Study on Effects of Surface Roughness Variations on Corrosion Resistance of Metal Components

By

Muhd Amirulnizam Bin Ahmad

Dissertation submitted in partial fulfillment of the requirement for the Bachelor of Engineering (Hons) Mechanical Engineering

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Approved by,

Saravanan Karuppanan)

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CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contain herein have not been taken or done unspecified sources or persons.

(MUHD AMIRULNIZAM BIN AHMAD)

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ABSTRACT

Duplex is the most commonly used stainless steels for offshore applications. It consists of ferritic and austenitic lattice structures which deliver both strength and ductility. It combines the basic toughness of the more common austenitic stainless steels with the higher strength and improved corrosion resistance of ferritic steels.

Duplex has made most significant contribution to fight against corrosion offshore. These have often been adopted on offshore structures in preference to carbon steel or other stainless steels. The outer surface of offshore metal components is widely exposed to the corrosion. Marine environment is the most aggressive environment for corrosion activities to take place. The dominant factors of marine environment are considered by extreme temperatures, humidity, and air contaminants.

The objective of this project is to study correlation between surface roughnesses of metals with its corrosion resistance behavior. The methodology consists of preparation of specimens, surface roughness measurement by using surface profiler, and corrosion testing in the corrosion chamber by applying salt spray test ASTM B 117 standard which is the most practical laboratory corrosion test to accelerate the corrodibility of the metals.

The outcomes of the testing indicate duplex which has best surface finishing is not affected by corrosion activities. Duplex with the surface roughness values less than 1.00μ m have the best corrosion resistance and preferable compared to same metal which have greater values of *Ra*. The lower the value of *Ra*, thus it may sustain failures of corrosion in longer periods.

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CHAPTER 1

INTRODUCTION

Duplex has made a most significant contribution to the fight against corrosion offshore. These have often been adopted on offshore structures in preference to carbon steel or other stainless steels. The greater corrosion resistance, heat resistance, and strength of duplex mean that stainless steel is eminently suitable for rigorous offshore applications - whether for topside construction or for down-hole oil flow applications. The optimum chemical composition of these steels provides a high level of corrosion resistance in chloride media together with high mechanical strength and ductility.

Sea water is highly corrosive and offshore installations are often exposed to temperature extremes. The corrosion resistance of a material is therefore equally as important as mechanical strength. Due to high contents of corrosive chloride in seawater, other than the potentially corrosive effects of hydrogen sulfide and acid conditions associated with the dissolved carbon dioxide which is often present, the steels which form the outer surface of the pipelines have to withstand the potential to be corroded.

1.1 **Problem Statement**

As common offshore metal components, the outer surface of duplex piping system is widely exposed to the risk of corrosion. Several survey data indicate the corrosion activities are taking place on the system. Hence, maintenance have been planned to prevent undesirable failure and deterioration which may cause millions. There are some considerations to be taken into account, not only limited to material selection in the fabrication stage, but also on the technical specifications which optimum design to prolong the physical life and the reliability of the components [1]. The specification we put our interest in this case of study is the surface roughness of the metal components. Corrosion is defined as the degradation of the material by dissolution or oxidation [2]. It is a destructive and unintentional attack of metal whereas chemical or electrochemical reactions with the environment are considered as the main contributors. Nowadays, metallic corrosion is very significant in the industrial world. Every year, millions have been spent to mitigate corrosion and some more lost due to failure caused by corrosion.

In scientific perspective, corrosion is the conversion of an element from zero or lower valence state to a positive or higher valence state, which is called as oxidation [2]. In the refining of metals, most metals occur naturally in their oxidized state, except perhaps for gold and other nobler metals like platinum. Thus, the stable state of a metal is in the oxidized state and corrosion being an oxidation process. Without any protection, most metals will oxidize or corrode, which cause the thickness to decrease and hence, compromise the integrity or reliability of the structures.

Different media can cause different types of corrosion attack that may vary in nature and appearance. The types of corrosion as uniform corrosion, atmospheric corrosion, and pitting are the common forms of corrosion occurs on metallic components and even stainless steels at offshore.

1.1.1 Uniform Corrosion

Uniform corrosion occurs when the passive layer on a stainless steel surface partly or completely breaks down [2]. The corrosion then propagates at a rate determined by a combination of the corrosive environment and the alloy composition. Uniform corrosion or general corrosion occurs on stainless steel in acid environments or hot alkaline solutions. Severe environments from a corrosive point of view are high concentrations of hydrochloric or hydrofluoric acid in which the corrosion may propagate at a rate that can be detrimental to a construction.



Figure 1.1: Common uniform corrosion takes place on the pipelines [2]

Uniform corrosion rate is also affected if the acid contains oxidizing or reducing chemicals. Reducing impurities, for example hydrogen sulfide, may increase the corrosion rate. An oxidizing acid that has a positive effect at lower concentration is nitric acid. It promotes passivation of the stainless steel surface at some concentrations rather than initiating uniform corrosion.

Nevertheless, there is a limitation of how oxidizing the environment may be from a corrosive point of view. A hot concentrated nitric acid can dissolve the passive layer and transpassive corrosion may occur. The mechanism of transpassive corrosion is not similar to uniform corrosion as the passive layer will be oxidized to a more soluble species but the consequence is the same, the passive layer breaks down partly or completely and uniform corrosion occurs. Even though the higher alloyed stainless steel grades are more resistant to uniform corrosion than the lower alloyed stainless steel grades, but the risk of corrosion is still there.

1.1.2 Pitting Corrosion

Pitting is a form of localized corrosion and is characterized by attacks at small discrete spots on the steel surface [2]. Pitting occurs mainly in the presence of neutral or acidic solutions containing chlorides or other halides. Chloride ions facilitate a local breakdown of the passive layer, especially if there are imperfections in the metal surface.



Figure 1.2: Discrete spots which contribute to the pitting corrosion [2]

Initiation sites may be non-metallic inclusions, e.g. sulfides, micro crevices caused by coarse grinding, or deposits formed by slag, suspended solids, etc. When the metal corrodes in the pit, dissolved metal ions generate an environment with low pH and chloride ions migrate into the pit to balance the positive charge of the metal ions.

Thus the environment inside a growing pit gradually becomes more aggressive and re-passivation becomes less likely. As a result, pitting attacks often penetrate at a high rate, thereby causing corrosion failure in a short time. The pits often appear to be rather small at the surface, but may have larger cross-section areas deeper inside the metal. Since the attack is small at the surface and may be covered by corrosion products, a pitting attack often remains undiscovered until it causes perforation and leakage. A higher chromium, molybdenum and nitrogen content in the steel increases the resistance to pitting.

1.1.3 Atmospheric Corrosion

Atmospheric corrosion occurs on a steel surface in a thin wet film created by the humidity in the air in combination with impurities [2]. Corrosive conditions for stainless steel can be the chloride depositions from a marine atmosphere on the steel surface in a humid atmosphere these; conditions may alter the choice of steel grade to a more corrosion resistant alloy.

This type of corrosion is most commonly local in the presence of chlorides, i.e. pitting or crevice corrosion. Molybdenum-alloyed are normally specified for a marine atmosphere, regardless of whether the application is a prestigious building in a coastal city or an offshore platform. However, this material has inadequate resistance if used close to the sea in tropical countries with high levels of humidity and high daytime temperatures.

1.2 Objectives

The objective of this project is to study the correlation between surface roughness variations and resistance behavior of stainless steels duplex.

1.3 Scope of Study

The focus of this project is the correlation between surface roughness and resistance behavior of duplex stainless steels which are commonly used for offshore applications. The mechanical properties of duplex will be accounted in determining its resistance behavior, for instance the density of the duplex. Its density is a variable used together with the weight loss to measure the corrosion rate. The key indicator for this project is to determine the correlation between the effects of surface roughness of duplex against corrosion.

CHAPTER 2

LITERATURE REVIEW

2.1 Stainless Steels

In many situations galvanic protection or painting of a steel surface is impractical. This is where the special oxide film formed on chromium alloyed stainless steels becomes so useful. Many types of stainless steels have been developed to resist different corrosion environments and working conditions. Stainless steels are chromium containing steel alloys [8]. The minimum chromium content of the standardized stainless steels is 10.5%. Chromium makes the steel 'stainless' this means improved corrosion resistance.

The better corrosion resistance is due to a chromium oxide film that is formed on the steel surface. This extremely thin layer, under the right conditions, is also self-repairing. Besides chromium, typical alloying elements are molybdenum, nickel and nitrogen. Nickel is mostly alloyed to improve the formability and ductility of stainless steel. Alloying these elements brings out different crystal structures to enable different properties in machining, forming, welding etc. There are four major types of stainless steels which are Austenitic, Ferritic, Ferritic-Austenitic (Duplex), and Martensitic. Provided that our interest is on duplex, further readings about the other types of stainless steels can be obtained in Appendix A.

2.2 Duplex 2205

Materials selections must be given detailed attention at every stage of the design, construction and operation of systems and equipment for application in offshore oil and gas production [9]. Attention must be given to corrosion resistance susceptibility in sour hydrogen sulfide environments if failures, loss of production and costly maintenance are to be avoided. Even more important than these considerations is the need to maintain offshore safety. Thus the specification and use of materials which

combine corrosion resistance with high mechanical strength is a fundamental requirement. A greater understanding of the offshore environment and more detailed knowledge of the conditions under which offshore structures and systems have to operate will obviously contribute to the selection of the correct materials.

The duplex can be defined as chromium-molybdenum ferritic stainless steels to which sufficient austenite stabilizers have been added to produce steels in which a balance of ferrite and austenite is present at room temperature. Such grades can have the high chromium and molybdenum responsible for the excellent corrosion resistance of ferritic stainless steels as well as the favorable mechanical properties of austenitic stainless steels. In fact, the duplex with about equal amounts of ferrite and austenite have excellent toughness and their strength exceeds either phases of ferrite and austenite itself.

The greater corrosion resistance, heat resistance, and strength of type 2205 duplex, and higher alloyed special grades, mean that stainless steel is eminently suitable for rigorous offshore applications - whether for topside construction or for down-hole oil flow applications. Duplex 2205 are the most widely used duplex stainless steel grade. It finds applications due to both excellent corrosion resistance and high strength.

Typical compositional ranges and mechanical properties for grade 2205 stainless steels are given in Table 2.1 and Table 2.2, respectively.

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Composition	Wt%
Carbon	0.030 (max)
Chromium	22.0 - 23.0
Manganese	2.00 (max)
Molybdenum	3.0 - 3.5
Nitrogen	0.14 - 0.20
Nickel	4.5 - 6.5
Phosphorus	0.030 (max)
Sulfur	0.020 (max)
Silicon	1.000 (max)

 Table 2.1: Composition ranges for duplex 2205 grade stainless steels [8]

 Table 2.2: Mechanical properties for duplex 2205 grade stainless steels [8]

Properties	Value
Density (kg/m³)	7805
Tensile Strength (MPa)	620
Yield Strength 0.2% Proof (MPa)	450
ElasticModulus (GPa)	200
Hardness: Rockwell C (HR C)	31 max
Hardness: Brinell (HB)	293 max
Specific Heat 0-100°C (J/kg.K)	450

2.3 Metallic Corrosion

Corrosion is defined as the degradation of the material by dissolution or oxidation. It is a destructive and unintentional attack of metal whereas chemical or electrochemical reactions with the environment are discovered as its main contributors. In real situation nowadays, metallic corrosion is very significant. Every year, millions have been spent to combat corrosion and some more lost due to failure caused by corrosion.

In scientific perspective, corrosion is the conversion of an element from zero or lower valence state to a positive or higher valence state, which is called as oxidation. In the refining of metals, most metals occur naturally in their oxidized state, except perhaps for gold and other nobler metals like platinum. Thus, the stable state of a metal is in the oxidized state and corrosion being an oxidation process. Without any protection, most metals will oxidize or corrode, which cause the thickness to decrease and hence, compromise the integrity or reliability of the structures.

Metal corrosion is a chemical reaction between a metal surface and its environment [7]. Corrosion can occur in a gaseous (dry) environment or a damp (wet) environment. This type of corrosion attacks the metal by removing the atoms on the metal surface. The metal atoms at the surface lose electrons and become actively charged ions that leave the metal and enter the 'wet' electrolyte. The metal ions join with/to oppositely charged ions from another chemical and form a new, stable compound. During corrosion the reacting components go from a higher to a lower energy state and release the energy needed for the reaction.

In the wet corrosion process, the electrons from the corroding anode metal move to the connected cathode where they recombine with the atoms of oxygen and water in the electrolyte to make a new hydroxyl ion (OH-). This new negatively charged ion then reacts to make a stable compound with the positively charged metal ions (M++) that originally lost the electrons. In this case, the electrons have a continuous pathway to escape the parent metal and the parent metal, which cannot develop a protective barrier, disassociates or falls apart. Once corrosion starts it continues until the ingredients are all used up.

The electrolyte in wet corrosion can be neutral, acidic or alkaline. For corrosion in near neutral solutions (pH 6 – 8) under oxygenated conditions the predominant cathodic reaction is the oxygen absorption reaction (O2 + 2H₂O + 4e- \rightarrow 4OH-). If instead the bi-metallic cell has no oxygen present in the electrolyte the hydrogen evolution reaction (H+ + e- \rightarrow H followed by H + H \rightarrow H₂ gas) becomes the cathodic process and the anode continues to corrode. This reaction is a much slower reaction (the H+ ion has a very low concentration in solution) than the oxygen absorbing reaction. In acidic solutions (pH 0 - 6) the hydrogen ion concentration is higher and the hydrogen evolution reaction is the predominant one. Corrosion rates become extreme as the pH drops as acid gets stronger.

Stainless steels are not natural noble materials in same way as gold or platinum, which are more or less inert to most environments. The corrosion resistance of a stainless steel is dependent on a thin invisible film on the steel surface, the passive film. The passive film consists mainly of a chromium oxide that forms in reaction with oxygen in the air. For spontaneous development, even after a damage of the passive film on the steel surface, the steel has to contain at least 12% chromium.

2.4 Marine Environment

The offshore environment, or will be changed interchangeably with marine environment is generally considered to be the most aggressive environment. For metallic components made of duplex, the maximum corrosion rate occurs in the splash zone, in which the alloy is wet almost continually with well-aerated seawater.

The factors of marine environment are considered by a variety of factors which affect the atmospheric corrosion behavior of materials [3]. These include the time of wetness, temperature, materials, air contaminants, solar radiation, biological species, and the composition of the corrosion products. In our case study, the most significant factors to be focused are the humidity, temperature, and air contaminants.

2.4.1 Humidity

For corrosion to occur by an electrochemical process there must be an electrolyte present. An electrolyte is a solution that will allow a current to pass through it by the diffusion of anions and cations. Water that contains ions is a very good electrolyte, as we can find in seawater which is rich in sodium and potassium ions. Therefore, the amount and availability of moisture present is an important factor in the rate of corrosion in marine atmosphere.

One of the measures of the effects of moisture is the 'time wetness' as corrosion resistance decreases as time of wetness increases. Other than that, it also depends on the hygroscopicity (tendency to absorb moisture) of the corrosion products and the contaminants [3]. In a hot and wet country, the Malaysian offshore is found to have more than 80% in humidity.

2.4.2 Air contaminants

The severity of the marine environment is related to the salt content of the sea spray or dew that contacts the surface of materials. Those contaminants found in the air could be natural or manmade, such as airborne moisture carrying salt from the seawater or carbon dioxide put into the atmosphere by gas-burning on the platform. The important contaminants from the seawater are chlorides, which is more than 5gm per 100ml of seawater [3]. Corrosive chlorides vigorously cause a direct relationship between atmospheric salt content (salinity) and measured corrosion rates.

2.4.3 Temperature

The temperature affects the relative humidity, in the dew point, the time wetness, and the kinetics of the corrosion process. For atmospheric corrosion, the presence of moisture as determined by the time of wetness is probably the most important role of temperature. However, the temperature of interest may not be the average daily temperature. Hence, it is recommended that the extreme temperature (>35°C) is considered.

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2.5 Surface Roughness Variations

Surface roughness has a significant influence on the corrosion resistance behavior of a metal. Surface quality or surface finish affects the sensitivity to corrosion. Roughness is measured by special precision instruments that measure the vertical deviations when traversing the metal surface [5]. **Ra** is the most commonly used parameter to describe the average surface roughness and is defined as an integral of the absolute value of the roughness profile measured over an evaluation length. The range of surface roughness (*Ra*) to be studied is between 0.07 μ m and 3.35 μ m, as the standard *Ra* for piping system is in the tolerable range of 0.5 μ m and 1.0 μ m. The results of surface roughness measurement using surface profiler are attached in Appendix C.

The average roughness is the total area of the peaks and valleys divided by the evaluation length; it is expressed in μ m (micrometer). The total area of the peaks above the mean line should be equal to the total area of the valleys below the mean line. Centre line average and arithmetic average are older designations for average surface roughness.

The intention is on distributed irregularities in the surface layer, which are characteristic of the different means of production and finishing of the steel product. In terms of strict definition, the concept "surface finish" can be said to describe the deviation from the ideal flat surface. This deviation is normally expressed in terms such as roughness, lay and waviness.



Figure 2.1: Y=Roughness, S=Lay, V=Waviness [5]

Roughness represents the size of the finely distributed surface pattern deviations from the smooth surface. Lay represents the dominant direction of the surface pattern, such as grinding scores. Waviness represents deviations, which are relatively far apart. Of these, waviness is the most difficult to detect with the naked eye.

A stainless steel may be corroded during use if it has a rough surface finish that provides a foothold for corrosive substances and corrosion products from the surroundings. Corrosion will also exist when the surface is contaminated by iron particles. In this case study, corrosion is caused due to exposure to a more aggressive environment than that for which that particular grade of steel is intended, e.g. highly polluted air, salt solutions or residuals of cleaning agents. In considering the effects of surface roughness, any sporadic surface defects will be regarded which simply has mechanical or metallurgical causes.

CHAPTER 3

METHODOLOGY

3.1 Preparation of Specimens

Six plates of duplex have been prepared as the specimens. These plates which have different surface roughness are measured by using Surface Profiler (Perthometer Concept) to obtain their Ra values. The range of surface roughness (Ra) to be studied is between 0.07µm and 3.35µm, as the standard Ra for piping system is in the tolerable range of 0.5µm and 1.0µm. Since the surface roughness of the original plates is 3.72µm (average), intensive polishing and grinding are very necessary to attain the desired range of study. The figures of the specimen can be obtained in Appendix B.

The characteristics of specimen to be used are stated in Table 3.1 below;

Specimen no.	Avg. surface roughness, <i>Ra</i> (µm)	Area (cm x cm)	Initial wt.(gm)
1	0.07	2.3 x 2.2	12.8599
2	0.24	2.3 x 2.5	14.4560
3	0.83	2.3 x 2.2	13.6080
4	1.25	2.3 x 2.8	15.7626
5	2.42	2.3 x 2.5	14.7918
6	3.35	2.3 x 2.0	11.4584

 Table 3.1: Initial profiles of duplex 2205

3.2 Measurement of Surface Roughness

The Perthometer Concept Roughness measuring station serves for determining all common surface texture parameters according to DIN EN ISO/ JIS/ ASME [5]. The efficient program package running under Windows controls the measuring station components and the measurements and documents all results according to requirements.



Figure 3.1: Surface Texture Measuring Station [5]

In order to measure surface roughness of the specimens, we are only interesting in some parameters. The normal program package is maintained as default except for a few parameters to be reset. Program package of this Perthometer Concept Roughness can be obtained in Appendix D. The parameters to be reset is as following, based on the requirements on the specimens;

- ✓ Measuring range: $\pm 250 \,\mu\text{m} / 5 \,\text{nm} (\pm 10\,000 \,\mu\text{in} / 0.2 \,\mu\text{in})$
- ✓ Profile type: R
- ✓ Filter types: Profile filter as per DIN EN ISO 11562
- ✓ Tracing length: 5.6 mm (0.224 in)
- ✓ Parameters/ Analysis: Ra

Ra is selected as the most desired parameter on the specimens as it is the most commonly used parameter to describe the average surface roughness. Ra is defined as the arithmetic average of the absolute values of the roughness profile ordinates.

$$Ra = (1/1) \left[[Z (x)] dx [5] \right]$$

3.3 Corrosion Testing

An experiment called salt spray testing is implemented as accelerated test for determining the corrodibility of the specimens. This test which is commonly known as Salt Spray Fog Testing ASTM B 117 is considered to be the most useful as accelerated laboratory corrosion test that similar the effects of marine environment [4]. The significance of the practice is to provide a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and even coatings exposed in the chamber. However, the reproducibility of results in the salt spray exposure is highly dependent on the type of specimens tested and the evaluation criteria selected, as well as the control of operating variables. In any testing program, sufficient replicates should be included to establish the variability of the results.

The apparatus required for salt spray exposure consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control [11].

The salt solution shall be prepared by dissolving 5 ± 1 parts by mass of sodium chloride, NaCl in 95 parts of water. A mixture of sodium chloride solution that can be varied in the range between 3.5% and 20%, do not contain more than 200ppm total solids and with the pH range of 4 to 7 will provide the salt fog. The temperature to be applied in the test is controlled to maintain over 35°C within the exposure zone of the closed cabinet.

Corrosion testing in the corrosion chamber is adapted from the marine environmental aspects. Three main variables; humidity, temperature, and contaminants will be applied in the test throughout the specified time. Corrosion testing able to quantify the corrosion resistance of material and is a common practice to submit material to harsher environment, hoping to accelerate the damage.

The duration of the test can rage from 8 up to 3000 hours, depending on the metals and its characteristics to be studied [4]. For this project, 738 hours (approximately 30 days) have been taken for the testing with credible assurance. The test was started on Tuesday, 9 March 2004 at 3.45 pm at Material Lab, Building 17 and ended on Thursday, 8 April 2004 at 3.45 pm. Corrosion chamber used is shown in Figure 3.3.



Figure 3.3: CCT Cabinet Model SF/450/CCT [6]

These cabinets are now widely used by the paint, chemical, surface coating, aerospace, offshore and defenses industries throughout the world as a method to accelerate the corrodibility of metals [6].

Standard features available on this apparatus are stated as below;

- MICROPROCESSOR/CONTROLLER A high specification unit for control with the capacity to hold up to 20 programs. The controller is easy to operate with rapid program selection complete with manual over-ride facility, bargraph display, program status display and cycles completed counter.
- TEMPERATURE RECORDER Continuous paper type chart recorder with ON/OFF control for individual test records.
- FULL VISUAL DISPLAY All events, cycles and test conditions.
- CABINET HUMIDIFIER Internal heated water bath with automatic level control ensures high Relative Humidity during the relevant periods of the test cycle.
- HEAVY DUTY PERISTALTIC PUMP with VARIABLE SPEED For accurate control of salt solution flow to the atomizer, indispensable for precise collection rates, also eliminates atomizer blockage.

- EXTERNAL SALT SOLUTION RESERVOIR and INTEGRAL FILTER -For easy cleaning and filling.
- INTERNAL HEAT EXCHANGER To pre-heat the salt solution to the required temperature before introduction to the atomizer.
- ACCURATE FLOWMETER Panel mounted, to monitor salt solution flow.
- SOPHISTICATED LUCITE ATOMIZER For baffle free mist generation ensuring precise fall-out readings throughout the chamber.
- AIR REGULATOR/PRESSURE GAUGE To control and monitor the air pressure required for precise salt fog collection rates.
- DRY/MOIST (humid) AIR CONTROLS A simple switch-over device for required setting, depending upon specified Salt Spray Standard procedure. A compact internal air saturation unit fully protected against overheating and low water. Automatic, self-filling system, complete with digital display of water temperature.
- AUTOMATIC AIR PURGE Incorporated into test program.

CCT cabinets enable to be simulated in two types of cycles; Salt Fog & High Humidity Cycles and Dry & Dwell Cycle. To establish a suitable condition for simulations in CCT, there are a few parameters to be set, which are percentage content of salt, humidity, temperature, and pressure. Content of salt functions to produce a nature-like salt fog and is desired to be identical to the content of chloride in seawater. To obtain an accurate result, natural seawater which has the exact content of chloride is preferable.

3.4 Corrosion Rate Expression

This corrosion rate expression is readily calculated from the weight loss of the specimen during the corrosion test by using the formula given as below;

Corrosion rate (in μ m/year) = $\frac{87.6 \text{ W}}{\text{DAT}}$

where; W = weight lost in grams D = density of the duplex (7.805grams/cm³) A = area in cm² T = time exposure in hours (738 hours)

The corrosion rate is expressed by mil per year as the most desirable way of expression of corrosion rates [12]. The conversion of one unit mpy into the SI unit is shown as below;

 $1.00 \text{ mpy} = 0.00254 \text{ cm/year} = 25.40 \mu\text{m/year} = 2.90 \text{nm/hour}$

The corrosion rate of all specimens will be recorded and scientifically compared. It is predictable to state that the coarser of the surface, so that the higher the value of Ra, the lower of its corrosion resistance behavior and the higher risk of the duplex to be corroded [7]. The validity of this prediction is not only applicable to duplex but also to most metals. Smooth surfaces, as well as freedom from surface imperfections, blemishes, and traces of scale and the foreign material, reduce the probability of corrosion. In general, a smooth, highly polished, and reflective surface, as well as having the lower value of Ra, will have greater resistance to corrosion.

CHAPTER 4

DISCUSSION

4.1 Results

Salt spray test ASTM B 117 has been used for over years as accelerated tests for determining the corrodibility of nonferrous and ferrous metals as well as the materials specifications. This procedure has been extensively discussed since its inception of the producibility relation of results related to the actual performance.

In corrosion testing, there some assumptions have been established to improve the understanding of data credibility. Provided that the corrosion testing is adapting the marine environment, there is no constantly exact temperature, humidity, and salt contents in air recorded except some average values which is practically adaptable. It is important to assume that the adapted environment in the chamber is uniformly identical to marine environment. The ambient temperature applied in the chamber is 35°C with 8% sodium chloride in salt fog spray.

Corrosion testing on the specimens has successfully been done for 738 hours which is approximately equal to 30 days. After the testing was over, the specimens were gently washed in clean running water at room temperature to remove salt deposits on its surface. Then it was immediately dried and weighed to get the final weight. The results of the testing are stated in Table 4.1.

Specimen no.	Initial wt.(gm)	Final wt. (gm)	Wt. gain (gm)
1	12.8599	12.8599	0.0000
2	14.4560	14.4560	0.0000
3	13.6080	13.6080	0.0000
4	15.7626	15.7627	0.0001
5	14.7918	14.7920	0.0002
6	11.4584	11.4586	0.0002

 Table 4.1: Findings for duplex 2205 after corrosion testing

Amount of weight loss is very significant in determining the corrosion rate of metal. Based on the testing, the amount of weight loss is equal the amount of weight gain. Assumption states that the amount of weight gain is due to formation of oxide. The amount of weight loss of metal then is assumed as metal which has been oxidized.

Weight gain	. =	Oxide formed
	=	Weight of metal oxidized
	=	Weight loss

The sample calculation for Specimen 6 duplex to calculate weight loss, % of oxidation, and corrosion rate are given as below;

Weight gain	_	Final weight -	Initial weight
		11.4586gm -	11.4584gm
	=	0.0002gm	
	-	Oxide formed	
	=	Weight of metal oxid	lized
	=	Weight loss	

% of oxidation= (Weight loss/ Initial weight) x 100 = (0.0002gm/ 11.4584gm) x 100 = 0.0017%

Corrosion rate (in μ m/year) = $\frac{87.6 \text{ W}}{\text{DAT}}$

Where; W = weight lost in gram D = density of the duplex (7.805gm/cm³) A = area in cm² T = time exposure in hours (738 hours)

Corrosion rate (in µm/year)	=	<u>87.6 (0.0002gm)</u> (7.805gm/cm ³)(4.6cm ²)(738 hours)
	=	6.6122 x 10E-7cm/hour
		5.7923 x 10E-3cm/year
	=	2.28mil/year

The results of calculation for all specimens are depicted in Table 4.2;

Specimen no.	Weight of metal oxidized/ Weight loss (gm)	% of oxidation	Corrosion rate (mpy)
1	0.0000	0.0000 %	0.000
2	0.0000	0.0000 %	0.000
3	0.0000	0.0000 %	0.000
4	0.0001	0.0006 %	0.815
5	0.0002	0.0014 %	1.824
6	0.0002	0.0017 %	2.280

Table 4.2: Findings for duplex 2205 after calculation of corrosion rate

The corrosion rate results are exactly identical to the predicted results in the hypothesis which says that the rougher a surface is, the higher corrosion rate will be. It is proven by the corrosion testing undergone by duplex 2205. Specimens which have greater value of Ra results the higher corrosion rate. However, results showed that the period of 738 hours was insufficient to run corrosion testing for duplex 2205. It was proven by three lowest values of Ra, out of six specimens which are not affected of corrosion.

It obviously caused by the excellent physical properties of the metals which put duplex in its own class as metal of strength and toughness. Corrosion testing in the chamber for 738 hours, with 8% sodium chloride as salt fog spray and temperature $35 \,^{\circ}$ C did not have any effect on duplex. The top three of the specimens are not corroded at all, even the remaining three are also least affected by corrosion. The weight loss for each specimen obtained from the testing shown in Table 4.1 and 4.2 was extremely in small amount.

4.2 Analysis

However, the amount of weight loss of duplex is insufficient to establish data credibility. The results of corrosion testing on duplex 2205 which produced small amount of weight loss or no corrosion at all, led to a pilot test to add credibility of the hypothesis. This pilot test used mild steel to replace duplex as the specimens. It consists of the same procedure, apparatus, and assumptions but in shorter period (46 hours) as have been used in previous testing. The initial and final data of the pilot test are shown in Table 4.3 and 4.4 respectively.

Specimen no.	Avg. surface roughness, <i>Ra</i> (µm)	Area (cm x cm)	Initial wt.(gm)
1	0.36	2.5 x 2.5	24.4470
2	0.72	2.5 x 2.5	24.0539
3	1.44	2.5 x 2.5	24.3417
4	2.03	2.5 x 2.5	24.3056
5	2.55	2.5 x 2.5	24.3018

 Table 4.3: Initial profiles of mild steel

The sample calculation for Specimen 1 of mild steel to calculate corrosion rate is given as below;

Corrosion rate (in µm/	$\frac{87.6 \text{ W}}{\text{DAT}}$
where;	W = weight lost in gram
	D = density of the mild steel (7.874gm/cm3)
	$A = \text{area in } \text{cm}^2 (6.25 \text{cm}^2)$
	T = time exposure in hours (46 hours)
Corrosion rate (in µm/	$(year) = \frac{87.6 (0.0306 gm)}{(7.874 gm/cm^3)(6.25 cm^2)(46 hor)}$

		(7.874gm/cm ³)(6.25cm ²)(46 hours)
	=	1.1841 x 10E-3cm/hour
		10.3728 cm/year
·	==	4.0838 x 10 ³ mil/year

Specimen no.	Final wt. (gm)	Wt. loss (gm)	% of oxidation	Corrosion rate (mpy)
1	24.4776	0.0306	0.1252	4.0838 x 10 ³
2	24.0870	0.0331	0.1376	4.4174 x 10 ³
3	24.3822	0.0405	0.1664	5.4050 x 10 ³
4	24.3488	0.0432	0.1778	5.7653 x 10 ³
5	24.3557	0.0539	0.2218	7.1933 x 10 ³

Table 4.4: Findings for mild steel after corrosion testing

From the results, mild steels yield greater amount of weight loss compared to duplex. The important point to be discussed here is the pattern of relationship between Ra value and the weight loss which is identical for both types of metal which have very contrast properties. This pattern is shown in Figure 4.1 and Figure 4.2, whereas the values displayed on the graphs are Ra values.



Figure 4.1: Surface Roughness Variations vs Weight Loss for Duplex 2205



Figure 4.2: Surface Roughness Variations vs Weight Loss for Mild Steel

There are a few scientific explanations to verify the results for corrosion testing on both types of specimens. Firstly, the surface area between surfaces of different values of Ra is comparatively different. In relative, the rougher a surface provides the larger its surface area. It is due to the presence of cripples and folds on its surface. Imagine surface as a piece of cloth, the cripples and folds are going to be flattened and obviously it will have larger surface area over same length of other surface [7]. The larger the surface area of a specimen, the higher its tendency to exposed to particles or contaminants which may cause corrosion. In practical, those specimens which have higher value of Ra hence rougher surface, the greater its surface to expose to corrosive chloride. When the chlorides drop onto its surfaces, there was larger probability for corrosion reactions to take place.

Secondly, the physical appearance of the rough surface itself contributes the ability to adhere and thus trap contaminants which may cause corrosion [7]. It contrasts to smooth surfaces which have higher ability to avoid adherence of contaminants and thus reduce the risk of corrosion activities to take place. In practice, a rough surface would trap the corrosive chlorides on its surface and allow the solution to react with the metal in corrosion reactions.

Thirdly, the presence of occluded cells on the surface contributes to the formation of corrosion cells [7]. Occluded cells can be formed from the original geometry or from a pit or crack on a surface. In these occluded cells, corrosion reactions are allowed to take place, thus stimulating attack at the latter. In any occluded cells, the pH will be significantly lower than that of the bulk solution and the chloride ion concentration will be significantly higher. The effect of occluded cells is its ability to make a passive metal in normal condition, becomes likely in active region.

4.3 Quality Assurance

There are some aspects throughout this project may not meet the criteria of perfection and thus providing space for improvement. The aspects consist of stages of preparation of specimens and the setup of the corrosion testing. At the stages of preparation of specimens, machined-grinding technique is more preferred to obtain a uniform surface of metal, which have higher persistency and lower variances. Manual-grinding technique is more conservative which produces lower persistency and higher variances of Ra values as well as very laborious. Technique of machined-grinding is much saving time and producing far better products.

In order to focus on single surface for corrosion exposure, any other surfaces must be coated. The technique of coating also is very important to ensure that there is no surface exposed to corrosive agents. Entire incorporated sides and edges have to be covered by coating and the coat must be good enough to prevent corrosion. For common type of coatings, paints are being used and sometimes failed when the corrosion activities are aggressively taking place. In practice, paints used for duplex are good enough to prevent the corrosive chloride to reach the surface of the metals. Meanwhile for mild steel, paints failed due to high-proneness of mild steel to corrode. For ideal purpose, high solid epoxy and aliphatic polyurethane are recommended coatings for maximum protection of the metals.

As has been stated, the duration of the testing can range between from 8 to 3000 hours, depending on the materials to be used. Generally, specimen has lower corrosion resistance behaviors may need shorter duration compared to specimen which has good corrosion resistance. Corrosion testing indicated that the period of 738 hours was insufficient to allow corrosion to occur on duplex. The excellence mechanical properties and integrities, as well as corrosion resistance behavior caused duplex needs much longer period when it is planned to undergo corrosion testing.

CHAPTER 5

CONCLUSION

Oil and gas industries standardize the recognized critical corrosion rate for metals at 2 mpy. In practice, industrial practitioners will never allow the rate even to reach more than half of the value, not only to their critical equipment but also to likely-failure equipment. The reliability of equipment is always in the assurance by maintaining its integrity and applying the safety factor into accounts. Disaster that might be caused by the failure and break-down equipment must be prevented.

According to this study on duplex 2205 as one of the most applicable metals for offshore components, we know that this type of stainless steel is very reliable to be applied in such rigorous environment. Based on the results of the corrosion testing, duplex which has Ra value below 1.00µm is not affected by corrosion activities throughout the testing. We conclude, duplex with the surface roughness values ($Ra < 1.00\mu$ m) have the best corrosion resistance and more preferable compared to same metal which have greater values of Ra. By applying interpolation, surface roughness of 1.00 µm is estimated capable to cater with the corrosion up to approximately ten years. The lower the value of Ra, thus it may sustain failures in longer periods.

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APPENDICES

APPENDIX A: Types of Stainless Steels

Austenitic

Austenitic is the most widely used type of stainless steel. It has a nickel content of at least of 7%, which makes the steel structure fully austenitic and gives it ductility, a large scale of service temperature, non-magnetic properties and good weldability. The range of applications of austenitic stainless steel includes housewares, containers, industrial piping and vessels, architectural facades and constructional structures.

This type of stainless steel is dominant in the market. The group includes the very common AISI 304 and AISI 316 steels, but also the higher-alloy AISI 310S and ASTM N08904.



Microstructure of austenitic stainless steel, type ASTM 304L.

Austenitic steels are characterized by their high content of austenite-formers, especially nickel. They are also alloyed with chromium, molybdenum and sometimes with copper, titanium, niobium and nitrogen. Alloying with nitrogen raises the yield strength of the steels. Austenitic stainless steels have a very wide range of applications, e.g. in the chemical industry and the food processing industry.

The molybdenum-free steels also have very good high-temperature properties and are therefore used in furnaces and heat exchangers. Their good impact strength at low temperatures is often exploited in apparatus such as vessels for cryogenic liquids. Austenitic steels cannot be hardened by heat treatment. They are normally supplied in the quench-annealed state, which means that they are soft and highly formable. Cold working increases their hardness and strength. Certain steel grades are therefore supplied in the cold stretched or hard rolled condition.

Ferritic

Ferritic stainless steel has properties similar to mild steel but with the better corrosion resistance. The most common of these steels are 12% and 17% chromium containing steels, with 12% used mostly in structural applications and 17% in housewares, boilers, washing machines and indoor architecture. These steels are, in principle, ferritic at all temperatures. This is achieved by a low content of austenite forming elements, mainly nickel, and a high content of ferrite forming elements, mainly chromium.

The older types, such as AISI 430, were mainly used for household utensils and other purposes where corrosion conditions are not particularly demanding. Steels with high chromium content, such as AISI 446 with 27% chromium, are used at high temperatures where their resistance to sulphurous flue gages is an advantage. However, the risk of 475 °C embrittlement and precipitation of brittle sigma phase in high-chromium steels must always be taken into consideration.

Today's ferritic steels, such as S44400 with extremely low carbon and nitrogen contents, find greatest use where there is a risk of stress-corrosion cracking. Ferritic steels have slightly higher yield strength (Rp 0.2) than austenitic steels, but they have less elongation at fracture. Another characteristic that distinguishes ferritic steel from austenitic material is that ferritic steels have much lower strain hardening.

Martensitic

Martensitic stainless steel contains mostly 11 to 13% chromium and is both strong and hard with moderate corrosion resistance. This steel is mostly used in turbine blades and in

knives. Martensitic steels have the highest strength but also the lowest corrosion resistance of the stainless steels.



Microstructure image of martensitic stainless steel

Martensitic steels with high carbon contents are used for tool steels. Due to their high strength in combination with some corrosion resistance, martensitic steels are suitable for applications where the material is subjected to both corrosion and wear. An example is in aydroelectric turbines.

APPENDIX B: Figures of Duplex Specimens



Specimen 1 (Surface roughness: 0.07µm)



Specimen 2 (Surface roughness: 0.24µm)



Specimen 3 (Surface roughness: 0.83µm)



Specimen 4 (Surface roughness: 1.25µm)



Specimen 5 (Surface roughness: 2.42µm)



Specimen 6 (Surface roughness: 3.35µm)

APPENDIX C: Results of Surface Roughness Measurement



Specimen 1



Specimen 2



Specimen 3



Specimen 4







Specimen 6

APPENDIX D: Program package of Perthometer Concept Roughness

iple of measurements	Stylus method		
ups	Type R, MFW, FRW (plug-in type), laser pick-ups Focodyn, LS 1		
	LS 10		
; units	PGK, PGK 120, PZK directly connectable; PRK via PAV 62		
	adaptable		
uring ranges/ resolution	$\pm 25 \ \mu\text{m}/ \ 0.5 \ \text{nm} \ (\pm 1000 \ \mu\text{in}/ \ 0.02 \ \mu\text{in}), \pm 250 \ \mu\text{m}/ \ 5 \ \text{nm} \ (\pm 10 \ 000 \ \mu\text{m})$		
	μ in/ 0.2 μ in), \pm 2 500 μ m/ 50 nm (\pm 100 000 μ in/ 2 μ in), with 102		
	538 steps/ vertical range, depending on the standard tracing length		
le types	D, P, W, R (profile inversion possible), ARC function		
types	Profile filter as per DIN EN ISO 11562 (digital, phase-corrected),		
	RC-filter (digital), special filter as per EN ISO 13565, and edge		
	filter		
offs	0.08/ 0.25/ 0.8/ 2.5/ 8 mm (0.003/ 0.010/ 0.032/ 0.100/ 0.320 in)		
ng lengths	0.56/ 1.75/ 5.6/ 17.5/ 56 mm (0.022/ 0.070/ 0.224/ 0.700/ 2.240 in)		
ation lengths	0.4/ 1.25/ 4.0/ 12.5/ 40 mm(0.016/ 0.050/ 0.16/ 0.50/ 1.60 in)		
ber of sampling lengths	1 to 5, selectable		
al tracing lengths	0.24 to 120 mm (0.0096 to 4.8 in). adjustable		
neters/ analysis	Ra, Rz, Rz max, Rmax, Rp, Rp max, Rt, Rq, R3z, R3z max, R Mr,		
	R Mr%, R Sm, R S, R Pc, R HSC, Rsk, Rku, Mr1, Mr2; A1, A2,		
	Rv, Rv max, Rdq; Vo, Pt, Pa, P Sm, P S, P Pc, P HSC, P Mr, P		
	M% Psk, Pku, Pdq, Wt, Wa, W Sm, W S, Wsq, Incl as per EN		
	ISO 13565: Rk, Rvk; Rpk, Rpkx, Rvkx as per EN ISO 12085: R,		
	AR, W, AW, Rx, Wx, Wte, Nr, Ncrx, Nw, CMP, Sr, Sar; Sw, Saw		
	Rz-L, Rp-L, Mr-L, R M%-L, R3z-L, Rv-L, P Mr-L, P M%-L		
cteristic curves	Material ratio curve (Abbott-Firestone), amplitude density curve		

Courtesy of MAHR® Catalog of Dimensional Metrology, Carl Mahr, Esslingen,