CHAPTER 1: INTRODUCTION

1.1 Background of the project

What is corrosion? Corrosion is the degradation of the material such as metal, polymer, and others. By undergo degradation, the material properties such as strength, appearances, and others will change and this will lead to many problems later. The corrosion phenomenon can be seen clearly at surface of the material. There are many types of corrosion such as galvanic corrosion, pitting corrosion, high temperature corrosion and others. In this report, the author will be focusing in high temperature corrosion. High temperature corrosion commonly occurs in the boiler, steam turbines, furnace, diesel engines and others. By undergo high temperature corrosion, the performance of the boiler, steam turbines and others will decrease and thus it can be broken. Hot corrosion is due to the use of low quality fuels which usually contain impurities such as Na and V, which then can form Na_2SO_4 and V_2O_5 salts on the surface of turbines blades (Mohsen, Abbas, & Akira, 2007). When the hot gas contact with the surface of the metal, the contaminant will deposit on the surface, thus corrosion will occur. Furthermore, the use of fuel in diesel engine is a great factor of corrosion to be happening. The fuels contain vanadium compound or sulphate and this two element will be form during combustion process. Vanadium and sulphate has a characteristic which is low melting point and this will make easy for them to melt during combustion and stick or deposit on the metal and it is highly corrosive to stainless steel.

Vanadium that was present in petroleum will be oxidize into vanadates and become in molten state and make it easy for it to stick into a metal and it can flux oxides scales and passivation layers. The present of vanadium enhance the diffusion rate of oxygen to the metal substrates to be happening quickly and thus increase the rate of oxidation to the metal. In addition, the availability of oxygen plays important roles in producing the corrosion agent form from vanadium. At lower oxygen level, the vanadium dioxide and vanadium trioxide will be formed and this do no contribute to corrosion but in high level of oxygen or process of burning at high temperature , the vanadium pentoxide will be formed and become a really good corrosion agent.

Corrosion that induces from the present of sulphate can be divided into two categories which were Type I and Type II. The different between Type I and Type II was only the process of corrosion occurs above or below the melting point of sodium sulphate. Type I take place above the melting point of sodium sulphate and Type II was vice versa and with presence of small amount of SO_3. In Type I, the molten salt has been dissolved with protective oxide scales and thus the sulfur was released from the salt and diffuses into the substrates. After it’s dissolved, discrete grey or blue colored aluminum or chromium sulfides can be observed and this will lead the steal to failure to rebuild a new protective oxide layer after the salt layer has been removed. Corrosion rate were determined by means of linear polarization resistance (LPR), electrochemical techniques and electrochemical impedance spectroscopy (EIS) (Tristancho-Reyes, et al., 2011).

1.2 Problem Statement

The corrosion process that take place in boiler, furnace, turbine and others high temperature equipment has make the equipment failure to operate at optimum level.

1.3 Objectives and Scope of Study

The objectives of this project was to compare the corrosion resistance of the coated substrate metal and uncoated substrate metal. The scope of study includes the causes of hot corrosion phenomenon. Besides that, the thermal spray techniques that were available in the industry should be study. Furthermore, the analysis that need to be done in order to approve the hypothesis need to be clarify and some study should be done.

CHAPTER 2: LITERATURE REVIEW

Nowadays, the depletion of high fuel grade due to some reasons has given negative effect to the energy generating system such as engine turbines, boiler and others. The element such as vanadium, sulphate, and sodium or we called it impurities that were present in the low grade oils will deposit on the substrate metal and because it has low melting point, it the melting process will become easier. The oxidation process or hot corrosion process were been accelerated by this molten solution that were deposit on the metal. To overcome this problem, many scholars have been taking action by conducting many experiments to study the behaviour of hot corrosion or oxidation and the thermal spray coating. The steels coated with a mixture of Na_2SO_4 + $NiSO_4$ and Na_2SO_4+ $CoSO_4$ show higher corrosion rates that either the na2so coated or transition metal sulphate coated steel at 923K (Malik.A.U, Amin.M.M, & Ahmad, 1984).To protect the turbine engines from the high temperature corrosion attack facilitated by these impurities, thermal sprayed coatings are deposited over the hot section components of turbine engines and boiler tubes (Kamal, Jayaganthan, & Prakash, 2008).

What was thermal spray coating was all about? In thermal spraying technique coating powders were melted and sprayed onto a surface of metal. Thermal spray can be divided into 7 types which are plasma spraying, detonation spraying, wire arc spraying, flame spraying, high velocity oxy-fuel coating spray (HVOF), warm spraying and cold spraying.

Nowadays, scholars have undergone many experiments to find a best coating powders and best substrate metal to overcome the hot corrosion phenomenon. Cr3C2–NiCr coatings, deposited on selected superalloys superni 75 superni 718 and superfer 800H using the detonation gun process, showed a higher hot corrosion resistance in the molten salt environment (Na_2SO_4+25 wt.% K_2SO_4) at 900 °C for 100 cycles as compared to the uncoated superalloys (Kamal, Jayaganthan, & Prakash, 2008). Besides that, Nickel based coating such as Ni-Cr, Ni3Al, NiCrBSi, and NiCrAlY have been found to exhibit excellent hot corrosion resistance (Sidhu, Prakash.S, & Agrawal). Even though until today, the scientist, researcher still continue their study on hot corrosion behavior and try to improve the coating process and coating powders and technique to be used in order to increase the life cycle of the substrate metal.

CHAPTER 3: METHODOLOGY

Figure 1: Methodology

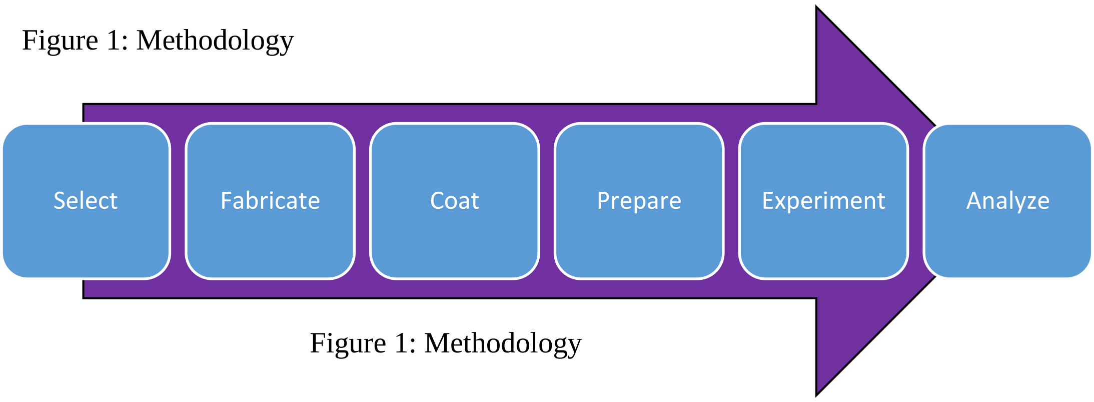


Figure 1: Methodology

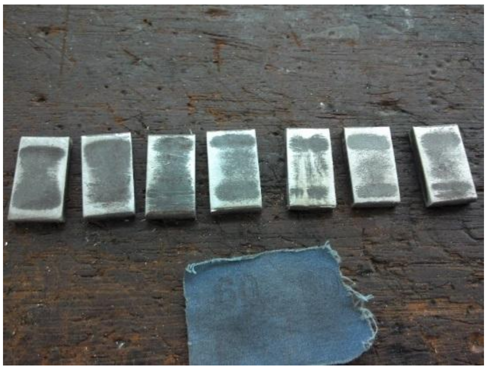
3.1: Select

Mild steel was been choose as substrate metal for this experiment. The reasons are the melting point of the mild steel was ranged from 1350 °c to 1500 °c. In this experiment, the substrate metal will be put in the furnace for several cycles at 800 °c and the mild steel can withstand the temperature and remain it physical appearances. Besides that, the mild steel has hard properties that enable the coating powder to stick to the surface by using the thermal spraying technique which is high-velocity oxy fuel. The coating powder will hit hard the surface of the substrate metal and the mild steel can withstand it. In addition, the mild steel can be easily be found and cheap compare to other metal.

Figure 2: Mild

3.2 Fabricate

The two pieces of mild steel was being cut into several pieces according to some dimension which is xxxx mm. The samples was been cut by using the abrasive cutter that were available in the laboratory. After that, the surface of the substrate metal was being cleaned by using the sand paper to remove some rusty and to make sure the surface is flat that enable



the coating powders to stick strongly to the surface.

Figure 3: Samples of mild

3.3 Coat

The author decided to use High Velocity Oxy Fuel (HVOF) techniques to deposit the coating powder to the surface of the substrate metal. The coating powders to be deposited to the surface was chromium carbide/ nickel chrome alloy powder. There are some advantages if the samples were coated with coating powder by using the HVOF techniques such as lower porosity, good resistance towards wear, high hardness and others. Before proceed with coating process, the samples need to undergo sand blasting process. Sand blasting is a mechanical equipment that spray the sand or abrasive material to the surface of metal. The sand blasting process objective is to remove the rust, oxide layer and to roughen the surface of the substrate metal that enhance the adhesion process of coating powder to the surface of substrate metal.

Figure 4: Substrate metal after sandblasting

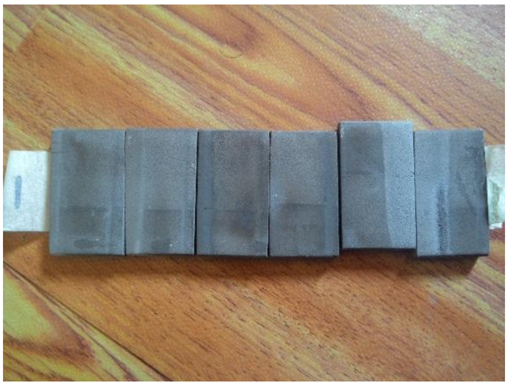
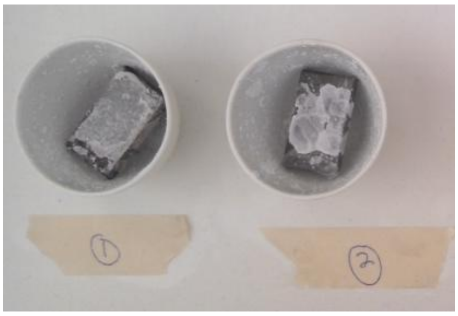


Figure 5: Substrate metal after HVOF

3.4 Prepare

The combination of Sodium chloride and Sodium Sulphate produce the dangerous salt solution. The samples were been coated by this salt solution by using the brush and oven. The oven operated temperature was set up to 150 °c. Then, the samples were preheated for 10 minutes and after that, the salt solution was been disposed to the samples. This step continuous for several cycles to enable the salt stick to the samples. The weight of



the samples before and after been put with salt solution need to be taken for the discussion.

Figure 6: Substrate metal after been coated with salt

3.5 Experiment

Two of the samples has been put in the furnace for hot corrosion testing. The first sample was the bare mild steel and the second sample was coated with coating powder and the first sample was labelled ad Sample 1 and the other sample was labelled as Sample 2. Before the samples been put in the furnace, the furnace need to set up the operating temperature before running. The technician set the furnace to operate at 800 °c and the time taken to reach 800 °c from room temperature was set up to 60 minutes or 1 hours. The samples undergo 2 cycle which is equivalent to 10 hours and 1 cycle is equal to 5 hours. After 1 cycle completed, the samples were left cooling in the furnace for about 20 hours before the author started the second cycle.

Figure 7: Furnace

3.6 Analyse

3.6.1 SEM/ EDAX

The samples were put under Scanning Electron Microscope to observe the surface profile of the samples and higher magnification and undergo Energy Dispersive X-ray to analyse the composition of element at the surface of the samples.

3.6.2 X- Ray Mapping

X-ray mapping provide the author of the images of two dimensional distribution of the element on the

Figure 8: PRO X machine

sample surface. X- ray mapping enable the author to focus on the region of interest that the author desired.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Weight gain analysis

Two samples were heated up to 800°c in the furnace for hot corrosion testing. The Sample 1(uncoated) and Sample 2 (coated) were undergo 2 cycles which is 1 cycle is equal to 5 hours. After been put in the furnace, the samples mass were recorded as below

	Before	**After**	**Weight gain**
Sample 1 (uncoated)	37.632g	38.143g	0.511g
Sample 2(coated)	37.929g	37.856g	0.073g

Table 1: Weight gain Analysis

From the table above, the Sample 1 shows the higher mass gain compare to Sample 2. The reasons are, there was a formation of oxides at coated sample which is Sample 2. The formation of oxide has blocked the air or oxygen from the surrounding to the surface of the sample and reduce the oxidation process to occur or corrosion. The oxide layer has become like a barrier for corrosion agent to diffuse into the samples. The formation of chromium oxide were easily been formed because of the chromium chemical properties that can easily react with oxygen. The formation of oxides that were deposited on the top surface or at coated layer and the pore of the samples has limit the growth of others oxide at the sample surface. As a conclusion, the weight gain of Sample 1 was higher that sample 2 is because, the rate of oxidation process at Sample 1 is higher than Sample 2. The salt solution that were put at the surface of the substrate metal, the oxygen from the surrounding and the high environment temperature, has enhance for hot corrosion to occur. Besides that, without the oxide layer that acts as barrier for oxidation to occur at Sample 1, rate of oxidation that occur at the surface of substrate metal is faster and higher compare to the formation of chromium oxide at the coating layer that reduce the speed of corrosion to occur or to increase the time taken for oxygen to diffuse into and penetrate the coating layer and reach substrate metal.

4.2 SEM/EDAX

Sample 1(bare steel)

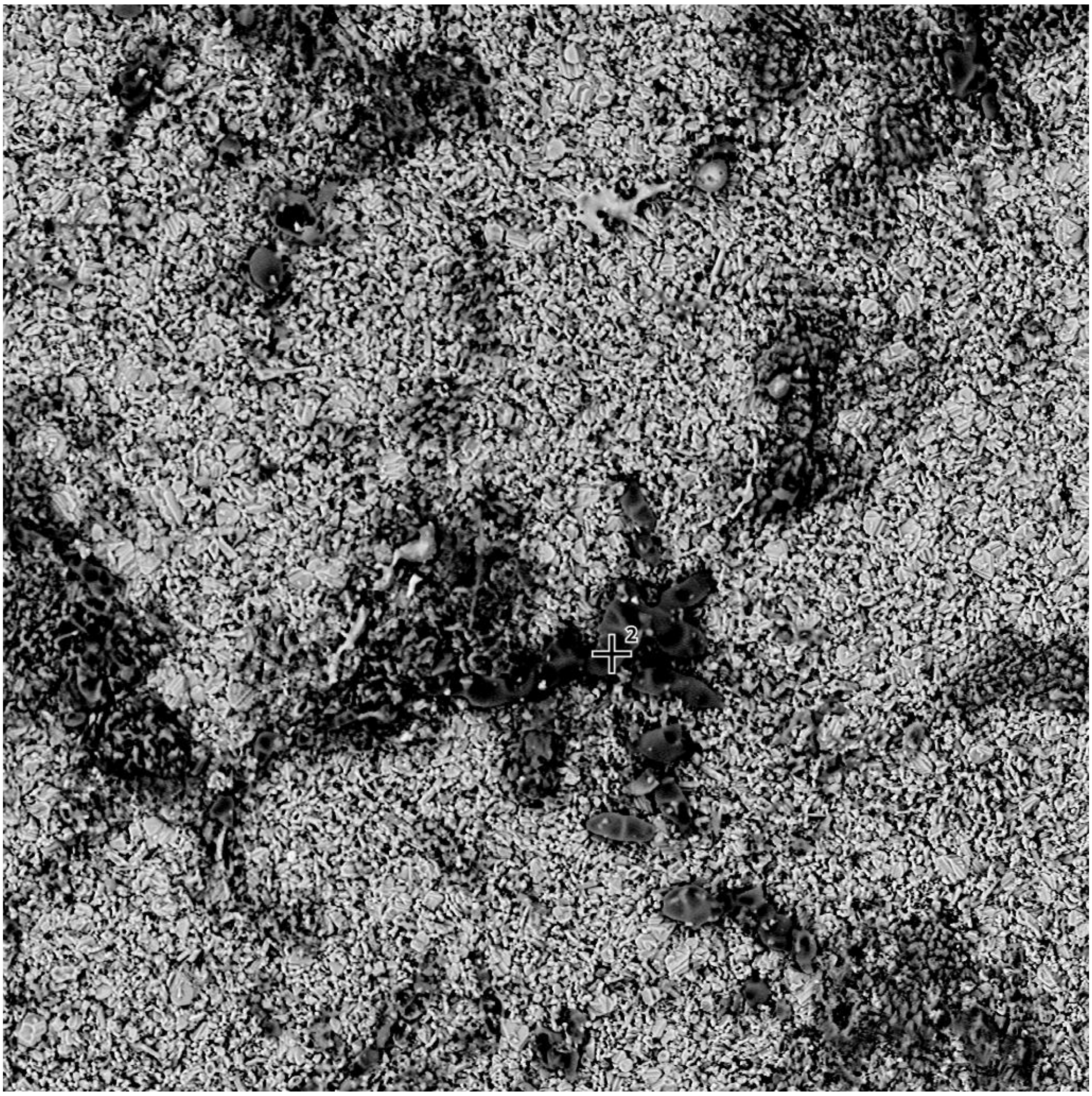
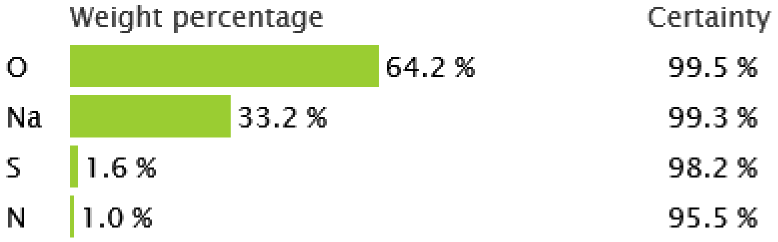


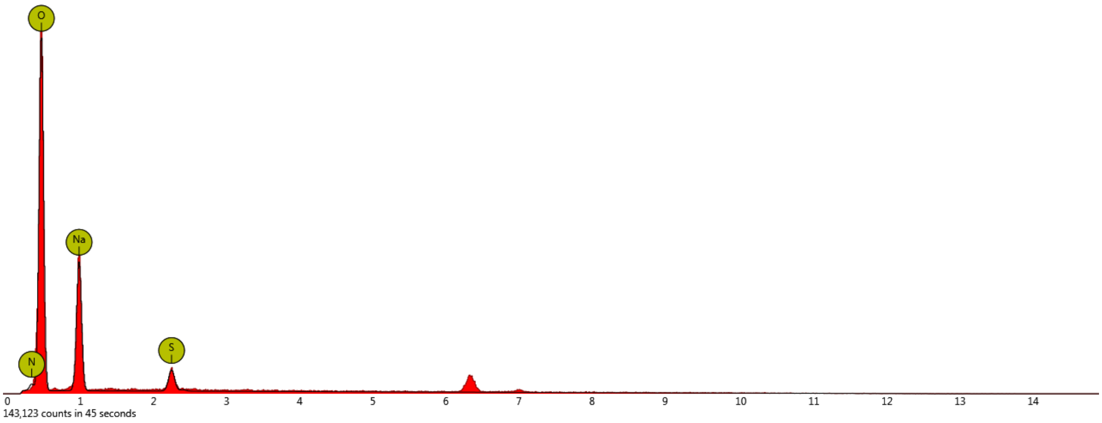
Figure 9: Image of Sample 1

Element Symbol	Element Name	Confidence	Concentration	Error
O	Oxygen	100.0	64.2	0.5
Na	Sodium	100.0	33.2	0.7
S	Sulphur	100.0	1.6	1.8

N	Nitrogen	100.0	1.0	4.5

Table 2: Composition of element (Sample





From the above image and table, we can observe that, the concentration of oxygen was the highest followed by sodium, sulphur and nitrogen. The concentration of oxygen was the highest because the substrate metal was oxidize with air during being heated in the furnace. The composition of air were nitrogen 78%, oxygen 20%, and water vapour 1% and other inert gases are approximately 1%. Due to high concentration of oxygen and the higher affinity of substrate metal towards oxygen, the substrate metal react easily with the oxygen to become a metal oxide. Besides that, the present of small concentration of nitrogen shows that, the oxidation process is the dominating or main process that occur during the sample were heated in the furnace for 10 hours at 800°c. The present of sodium and sulphur shows that, the salt solution which is the mixture of sodium sulphate and sodium chloride stick to the surface of the metal during preparation process before hot corrosion testing. The heat energy that were produced by the furnace and flow into the substrate metal, enable the element in the substrate metal to absorb enough energy for them to move and react with the air. The process of oxidation that occur was aggressive and fast because the substrate metal has a characteristic of higher affinity towards oxygen or can react with oxygen easily.

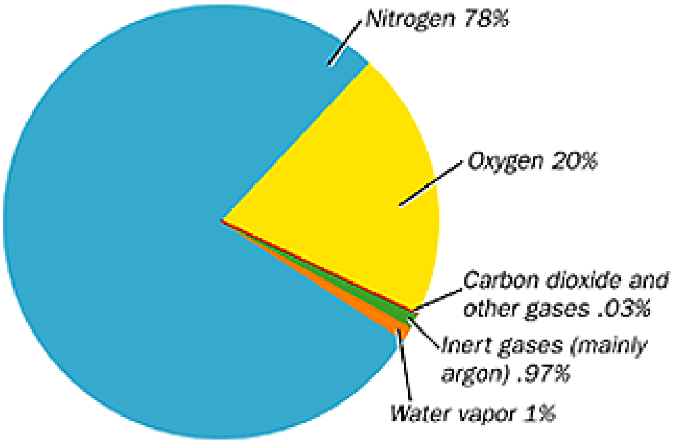


Figure 10: Composition of air

Sample 2

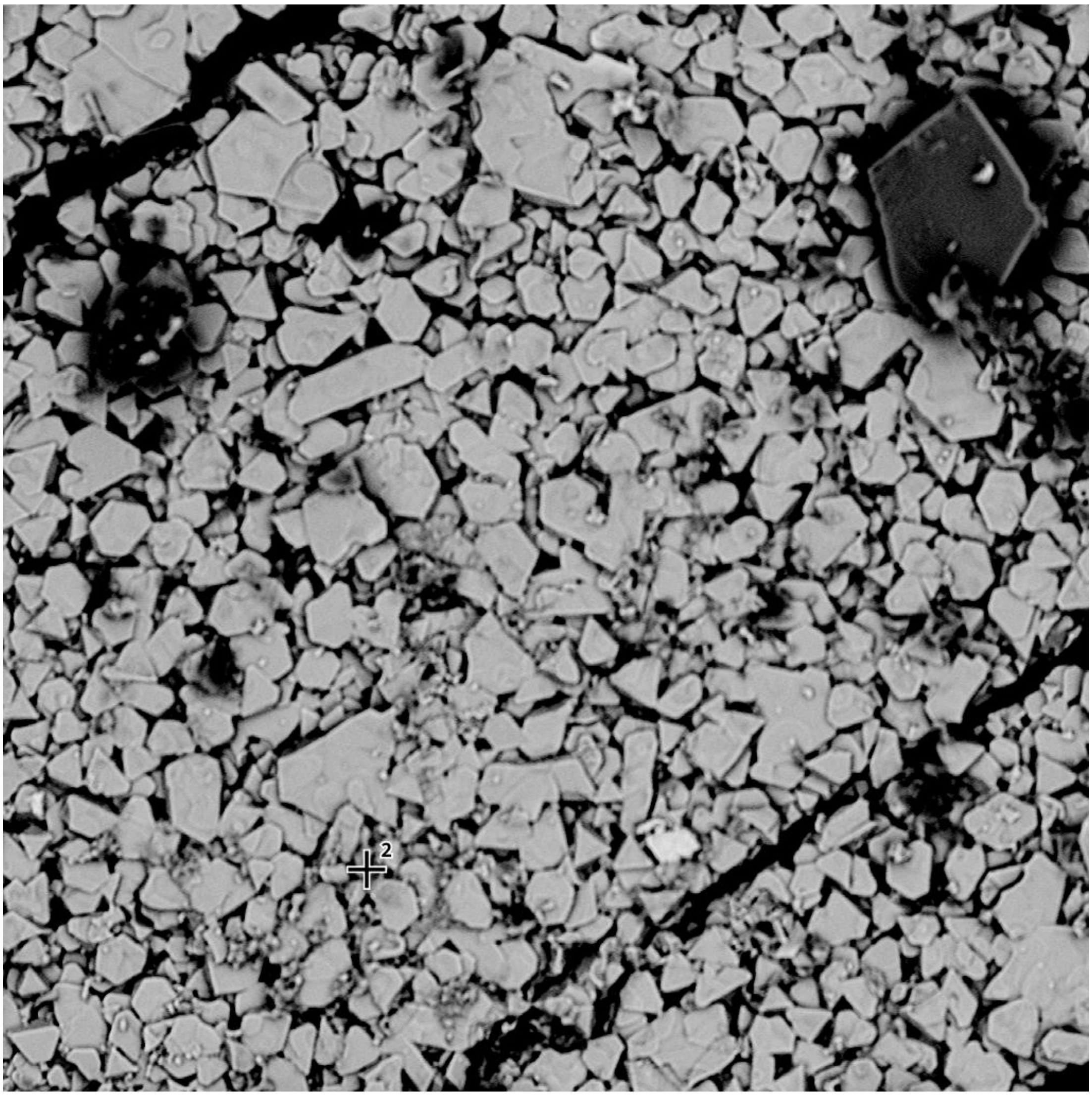
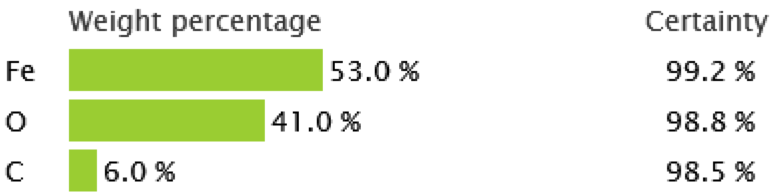
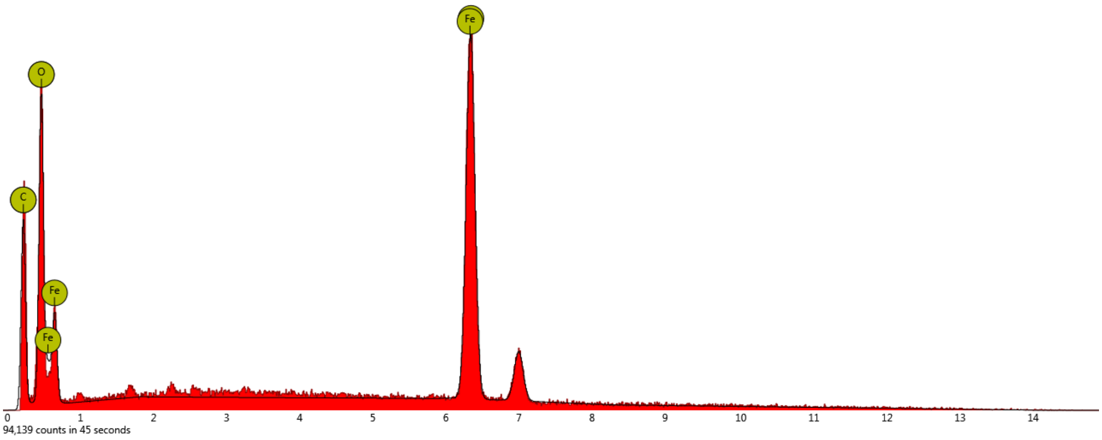


Figure 11: Image of Sample 2





Element Symbol	Element Name	Confidence	Concentration	Error
O	Oxygen	100.0	41.0	1.2
Fe	Iron	100.0	53.0	0.8
C	Carbon	100.0	6.0	1.5

Table 3: Composition of element (Sample 2)

From the image, table and graph above, its shows that, the concentration of iron was the highest followed by oxygen and carbon. The reasons are during the heating process, the substrate metal element which is iron absorb the heat energy from the source and enable it’s to obtain enough energy to flow into the surface through the pore and passed the coating layer of coating powder that were deposited at the top surface. After that, the iron will react with oxygen from surrounding or oxidise and metal oxide were deposited. The iron oxide that were deposited at the pore acts as a one of the defensive barrier to prevent the corrosion agent to penetrate through the coating layer and went to the substrate metal. Besides that, the pointed area does not show the composition of coating powder elements such as chromium or nickel because, at that point, at the pore that were exist, the iron element was dominating compare to the nickel and chromium. The existing of coating powder element can be seen by using the x-ray map analysis that will be explained at the few next pages.

4.3 X-Ray mapping

Sample 1(uncoated)

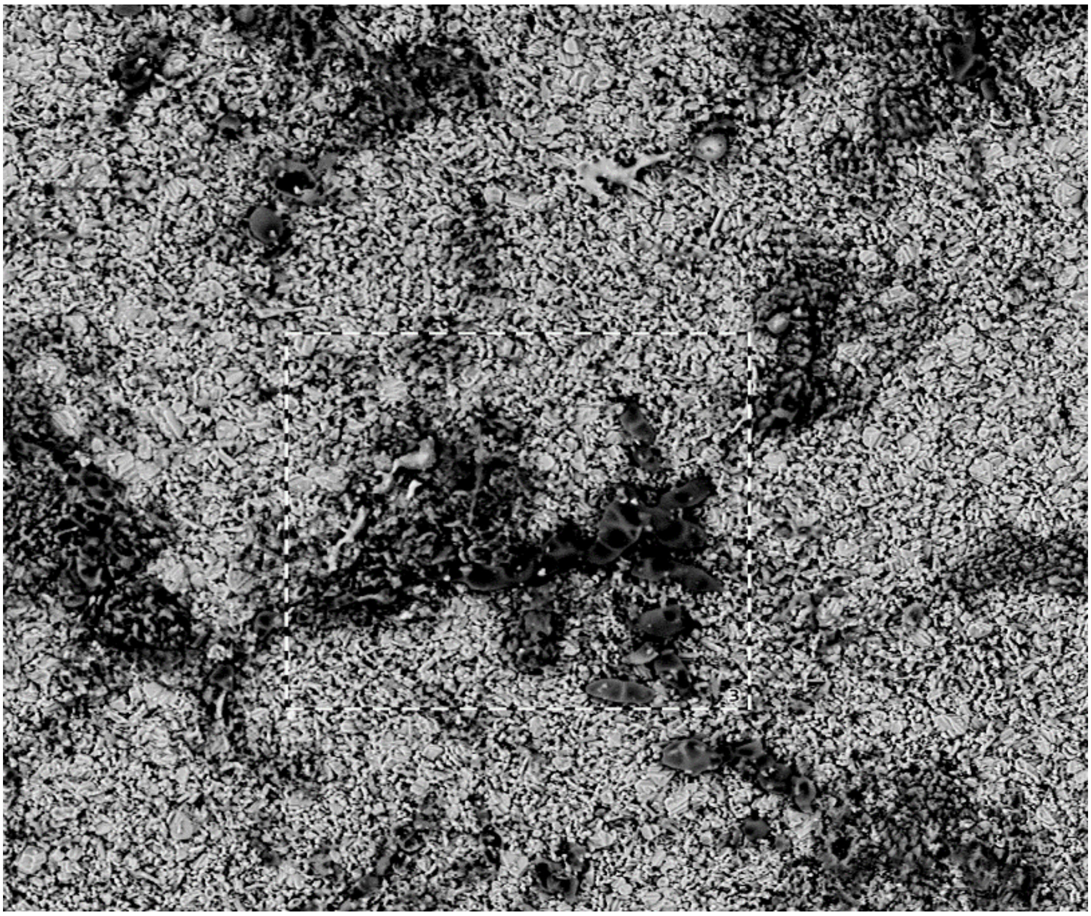


Figure 12: Image of Sample 1(Mapping)

Based on the figure and table above, the concentration of oxygen is the highest followed by iron, sodium, sulphur and nitrogen. The higher concentration of iron and oxygen shows the precipitation of iron oxide. When the samples were put in the furnace that operated at 800 °c, the iron element in the substrate metal acquire enough energy to move out from the substrate metal and react with oxygen. The oxide layer that were formed acts as a barrier for corrosion agent to penetrate. Even though the oxide layer protected the substrate metal, the corrosion agent will slowly killing the oxide layer thus the new oxide barrier is needed to overcome that and this process is continuous process. The formation of oxide layer that results from reaction of substrate metal with oxygen induce precipitation that increase the weight of the samples after hot corrosion testing has been done.

Element Symbol	Element Name	Confidence	Concentration	Error
O	Oxygen	100.0	43.3	0.5
Fe	Iron	100.0	23.5	0.5
Na	Sodium	100.0	29.4	0.7
S	Sulphur	100.0	2.7	1.2
N	Nitrogen	100.0	1.2	3.8

Sample 2 (coated)

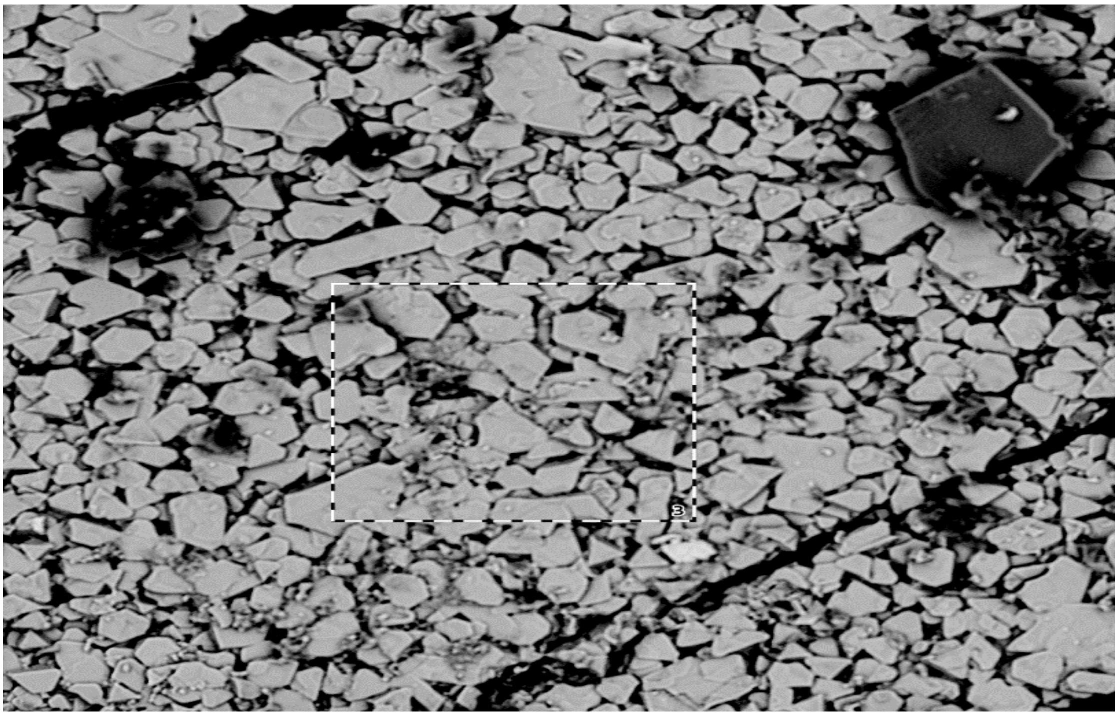


Figure 13: Image of Sample 2(Mapping)

sed on the figure and table above, the concentration of chromium is the highest followed by nickel and oxygen, iron and sodium. The higher concentration of nickel and chromium and oxygen shows the precipitation of nickel and chromium oxide. Even though the concentration of iron is low compare to nickel and chromium, the precipitation of iron oxide cannot be deny. The reasons for the highest concentration of chromium, followed by nickel and iron were because, the chromium reacts faster towards oxygen compare to nickel and iron. The chromium oxide acts as top defensive barrier compare to nickel and iron because the chromium oxide has a corrosion resistance is higher than nickel and iron. The present of higher concentration of oxygen shows the oxide layer was been formed during the hot corrosion testing.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, the coating powder (chromium carbide- nickel chrome) deposited on the substrate metal using HVOF techniques showed a high corrosion resistance in molten salt solution (sodium sulphate + sodium chloride) at 800 °c for 2 cycles (10 hours). This can be proved by the increase in the weight gain of both sample which is Sample 1 and Sample 2. The weight gain of Sample1 is higher compare to Sample 2 because the higher formation of iron oxide at Sample 1 compare to formation of chromium, nickel and iron oxide that were deposited at Sample 2. The higher formation of iron oxide show that the higher oxidation rate that occur at Sample 1.

Based on the images from the Scanning Electron Microscope, and the Energy Dispersive X- ray and the X-ray map analysis, the author can conclude that, the higher concentration of oxygen and iron at Sample 1 shows that the formation of iron oxide. Samples 2 shows the higher concentration of coating powder element such as chromium and nickel and followed by the iron. The present of coating powder element in Sample 2 shows the present of chromium oxide, nickel oxide and iron oxide that acts as a defensive barrier towards hot corrosion or oxidation. The precipitation of the oxide layer at Sample 2 proved that, the coating powders play its role and purpose. As a conclusion the coating powder that were deposited on the surface of substrate shows a high resistance towards hot corrosion.

5.2 Recommendation for the future

The number of cycle or the total time the samples was put in the furnace for hot corrosion testing can be increased to study the life span of the coating powders. By increasing the number of cycles, the result will be more accurate and we can determine exactly the number of hours or the base line for the coating powder to withstand the corrosion agent that are dangerous. Besides that, the operating temperature of the furnace can be increase up to 1500 °c. Based on the study, the increase in the operating temperature effect the oxidation process. By doing so, we can do a further study to analyse the hot corrosion behaviour at a new level and more detail and specific. In addition, the cross section analysis should be done. The reasons are, by doing the cross section analysis, we can observe how much the corrosion agent penetrate through the coating layer and go into the substrate metal. Besides that, by doing cross section analysis, we can see clearly the images of the coating powder layer and the thickness of the layer. XRD analysis or X-ray diffraction analysis should be done in order to study the atomic arrangement, crystallite size and others.

CHAPTER 6: REFERENCE

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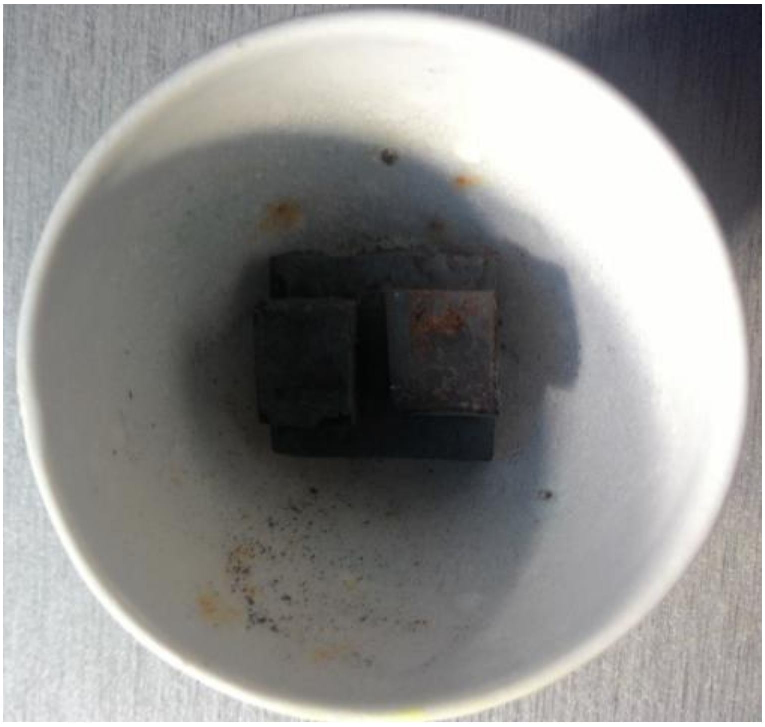
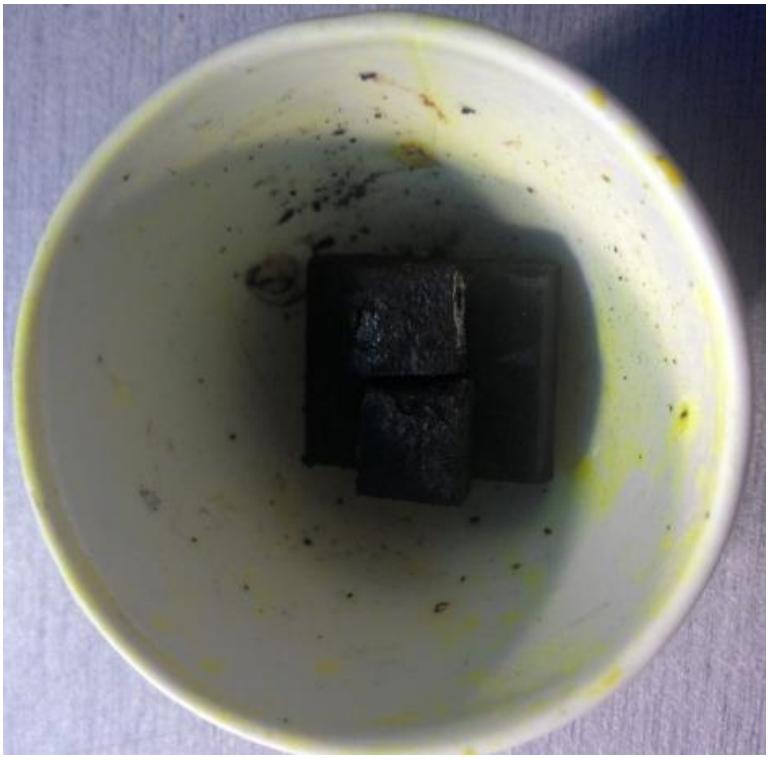
APPENDIX

Sample 1 after hot corrosion testing



Sample 2 after hot corrosion testing



Sand blasting machine that were used

Coating powder that were deposited on the surface of substrate metal