The Influence of Oxidizing Parameters on the Formation of Oxide Layer as a Precursor for the Fabrication of Carbon Fiber-Steel Laminate

by

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22537

Dissertation submitted in partial fulfilment of

the requirements for the

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify and confirm that I am responsible for the work that is done and submitted in this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have been undertaken or done by unmentioned sources or person

DHARMESH KUMAR A/L CHANDRASHAKERAN

ABSTRACT

The application of fiber metal lamination has been increasing in the engineering industries such as the aerospace, automotive, construction and processing industries. Fiber metal lamination are able to provide a solution to improve metallic materials' characteristics while improving the fibers' properties at the same time. With high reliability and cheaper alternative to provide superior properties in material, in fabricating the fiber metal laminates, the surface of contact between the metal and the fiber is a fundamental criterion. The stability of the surface of the metallic substrate is key in avoiding delamination of the fiber metal laminate due to corrosion under insulation where the metallic surface that is bonded with the fiber are decomposed. In this paper, the influence of oxide formation on carbon steel which is a precursor to carbon fiber steel laminate surface discussed with different oxidizing parameters, which are temperature, time, heating rate and surface roughness on the formation of stable oxide layer. An optimum set of oxidizing parameter and levels are determined using the Analysis of Mean (ANOM) technique in Taguchi's method, and the contribution of each oxidizing parameter in the formation of magnetite layer is done using the Analysis of Variance (ANOVA) method. The properties of the oxide are then determined using the X-Ray Diffraction (XRD) analysis. From the setup of the experiment, appearance of different oxides can be observed physically on the surface of the oxidized steel and optimization of the magnetite formation parameter shows that the hardness of the oxidized steel is directly proportional to the percentage of magnetite formation on the optimized parameter. The numerical study with ANOVA showed that the surface roughness has the highest significance on the formation of magnetite on the surface of carbon steel followed by temperature and giving time and heating rate a not significant effect. Based on the Taguchi's analysis and XRD results, run number nine has the optimum stable oxide formation parameters where high temperature, surface roughness and time yields a higher magnetite content oxidation on the surface of the carbon steel.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In most of industrial and structural applications, the parameters in material selection such as the specific strength, weight and cost have become a fundamental criterion. The introduction of composites has become revolutionary in improving the material properties and in the current era, mixture of composite and non-composite structures has become a normality especially for industrial use in enhancing the material properties to provide a protection such as insulation and corrosion inhibitors. One of the most common hybrid composites is the Fiber Metal Laminate (FML) that is a family of hybrid composite structure formed from the combination of metal layers sandwiching a fiber-reinforced plastic layer. The current metals that are used in the structure are aluminum, magnesium or titanium and the fiber-reinforced composites are either glass fiber, carbon fiber or aramid fibers [1].

FML’s are composed of alternatively stacked metal and fiber reinforced composite layers. The hybrid composite provides an advantage of hybrid nature from two different constituents that are metal and fiber reinforced matrix systems. For instance, metals are isotropic, can bear high strength and is impact resistance but they are easily prone to corrosion due to chemical reaction of metal with the environment, which causes the metal to deteriorate. Composite fibers such as fiberglass and carbon fibers on the other hand provide high corrosion resistance and provides excellent fatigue characteristics with high strength and stiffness [2-6]. The fatigue and corrosive characteristics that the metals inhibit and the low bearing strength, impact resistance and the reparability of a fiber composites can be overcome with the hybrid combination of the two constituents [7,8].

In the industry, FMLs are commonly used in the aircraft industry for high performance and lightweight structure, which is where the strong development of these fiber-metal laminate structures started where in this industry Aramid Reinforced Aluminium Laminate (ARALL), Carbon Reinforced Laminate (CARALL) and Glass Reinforced Aluminium Laminate (GLARE) are implemented [9]. Other industries started implementing the FML following the aircraft industry viewing its advantageous properties. Some of the industries include the construction industry where carbon fiber reinforced polymer (CFRP) are used in strengthening the concrete beams and FML are used in offshore and naval industries such as improvising stealthier hull technologies and online pipe repairs which are caused due to galvanic corrosion.

1.2 PROBLEM STATEMENT

Carbon fiber steel laminate is a common fiber metal laminate such as in the application of concrete rebar protection from corrosion and remediation of corroded industrial pipelines. In the fabrication of fiber metal laminate structure, such that steel is the substrate material the quality of surface of the steel affects the surface bonding with the carbon fiber. Failure on the surface of the steel especially due to reduction of the surface due to corrosion can disrupt the bonding of the laminate. The type of oxides form on the surface of the steel plays a factor in acting as a passivation of the coating which will reduce the probability of delamination with a condition of being a stable oxide at a presence of electrolyte environment such as air and brine water. Different oxides provide different reaction towards the environment and the common oxides that are commonly known consist of hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO). Wustite (FeO) is highly sensitive type of oxide which despite being one the stable oxides at high temperature is a metastable oxide which easily transforms into a stable magnetite (Fe_3O_4) under normal oxidizing environment. In addition, normal oxidation at lower temperature can yield to hematite (Fe_2O_3) or typically known as rust which is unstable oxide in normal environment that can deteriorate the bonding in the laminate. To overcome this issue, oxidizing parameters that are crucial to dictate the formation of magnetite oxide layer should be controlled such as the temperature, time, heating rate and surface roughness. Therefore, it is vital to evaluate these parameters as the formation of stable oxide layer on steel is a contributing to the decisive factor for the interfacial fracture toughness for the carbon fiber-carbon steel laminate structure.

1.3 OBJECTIVES

The purpose of this research is to investigate the influence of oxidizing parameters on the formation of stable and passive oxidized steel as a precursor to carbon fiber steel lamination. This research is subdivided into the following objectives:

i) To study the influence of oxidizing parameters which are temperature, time, heating rate and surface roughness on the formation of oxide layer on carbon steel

ii) To investigate the significance of each oxidizing parameter using an appropriate design of experiment with a statistical model and Analysis of Mean (ANOM) using the signal-to-noise (S/N) ratio along with Analysis of Variance (ANOVA).

iii) To verify the yield of stable oxide formed on carbon steel after oxidation based on the optimized parameters provided by ANOM analysis.

1.4 SCOPE OF STUDY

To achieve the objectives that have been laid out based on the problem statement, a precise scope of study to ensure that the research is in-depth and relevant to the problem statement thus not getting out of track from the research done. The main goal of the research is to investigate the influence of oxidizing parameter on carbon steel as a precursor for fiber metal lamination with low probability of delamination:

1) To study the influence of temperature, time, heating rate and surface roughness on the formation of oxide layer on the carbon steel.

- By creating an oxide layer on the carbon steel using four different parameters at three different levels, which provides significant effect on the formation of stable oxide.

2) To investigate the significance of each oxidizing parameter using an appropriate design of experiment with a statistical model and Analysis of Mean (ANOM) using the signal-to-noise (S/N) ratio along with Analysis of Variance (ANOVA).

   - Using Taguchi's design of experiment with statistical orthogonal array arrangement to obtain different combination of parameters for sample preparation.

   - Measuring the hardness of the oxidized sample using Micro hardness test as a mechanical performance optimized from the design of experiment

   - The ANOVA technique is used to analyse the effect of each parameter in the oxidizing process and identify the significance of each parameter in the process

3) To observe and analyse the yield of stable oxide formation due to the oxidizing parameters using the X-Ray Diffraction (XRD).

   - By using X-Ray Diffraction (XRD) to analyse the percentage of stable oxide form on the surface and verify the percentage of formation with the statistical study

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 OVERVIEW OF CARBON STEEL

Carbon steel is an alloy which where it is iron carbon compounded. The carbon steel content makes up to 2.1% of the steel's total weight and it is known to be one of the primary categories of steel. Carbon steel are made up as much as 90% of steel manufactured around the world [10]. There are five sub-categories of carbon steel which are:

- Ultra-low Carbon-Steel: With Carbon content less than 0.015%
- Extra-Low Carbon Steel: With Carbon content between 0.015% to 0.05%
- Low Carbon Steel: With Carbon content between 0.05% to 0.19% carbon
- Medium Carbon Steel: With Carbon content 0.2% to 0.49%
- High Carbon Steel: With Carbon content over 0.5%

and these characteristics must have lower than 0.6% copper, 0.6% silicon and 1.65% manganese in order to meet the requirements to be classified as carbon steel [10].

Carbon Steel is an ally that is created such that the high strength in the carbon characteristic able to unite with the malleability of iron. Heat treatment is usually done on the carbon steel alloy to improve its toughness and tensile strength. Despite the high strength and toughness of the carbon steel, it is still prone to corrosion such as oxidation where oxide layer is formed on the carbon steel in a oxygen existing environment where degradation of the carbon steel occurs which then leads to failure of the material.

2.2 OXIDATION OF CARBON STEEL

Oxidation is a process where oxygen reacts with the iron content on the carbon steel producing oxide. The formation of oxide on the surface of the steel consumes the iron element on the carbon steel making the steel to reduce or corrode. In the mill scale created in the carbon steel production process consists of three variations of iron oxides which are wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3). [11, 12].

2.2.1 Wustite (FeO)

Among the three iron oxides, wustite is known as a metastable as wustite displays great stability at higher temperatures than 570^{o}C and wustite is the least stable at low temperature which breaks down into magnetite and iron below 570^{o}C [11,13].The breakdown of wustite to magnetite occurs as such reaction:

$$4FeO \rightarrow Fe_3O_4 + Fe \quad (1)$$

The formation of wustite oxides only exist at high temperatures or the oxides have to be quenched at room temperature to avoid the immediate change in formation which happens between 400^{o}C – 480^{o}C. [11,14]. Due to the transformation of wustite to magnetite at below the stability temperature, thus wustite is rarely found in the presence of normal environment.

2.2.2 Magnetite (Fe_3O_4)

Magnetite is stable iron oxides, such that the crystal habits of the magnetite makes the metal substrate inert against new type of corrosion under low oxygen content. Magnetite used to passivate surface of steel, which acts as a protection from the surface corrosion while hematite type is a common oxide that forms on steel that is more porous and less stable thus being less desirable to be on a steel surface [15]. The formation of magnetite from steel surface at high temperature can be deducted with the reaction:

$$Fe + 4\ Fe_2O_3 \leftrightarrow Fe_3O_4\ Fe \quad (2)$$

Where the presence of hematite on the surface of the steel such that due to presence of water the hematite reduces with the iron metal. Magnetite-epoxy nanocomposites are used as protective coating for marine application due as damaged epoxy layer compromised with magnetite that heals the cracks. [16] In similar application, increment of magnetite presence in the epoxy hybrid nanocomposites improves the adhesion of the epoxy with the steel network. [16]

2.2.3 Hematite (Fe_2O_3)

Hematite or generally known as rust is commonly seen as the iron oxide forms at normal oxidizing conditions regardless of pH and are active corrosion substance which makes the steel much brittle as it continuously reacts with them. At high oxygen concentration, magnetite starts to break down to hematite. Hematite are very reactive with high concentration of oxygen and speeds up the corrosion process. The formation of hematite with the presence of oxygen in moist air can be deducted such as:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3\ Fe \tag{3}$$

The characteristics of the iron oxides can be clearly viewed by the iron oxide phase diagram as shown in Figure 2.1.

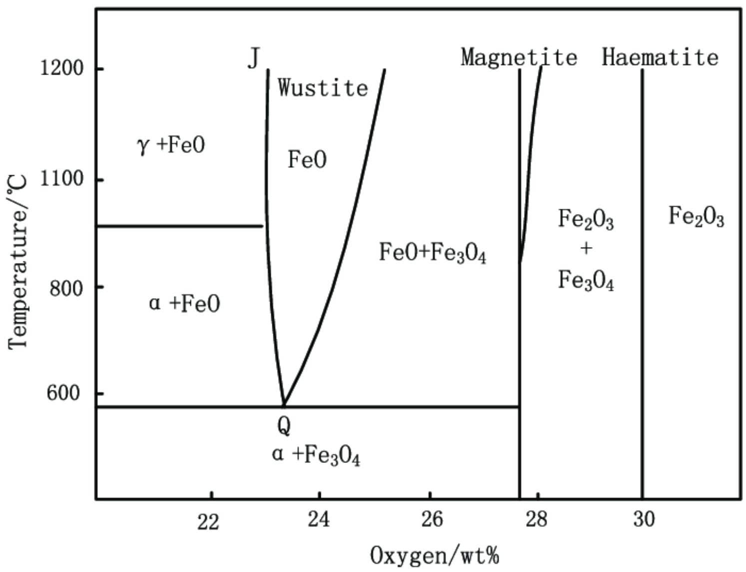


Figure 2.1: Iron Oxide Phase Diagram [17]

The oxide forms also differ in property of pure and complex oxides. Pure oxides are oxide that consist of purely a single type composition with low to negligible other compositions while complex oxides are mixture of different oxides which is the most common on the formation of steel as due to the temperature and heating rate. Besides that, increasing temperature will increase the oxide stability in the standard environment and be less corrosion resistance.

Another factor that differ in different oxides is the hardness properties of the oxides as shown in the Table 2.1.

Table 2.1: Comparison of hardness of pure and complex oxides of hematite and magnetite using Instrumented Indentation [18].

Mechanical Properties	Pure Oxides		Complex Oxides	
Instrumented Indentation	Magnetite	Haematite	Magnetite	Haematite
B(GPa)	223	237	52	65
Real Hardness, H0 (GPa)	6.3	8.2	5.3	2.7
Hardness length scale factor, HLSF	9.8	8.1	5.2	3.8

In the Vickers hardness test, the hardness properties of hematite and magnetite differ for pure and complex oxide such that the hardness value of the pure hematite is higher that of magnetite while the complex magnetite has higher hardness value in comparison to complex hematite [18]. From the oxides form, one correlation can be deducted is that increasing stability of oxide as steel production have higher hardness value in complex form which is the common type formed on surface of metal.

2.3 INVESTIGATION OF THE OXIDIZING PARAMETERS

In studying the influence of the oxidizing parameters on carbon fiber steel lamination, four key parameters must take into consideration for the research that involves temperature, time, heating rate and surface roughness. With these parameters, the effects of oxide formation on steel investigated.

2.3.1 Temperature

Temperature is one of the fundamental parameters that affects the iron oxide formation as at different temperature, the different energy applied in the reaction of steel with oxygen forms different iron oxide layers as can be referred in Figure. At a normal oxygen present environment, wustite is metastable such that at temperature higher than 570^{o}C, the wustite is unstable and when temperature drops below 570^{o}C it starts to decompose into magnetite and iron [19]. temperature increases. Magnetite also exist in low temperature but that is influenced by oxygen percentage as shown in Figure. The change in temperature not only influences the iron oxide formation but it influences the grain size of the steel substrate where the size of grain of steel reduces at high temperature. Therefore, higher iron oxide formed on steel affects the hardness of the material. Increasing the temperature reduces the oxygen weight % in the composition in iron oxide layer [20].

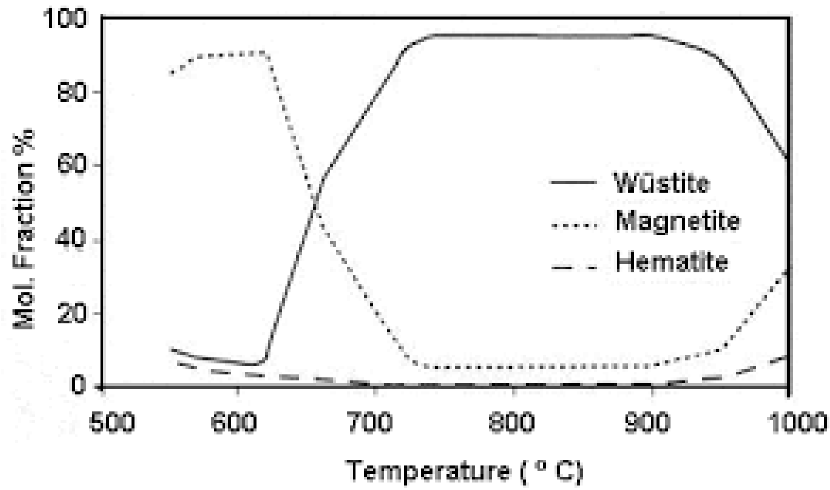


Figure 2.2: Graph of temperature versus mol fraction % of the three types of oxides formed [20]

2.3.2 Time

The time of oxidation is another important parameter in the formation of different oxide layers as at different time rates, with the exposure to the heat or environment, different oxides are formed. Time works cohesively with temperature as at a certain temperature and time, different types of oxides can be formed due to the shortened or prolonged exposure to the different temperatures or oxidizing environment. The different time and temperature can provide different rate of reactions to the oxidation process on the surface of the steel. The longer the exposure to the high temperature of oxidizing environment, the thicker the oxide layer formed and can be fully developed wustite layer as the surface is allowed for full diffusion of the reaction. Increasing time of exposure of steel surface to oxygen present environment will increase the thickness of oxide layer formed, which can be seen in Figure 2.3.

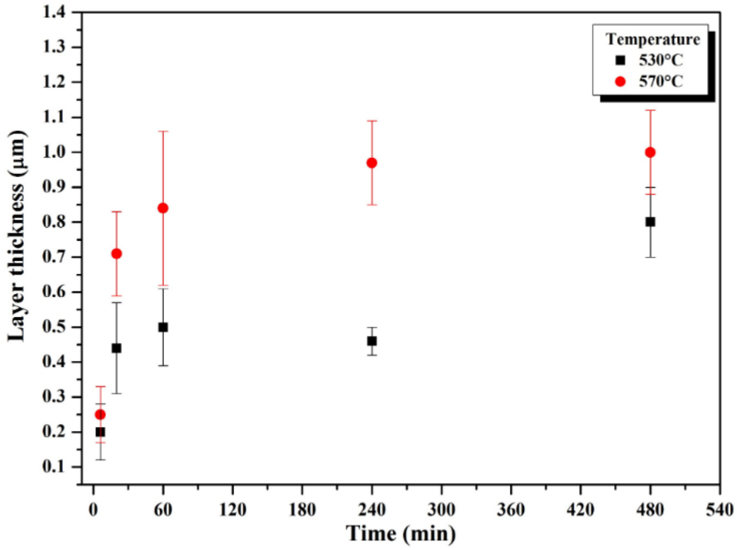


Figure 2.3: Graphical representation of oxide layer thickness (μm) for all evaluated samples [21].

2.3.3 Heating Rate

As important as time and temperature in the formation of different oxide layers, heating rates also effects the oxidation rate on the surface of the steel. At high heating rates, the faster the reaction of oxide formation may occur rather than the slow heating rate. When the heating rate reaches the peak temperature, the rate is held at constant temperature where usually the phase changes can occur evenly on the surface of the metal rather than the slower heating rate that causes delay in the formation of oxide. Despite that, high heating rate can cause unstable growth of the particles due to fasten kinetics of the particles which may affect the formation of oxide film on the surface of the steel varying in thickness of the film and the type of oxide formed.

2.3.4 Surface Roughness

One of the key parameters that would influence the formation of oxide layer is the surface roughness of the steel. Higher surface roughness produces a thicker oxide films as the contact of oxygen to the surface of the metal varies instead that of smoother surface were the contact is near to constant throughout the surface of the steel. Despite that, the higher surface roughness has a much slower time for the oxide layer to smoothen out. The weight gain analysis indicated increased oxide thickness with coarser surface finish where the polished sample exhibited a thinner oxide than that of a chemically etched sample [22,23]. Some of the results obtain from the research, the Figure 2.4.

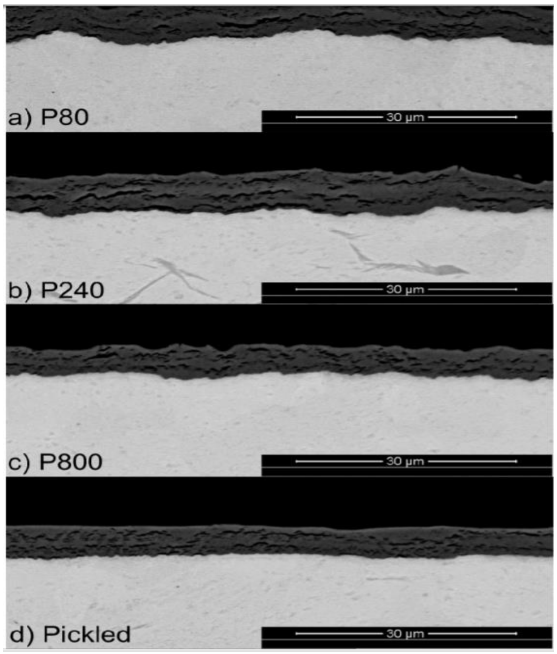


Figure 2.4: The formation of oxide on different surface roughness of Zircaloy-4 [22]

2.4 CARBON FIBER METAL LAMINATION

Carbon Fiber metal laminates are mainly designed for producing high strength with low weight ratio material for industrial application. Carbon fiber reinforced composite upholds a high specific strength, the carbon composites are at twice as strong as steel, thus combining obtains the required strength of the steel without increasing the composition and density of steel thus reducing the weight by half [24]. Despite that the carbon fibers in the carbon fiber reinforced polymers causes the overall metal laminate to be electrically conductive thus making it more vulnerable to galvanic corrosion especially when coupled with small metallic parts such as fasteners, nuts and bolt [24]. One way to reduce the occurrence of the galvanic corrosion is by formation of protective stable oxide layer, which acts as a passivation on the surface of metal [24]. Passivating the surface between the epoxy and steel lamination improves the adhesion between the steel and the epoxy network. [16]

CHAPTER 3

METHODOLOGY

3.1 OVERALL PROJECT PROCESS FLOWCHART

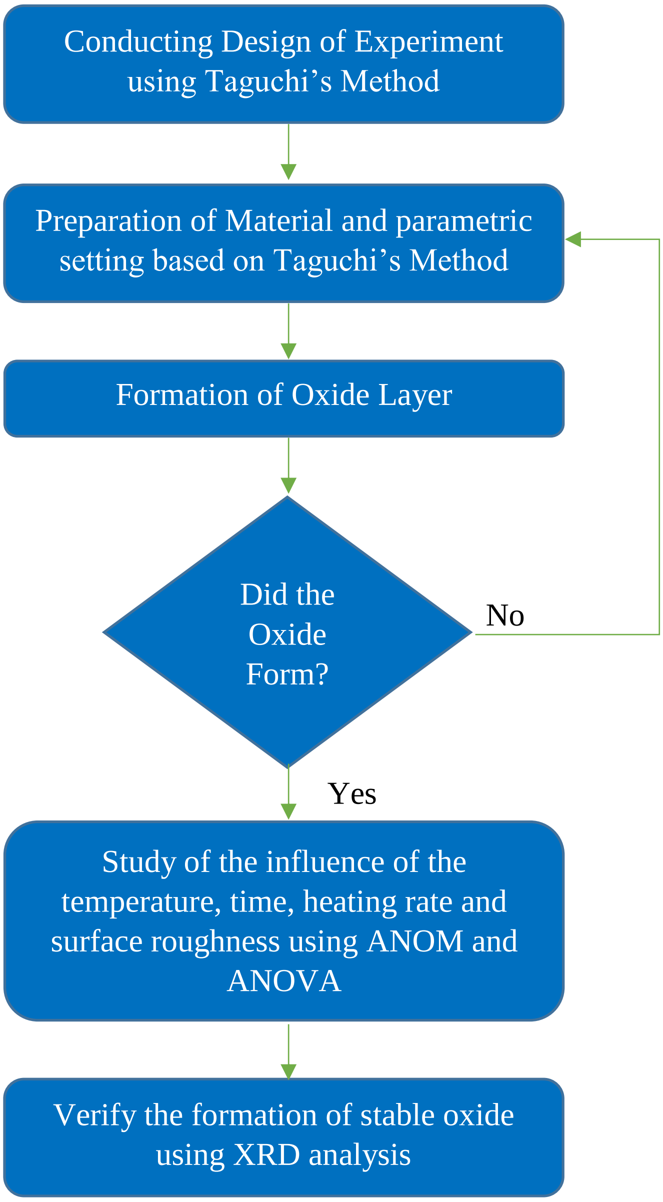


Figure 3.1: Project Flowchart

3.2 DESIGN OF EXPERIMENT USING TAGUCHI'S METHOD

Factorial design of the experiment is a system laid out arrangement for an experimental investigation with a variety of parameters and level of parameters. Adequate factorial outlines can distinguish all possible combination for a given arrangement of parameters [25]. Despite being able to produce different combination of experimental design, the factorial design provides a drawback in terms of increasing number of parameters will increase the combination of experiments that are not feasible and there are no broad rules for the investigation of the outcomes obtained from the tests. A unique combination of general planned rules for factorial experimental testing that fulfills different engineering applications known as the Taguchi's Method that is introduces by Dr Genechi Taguchi who was an engineer in providing statistics to improved manufacturing products.

A comparison can be done with factorial experimental design with Taguchi's method that shows the reduction of number of experimental runs while able to obtain the effects and on the influencing parameters. In this research study, there are four levels where each parameter has three sets of value or levels in investigating and obtaining the most optimized parameter of the oxide formation as detailed in Table 3.1.

Table 3.1: Comparison of Factorial Design and Taguchi's Method of Number of Experiment

Factors	Level	Total number of experiments	
		Factorial Design	Taguchi's Method
2	2	4 (2^2)	4
3	2	8 (2^3)	4
4	2	16 (2^4)	8
7	2	128 (2^7)	8
15	2	32,768 (2^{15})	16
4	3	81 (3^4)	9

To determine the combinations of the Taguchi's Method experimental analysis, orthogonal arrays are to be used. The orthogonal array provides a well-balanced, minimum number of experiments that serve as an objective function for optimization thus providing a detailed prediction and analysis of results [25, 26]. Therefore, different parameters can be studied in an orthogonal array design.

As there are different standards for orthogonal arrays, each of the arrays depends on the specific number of independent design parameters and levels. In this research, three levels of variation were selected for each variable as analyzing three levels for controlling factors can produce a non-linearity over the range of controlling factor compared to two levels that can only evaluate a direct linear change between one and two. [27] Therefore, three levels able to provide a more accurate average of the optimized parameters than two levels. The orthogonal design can be formed using the following equations:

$$k = (n-1) / 2 \qquad L_n(3^k) \tag{4}$$

L = Latin Square layout

n = number of experiments

k = greatest number of factors that can be investigated using the design layout

The minimum number of experiments need to be conducted by Taguchi' Method can be determined from the calculation the degree of freedom.

NTaguchi = 1 + Σ (number of levels for each factors−1)

NTaguchi = 1 + Σ ((3−1) + (3−1) + (3−1) + (3−1))

NTaguchi = 9 experiments

From the calculations, the $L_9(3^4)$ design was chosen for the research being suitable for the processing parameters and levels that was set for the experimental procedure in determining the influence of oxidising parameter on the formation of oxides on the carbon steel as a precursor of carbon fibre lamination on the carbon steel. The orthogonal array with nine experiments can be portrayed in Table 3.2 with vertical columns being the parameters of the experiment and the values in each column representing the number of levels. Each row in the orthogonal array for nine experiments shows the suitable combinations for each experiment.

Table 3.2: L_9 (3^4) Orthogonal array experimental design

$L_9(3^4)$ Orthogonal Array					
Experiment #	Parameter 1	Parameter 2	Parameter 3	Parameter 4	Performance Parameter Value
1	1	1	1	1	Ex 1
2	1	2	2	2	Ex 2
3	1	3	3	3	Ex 3
4	2	1	2	3	Ex 4
5	2	2	3	1	Ex 5
6	2	3	1	2	Ex 6
7	3	1	3	2	Ex 7
8	3	2	1	3	Ex 8
9	3	3	2	1	Ex 9

In the first part of studying the oxidizing parameter of carbon steel was the formation of oxides on the carbon steel. Based on the Taguchi's design of experiment nine parameters were produced based on the L_9 orthogonal array as shown in Table 3.3 with each oxidizing parameter discussed in the literature review with three sets of level such as in Table.

Table 3.3: Process parameters and each level for the parameter

Process parameter	Process parameter	Level 1	Level 2	Level 3
A (°C)	Temperature	400	600	800
B (min)	Time	60	90	120
C (°C/min)	Heating Rate	10	15	20
D	Surface Roughness	P80	P240	P800

Based on the processing parameter that have been set for the parametric study as tabulated in Table 3.3, the parameter is then combined with the orthogonal array to obtain the set of experiment with fair distribution of each parameter and level as tabulated in Table 3.4. The values of temperature was determined based on the transition of unstable to stable oxide changing temperature, which is at 570^{o}C [20]. Time of the oxidation is set based on the average time used to heat the sample, which is the average time required for oxide layer start to form based on the set heating rate [11]. Besides, the lowest time is set based on the minimum requirement of the normalizing furnace at Block 17, Universiti Teknologi PETRONAS. The heating rate is set based on the appropriate setting of the normalizing furnace in block. Finally, the roughness of the sandpaper used for sample preparation was based on the formation of oxide on different surface roughness of Zircaloy-4 [22].

Table 3.4: Processing parameter based on the $L_9(3^4)$ Orthogonal Array

$L_9(3^4)$ Orthogonal Array				
Experiment #	Temperature (°C)	Time (min)	Heating rate (°C/min)	Surface Roughness (Grit Paper)
1	400	60	10	P80
2	400	90	15	P240
3	400	120	20	P800
4	600	60	15	P800
5	600	90	20	P80
6	600	120	10	P240
7	800	60	20	P240
8	800	90	10	P800
9	800	120	15	P80

3.2 EXPERIMENTAL PROCEDURE

In the experimental procedure, the oxidized steel is prepared based on the Taguchi's design of experiment and Micro hardness test is done to be used as the performance parameter in the evaluation of stable oxide in the design of experiment. X-Ray Diffraction analysis is done to verify the result of the design of experiment with the percentage of magnetite formation on the steel substrate.

3.2.1 Sample Preparation of Oxidized Carbon Steel

As the experimental setup is done for each parameter and level prepared using the $L_9(3^4)$ orthogonal array the material sample is prepared first by cutting the carbon steel to 2.5cm x 2.5cm x 0.5cm. The material is cut utilizing the metal cutting machine such that nine pieces with similar dimensions were cut and chippings and steel burrs were removed.

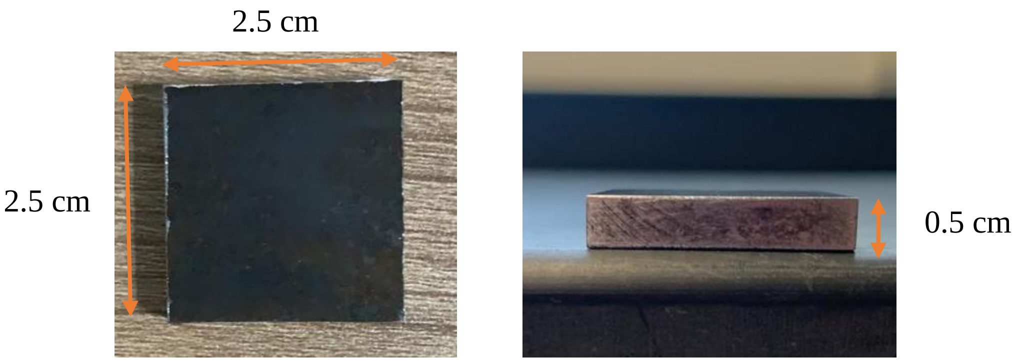


Figure 3.2: Dimension of the sample

Next, existing surface oxide protection on the carbon steel is removed using P80, P240 and P800 grit sandpapers depending on the experimental setup with Taguchi's design of experiment before being oxidized. This is done so that oxide can be properly formed on the surface of the carbon steel and fair evaluation can be done for all the carbon steel sample with no surface deposits.

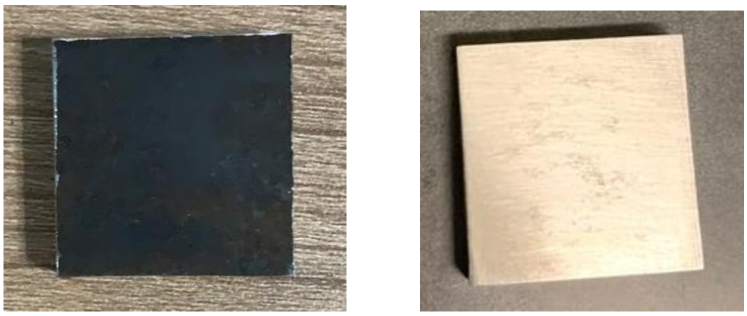


Figure 3.3: Surface preparation for a) before b) after

The formation of oxide is executed by heating up the surface prepped carbon steel which is placed in the normalizing furnace with temperature, time and heating rate for the samples based on the designed experimental setup using the orthogonal array. The setting in the furnace is done such that it obeys the oxidizing cycle for each process based on the combination of the three-heating parameter as displayed in Figure 3.4.

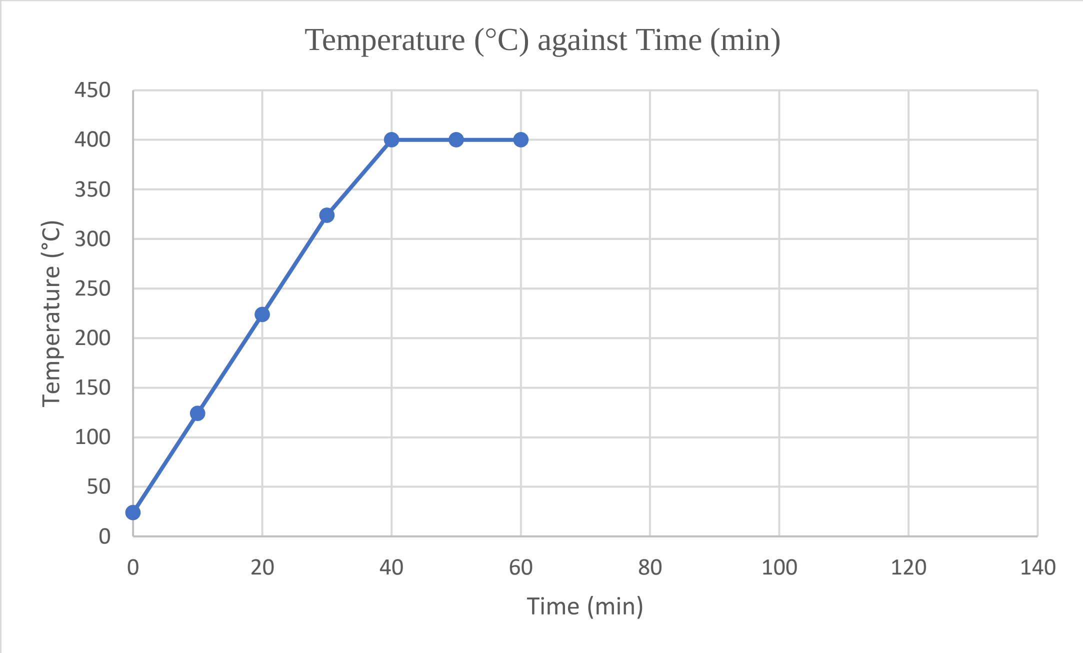


Figure 3.4: The oxidizing cycle with max temperature of 400^{o}C at 60 minutes with the heating rate of 10^{o}C/min

Once the sample have started the oxidizing cycle in the furnace, the carbon steel sample is left in the furnace throughout the day for it to be cooled and the oxidized steel is retrieved the following day.

3.2.2 Microhardness Testing

To study the influence of the oxidizing parameter, the hardness value is used to determine the significance of each parameter. As for this research, the Vickers hardness testing is done on the surface of the oxidized steel as . The Vickers hardness testing used for this research is because the Vickers hardness test method is used for determining hardness in the micro scale thus the testing being known as the micro hardness test. The main purpose of using the micro hardness testing is that is useful for small parts or thin materials where the focus of the hardness in this experiment is on the thin oxide layer formed on the surface of the steel. The micro hardness test is done based on the ASTM E-384 standard where light loads are used with a diamond indenter to make the indentation and measure the hardness value.

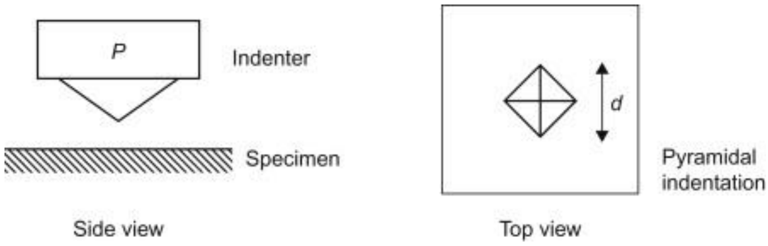


Figure 3.5: Vickers diamond indenter for hardness measurement

As for this experiment, the load is set to 1kgf on the Vickers hardness machine with the dwell time of 15 s to ensure the indentation is clear on the surface of the oxidized steel for accurate data measurement. To ensure a more accurate data, each sample microhardness testing is done three times and the average value is taken for the parametric study

3.2.3 Analysis of the Parameters using the ANOM and ANOVA

After the nine experiments have been performed based on the Taguchi's design of experiment, the average hardness value for each of the experiment run is evaluated using the signal-to-noise (S/N) ratio. As for the statistical approach, the S/N ratio can be categorized in smaller values are better, nominal is the best and larger value is better approach. [28] As for this case study the larger the better S/N ratio approach is selected as based on research done on formation of stable oxide, the higher hardness value yields higher formation of the magnetite. The S/N ratio can be evaluated as such:

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{R_i^2}\right) \quad (5)$$

Where

n = Total number of experiments run for each set of experiment

R_i = The score for the separation efficiency performance in the separator.

i = The current experiment being run with the same experimental condition

From the S/N Ratio calculated for each parameter and levels, the effect of the parameters with the average hardness can be determined from the cast study such that the higher response of S/N ratio level for its respective parameter, displays the best value for hardness, which is for the stable oxide formation which is mathematically represented as shown:

$$(M)_{Level=i}^{Factor=F} = \frac{1}{n_{Fi}} \sum_{j=1}^{n_{Fi}} [\left(\frac{S}{N}\right)_{Level=i}^{Factor=F}]_j \qquad (6)$$

Where $[(M)_{Level=i}^{Factor=F}]$ represents the mean of the S/N ratio with F as the factor and i level, $[\left(\frac{S}{N}\right)_{Level=i}^{Factor=F}]_j$ describes the value of S/N ratio with F as the factor at 'i' level in the the number of appearance, j in each experimental setup. This approach of determining the optimized parameter is known as the Analysis of Mean (ANOM). [28].

An Analysis of Variance (ANOVA) can be studied to determine the percentage of contribution of each parameter in the average hardness on the experimental setup and the percentage of contribution can be determine using [28]:

$$\rho_F = \frac{SS_F - (DOF_F\, V_{Er})}{SS_T} \times 100\% \qquad (7)$$

Where

SS_F = Factorial sum of squares

DOF_F = Degree of freedom for each factor

V_{Er} = Error of the variance

SS_T = The total sum of squares

3.2.4 Investigation of Existing Oxides Layer on the Oxidized Sample

Based on the optimization done using the ANOVA method to determine the best parameter to obtain a high hardness value. To ensure that the optimization done provides the stable magnetite formation on the oxidized steel a verification should be done to determine the compound existing on the carbon steel and X-Ray Diffraction (XRD) is done on all the prepared sample to determine the composition of the oxide formed and its thickness on the carbon steel metal [11,12]. The main purpose of conducting the XRD is that it can provide pattern of the iron oxide formed which are relatively close to the main oxide and provides several different transition phases can be simultaneously present. [29] To obtain the different oxide compound exist on the oxidized steel, The XRD is set with a scan range of $10^o < 2\theta < 80^o$, to obtain a larger range of peaks which can be analyzed to obtain more detail of oxide on the surface and the exposure time is set to 100 s/step at a step size of 0.02^{o}/step with copper diffractometer which are the standard setup used at UTP's Centre of Analytical Laboratory (CAL).

3.3 EQUIPMENT AND MATERIAL

Table 3.5 shows the planned list of equipment to be used and Table 3.6 is the list of core material needed for the experimental procedure.

Table 3.5: List of Equipment Required for the Research

No	Equipment	Location
1	Metal Cutter	Block 21, EPIC, UTP
1	Normalizing Furnace	Block 17, UTP/ Block 20, UTP
2	Microhardness Testing Machine	Block 17, UTP
3	Powder X-Ray Diffraction (XRD)	Block P, CAL, UTP

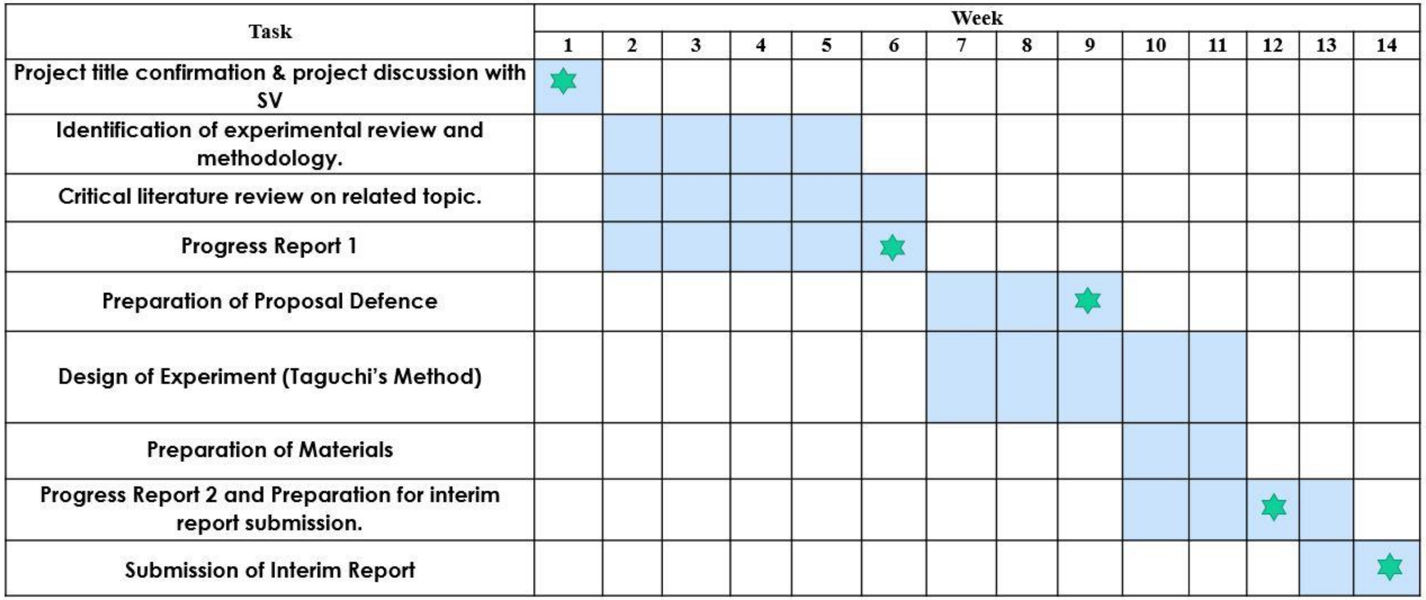
Table 3.6: List of Raw Materials for the Experimental Procedure

No	Materials Used
1	Mild Carbon Steel
2	Sandpaper with Grit P80, P240 and P800

3.4 GANTT CHART AND MILESTONES

The research and the critical literature review were carried out for 7 weeks to get enough and accurate information. The preparation for the materials took 2 weeks to be completed as there was several students who needed to use it. All bookings for the equipment and tests were done during FYP 1 except for the linear polarization resistance (LPR) corrosion test and the scanning electron microscope (SEM) test All tests and analyzation of acquired data was completed within the allocated time.

Table 3.7: Project Gantt Chart and Milestones for FYP 1



= Key Milestones

Table 3.8: Project Gantt Chart and Milestones for FYP 2

Task	Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Experimentation on the formation of oxide layer with different oxidizing parameter on carbon steel														
Conduction of Micro hardness Test														
XRD Analysis of the experimentation														
Preparation and Compilation of Results and Discussion														
Preparation for VIVA														
Preparation of Dissertation														

= Key Milestones

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PHYSICAL OBSERVATION OF SAMPLE TRANSFORMATION

When the carbon steel undergoes the oxidation process using the parameters and level decided by the Taguchi's design of experiment, the physical appearance of the oxidized steel changes such that there is formation of black and red substrate on the surface of the oxidized steel as shown in Figure 4.1.

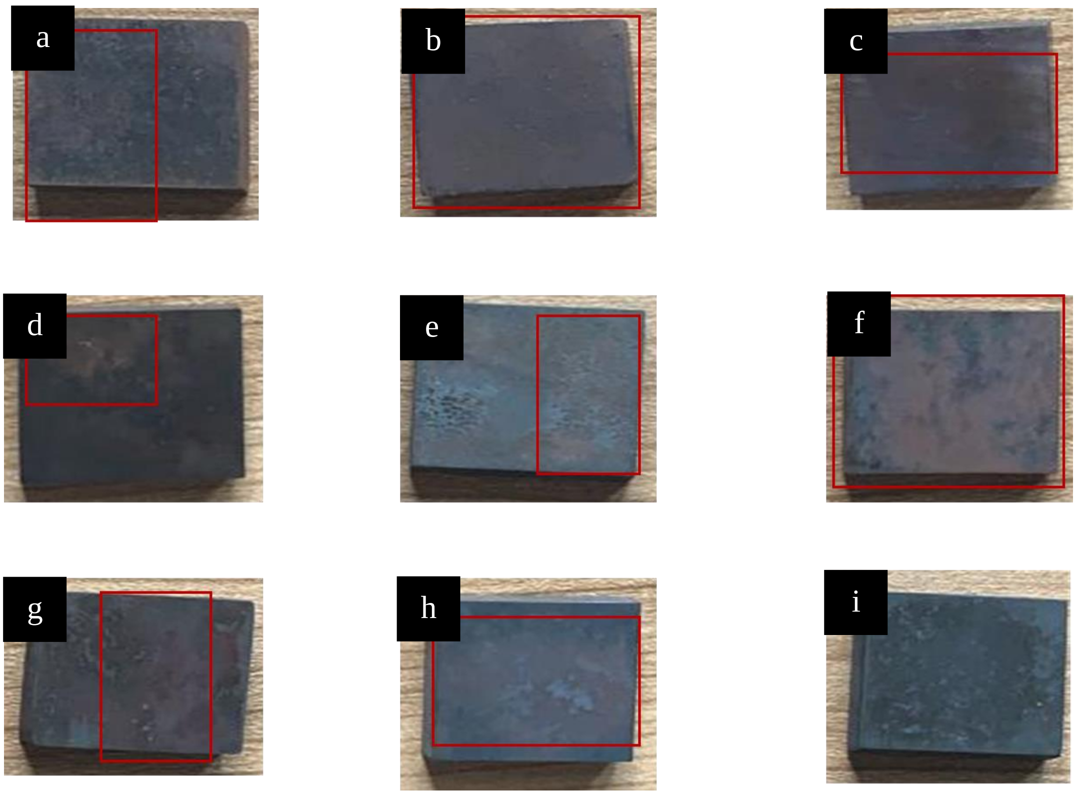


Figure 4.1: Formation of oxide on carbon steel for a) Experiment 1 b) Experiment 2 c) Experiment 3 d) Experiment 4 e) Experiment 5 f) Experiment 6 g) Experiment 7 h) Experiment 8 i) Experiment 9

Based on the Figure 4.1, the first eight run of experiment display a mixture if red oxide (hematite) and black oxide (magnetite) on the surface of the oxidized steel while the run number nine displays only the black oxide where it shows that the formation of magnetite is higher on the experiment number nine compared to the other experiments. Therefore, the first eight experiment the unstable oxide is presence and can be observed clearly and the last experiment run shows no visible unstable oxide thus making it a more passive oxide on the surface. Physically observed, the temperature it can be deducted that the formation of oxide varies from each level of temperature mainly as there are higher browning on the first three samples which are oxidized at 400^oC followed by the fourth to sixth sample which is oxidized at 600^oC. Finally, lesser brown colorization on the surface of carbon steel oxidized at 800^oC.

4.2 MICROHARDNESS TEST RESULT FOR DETERMINING THE SIGNIFICANCE OF THE PARAMETER AND LEVEL

Based on the four parameters and three levels the $L_9(3^4)$ orthogonal array experimental design have been created as shown in Table 4.1 to determine the nine combination of experiments that needed to be conducted to obtain the optimum parameters and also the signal to noise ratio to obtain an optimised data for producing a stable magnetite. Before the S/N Ratio is calculated, a micro hardness test is done using Vickers hardness machine to determine the hardness value which is the base of determining the influence of each oxidizing parameter. The hardness value is based on the average of three times of each sample where the hardness test is done three times on the similar sample to obtain a more accurate hardness value as hardness varied on the surface of the oxide due to roughness of the surface and the distribution of oxide formed across the oxidized steel surface.

Table 4.1: Average hardness value for bare steel and oxidized steel for each experiment run

Experiment Run	Hardness No 1	Hardness No 2	Hardness No 3	Average Hardness
Bare Steel	257.50	258.30	254.70	256.83
1	331.7	321.8	320.40	324.65
2	303.90	307.80	301.10	304.26
3	290.50	290.70	293.10	291.43
4	319.50	310.50	308.50	312.77
5	344.50	340.90	359.80	348.40
6	331.30	324.80	329.60	328.57
7	318.94	311.78	312.18	314.33
8	301.00	317.70	337.80	318.83
9	372.90	366.20	351.70	363.60

Based on the micro hardness test, it is observable that the oxidized steel has higher hardness compared to that of bare steel. Besides, the experiment run number nine yields the highest average hardness value among the other experiment runs.

Using equation (5) the S/N ratio of each experiment and the average S/N ratio value can be calculated and is tabulated as shown in Table 4.2.

Table 4.2: Signal-to-noise ratio based on the average hardness value

Experiment Run	Average hardness Value	Signal to Noise Ratio (S/N)
1	324.65	50.228
2	304.26	49.665
3	291.43	49.291
4	312.77	49.905
5	348.40	50.842
6	328.57	50.333
7	314.33	49.947
8	318.83	50.071
9	363.60	51.212
Mean S/N Ratio		50.166

4.3 EFFECT OF HARDNESS ON THE SIGNIFICANCE OF EACH PARAMETER

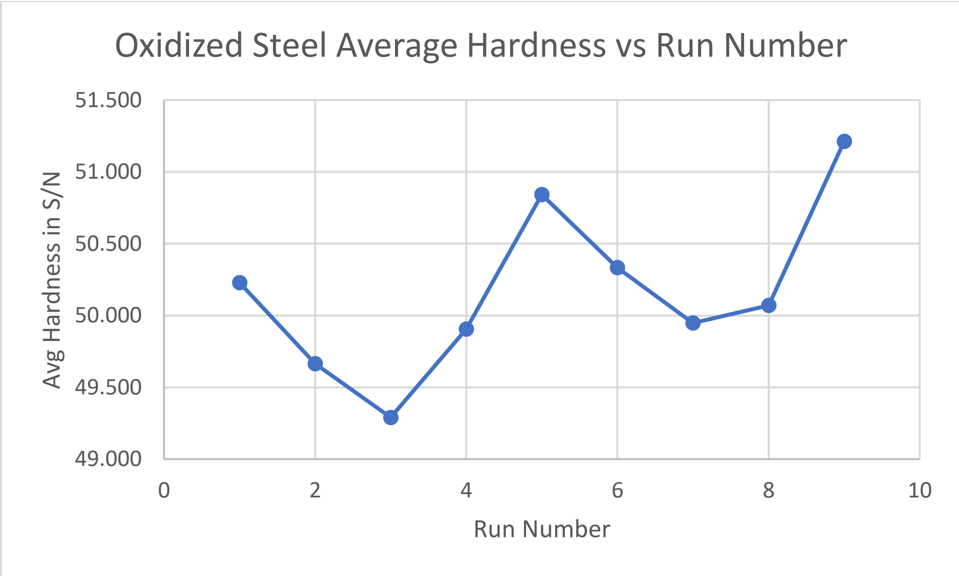


Figure 4.2: Oxidized Steel Average Hardness vs Run Number

On Figure 4.2 shows, the graph of average hardness signal to noise ratio against the number of experiments based on Taguchi's design of experiment. This graph shows the overall effect of all the factors combined to the hardness of the oxidized sample.

Based on equation (6) the optimize process can be determined by selecting the highest S/N ratio of each parameter at a certain level and can be plotted as Figure 4.3 – 4.6.

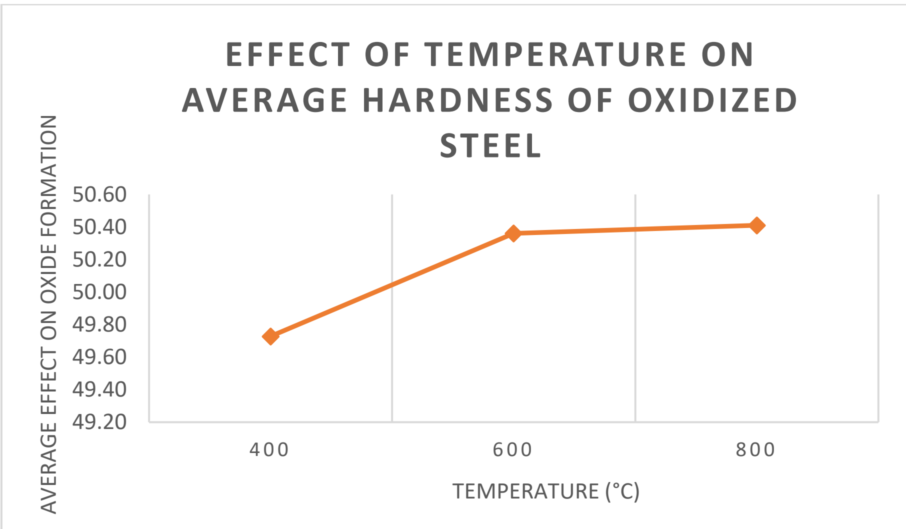


Figure 4.3: Effect of Temperature on Average Hardness of Oxidized Steel

The Figure 4.3 shows the effect of temperature on the formation of iron oxide based on the effect of temperature to the hardness. From the graph it can deducted that the higher the temperature, the higher the average hardness of the sample.

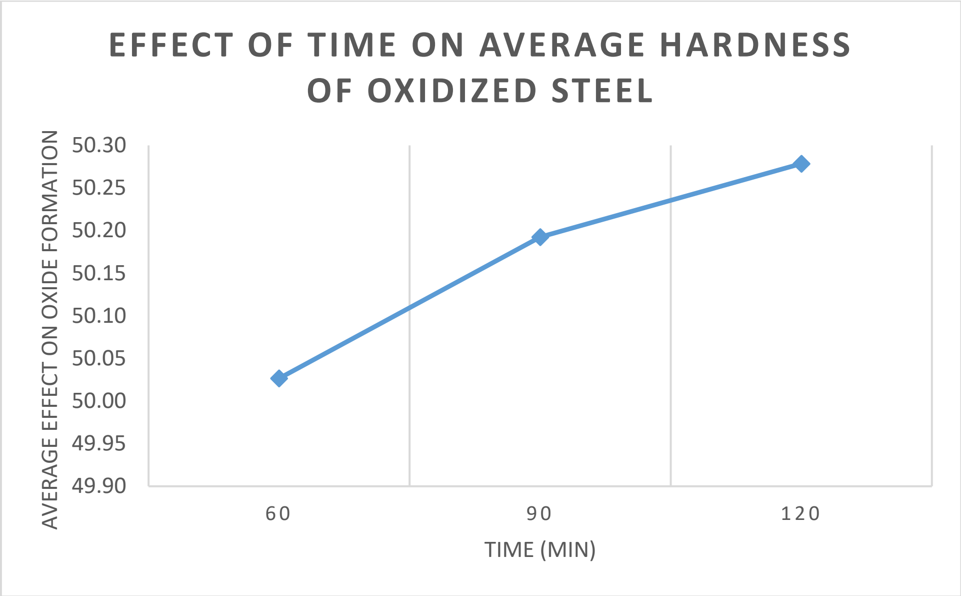


Figure 4.4: Effect of Time on Average Hardness of Oxidized Steel

The Figure 4.4 shows the effect of time on the formation of iron oxide based on the effect of time to the hardness. The graph shows that the increase in time in oxidizing the sample increases the hardness of the sample.

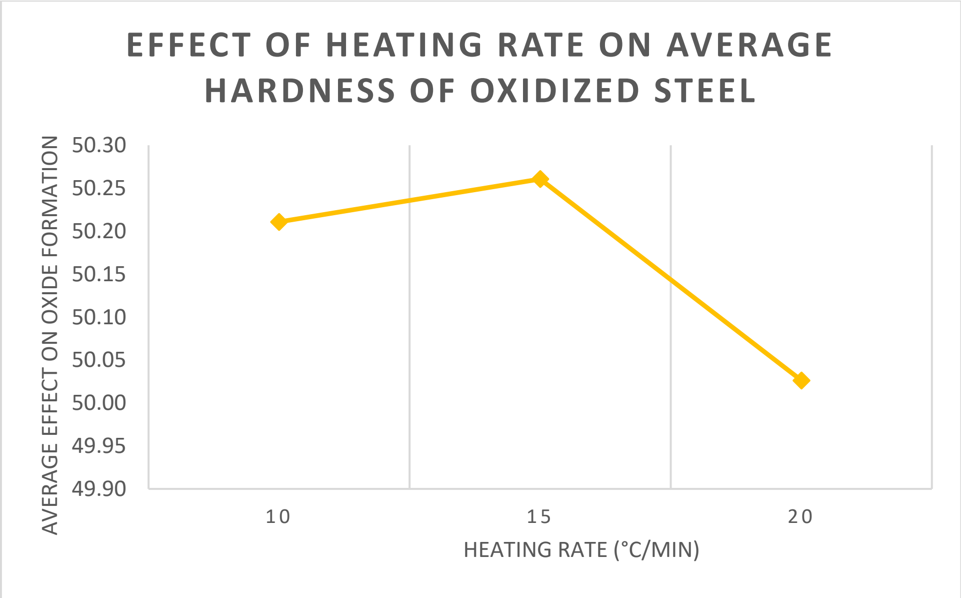


Figure 4.5: Effect of Heating Rate on Average Hardness of Oxidized Steel

The Figure 4.5 shows the effect of heating rate on the formation of iron oxide based on the effect of heating rate to the hardness. From the graph, based on the signal to noise average hardness, it can be deducted that the heating rate does not significantly affect the hardness of the sample. The peak of hardness is when the heating rate is set to 15^{o}C/min and the higher heating rate shows a much more significant drop of hardness than the lower level of the heating rate.

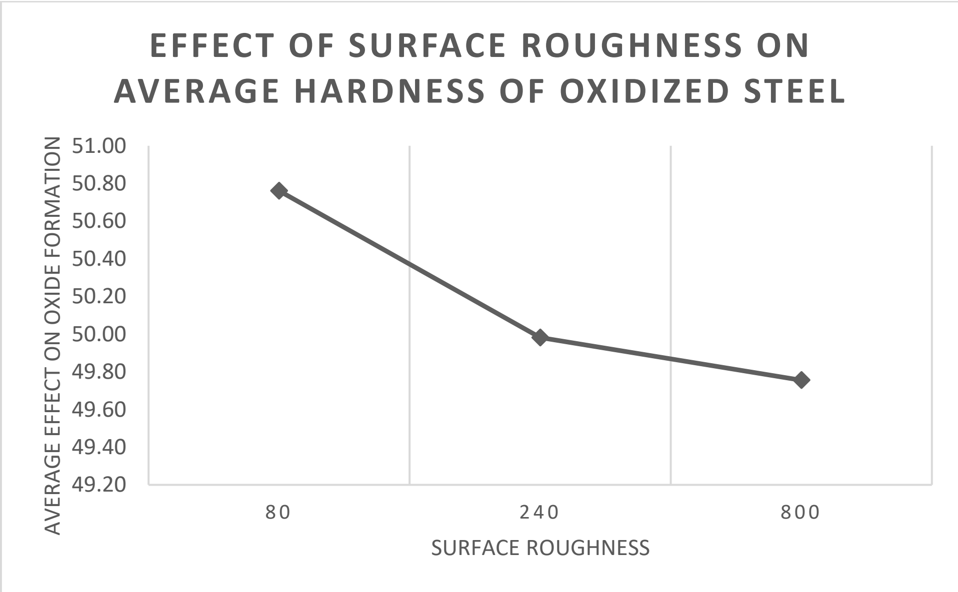


Figure 4.6: Effect of Surface Roughness on Average Hardness of Oxidized Steel

The Figure 4.6 shows the effect of surface roughness on the formation of iron oxide based on the effect of surface roughness to the hardness. Surface roughness effects the hardness inversely from the other parameters such that smoother surface which is the higher grit has lower hardness value.

Based on the analysis of variance (ANOVA), the determination of the percentage of contribution of each parameter in the research can be done using the S/N ratio of each factor such that the combinatorial effect of the average hardness on oxide formation is determined. From the combinatorial effect he overall significance of each parameter can be determined.

Table 4.3: ANOVA study on the contribution of each parameter on the average hardness of the oxidized steel based on equation (7)

Column	Factors	DOF	Sum of Squares	Variance	Percent
1	Temperature	2	0.867	0.433	31.803
2	Time	2	0.098	0.049	3.612
3	**Heating Rate**	**2**	**0.091**	**0.046**	3.351
4	Surface Roughness	2	1.669	0.835	61.234
	All others/Error	0			
	Total	8	2.726		100.000

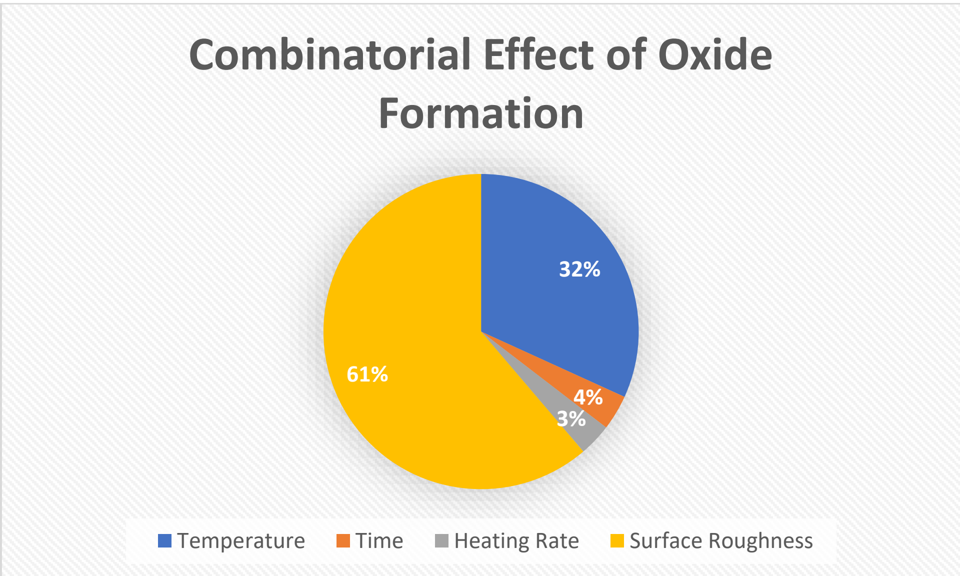


Figure 4.7: Combinatorial Effect of Oxide Formation based on Average Hardness

Based on Figure 4.7, this experiment shows that surface roughness have the highest impact on the average hardness on the sample at with 61% contribution followed by temperature at 32%, time at 4% and finally the heating rate providing the least effect on the hardness value with a contributing percentile of 3%. To determine the significant parameter that have the highest influence in the average hardness value and formation of stable oxide, the parameter with the lowest contribution percentage is pooled which is the heating rate such as in the Table 4.4.

Table 4.4: Results of ANOVA study for the significant parameter (Pooled factor '*')

Column	Factors	DOF	Sum of squares	Variance	F	Percent
1	Temperature	2	0.867	0.433	9.491	28.452
2	Time	2	0.098	0.049	1.078	0.261
3*	Heating Rate	{2}	{0.091}	-	-	-
4	Surface Roughness	2	1.669	0.835	18.275	57.884
	All other/ Pooled Error	2	0.091	0.046		13.403
	Total	8	2.726			100

The main criteria for a parameter to be significant is when the percent or p value is more than 5%. Based on the Table 4.4, the surface roughness yields the highest contribution percentage at 57.88% followed by temperature at 28.45%. Thus, from the study of variance, it can be deducted that from the four parameters that have been analyzed in the research that are temperature, time, heating rate and surface roughness, the surface roughness and the temperature are the significant factor in affecting the average hardness on the oxidized sample along with the formation of stable oxide.

From the results of the signal to noise ratio for each of the parameter, an optimized parameter with its level can be determined from the highest point in each parameter. From this experiment, the optimum parameter based on the signal to noise ratio is as displayed in Table 4.5. The final optimum parameters and level shows the similar case of experiment run number nine.

Table 4.5: Optimum Processing Parameter for Stable Oxide based on Average Hardness

Processing Parameter	Optimum Level	Value
Temperature (^oC)	3	800
Time (min)	3	120
Heating Rate (^oC/min)	2	15
Surface Roughness (Grit)	1	P80

4.5 XRD ANALYSIS ON THE FORMATION OF OXIDE ON CARBON STEEL

The X-Ray Diffraction analytical method was used to obtain and compare the different oxides and the percentage of oxides formed on the carbon steel samples.

From the nine experiments that have been conducted, the XRD analysis was done to verify the formation of iron oxides on the surface of the oxidized steel and determine the sample with highest formation of magnetite.

a)

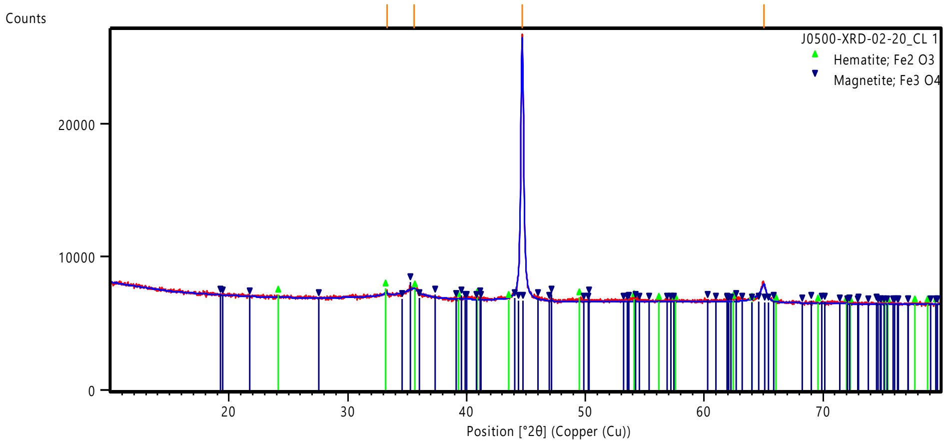


Figure 4.8: XRD result on sample number 1

b)

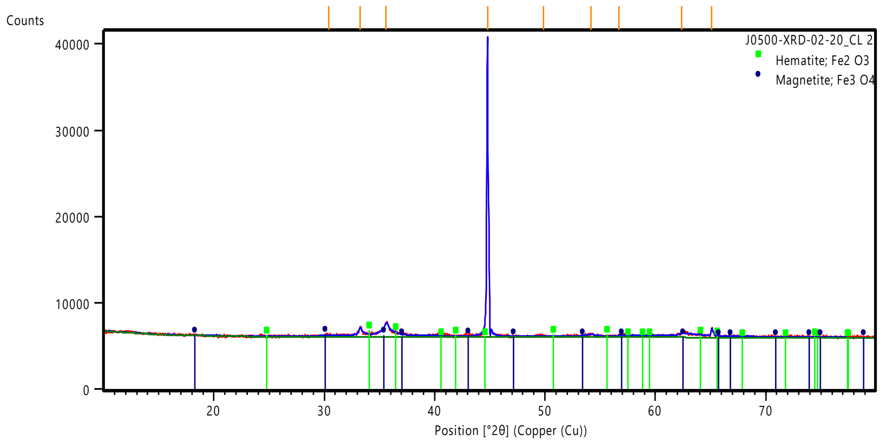


Figure 4.9: XRD result on sample number 2

c)

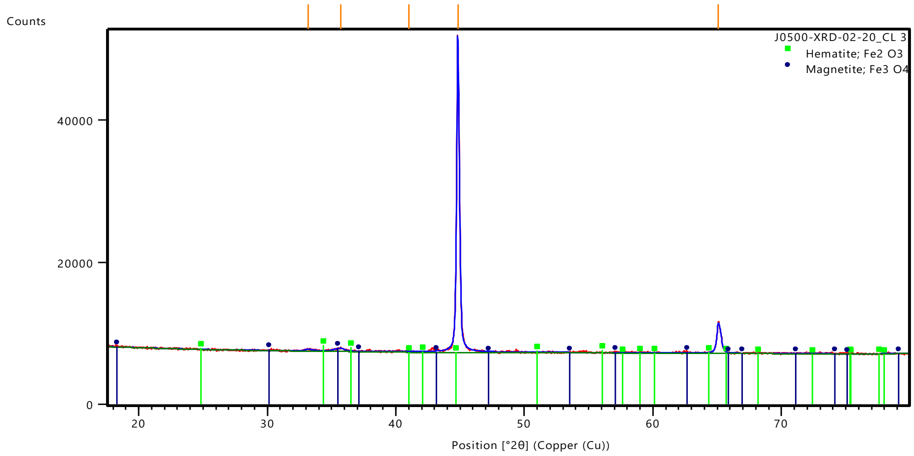


Figure 4.10: XRD result on sample number 3

d)

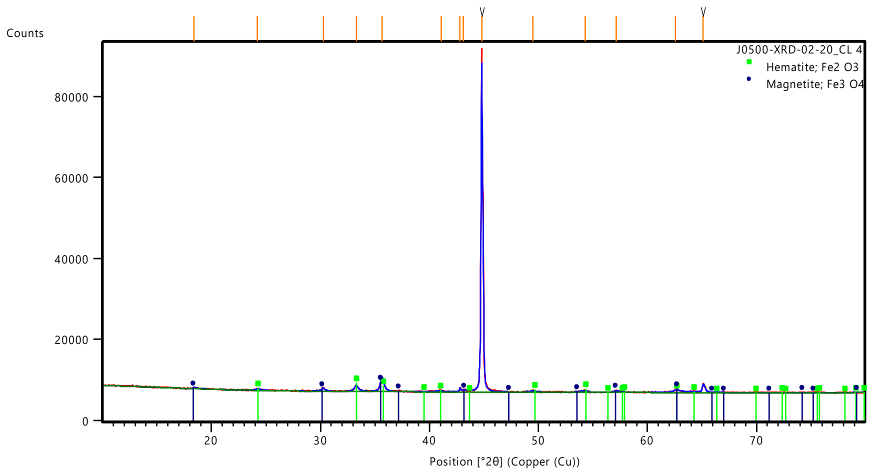


Figure 4.11: XRD result on sample number 4

e)

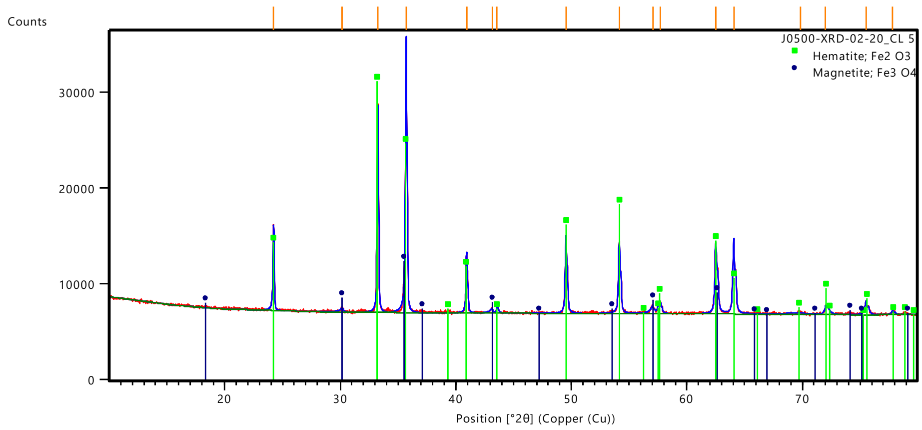


Figure 4.12: XRD result on sample number 5

f)

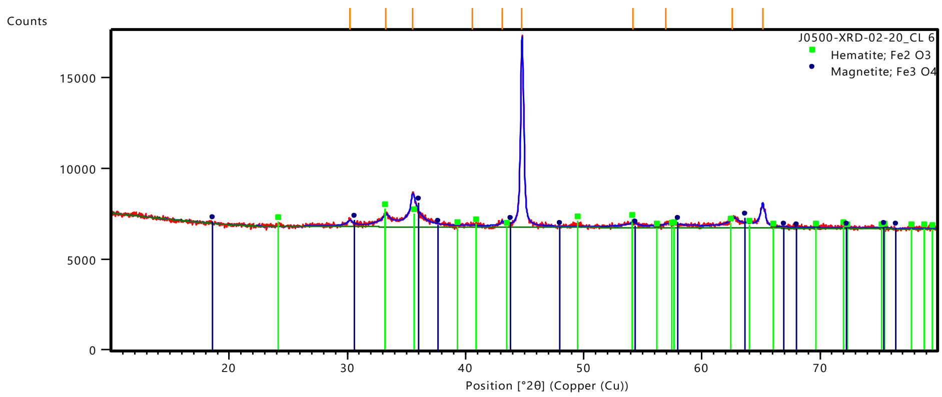


Figure 4.13: XRD result on sample number 6

g)

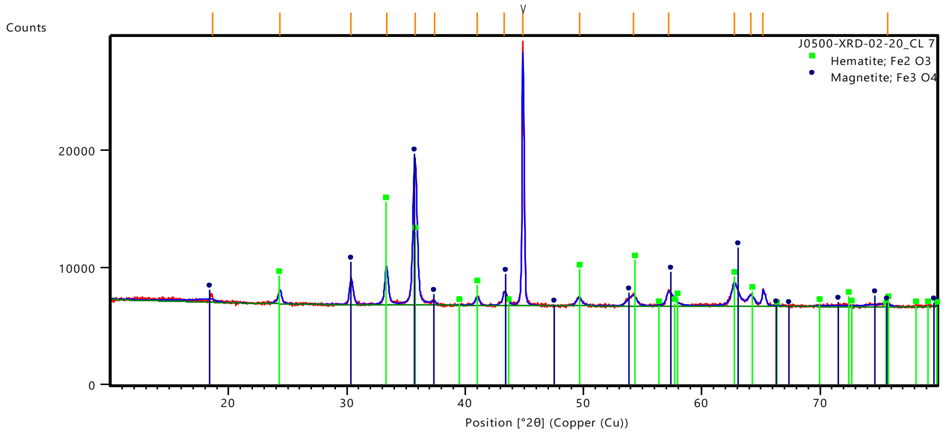


Figure 4.14: XRD result on sample number 7

h)

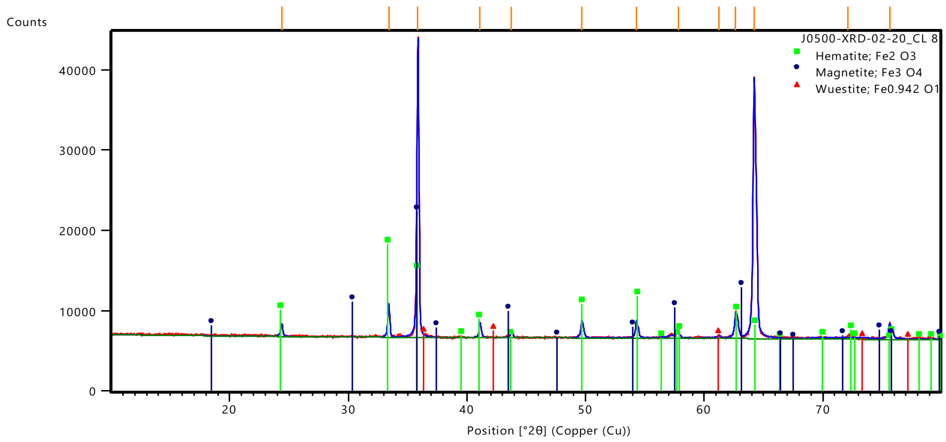


Figure 4.15: XRD result on sample number 8

i)

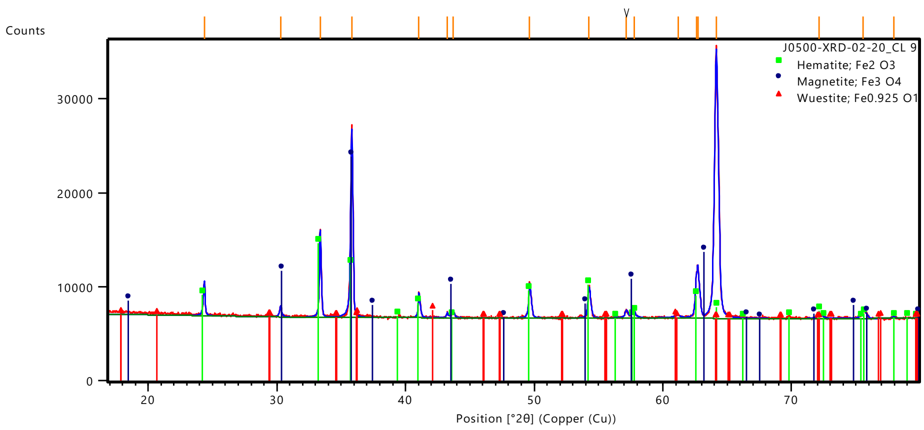


Figure 4.16: XRD result on sample number 9

Based on the XRD analysis for all the nine experiment runs, run number eight and run number nine are the only ones with a content of wustite on the oxidized steel.

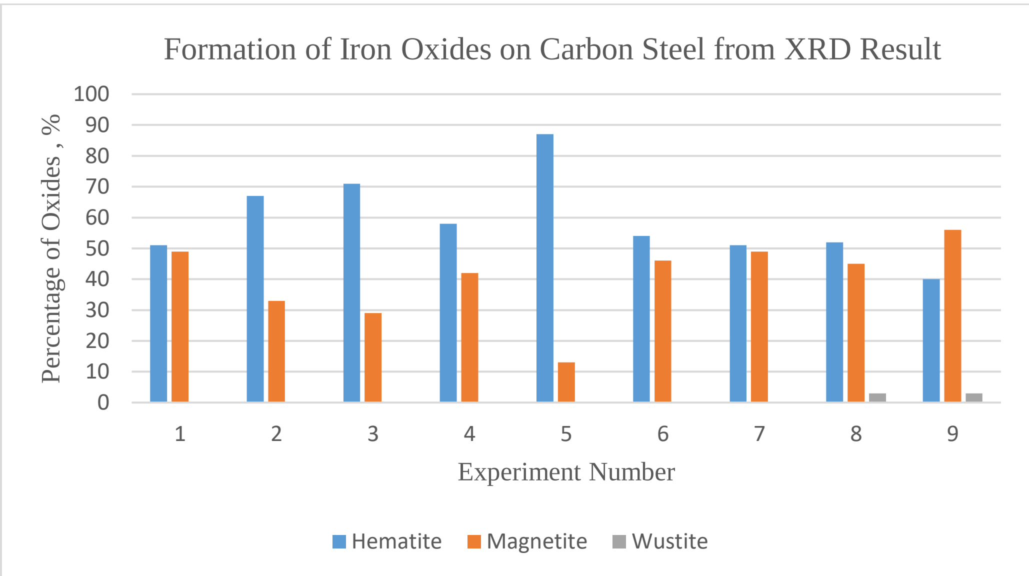


Figure 4.17: Graph for the type and percentage of oxide formed against the experiment

Based on the XRD results obtain on the nine experiments run, it can be confirmed that each run of experiment has iron oxides form on the carbon steel. Based on the formation of iron oxides, all nine experiments have presence of hematite (Fe_2O_3) and magnetite (Fe_3O_4). It is also observed that there are some matching peaks of wustite formation in experiment run number eight and nine. Besides that, from the XRD analysis, the experimental setup number nine have the highest percentage of magnetite formed on the sample which is the stable oxide compared to the other eight which is dominated by the presence of hematite.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This research paper experimentally investigates the influence of oxidizing parameter on the formation of oxide layer on carbon steel as a precursor for carbon fiber steel lamination and determines the effect of each oxidizing parameter which are temperature, time, heating rate and surface roughness on the formation of a stable oxide which is the magnetite. The parameters are studied and an optimised parameter is obtain using the Taguchi's method of design of experiment where each optimise result for each parameter and its level can be determined using the average S/N ratio with analysis of mean (ANOM) and the contribution of each parameter on the formation of magnetite is determined using the analysis of variance (ANOVA). X-Ray diffraction (XRD) technique is used to verify the presence of magnetite on the oxidized carbon steel.

The results in this research proves that the presence of black oxide on the surface of an oxidized steel shows the presence of the magnetite and presence of red or brown oxide represents the formation of hematite. Besides that, from the results, the increase in temperature, time and the roughness of the surface (low grit sandpaper) can form higher percentage of magnetite during oxidation. The combinatorial effect of each parameter on the formation of oxide shows that the surface roughness and temperatures have the highest significance on the formation of magnetite while time and heating rate are quite insignificant as the percentage of contribution is below 10%. The hardness of the oxidized steel influences the formation of oxide as well where the higher hardness shows the more formation of magnetite as shown in the XRD analysis where the highest content of magnetite is from the sample with the highest hardness. Thus, it can be deducted that the hardness of the oxidized steel is directly proportional to the percentage of oxide compound formed based on the four parameters that has been analysed.

5.2 RECOMMENDATION

The stable oxide formed from the parametric study should be further validated by laminating it with carbon fiber reinforced polymer and comparing with the time of lamination of bare carbon steel with carbon fiber reinforced polymer with mechanical test such as the impact test and corrosion test of the bond surface between the carbon fiber and the substrate. Microstruture analysis should be done on the experimental samples to show the interaction of the oxides with the steel substrate.

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