology of WC-Ni coating layers which demonstrate sound adhesion between the coating layer and the substrate.

![Figure 2.1](image1.png)

Figure 2.1: The micrographs of (a) cross-sectional, and (b) surface morphology of WC-Co coating (Cho et al., 2006)

![Figure 2.2](image2.png)

Figure 2.2: The micrographs of (a) cross-sectional, and (b) surface morphology of WC-Ni coating (Cho et al., 2006)

It is important to have a good understanding of the coating corrosion and wear properties on the component which will be exposed to a potentially corrosive and wear service environment. A binder with poor corrosion resistance in a service environment can cause delamination between coating and substrate (Aw et al., 2008). It is proven that use of coatings would enhance the wear resistance as well as anti-
friction resistance of the materials (Ramesh & Seshadri, 2003; Shipway & Hutchings, 1995) and improve tribological performance of the coatings (Shipway & Hutchings, 1995). Thus, the preparation of appropriate surface coatings on the metal/alloy substrates is often necessary to reduce cavitation damage of the components (Wu et al., 2012).

2.2.1 Metal matrix composite coatings

Metal matrix composites (MMCs) coatings have attracted scientific and technological interest due to the enhanced properties exhibited by these coatings (Srivastava et al., 2007). Metal-matrix composite are materials in which the properties of a metallic host material are modified with the addition of a second phase of ceramic (Surender et al., 2004). Composite coatings can be prepared by various techniques, such as thermal spray, physical vapor deposition, chemical vapor deposition and electrodeposition (Juneghani et al., 2013; Ramesh & Seshadri, 2003). Coatings often provide a very cost-effective means to achieve properties that would be difficult or impossible to obtain with monolithic materials (Fildes et al., 2013; Ramesh & Seshadri, 2003).

The characteristic of metal matrix composite coatings processing excellent tribological properties (Ramesh & Seshadri, 2003), and are improved with the presence of binder which will increase toughness and adhesion in the bonding (Aw et al., 2008). The significance of metal matrix composites is to develop a material with superior mechanical properties which include increased toughness, stiffness and wear resistance) compared to those inherent in a matrix component (Trueman et al., 1999). Metals can be added during the deposition process and thus could modify the physical properties of the MMC as well as changing its corrosion susceptibility (Trueman et al., 1999).

2.2.2 Cermet coatings

Cermet which came from the words ceramic-metallic materials are often considered in service involving high erosion and corrosion conditions. In fact, there has been
extensive consideration of thermal-sprayed cermets as surface coatings on conventional metallic materials (Hodgkiess et al., 1999; Shrestha et al., 2005). Protection of the metallic particles by cermet is an effective method to reduce erosion and corrosion (Toma et al., 2001). Cermet can be applied on many different substrates such as steel, plastic materials, titanium, copper, aluminum, and other different metallic alloys (Magnani et al., 2008). Ceramic-base materials represent attractive possibilities for service in high-wear conditions (Hodgkiess et al., 1999).

This coating are being increasingly used to combat erosion-corrosion in industries especially in offshore piping, production systems and machinery involving fluid and/or slurry flowing corrosive media which often contain solid particles such as sand (El Rayes et al., 2013; Toma et al., 2001). For example, tungsten carbide based coatings can be used to increase the wear, oxidation and erosion-corrosion resistance of the metal/alloy materials (Wu et al., 2012). However, cemented carbides or hard metals are heterogeneous material which certainly suffer galvanic corrosion (Sutthiruangwong & Mori, 2003). Figure 2.3 shows the micrograph of untreated WC-Co coating. It can be seen that, most of WC grains are of truncated triangular prism shape with heterogeneous distribution of carbide and a wide variety of carbide size can be observed.

![Micrograph of untreated WC-Co coating](image)

Figure 2.3: SEM micrograph of untreated WC-Co coating (Gu et al., 2015)

There are various type of techniques available to produce the cermet coatings includes cermet coatings applied by HVOF spraying have been developed primarily for their wear-resistant properties in dry (sliding) or pure tribological conditions. Besides, it can be produced by using electrodeposited techniques as well by apply
metallic coatings and binder particles to a conductive surface or substrate by electrochemical process. In previous researches, it has been reported that the corrosion and wear resistance can be affected by the particles size of SiC during the co-deposition process (Gyfiou et al., 2008).

Cemented carbides consist of the hard carbide phase embedded in a ductile metallic matrix usually preferred to as binder phase (Su et al., 2015). Thus, in order to increase the corrosion resistance and mechanical properties of the surfaces, cermet materials have been largely used for application on steels, generally using the high velocity oxygen fuel (HVOF) technique and electrodeposited process (Magnani et al., 2008). At room temperature, cemented carbides show an excellent resistance in basic and neutral aqueous solutions (Sutthiruangwong & Mori, 2003).

2.3 Tungsten carbide based materials

Tungsten carbide (WC) is one of the most interesting carbides due to an array of mechanical, electrical, and chemical properties which offer applications in tribology (Asl et al., 2006; Gaston & Hendy, 2009). Tungsten carbide consists of hard hexagonal particles shape (Gu et al., 2015). The refractory carbides combine the physical properties of ceramics and the electronic properties of metals (Lekatou et al., 2008b). In fact, hard coatings applied to cutting tools increase the life by two to ten times that of uncoated tools (Kennedy & Hashmi, 1998).

Figure 2.4 shows the XRD pattern observed in the coatings and the powders of WC-17Ni and WC-17Co. Traces of W2C are observed in the XRD pattern for both coatings as the typical features of thermal spray coating as the result of extremely high processing temperatures (Aw et al., 2008). Many studies have shown that during the thermal spray coating, decarburization of WC coating powders occurred (Cho et al., 2006). It means, the coatings have significantly lower carbon levels than their respective powders (Stewart et al., 2000). The addition of tungsten carbide causes changes in microstructure of the matrix. Most of these changes are visible on the carbide-matrix boundary which revealed the presence of precipitates with spherical or irregular shape (Bartkowski et al., 2015).
Figure 2.4: XRD patterns of tungsten carbide based coatings and their respective starting powders (Aw et al., 2008)

The main parameters influencing their properties are carbide grain size and volume fraction and binder mean free path (Chivavibul et al., 2007; Stewart et al., 1999). In fact, the tungsten carbide based coatings produced are well established wear resistance coatings (Aw et al., 2008; Souza & Neville, 2005). Previous investigation reported that thermal spray WC cermet coatings exhibited poor corrosion resistance in an aqueous solution, resulting in a delamination between coating layer and substrate, mainly due to inner stress of coating layers and interconnected pores (Cho et al., 2006).

Among different types of thermal spray coatings, the tungsten carbide-based ones are widely used when abrasion, sliding, fretting, and erosion resistance are required (Magnani et al., 2008). Hard coatings consist of many types that are readily available such as diamond-like-carbon (DLC) coatings, nitrides, carbides, and oxides (Fildes et al., 2013). The corrosion resistance of hard metals strongly depends on the binder composition (Lekatou et al., 2008b). In fact, the strength of hard metals in wood-cutting environment is adversely affected by corrosive attack (Sutthiruangwong & Mori, 2003).
2.3.1 Tungsten carbide nickel

WC-Ni coating have a lower porosity which can provide a better barrier and effectively prevented corrosion attack when it was deposited on steel. As stated in previous journal, it was found that nickel binder in the WC-Ni coating have a better corrosion resistance than the cobalt binder in the WC-Co coating (Aw et al., 2008). This is consistence to a study prove that nickel in the binder has been found to induce lower corrosion rates than the cobalt, but also higher susceptibility to localized corrosion (Lekatou et al., 2008b). Figure 2.5 shows the micrograph of HVOF sprayed of WC-17Ni with average porosity 2.12%. The low percentage of porosity shown that the process have been conducted with careful (Aw et al., 2008).

![Image](image-url)

Figure 2.5: Micrograph of HVOF sprayed WC-17Ni coating with 2.12% average porosity (Aw et al., 2008)

Nickel is one of the most commonly used materials as an alternative binder to cobalt in hardmetals (cemented carbides) composites coatings (Tarragó et al., 2015). However, some of the carbide particles are found to decarburize and dissolve in the liquid metal binder during spraying resulting in a brittle binder phase in the coating (Stewart et al., 1998). The binder material such as nickel provides toughness and adhesion for a coating. The denser coating structure on nickel serves as a better barrier and has a better resistance against the electrolyte attack (Aw et al., 2008). For corrosion resistance, cobalt could be replaced by nickel which has a similarity in structure and properties and lower toughness than that of Co-bonded carbides (Lekatou et al., 2008b; Tarragó et al., 2015). Besides, the toxicity and high price of
cobalt metal and the eagerness to improve the performance of cemented carbides under severe working conditions with corrosion exposure have promoted the search and usage of grades with alternative binders such as nickel (Tarragó et al., 2015).

2.3.2 Tungsten carbide cobalt

The most commonly applied HVOF cermet coating are the tungsten carbide-cobalt (WC-Co) coatings, because of their excellent wear resistance (Lekatou et al., 2008b; Stewart et al., 1999) and high hardness (Tarragó et al., 2015; Wu et al., 2012). WC-Co cermet are widely used by thermal spray processes to deposit protective coatings on engineering surfaces against wear condition such as abrasion and erosion (Souza & Neville, 2005). WC-Co hard metals are well known as materials with high resistant to wear in a wide variety of situations. The main parameters influencing their properties are carbide grain size and volume fraction (Shipway et al., 2005).

WC-Co cemented carbides have been widely used for a variety of machining, cutting, drilling, mining and woodworking due to the desired properties of abrasion resistance, heat resistance and the good balance of hardness and toughness (Asl et al., 2006; Espinosa et al., 2011; Gu et al., 2015; Stewart et al., 1998). A typical cross sectional view of WC-17Co coating is shown in Figure 2.6. The coating porosity as indicated by the arrows with dark grey phases usually inherent flaws of thermal sprayed coatings.

Figure 2.6: Micrograph of HVOF sprayed WC-17Co coating with 2.21 % average porosity (Aw et al., 2008)
WC-Co coatings with larger grain size exhibit ductility, whereas small grained materials characteristically brittle. It consists of a high volume fraction of the hard hexagonal WC phase within a soft and tough Co binder phase (Gu et al., 2015). Besides that, compressive or tensile strength increases with decreasing WC grain size (Okamoto et al., 2005). The cobalt content, size, and quality of the starting powder may affect the chemical composition and microstructure subsequently give effect to their wear behavior (Espinosa et al., 2011). Figure 2.7 shows the cross-sectional SEM micrographs of WC-17Co HVOF sprayed coating. The bright fields are the WC grains and dark areas are cobalt with a sharp interface can be seen between the WC and cobalt (Asl et al., 2006).

![Figure 2.7: Back-scattered SEM micrographs on the cross-sectional view of WC-17Co sprayed coating (Asl et al., 2006)](image)

WC-Co hard metals exhibit excellent wear resistance, due to unique combination of high hardness and high fracture toughness (Chivavibul et al., 2007; Lekatou et al., 2008b). In general, the failure of WC-Co coatings is always related with the following mechanisms: (i) delamination of coating, (ii) micro-cutting, (iii) fracture of carbides, cracks generated at the binder phase and disruption of the carbide-binder interfaces, (iv) extrusion of the binder phase and removal by plastic deformation and fatigue, and (v) undermining of the particles and subsequent particle pull-out. Usually cobalt is used in the fabrication of cutting tools and also been used as a hard facing material as it combines a properties of hardness and ductility (Trueman et al., 1999).
2.4 High Velocity Oxygen Fuel (HVOF)

The high velocity oxygen fuel (HVOF) spray technique is a thermal spraying process in which gas and oxygen are fed into a combustion chamber to produce a supersonic flame (Aw et al., 2008; Lekatou et al., 2008b; Souza & Neville, 2005, 2007). A very dense and superior bond strength coating is produced through HVOF spray process (Asl et al., 2006; Aw et al., 2008; Sahraoui et al., 2004). This is due to the high velocity of particles hit the substrate during the process. Powder material is fed into this stream and accelerated to an extremely high velocity. These high kinetic energy particles strike the substrate and produce coating with good adhesion to the substrate (Lekatou et al., 2008b).

HVOF is a thermal spray system utilizing the combustion of gases, such as hydrogen or a liquid fuel such as kerosene. Fuel and oxygen mix and atomize within the combustion area under conditions that monitor the correct combustion mode and pressure. This thermal spray technology has their own characteristics such as particle velocity and flame temperature which produces a coating layer that has different microstructure and properties (El Rayes et al., 2013; Toma et al., 2001). The process creates a very high velocity which is used to propel the particles at near supersonic speeds before impact onto the substrate. The process of HVOF sprayed technique as shown in Figure 2.8.

![Figure 2.8: HVOF spray process (FST, 2016)]
High velocity oxy-fuel (HVOF) thermal spraying has shown itself to be one of the better methods for depositing conventional WC-Co feedstock powders (Sahraoui et al., 2004; Stewart et al., 1999). One of the key benefits of this system's high velocity is the extremely high coating density and low oxide content. The low oxides are due to the speed of the particles spending less time within the heat source and also due to the lower flame temperature (around 3000 °C) of the heat source compared with alternative processes (Asl et al., 2006; Stewart et al., 1999).

According to Souza and Neville (2005), one of the great advantages of the HVOF process is the higher velocity reached by the particles and the low temperatures involved which minimizes any potentially damaging effects to the coating and substrate (Souza & Neville, 2005). However, many studies have shown decarburization of WC coating powders during coating process (Aw et al., 2008; Cho et al., 2006). The coating contain W_{2}C and metallic W, which were formed due to the loss of carbon and degradation of tungsten carbide coating during coating process (Cho et al., 2006). Another study also said that the XRD analysis of starting powders showed that they consist solely of WC grains in a cobalt matrix (Stewart et al., 1999). Figure 2.9 shows the diffraction patterns of the powders and corresponding as-sprayed (a) WC-12Co and (b) WC-10Ni of HVOF coatings.

![XRD patterns](image)

Figure 2.9: XRD patterns of the powders and corresponding as-sprayed (a) WC-12Co and (b) WC-10Ni of HVOF coatings (Cho et al., 2006)
In addition, crystal structure of WC was found as hexagonal with one tungsten and carbon atom per unit cell and close lattice parameters with triangular prism as the stable shape of WC (Gu et al., 2015). The microstructure of a thermally sprayed coating is usually inhomogeneous (El Rayes et al., 2013). In addition, measurement of WC mean grain size can be done by using SEM as well, by the linear intercept method (Gu et al., 2015). As shown in Figure 2.10, the micrograph of HVOF WC-Co-Cr coating shows the complex microstructure presenting a very distinct hard phase characterized by the angular-shaped particles embedded in the binder (Souza & Neville, 2005).

![Figure 2.10: SEM micrograph of HVOF WC-Co-Cr surface (Souza & Neville, 2005)](image)

### 2.5 Electrodeposited coatings

Electrodeposition is the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes. Electrodeposition of composite coatings, based on second phase hard particles dispersed in a metallic matrix is gaining significance attention for potential engineering applications (Surender et al., 2004). This is a second phase to enhance their mechanical / tribological properties (Narasimman et al., 2012; Ramesh & Seshadri, 2003). It also known as a method of co-depositing micron or nano sized particles of metallic or non-metallic compounds and polymers with a metal or alloy matrix (Gyftou et al., 2008). Electro-codeposition of inert ceramic nanoparticles such as SiC in a metal matrix is a good way to produce a hard plated layer on a metallic surface (Juneghani et al., 2013). The second phase
can be hard oxide, or carbides particles such as SiC and WC or diamond, or solid lubricant such as polytetrafluoroethylene (PTFE) and graphite (Surender et al., 2004). Figure 2.11 shows the morphology of electrodeposited Ni coating which consisted by very well formed crystallites with grain size that exceeded few microns.

![SEM image of pure Ni deposit coating](image)

**Figure 2.11: SEM image of pure Ni deposit coating (Gyftou et al., 2008)**

This method is considered as ergonomic as it required less cost and occurred at room temperature to produce large area samples in industrial production (Narasimman et al., 2012). The low cost and low processing temperature at room temperature approximately give advantages such as minimize interdiffusion or chemical reaction between the substrate and coating synthesized (Narasimman et al., 2012; Ramesh & Seshadri, 2003). Particles size plays an important role in the electro-codeposition process and hence in the mechanical properties of the Ni/SiC composite coatings (Gyftou et al., 2008; Juneghani et al., 2013). Besides, there are other factors that might affect the quality of coatings such as operating pH, temperature, plating bath composition, bath solution stirring rate, current densities, current type, and particles concentration (Juneghani et al., 2013).

Electro-codeposition is also known for their ease of fabrication and high quality deposits, free from porosity and uncontrolled oxide inclusion (Ramesh & Seshadri, 2003). As shown in Figure 2.12, the micrograph of electrodeposited Ni-SiC coating exhibited a “cauliflower” structure that was formed by microcrystalline aggregates (Gyftou et al., 2008).
However, the major challenge in electroplating process is the aimed to achieve of high co-deposition rates and homogenous distribution of the particles in the metallic matrix (Gyftou et al., 2008). In fact, co-deposition of nanosized particles into metal deposits is more difficult than the micron sized particles as it exhibits a higher tendency to agglomeration of particles towards the coatings (Narasimman et al., 2012). Thus, high amount of particle agglomeration will cause inhomogeneity on the coatings which would be detrimental to the mechanical properties of the deposits (Gnjidić et al., 2001).

2.6 Corrosion

Corrosion mechanism can be determined from the corrosion product films characterization (Bai et al., 2014). The corrosion performance of a coating in a service environment are usually affected by the properties of the as-sprayed coating structure and the binder material (Aw et al., 2008). In fact, corrosion resistance of the thermal spray coating layers is primarily determined by the corrosion behavior of metallic binders which provide toughness and adhesion of coatings (Cho et al., 2006). However, there is increase in the occurrence of galvanic corrosion problems associated with the use of different dissimilar materials, which has garnered much attention (Finšgar & Jackson, 2014). Besides that, corrosion activation along lamellae boundaries may cause damage to the coating after a period of time (Bolelli
et al., 2008). The charge transfer rate can be accentuated by the increased of mechanical impacts as a result of an impinging flow (Souza & Neville, 2005). The corrosion mechanisms at the hard phase/matrix interface and on the WC particles as presented in the Figure 2.13. It can be seen that how this affects the local region in the vicinity of the original hard phase particle.

![Figure 2.13: Sketch of the corrosion of binder and hard phase on the thermal spray coatings (W species represent WC and W2C) (Souza & Neville, 2005)](image)

The binder chemical composition and micro crack control are the most crucial factors for the corrosion resistance of cemented coatings (Lekatou et al., 2008b). Corrosion resistance are mainly attributed by the hardening of the metal matrix by finely dispersed particles which gradually reduce the plowing effect and adhesive wear and retard the grain growth in the matrix at elevated temperatures (Gyftou et al., 2008). Thus technically improve the mechanical properties. In cermet carbides, corrosion usually governed by the binder dissolution in both acidic and neutral solutions during the anodic polarization. A reduction of corrosion resistance with increasing WC content in coating was also discovered (Bartkowski et al., 2015). Whereas in alkaline solutions, the dissolution of the WC phase becomes more significant while Co passivates (Lekatou et al., 2008b).

In fact, main contribution to the corrosion degradation includes the sequence of corrosion reactions occurring on the metal binder, at the interface between the
binder and the ceramic hard phase and on the hard phase itself (Souza & Neville, 2005) regardless how the coatings were produced.

2.6.1 Galvanic corrosion

Galvanic corrosion usually occurs in the most common situation of coupling dissimilar materials in wells consists of a tubing string made of corrosion-resistant alloy in contact with lower-grade steel casing (Finšgar & Jackson, 2014; Schneider et al., 2014). It is one of the most common forms of corrosion in practical applications which also known as a bimetallic corrosion (Fasuba et al., 2013). By definition “galvanic corrosion” is the corrosion between various electronic conductive or semi-conductive materials which are in contact and exposed in the same electrolyte (Schneider et al., 2014). The macrogalvanic corrosion tend to occur at the interface of the coating layer or substrate when the acid solution infiltrates along the microcracks that exist at those interface (Cho et al., 2006).

The highest value of corrosion current, Icorr may cause by its multi-phase microstructure which then triggered severe galvanic corrosion (Bolelli et al., 2008). Based on a previous research, the experimental results revealed that a considerable galvanic corrosion occurred between WC particles and metallic binders in the aerated 5 wt% H2SO4 solution (Cho et al., 2006). This galvanic corrosion is a phenomenon where an accelerated corrosion of metals occurred in an aqueous environment which electrically coupled to another more noble metal (Fasuba et al., 2013).

Thus the formation of galvanic cells between coating and substrate basically can affected by its porosity since a network of pores can lead the electrolyte to the substrate (Lekatou et al., 2008b). Metal contacts cause crevice corrosion in the occluded area between tubing and casing (Finšgar & Jackson, 2014). It somehow can be eliminated by barrier coatings which preclude electrical contact between dissimilar metals (Fasuba et al., 2013). However, in practicing such methods are unavoidable due to the mechanical and electrical demands in engineering design. The galvanic dielectric usually has its root causes in the adhesive microcracks, thus understand in the integrity loss of the bonding adhesive is necessary to fully characterize the failure (Anes et al., 2016). The galvanic corrosion process can be
due to electrical conduction by these materials which have different reactivity in an electrolyte (Mandel & Krüger, 2013).

2.6.2 Pitting corrosion

Pitting corrosion in any metals is usually determined by its microstructure (Murer & Buchheit, 2013). It is a form of extremely localized attack that results in holes in the metal which may be small or large in diameter, but in most cases they are relatively small (Fontana, 2005). Extensive pitting corrosion of steel materials is very common in solutions containing high concentration of chlorides (Finšgar & Jackson, 2014). A weight loss experiment could show a small mass loss, but the pits formed might already be deep (Smith et al., 1994). Extensive localized attack can lead to severe damage to the components which can cause the leakage of fluid or gases (Finšgar et al., 2009).

Usually extensive pitting occurs when inhibitor concentrations are reduced to their absolute minimum (Smith et al., 1994). In potential-controlled conditions, pitting is characterized by two types of conditions which are metastable and stable usually occurred before and after the pitting potential, respectively (Mandel & Krüger, 2013; Murer & Buchheit, 2013). Figure 2.14 shows an example of autocatalytic process occurring in a corrosion pit in an aerated sodium chloride (NaCl) solution.

Figure 2.14: Autocatalytic process occurring in a corrosion pit in an aerated sodium chloride (NaCl) solution (Fontana, 2005)
Pitting corrosion in the passive layer can be evaluated by the potentiodynamic polarization curve which indicates that metastable pit growth can be referred to the arising passive region, while stable pit growth can be assumed in the transpassive region (Mandel & Krüger, 2013). In certain condition, a critical distance for galvanic induced pitting corrosion at the aluminum alloy surface (Mandel & Krüger, 2013). In the case of WC-CoCr, the absence of passivation resulting in the absence of pit corrosion, due to the superior corrosion resistance of the coating in 0.1 M HCl. Pitting corrosion can be considered as a stochastic process which allowed computing tools to be used to model and predict pitting-related accumulation damage and thus assesses the lifetime of structural materials (Murier & Buchheit, 2013).

2.6.3 Pourbaix Diagram

The application of Pourbaix diagram which is also known as equilibrium diagram in corrosion phenomena is fairly obvious. It usually presents the thermodynamically stable state of a material at different potential and pH values (Weidman et al., 2012). Pourbaix diagram is a diagram which applies to conditions where the metal is in equilibrium with its environment. Usually it indicates certain regions of potential and pH where the metal undergoes corrosion and other regions of potential and pH where the metal is protected from corrosion (McCafferty, 2010). In previous study, the potential-pH equilibrium diagrams and pertinent reactions of W-water systems, under conditions of thermodynamic equilibrium at 25 °C, in the absence of precipitating substances, taking into account the \( \text{WO}_4^{2-} \) and the solid substances of W, \( \text{WO}_2 \), \( \text{W}_2\text{O}_5 \) and anhydrous \( \text{WO}_3 \), have been generated by Pourbaix (Koutsospyros et al., 2006). Figure 2.15 shows a Pourbaix diagram for Cobalt in \( \text{H}_2\text{O} \) system.
REFERENCES


