SURFACE MODIFICATION OF ALUMINIUM ALLOY 5052 AND ITS CORROSION CHARACTERIZATION

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RESEARCH REPORT SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF MATERIALS ENGINEERING

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ABSTRACT

Aluminum (Al) casting alloys are important materials for the fabrication of engine components such as engine block, pistons and cylinder head. In the present study, a self-organized nanostructured Al_2O_3 layer on AA5052 H32 series was fabricated and followed by heat treated at 450 °C for 1.5 h. The microstructural features and corrosion characterization was the interest part to study. In addition, mechanical and corrosion behavior of Al_2O_3 nanoporous after anodizing and heat treatment were investigated. From the microstructural point of view, the average length and diameter of the optimized nanoporous arrays ranged from 0.5 μm and 20 nm. Scratch test conducted to nanoporous layer and reveal that scratch hardness of heat treated AA5052 is 15.32 MN/m², higher than anodized sample 9.68 MN/m². Besides, anodization increase the hardness of AA 5052 from 50.5 HV to 85.3HV. Then, it being enhanced by heat treatment process and reduce to 60.7. Besides, the heat treated nanoporous layer show the hydrophilic properties where water contact angle value is only 13.7°. The results of corrosion tests in artificial sea water (ASW) showed that the corrosion rate values significantly decreased from after anodization and subsequent heat treatment compared to the substrate. Specifically, anodized sample corrosion protection improved 40.08% and while heat treated sample improved 88.17% from AA 5052 bare substrate.

ABSTRAK

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Aluminium adalah unsur bahan yang penting untuk pembuatan komponen enjin seoerti enjin blok, piston and kepala silinder. Dalam kajian terkini, nano pori Al_2O_3 layer boleh terhasil dengan sendirinya melalui proses anodisasi di atas permukaan AA5053. Oleh yang demikin, ia menarik minat untuk mengkaji ciri-ciri struktur mikro serta kebolehbasahannya. Selain itu, ciri-ciri mekanikal serta karatan selepas anodisasi serta rawatan haba turut dikaji. Dari kaca mata struktur mikro, purata panjang dan diameter nano-pori adalah antara julat 0.5 μm kepada 20 nm. Ujian cakaran yang dilaksanakan membuktikan sample teranodisasi mempunyai 9.68 MN/m^2 berbanding 15.32 MN/m^2 untuk sampel terawatt haba. Proses anodisasi jugak meningkat lagi kekerasan AA 5052 daripada 50.5HV kepada 85.3 HV. Selepas itu, proses rawatan haba membantu mengawal kekerasan dan mengurangkan kepada 60.7HV. Disamping itu, rawatan haba juga membuktikan mampu meningkatkan kebolehbasahan. Hasil ujian karatan didalam air laut articial mendapati kadar karatan berkurang selepasa proses anodisasi dan rawatan haba. Perlindungan karatan meningkat sebanyak 40.08% untuk sample teranodisasi dan peningkatan sebanyak 88.17% untuk sample terawat haba berbanding dengan sample asli AA5052.

ACKNOWLEDGEMENTS

First of all, I would like to express gratitude to my parent for their pray and encouragement along my two years study as Post Graduate student in University of Malaya. I would like to thank to Dr. Nazatul Liana Sukiman for her support along conducting the research project. On top of that, I also would like to express deep appreciation to Dr. Masoud Sarraf for his sincere support and never exasperate to keep repeat explaining on fundamental concept and idea of the project. Without support from these expert it almost impossible for me to produce this report and complete my master degree in Materials Engineering. Last but not least, support from collogue especially Shalini and Faculty of Engineering Dean Office also assist so much in this project completion.

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LIST OF SYMBOLS AND ABBREVIATIONS

AA	:	Aluminium Alloy
Al_2O_3	:	Aluminium Oxide
ASTM	:	American Standard Testing Materials
CVD	:	Chemical Vapour Deposition
EDS	:	Energy Dispersive Spectrscopy
FESEM	:	Field Emission Scanning Electron Microscopy
FML		Fiber Metal Laminate
H_2SO_4		Sulphuric Acid
HNO_3	:	Nitric Acid
Mg	:	Magnesium
NAB	:	Nickel-Aluminium-Bronze
NaOH	:	Sodium Hydroxide
PVD	:	Physical Vapour Deposition
SCE	:	Saturated Calomel Electrode
XRD	:	X-ray Diffractometry

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CHAPTER 1: INTRODUCTION

1.1 Background of Study

Aluminium had been used for various engineering applications since 1980s when the considerable of weight saving in vehicle and improvement in fuel economy becoming the priority for car manufacturer. Due to that, a number of improvement had been conducted to aluminium such as alloying to certain element in order to improve resistance to heat, wear and corrosion. One of the alloying elements are aluminium 5052. Magnesium is added to aluminium to enhance their strength. It was achieved through solid hardening process (Huang, Li, Xiao, Huang, & Ren, 2016).

Study on inserting element to aluminium lead to various innovation on producing and synthesis of metal matrix composites. Usually, common element that use for aluminium reinforcement are alumina, graphite and carbide. As time pass, magnesium becoming interest element to be add especially for application of aerospace, automobile and marine(Shanavas & J. Edwin, 2018). Magnesium is employed to tackle corrosion attack issue which commonly occur at region of high iron concentration. Pitting which usually occur at this area was overcome by Mg_2Si intermetallic supersaturated solution which demonstrate the anodic behaviour. Main surface of aluminium alloy is preserve due to partial dissolution. In other word, the Mg_2Si assist in selective leaching and preserved the life time of aluminium alloy.

Due to that, manufacturing method should be altered to reduce defect during machining and casting especially residual stress, hot cracking and lamellar tearing defects. Since demand for performance in transportation is quite extensive, aluminium must endure to critical condition of aeronautic or automotive application. Aluminium need to be pretreated by conversion coating and anodizing (Mui, SIlva, Prysiazhnyi, & Kostov, 2017). Main concern during pretreated is poorly distributed coated layer and homogenous issue(Joel & M. Anthony, 2018). Besides, joining method of AA 5052 should evaluated to avoid welding defect. Welding parameter such tools transverse speed, rotational speed, voltage supply, welding angle and other need to be review in order to ensure maximum strength and joint efficiency of aluminium alloy especially series five could be maximized.

1.2 Problem Statement

It had been reported that 20% of the material degradation in engineering parts occurs due to corrosion related issues. The corrosion characteristics of cast aluminum alloys have been extensively studied, however, there is very limited information available in the literature related to the corrosion behavior of Al casting alloys. Many aspects of the mechanism of corrosion are not yet fully understood due to the complexity of the chemical, electrochemical, physical, and mechanical processes involved and also need to improve the mechanical and corrosion properties of aluminium alloy especially for series of AA 5052(Moshwan, Farazila, Hasan, & Rahmat, 2014).

Besides of harsh environment in engine, moisture is another factor that lead to corrosion. Surface modification is proposed to overcome the issue of corrosion in aluminium alloy engine block and components. There are a number of surface modification method such nitro-carburizing, carbo-nitriding, PVD, CVD and other. However, not every method is suitable for aluminium alloy especially for engine block application.

Through polymerization of surface modification, it able to reduce surface roughness and increase hydrophobicity of aluminium sample (Rahimi, Fojan, Gurevich, & Afshari, 2014). Thus, in reduce the risk of frost formation or moisture trapped due to presence of water vapour which may lead to deterioration of engine equipment. However, polymerization method is hard to control. We cannot ensure on location of polymerization either at samples or bulk of solution. On the other hand, the reaction is dependent on morality the substrate and reactant only, where reactant and substrate option are also limited.

Anodization is a popular method for surface modification of Al-based alloys. Anodization is an electrolytic passivation process used to increase the thickness of natural oxide layer on the surface of metal parts. Instead of improved wettability, it is able to contribute as wear resistance, corrosion resistance, non-conductive barrier and facilitate penetration of the electrolyte within oxide layer.

Surface modification of AA 5052 is conducted by Gonzalez-Canche et al. The surface of AA 5052 is modify by introducing fiber metal laminates (FML). This FML found to improved strength and stiffness of AA5052. However, there are gap on how anodization able to improved AA5052 especially on corrosion resistance properties. Thus, this research is focused on how corrosion of AA 5052 could be improved through anodizing process. However, there are also other factor that influence the corrosion resistance such grain boundary distribution, constituent particles, grain size and grain morphology (Huang et al., 2016). All of these factor shall be taken into consideration.

1.3 Research Objective

The objectives of this research are

1. To fabricate aluminium oxide nanoporous on AA 5052 through anodization process.
2. To characterize the microstructural features, mechanical properties and corrosion behavior of nanoporous alumina on AA 5052.

1.4 Research Scope

This study would like to determine the effect of surface modification and effect to the mechanical properties of AA 5052. It also to determine desirable surface medication to overcome current problem in AA 5052 application especially in susceptibility to corrosion. In order to modify the surface of AA 5052, anodization method followed by heat treatment was used in order to fabricate nanoporous layer on the AA 5052 substrate. The fabrication of substrate is confirmed by X-ray diffractometry (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS). Mechanical strength of nanoporous layer then tested through adhesion test and Vickers Micro-hardness. Wettability of nanoporous layer also tested. Lastly, corrosion test is conducted to in order to determine their corrosion protection efficiency.

1.5 Thesis Outline

Current chapter is an overview of the project which shortly summarize the background, research objectives, problem statement and research scopes. Chapter two is a comprehensive explanation of aluminium and anodization process. It also outlining previous study and outcome of previous research on aluminum especially on series 5. Some result of mechanical studies also includes for reference purposes. Chapter three is a highlight on how research were carried out. Methodology is explaining details of step taken from sample preparation, equipment use, consumable applied and analyses performed. Each parameter on each testing also mentioned. Chapter 4 is presentation of result of the study. It also explaining the result obtain. In the discussion also comparing between three types of samples as well as comparing to the literature. Chapter 5 is conclude all the result and provide recommendation for improvement. The flow of project activities is summarized below in Figure 1.1.

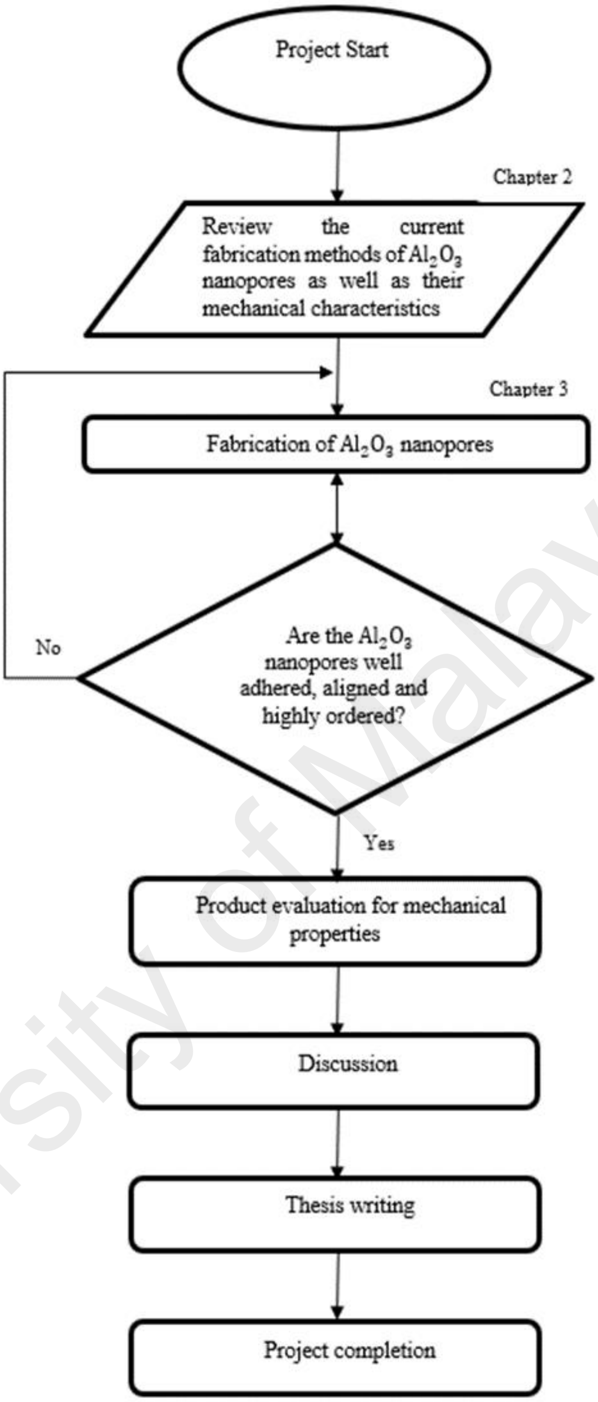


Figure 1.1: Flow of project activities

CHAPTER 2: LITERATURE REVIEW

This chapter will provide comprehensive knowledge of aluminium alloy, surface modification and corrosion study

2.1 Aluminium and Their Basic Properties

Aluminium is one of the elements that listed in periodic table and occupied eight percent of the Earth's land mass ("Aluminium Fact," 2018). Despite of that, we could not found aluminium in metallic form but it was extracted from bauxites, iron oxide, clay and mixture of aluminium oxides (Izbire, 2013). It has atomic mass about 26.982 g/mol. Number 13 seem to be familiar to Al as it come from group 13 and have 13 atomic numbers. Due to that, it is strongly electro-negative metal and holds a strong affinity for oxygen apparently from high heat of formation of its oxide. Aluminium Federation one of the organization from United Kingdom (UK) had termed the aluminium as magic or wonder metal. This is because of their diverse range of physical, mechanical and chemical properties of pure aluminum metal and its alloys regardless in cast or wrought forms.

In general, aluminium is a strong and ductile materials yet furnished with low density. Davis had mentioned in his writing that density of Al (2.7 gm/cm^3) is only about 30% of steel's density with 7.83 gm/cm^3 (Davis, 2001). Thus, it has been extensively studied in transportation industry as alternative to iron and steel application(" UK Aluminium Industry Fact Sheet 6 : Aluminium - The Metal," 2018). The study was include the application of aluminium and aluminium alloys in space vehicles, aircraft, and automotive (Davis, 2001). The main objectives to utilize aluminium in this sector was to offer lightweight body of vehicles (Lumley, 2018).

Even though it only one half from the copper conductivity, it frequently used as electrical conductor in various electrical appliances (Callister & Rethwisch, 2010) due to weight and cost factor. The electrical and mechanical quality of aluminium able to be used in long line, high voltages and aluminium-steel core reinforced transmission cable (Davis, 2001). Furthermore, aluminium have very good electrical conductivity compare to brass, iron and platinum. Besides, it also can be doped with silicon or germanium for p-type extrinsic semiconductor application (Callister & Rethwisch, 2010).

On top of that, aluminium is highly resistant to most form of corrosion. It naturally coated by its own oxide and becoming effectives barrier to the ravages of air, temperature, moisture and chemical attack (" UK Aluminium Industry Fact Sheet 6 : Aluminium - The Metal," 2018). As mentioned in paragraph 1, aluminium have strong affinity to oxygen and basically it contribute to their excellence corrosion resistance properties (Sheasby & Pinner, 2001). Strong affinity to oxygen could be easily understand as when aluminium in ambient environment, it instantaneously form a layer of oxide. A few micron layer of oxide are sufficient to protect aluminium against severe corrosion and chemical attack (Jacobs, 1999). In addition, aluminium have the capability of reform their oxide layer when ruptured (Sheasby & Pinner, 2001). Nevertheless, there are a number of research conducted on aluminium to improve their corrosion and mechanical strength especially in harsh environment (Wang & Guo, 2018).

2.2 Aluminium Alloys

Alloying is the process of adding another elements to the main metal in order to improve strength, workability, corrosion resistance and electrical conductivity. Aluminium alloy is made by mixing aluminium with another elements including iron, copper, magnesium, silicon and zinc in molten state which then cooled to forms homogeneous solution (Helmenstine, 2017). According to Mukhopadhyay, aluminium alloy can be strengthen using strengthening mechanism along with solid solution. Among the proposed mechanism was include grain boundary strengthening, age hardening and work hardening (Mukhopadhyay, 2012).

Aluminium alloy categories are easily differentiate by two major categories which are cast composition and wrought composition (Davis, 2001). Aluminium with cast composition type was form directly to their desire shape while wrought composition type usually come in form of billet and ingots (Sheasby & Pinner, 2001). Wrought alloy could be heat treatable or non-heat treatable. The main classes of alloys are the 2000 series (Al-Cu alloys), which are high-strength materials used mainly in the aircraft industry, the 3000 series (Al-Mn alloys) used mainly in the canning industry, the 5000 series (Al-Mg alloys) which are used unprotected for structural and architectural applications, the 6000 series (Al-Mg-Si alloys) which are the most common extrusion alloys and are used particularly in the building industry, and the 7000 series (Al-Zn-Mg alloys) which are again high strength alloys for aircraft and military vehicle applications(Sheasby & Pinner, 2001). In section 2.2.1, we are going to have an overview to aluminium alloy designation

2.3.2 Aluminium Alloy Designation

Cast aluminium alloy consist of four numerical digits where there are decimal place between third digit and fourth digits. It notation could be represented as “Wxx.x”. The first digits will indicate the principal alloying elements. Second and third digits indicate the specific alloy designation. This two digits was not too significance but unique. The last digits will be only either representing casting type or ingot type. Casting type will be represented by digit 0 while ingot type represented by digit one or two ("Aluminum Alloy Selection and Applications," 1998).

Wrought aluminium alloy consist of four numerical digits as “Wxxx”. The first digit indicate of principal of alloying elements. If alloy is mainly of aluminium, the “W” will be indicate by number one (1xxx). Specific guidance had been provided and it shall be in order of pure aluminium, copper, manganese, silicon, magnesium, magnesium & silicon, and zinc("Aluminum Alloy Selection and Applications," 1998). It is similar to the order of cast aluminium alloy as well. For example, aluminum-copper alloy shall be represent by 2xxx, aluminium-manganese alloy represent by 3xxx, while aluminium-zinc alloy shall be represent by 7xxx. Second digit referring to alloy variation. If the second digit is 0, it generally indicate the bulk of alloy is a pure aluminium. When the second digit is any integers between one until nine, it indicate special control has been placed to suit certain application and achieving certain performance(Kaufman, 2000). The third and fourth digit will served as product identification without carry any special significance information(Kaufman, 2000).

2.2.2 Overview of Aluminium Alloy Properties

Each of the aluminium alloy will have different strengthening mechanism. It is beneficial to the user and manufacturer to understand their characteristic. The following is a brief information on some of aluminium characteristic.

2.2.2.1 Pure Aluminium,1xxx,

Pure aluminium relatively have good electrical conductivities and resistance to almost all kind of corrosive environment. On top of that, it has high ductility and formability. However, it relatively have low strength even though strain hardened was applied(Kaufman, 2000).

2.2.2.2 Copper, 2xxx

Unlike pure aluminium, copper could be strengthen using hardening process. Copper is popularly use as constituent for aluminium alloy in commercial as these alloy naturally aged at room temperature. Aging mechanism resulted hardness improvement and ultimate tensile strength to 2 series aluminium alloy (Ashwath et al., 2018). Besides, forming work and other required work that shall be done after quenching could be performed easily. The drawback of this alloy is their weldability is poor. However, series of 2219 and 2195 had been specially develop for application that require welding(Kaufman, 2000).

2.2.2.3 Manganese, 3xxx

Manganese offer modest strength increase even after strain hardening. On the other hand, it has good resistance to nearly all corrosive environment. It reasonably easy to be formed and relatively high ductility. Unlike aluminium-copper alloy, aluminium alloy 3 series are readily weldable and among the best for brazing and soldering application (Kaufman, 2000).

2.2.2.4 Silicon, 4xxx

There are two types of silicon-bearing aluminium alloys: those with silicon alone, which are not very strong but provide excellent flow and finishing characteristics, and those that also include copper and/or magnesium as well as silicon and so gain strength by solution heat treatment and aging. The 4xxx alloys are not highly resistant to atmospheric corrosion and tend to “gray” with time in humid environments. Interestingly, this characteristic is used to advantage with finishing techniques such as anodizing to obtain a variety of rich gray shades. This series also have good weldability (Kaufman, 2000).

2.2.2.5 Magnesium, 5xxx

Aluminium magnesium (Al-Mg) 5xxx series is non treatable alloy. They are exceptionally tough, absorbing a lot of energy during fracture and could be applied to equipment which require toughness properties as priority during materials selection stages. On the other hand, it is readily to be weld as 2xxx, 3xxx and 4xxx aluminium alloy series (Kaufman, 2000).

On top of that, Al-Mg alloys always becoming an attention to automotive industry. It is because of their excellent in corrosion resistance, recycling potential and the most important is strength to weight ratio. Since they are simple elements system and have weak anisotropy properties, their mechanical properties mainly rely on grain size and dislocation density (Sharifitabar, A. Sarani, & Afarani, 2011).

There are a few series of Al-Mg alloy which could be used in vast application. As example is 5052 series where it could be use as traffic sign, home appliances, heavy duty cooking utensils and bulk food processing ("5000 Series Aluminium Alloys," 2018). Besides, it could be involve in more heavy industries application such as marine application and transportation. Bhowmik and Mishra claimed in their report that Al-Mg5052 possessed high fatigue strength which suitable to be used in high excessive vibration application (Bhowmik & Mishra, 2016).

Some Al-Mg is not suitable to be used to the application that continuously exposing to high temperature because some sensitization to SCC may develop(Kaufman, 2000). It had been prove by a study where ultimate tensile strength (UTS) and yield strength (YS) of Al-Mg 5052 H32 decrease dramatically after annealed up to 350˚C (Bhowmik & Mishra, 2016). Thus, early statement is proven that Al-Mg in non-heat treatable and their UTS and YS could be enhanced through cold working.

With both magnesium and silicon present, aluminium forms a quasi-binary section with the Mg2Si phase of the magnesium-silicon system, which in turn provides excellent precipitation- hardening capability. This results in modestly higher strengths than possible with non-heat-treatable alloys, combined with generally excellent corrosion resistance. Alloys of the 6xxx type are among the easiest of aluminium alloys to extrude, and are thus widely used for complex (e.g., multi-hollow or finned) shapes produced in this manner. In addition, they are readily joined by almost all commercial processes (Kaufman, 2000).

Base on Rodrizues *et al.* mild anodization of AA 6016 produce aluminium alloy oxide (AAO) layer of 31nm with very low porosity. The oxide layer was improved through two step of anodization where layer of 205nm was form with higher porosity. Porous structure gave rise to superhydrophilic wettability behaviours, typical of Wenzel state (Rodriques, Alves, Cavaleiro, & Carvalho, 2017).

There are a number of parameter that affect efficiency of anodization process. There are temperature, anodization time, voltage supplied and type of electrolyte. Usual type of electrolyte use are NaOH solution and HNO_3 solution. It also common to use malonic acid. Common anodization time is 60 minutes (Lu, Wei, Yu, Guo, & Jiang, 2018). Early study of aluminium anodization mentioned that the higher the anodization temperature the better the nanoporous produce (Charles, 2007). However, Theohari and Kontogeorgou in his study on effect temperature to AA5052 found that anodization at 30˚C will produce highest density of nanoporous. The increasing of temperature will only introduce blocking effect to nanoporous growth (Theohari & Kontogeorgou, 2013).

2.2.2.7, Zinc, 7xxx

It has the highest strength compare to other if combining with copper and magnesium. As a whole it relatively poor to atmospheric corrosion attack. Special treatment still in research to improve this characteristic(Kaufman, 2000).

2.3 **Surface Treatment**

Surface treatment is essentially importance not only to aluminium but to other metal as well. Purpose of surface treatment could be improving mechanical properties, corrosion prevention and decoration purposes. The surface modifications are also able to extending life of metals components such as automotive bodies and construction materials("Surface Treatment of Metals," 2018). There are a numbers of surface treatment type and methods such electroplating, hot dipping, thermal spraying, anodic oxidation etc.("Surface Finishing Tutorial," 2011). Anodization is one of the commonly used for aluminium alloy and aluminium surface modification tools.

2.3.1 Anodization

Anodizing method was emerged since 1960. It is an electrolytic process in which surface layer of a metal, such as aluminium, magnesium or zinc is converted to a coating, usually an oxide. This oxide were having properties of protective or decorative. In 2006, European Commission had mentioned in their report that aluminium anodizing come prior to photosensitive treatment("Surface Treatment and Plastics," 2006). Report also mentioned that anodizing of aluminium could be divided by two type. First type is normal anodizing. It is for automotive components, aerospace wing, fuselage panels, building doors, packaging and consumer goods. Another type of anodizing known as hard anodizing. It specially design for bearing surface in turbine compressor housing and automotive engine.

As mentioned before, anodizing is an electrolytic process. Normally, sulphuric acid, oxalic acid, chromic acid and other organic acid will be employed as electrolyte. Sulphuric acid is the most prefer electrolyte since it produce colorless layer, low power supply and voltage consumption and economical for colour part production("Surface Finishing Tutorial," 2011). Each cycle of anodization process will require specific temperature, power source, and electrical form so that the incoming layer produce will suit the specification needed. Oxygen at anode produces porous layer with good electrical isolation characteristic, corrosion resistance and wear resistance properties("Surface Finishing Tutorial," 2011). Properties of anodized layer rely on crystalline structure of the oxide and chemical composition. Besides, electrolyte type, concentration and current density also affect the anodizing process and properties of anodizing layer(Canyook, Seubsom, Sang-ngean, Trirujirapapong, & Taweesup, 2018). The basic anodize process diagram could be refer at figure 2.1.

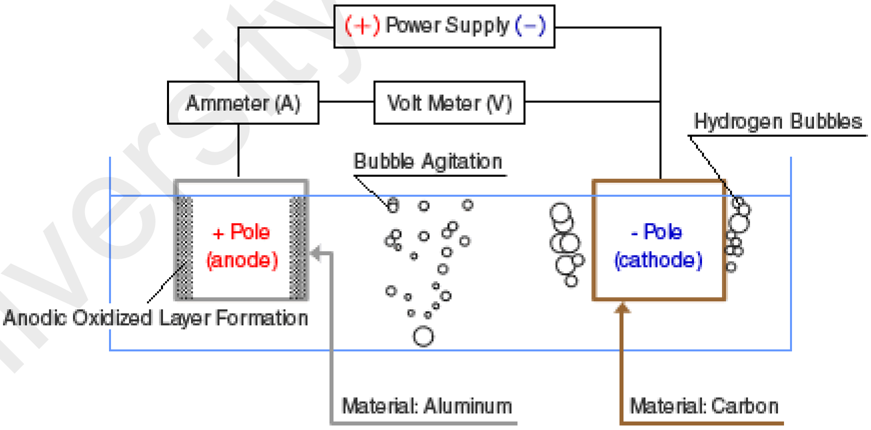


Figure 2.1: Basic Anodization Circuit

Surface preparation before anodizing is crucial. It begin with cutting the samples to desire size. Budsarakham *et al.* choose to cut cast aluminium alloy from ingot into size of 15 × 20 × 10 mm^3 (Budsarakham, Riyaphan, Canyook, & Taweesup, 2018) while Canyook *et al.* choose dimension of 2 × 2.5 × 4 mm^3. Eventually, the size of specimen rely on their experimental set-up and characterization tools. Regardless of any size, specimen need to be polished thoroughly prior anodizing process. Wheeler *et al.* in their study on “hard anodizing and plasma electrolytic oxidation effect to AA 5052” had polished the samples using SiC abrasive papers from 360-grit to 1200-grit(Wheeler, Curran, & Shrestha, 2012). After polished, the samples rinsed with distilled water. While study on “anodized layer of AA 7075”, Canyook *et al.* also used SiC abrasive paper in the order of 320-grit, 600-grit, 800-grit and 1200-grit before rinsed with niric acid for degreasing, bath with distilled water and air dried (Canyook et al., 2018). Some other using acetone as degreasing medium before etched samples to 100g/L NaOH solution at 40˚C(Theohari & Kontogeorgou, 2013). Besides of SiC abrasive paper, metallographic emery paper with different granulation (from 1000 to 2500 mesh) also could be use during polishing (Lu et al., 2018).

Determination of voltages applied may affect the nanoporous layer. In general, higher voltages will induced rapid growth of nanoporous (Wu & Ji, 2018). This is because rate of barrier dissolution is highly depending on the voltages supply. It also related to current density flow through the samples. Figure 2.2 reveal that higher voltages will induced more current density. However, their behaviour were similar regardless on voltages applied. Consist of four region where each region indicating the nanoporous growth from (I) emergence of dense Al_2O_3 ion, (II) formation of organized nanoporous Al_2O_3, (III) steady state of nucleation and growth of nanoporous Al_2O_3 and (IV) indicate the end of aluminium ion consumption. On top of that, lower voltages supply (< 5V) will promote fabrication of nanoporous with high porosity (Alaa, A.M, Waleed, & M.A, 2014) which is mechanically unfavorable. Besides, voltages applied also could affect anodization time.

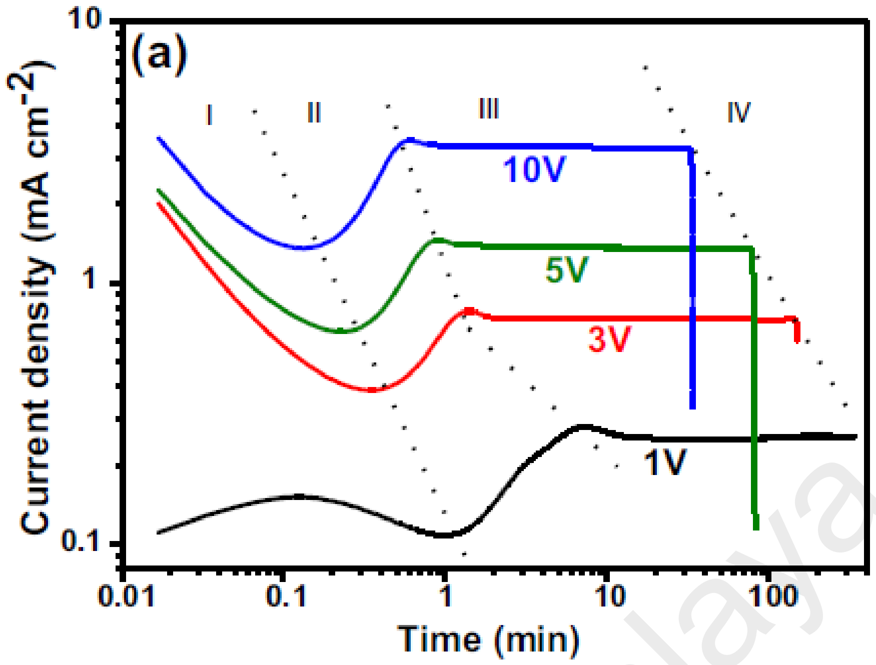


Figure 2.2: Effect of voltages supply to the current density during anodization process (Alaa, A.M, Waleed, & M.A, 2014)

Another factor that affect anodization process are anodization time. Anodization process consider complete when all aluminum ion is completely oxidized and the illustration could be refer at figure 2.2 As mentioned previously, time of anodization also depending on voltage supply. In other word, there are inter-related. The higher voltage supply the shorter anodization time. There are study that able to reduce anodization time from 6 hours to 0.5 hour by increasing the voltages from 1V to 10V (Alaa, A.M, Waleed, & M.A, 2014). However, shorter anodization time may lead no incomplete and defective nanoporous layer formation. Study of fabricating anodic film in 0.3 oxalic acid on pure aluminum reveal that shorter anodization time will hindering the formation of anodic film. The anodic film is still in nucleation mode array of nanoporous still cannot be seen. Along the time, the nanoporous self-aligned themselves and becoming organized and amorphous dense layer (Maryam, Mansour, & Ali Reza, 2019). When anodization complete, we could see the porous and well-ordered layer form on aluminium substrate as in figure.

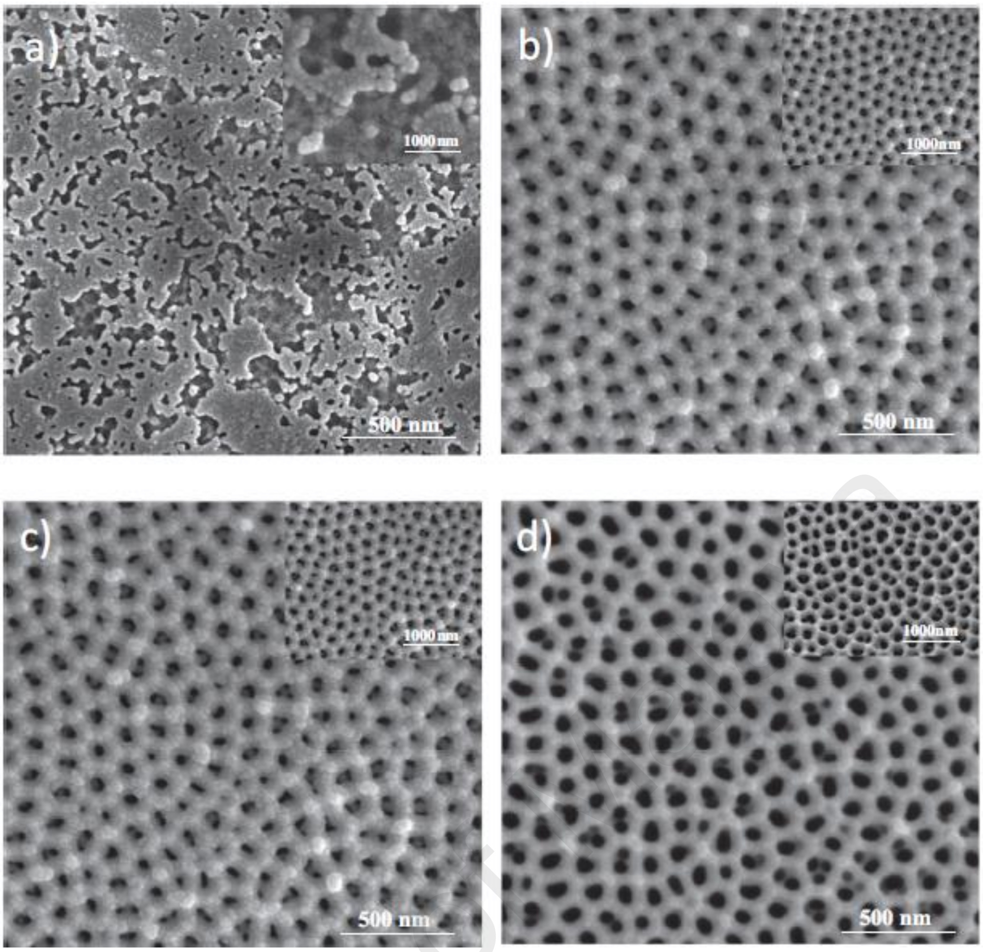


Figure 2.3: FESEM image of anodic film anodized at difference time (a) 60min, (b) 90min, (c) 120min and (d) 150min (Maryam, Mansour, & Ali Reza, 2019)

Determining the electrolyte are another significance step in anodization. As mentioned before, sulphuric acid is the most popular electrolyte use for anodization purpose. Surprisingly, for aluminium alloy especially Al-Mg alloy it still not attract great attention from researcher(Theohari & Kontogeorgou, 2013). One of example which use sulphuric acid as electrolyte to anodized AA5052 was conducted by Theohari and Kontogeorgou. Aluminium sheet was choose to be counter electrode. After thorough surface preparation which involve degreasing of samples with acetone, etched with NaOH, immersed with HNO_3, and cleaned with deionized water after each process, the samples anodized at constant voltages of 15V under agitation of magnetic stirrer for 40 minutes. Anodizing temperature was manipulated from 10˚C until 40˚C by 10˚C order. After anodizing, samples were rinsed with deionized water for a minute and dried in cool air stream.

Anodizing layer (porous oxide film) then measure using eddy current techniques. Anodizing thickness increase proportionate to the increasing of anodizing temperature. However, the thickness reducing after 30˚C to 40˚C. It due to chemical dissolution rate and side reaction decrease the porous growth when surrounding is exceed 30˚C(Theohari & Kontogeorgou, 2013). They also study the relationship of anodizing temperature toward current density. The higher anodizing temperature the higher the current density. Current density will determine the speed up of oxide layer growth(Theohari & Kontogeorgou, 2013).

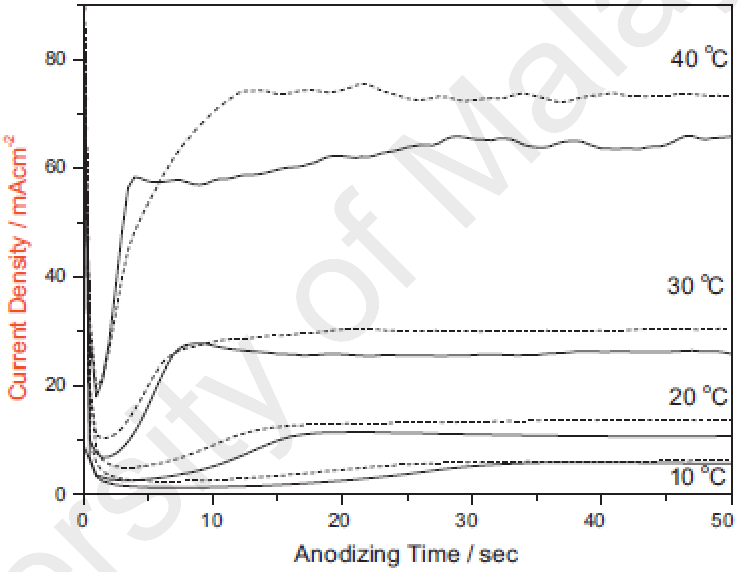


Figure 2.4: Current density-time response (Theohari & Kontogeorgou, 2013)

Anodizing using sulphuric acid as electrolyte also could be combine using another surface treatment method such plasma electrolytic oxidation (PEO). PEO will assist in formation of relatively thick, predominant crystalline oxide-based surface layers formed primarily by oxidation or conversion of substrate alloy. Another method, PEO also worked by co-deposition from electrolyte constituents(Wheeler et al., 2012). PEO will require higher voltages so that repeated local dielectric breakdown and plasma discharge are generated across the growing oxide. Wheeler, Curran and Shrestha had setup the anodization process almost similar to Theohari and Kontogeorgou. Then it followed by PEO coating using commercial AC Bipolar 50kW Keronite PEO equipment. Anodization only require DC type voltage supply. However, PEO require AC type voltage supply.

Nanoporous structure represent the transition from atom to solid. It important to obtain particles or pores with uniform diameters and shape and, for the purpose of particular application, to arrange and embed them in a superstructure. Two step anodization could assist in developing the nanoporous layer at metal especially alumina oxide type(Ates, Baran, & Yazici, 2018). As usual, sample preparation was require cutting, degreasing with acetone and washed with rinsed water. However, for two step anodization, Ates et al. had annealed Al electrode at air furnace for 5 hours. Prior anodizing, Al samples was electrochemically polished in mixture of perchloric acid (60wt%) and ethanol for 1 minute at 5˚C and constant voltages of 20V was supplied. First step anodization using 0.3M oxalic acid as electrolyte. Al sheet anodized at 50V for 1 hour. After complete the irregular oxide layer of Al sheet is removed by chemical etching. Second anodization also using oxalic acid and 50V, however, the anodization time is manipulated at set of 1hour, 2 hour and 4 hour (known as sample A) and 2 hour, 4 hour and 8 hour (known as B). In this research, self-ordered of alumina oxide were obtained through two step anodization. The longer the anodization time, the preferred layer of shorter length and smaller diameter of pores are obtained (proven by SEM). On the other hand, linear increase in the average pores diameter and oxide layer thickness with increasing anodization time were observed and the increased in BET surface area has been detected accordingly. It proven by micro-hardness result that proven sample B have highest hardness.

Heat treatment after anodization is another effort to improve the nanoporous layer. Heat treatment basically will assist to align the microstructure in more structured order (Marsal, Vojkuvka, Formentin, Pallares, & Ferre-Borrul, 2009). It improve intermetallic layer between substrate and coating layer (Zhou, Yang, Wang, & Pang, 2017). According to Zhou *et al*. anneal temperature shall be properly decided. Excessive annealing temperature could lead to the formation of cavities and voids. During annealing, we need to ensure the initial substrate shall be the main phase. Annealing also assist to remove the microstructure defect during nanoporus fabrication. Through self-ordered mechanism, annealed contribute to removed dislocation. It due to recrystallization that occur during annealing which rearrange grain and subgrain to certain degree of coarsening and growth (Jinlian, Jun, & Feng, 2018)

2.4 Adhesion Strength

Adhesion strength test is a method to measure the bonding strength between substrate and coating materials. Coating materials could be either nanotubes, nanoporous, lamination, spray coated etc. There are also various method to conduct adhesion strength test for aluminum. This test basically related to susceptibility of materials to corrosion protection, along with hardness and wea (Choudhary et al., 2015).

The easiest way to test adhesion strength of anodized layer on aluminium is through scratch test. It provide crucial information regarding the critical load on adhesive failure. In order to study adhesion strength of anodization layer of aluminium in 30˚C oxalic acid, Chaudhary *et al.* put parallel vertical tips on samples and induced crack. Normal load apply is 1 N and increasing along the distance(Choudhary et al., 2015). Jang et al. measure their aluminium alloy (Al 6061) composite armor through drop weight impact test. It is a part of study on how complete delamination of aluminium and alumina) resist the crack from impact occur. Based on result, nanostructured of interfacial adhesion led to better protection against impact than those of their counterparts without any surface treatment(Jang et al., 2017). Another method of adhesion strength was through shear adhesion test according to ASTM D1002 where Gonzalez-Canche et al would like to study on effect on surface treatment to interfacial adhesion between aluminium alloy and polypropylene. Sample (treated and untreated aluminium) were put in mold and bonded by single lap joint configuration via strip of polypropylene as per figure 2.3 Test proved that aluminium substrate with chemically treated has 76% (15.7 MPa) stronger than untreated sample. It is because, chemically treated aluminium substrate improve in roughness and increase their mechanical interlocking(Gonzalez-Canche, Flores-Johnson, Cortes, & Carillo, 2018).

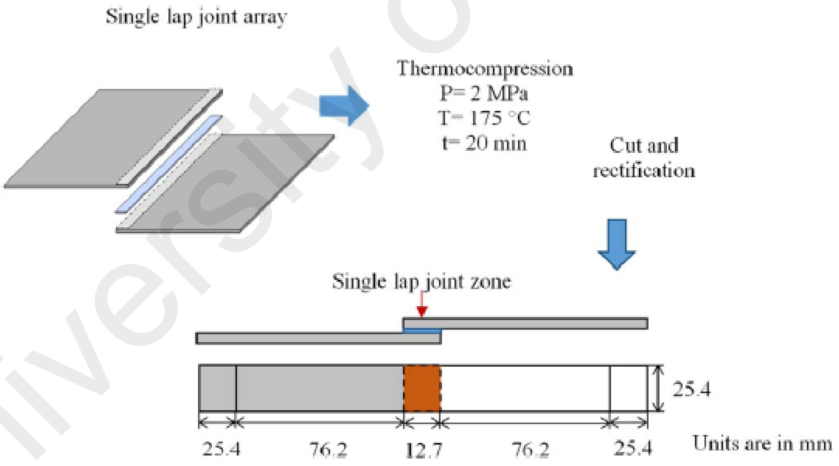


Figure 2.5: Single lap joint configuration of Aluminium (Gonzalez-Canche, Flores-Johnson, Cortes, & Carillo, 2018)

On top of that, adhesion strength also could be improved through heat treatment. Heat treated up to 500˚C able to improved adhesive strength of $Cu\text{-}Al_2O_3$when necessary moisture is removed (Lim, Susan, Daniel, Leong, & Wong, 2013). Furthermore, it improved the surface contact area. Based on Lim *et al.*, this greatly assist in improving adhesive strength at interface because more energy require to initiate bond breakage

2.5 Microhardness Testing

One of the challenge in producing good anodization nanoporous layer is to ensure their hardness. Lu *et. al* also mentioning that through mirohardness and nanoindentation, it the best way to extract elastic modulus and speciment hardness from load displacement curves. It is assume that only elastic deformation is available during unloading stage. Anodization Hardness of anodized layer could be differ by anodization method. It mainly affect by their temperature and duration of anodization process (Lu, Wei, Yu, Guo, & Jiang, , 2018). Low anodization process will lead to higher hardness compare to high temperature(Lee et al., 2017).Lee et al. had proove that anodization of die cast Al alloe at only 20˚C produce oxide layer as high as 170HV rather than anodization at 25˚C where only 120HV recorded

Hardness also could be improved by chemical environment. Study by Lee *et al.*, micro-Vickers anode of Al Alloy (ADC12 Al-Alloy) improved in higher concentration of $NaAlO_2$. Low concentration of $NaAlO_2$electrolyte, unable to produce good density of oxide layer (Lee et al., 2017). In addition, oxide layer produce have various defect and require for mechanical properties enhancement.

On top of that, annealing also is another mean to improve hardness of materials. Study of laminated composites of Ti and Al shown that Al layer hardness increase in the range of 50 to 100 HV after annealing at 700˚C. In this case, it mainly due to uniform distribution of Al and Ti particle (Jafari, Eghbali, & Adhami, 2018).Thus, this is new potential method to enhanced mechanical properties of metal matrix composites.

2.6 Wettability

Method of analysis that measure the degree of interaction between liquid and solid surface known as wettability (Darmanin & Guittard, 2015). Hydrophobic or hydrophilic character could be enhanced through surface modification which not only modify on surface roughness or topography, but also change it surface chemistry (Darmanin & Guittard, 2015). On the other hand, contact point is highly depend on interaction of three phases of solid-liquid-vapour (Rodriques et al., 2017).

Rodriquez *et al.* had study on effect of surface finishing prior anodization effect to the wettability of water and oil. It was found that non polishing aluminium alloy show indication of hydrophobicity compare to those with treat with proper finishing. However, the surface of aluminium alloy were slightly change after anodization where a dimple structure were found. It tremendously affect the anodization since porosity of Al_2O_3 is forming. Generally, anodization cause substrate becoming more hydrophilic and contact angle reduce as shown in figure 2.4. It mainly due to porosity and new surface texture produce after anodization. In the case where sligh higher surface angle require, salinization treatment could be performed. Salinization agent such KH560 could be used for this purposes (Pan et al., 2018)

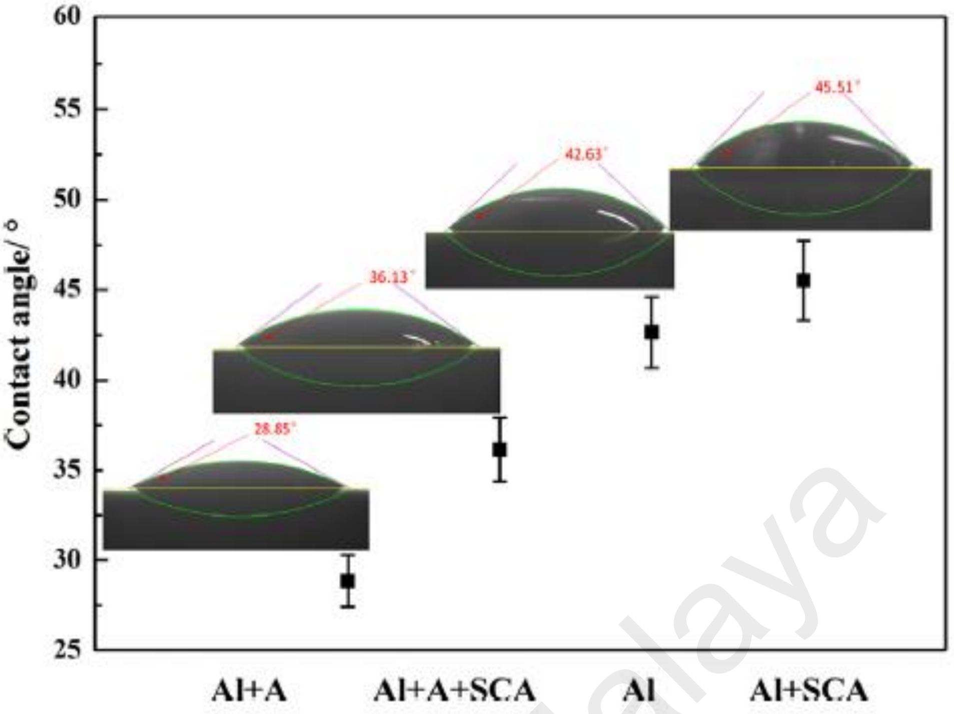


Figure 2.6: Comparison of Aluminium contact angle base on treatment (Pan, et al., 2018)

2.7 Corrosion Study of Aluminium

In general, higher aluminium content with certain materials will provide greater resistance to the corrosion. As example, Nickel-Aluminium-Bronze (NAB) which usually use in marine application will provide their suitable mechanical and corrosion resistance at composition of 9-12% of aluminium (Hanke, Fisher, Beyer, & Santos, 2011). Phase selection of corrosion mechanism will applied to NAB however, aluminium layer will becoming the protective layer to the structure.

On top of that, surface modification is another important tricks to improve the aluminium corrosion resistance. One of the study by Wang and Guo using layer double hydroxide techniques (LDH). This method will modify the surface of Mg-Al becoming superhydrophobic. The superhydrophobic layer were produced by immersing the sample into deionized water, ethanol and FAS-13 of 50 mmol/L and drying them in air. During the sample preparation, it was using different pH value. Based on corrosion test, bare Mg-Al will have highest I_{corr} compare to those treated with LDH. However, samples with treated in high pH value will have higher corrosion resistance compare to those treated in lower pH value (Wang & Guo, 2018).

Another method to improve corrosion resistance by using sulfate-reducing bacteria (SRB). This method is suitable to be used for AA5052 that being applied for oil pipelines and marine facilities (Muyzer & Stams, 2008). Guan et al. had extracted desulfovibrio caledoniensis to produce SRB. SRB culture were inoculated in sterile postgate C medium which consist of 0.5 g K2HPO4, 1.0 g NH4Cl, 0.06 g CaCl2·6H2O, 0.06 g MgSO4·7H2O, and 6 mL of 70% sodium lactate. Process of purging with nitrogen and injected of assisting bacteria into electrochemical reactor. Temperature is maintained at 10˚C to 15˚C.

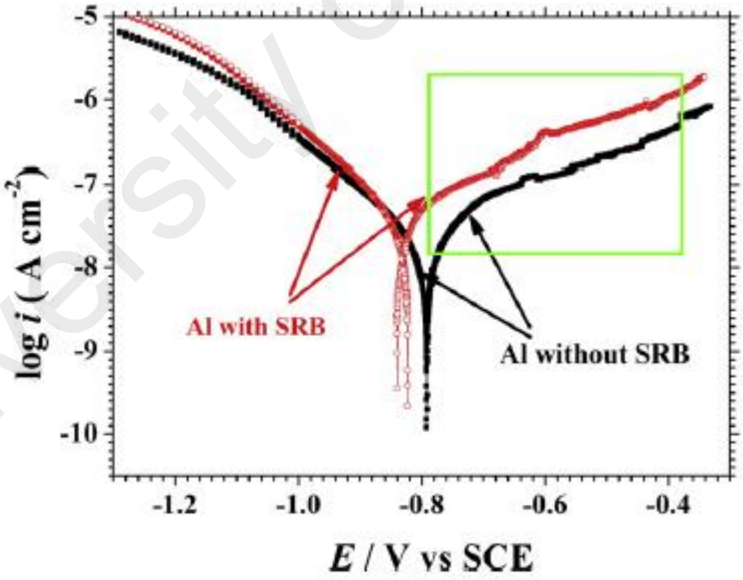


Figure 2.7: Polarization curve of aluminium alloy exposed to media with or without SRB (Guan, et al., 2017)

Through corrosion test result as per figure 2.5, AA 5052 with SRB found that samples with treated SRB have better corrosion resistance. Guan *et al.* recorded that I_{corr} of Aluminium treated with SRB media has higher anodic polarization curve. It an indicating of higher indicating anodic solution reaction due to presence of SRB metabolic activity.

This activity basically will kill the corrosive ions and enhance corrosion resistance of AA 5052.

Another method of to improved corrosion resistance of AA five series by homogenization. A study conducted to homogenization heat treatment and omission of homogenization of heat treatment for AA5083-H321 found that treated sample has lower corrosion susceptibility. It were assist by the presence of large intermetallic particle. On top of that, not treated sample have smaller grain size and less texture owing to fractional recrystallization. It in favour with general understanding that high penetration depth always occur at small grained microstructure(Huang et al., 2016). Figure 2.6illustrated the difference between non-treated (AR=as received) and treated sample (TT=temper condition and treated)

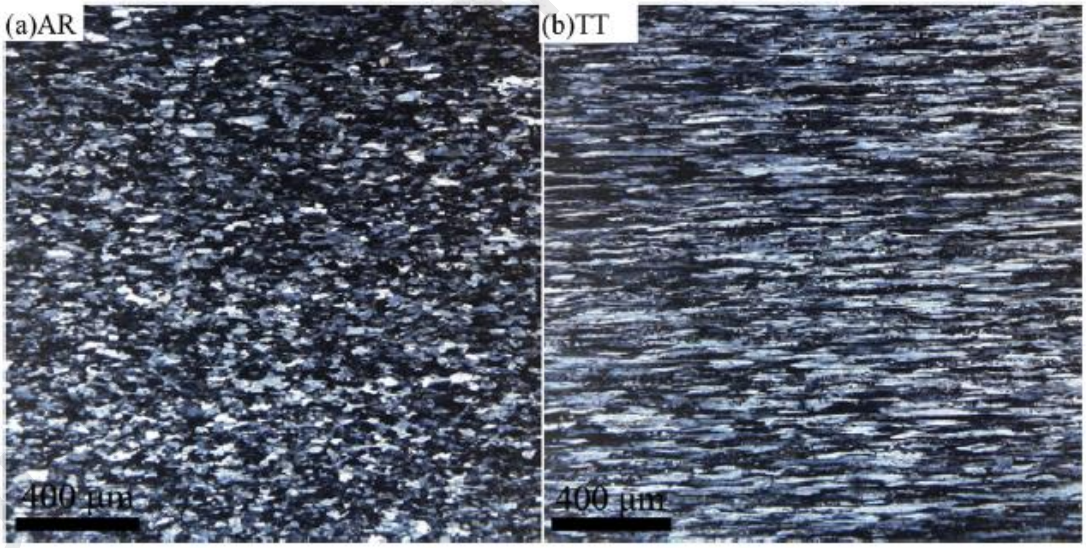


Figure 2.8: Micrograph of plate specimen taken perpendicularly to the major deformation direction (Huang, Li, Xiao, Huang, & Ren, 2016)

Anodization is another method to improve corrosion resistance. Anodization mentioned above is a process of fabricating nanoporous layer so that it may resist to corrosion agent. Anodization not only able to perform at wrought aluminium but also at die cast aluminium alloy. On study of die cast aluminium casting type ADC12, which is higher in silicon content show improvement of corrosion resistance after anodized. The anodizing process was accomplish in electrolyte of 0.3M sulfuric acid. Sulfuric acid use eventually is a type of high concentration of aluminate. This anodization produce high amount of AlO_2^- which assist to improved surface morphology. As a result, lower corrosion rate of anodized sample compare to bare substrate is achieve. It indicated by I_{Corr} value where anodized sample have 5.64×10^{-6} mA/cm² while bare substrate have as much as 1.10×10^{-5} mA/cm². This 48% improvement due to dense and thick nanoporous produce from anodization process had cover defect site (Lee, et al., 2017).

CHAPTER 3: METHODOLOGY

3.1 Flowchart for Methodology

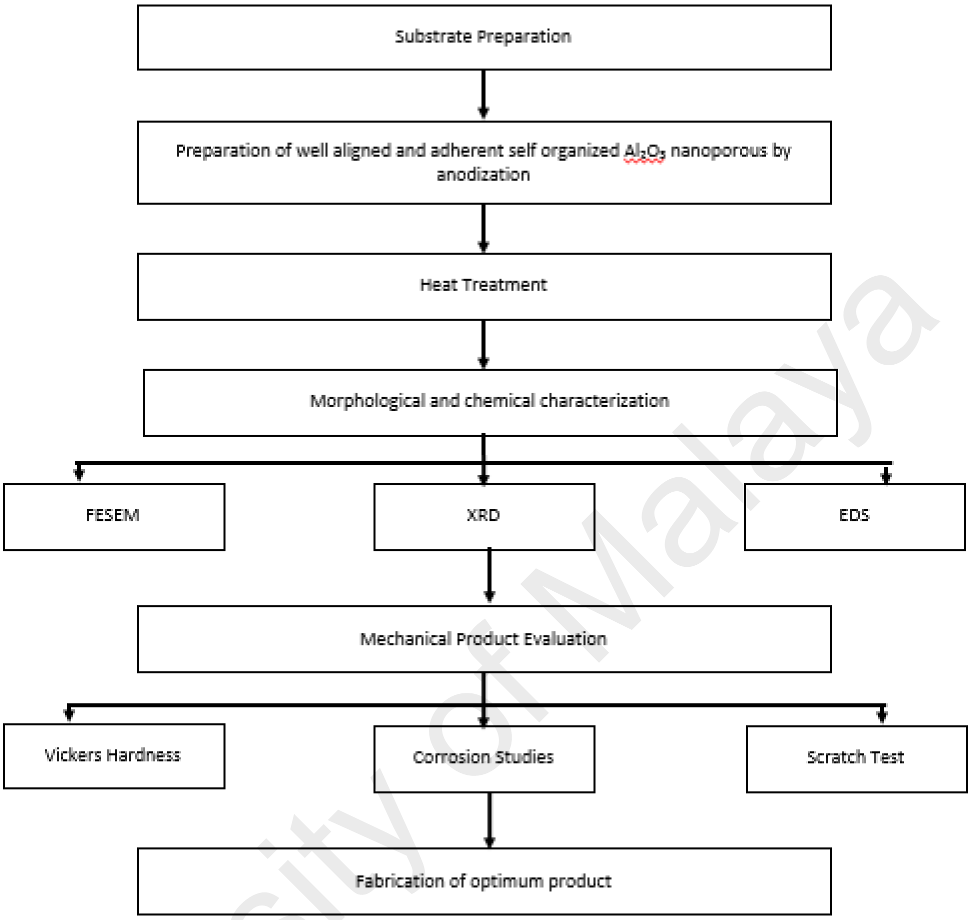


Figure 3.1: Flowchart of methodology

3.2 Substrate preparation

Substrates of aluminium alloy series 5 were fabricated (KAMCO ALUMINIUM SDN BHD, Kuala Lumpur, Malaysia) plates with dimensions of 15 mm × 15 mm × 2 mm. The specimens were set by polishing using 800–2400 grit silicon-carbide emery papers, tailed by wet-polishing using a diamond slurry and sonication in acetone at 40˚C for 10 minute. Using distilled water, substrates were then washed three times, trailed by drying at 100 °C for an hour. It conducted for each experiment in order to produce thin film of Al_2O_3 nanoporous arrays.

3.3 Preparation of Self-organized Al_2O_3 nanoporous arrays

Two-electrode were employed to conduct electrochemical anodization. During the process, graphite rod of diameter 7mm was attached to both cathode and anode as per figure 3.1. Throughout experiment, distance between electrode were fixed at 20mm. Anodizing was carried out using a direct current (DC) power source (Model E3641A, Agilent Technologies, Palo Alto, USA) at 12V for 1 h in an electrolyte containing 15 wt% H_2SO_4.. De-ionized water were use to washed samples right after anodization process. In order to improve crystallinity of nanoporous, anodized samples were annealed at 450˚C for 90minutes. Then, it is cooled with rate of 5 °C/min under normal atmosphere.

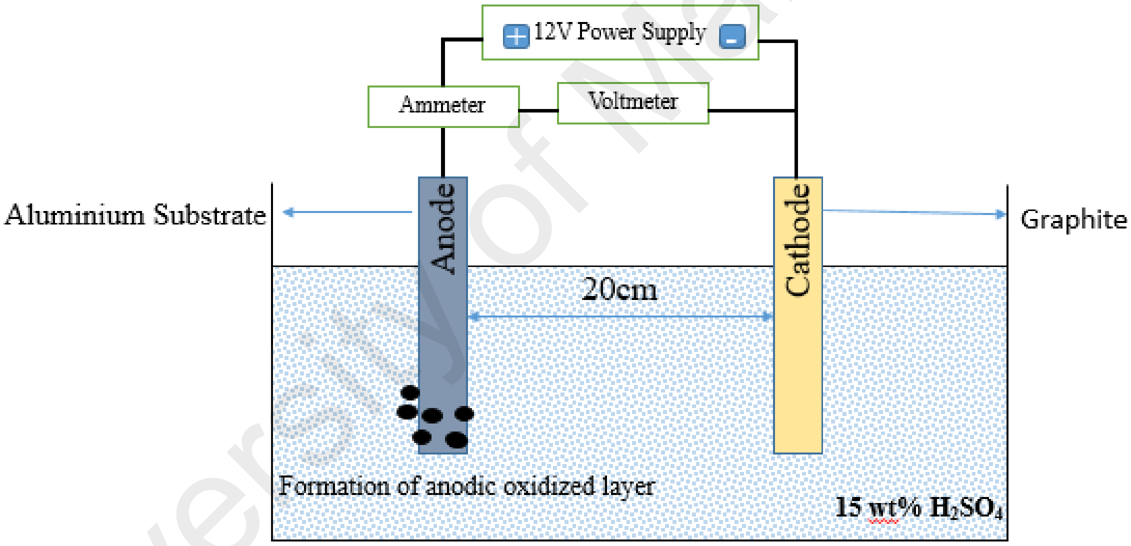


Figure 3.2: Schematic view of the anodization process to produce nanoporous array

3.4 Phase Analysis and Microstructural Characterization

By using a field emission scanning electron microscope (FESEM, SU8000, Hitachi, Japan) with an acceleration voltage of 1 to 2 kV, morphology of nanoporous of anodized sample were investigated. The cross-sections of the specimens were prepared with a destructive technique using a high-precision cutter equipped with a diamond blade. The phase composition and cleanliness of the substrates, Al_2O_3 nanoporous arrays annealed

Al_2O_3 nanoporous arrays on series 5 specimens were analyzed by X-ray diffractometry (XRD; Philips PW1840, the Netherlands) with Cu Kα radiation (λ=1.54178Å) functioning at 30mA and 45 kV , 2 theta range of 30°-80°, step size of 0.026° and scan rate of 0.1°.s^{-1},. The "*PANalytical X'Pert HighScore*" software was also engaged to analyze the XRD patterns, wherein all the reflections were equated with the standards gathered by the Joint Committee on Powder Diffraction and Standards (JCPDS, card #005-0682). Energy dispersive X-ray spectrometry (EDS) is employed to check on atomic absorption as well as dispersion of constitutive elements in the samples.

3.5 Adhesion Strength

The adhesion strength of the coatings was measured quantitatively using a Micro Materials Nano Test (Wrexham U.K). It come with a diamond indenter with radius of 25.0 ± 2.0 µm and angle of 90.0 ± 5.0°, respectively. Velocity use during experiments is 5 mm s^{-1} and the loading rate steadily increased to 9.2 mN s^{-1}. Each sample will undergoes scratch tests and the destruction profile was explored under a light optical microscope (Olympus BX61, Tokyo, Japan). In other word adhesion strength is method to define the severity of total coating failure. The sample was relocated perpendicular to the scratch probe whilst the contact was either held constant or ramped at a user-defined rate. Outcome that continuously monitored throughout the test is probe penetration depth and frictional load. A pre-scratch scan was conducted using an ultra-low contact force in order to assess baseline sample topography. After that, the scratch test was recurrent three times within the specified load range using a diamond indenter.

For further investigation, the scratch hardness test was performed on the Al_2O_3 nanoporous arrays, annealed Al_2O_3 nanoporous arrays thin films at 450°C for 90 minutes. Objective of this test is to quantity the resistance of the thin films to permanent deformation under the action of a single point (stylus tip). It involves a different arrangement of properties of the surface because the indenter, in this case, a diamond stylus, moved tangentially along the surface. The scratch hardness test, is more proper procedure to measure the coating failure of a material, like the two-body abrasion. This procedure is valid to several of materials type including metals, alloys and some polymers. This experiment will provide scratch hardness number. It is based on the measurement of the residual scratch width, after the stylus is removed. Therefore, it reveals the permanent deformation consequential from the scratch. It is another evidence that permanent deformation is not result of instantaneous state of combined elastic and plastic deformation of the surface. Since the state of stress at the stylus tip is a function of contact geometry and applied force, the degree of the scratch hardness number is reliant on upon both the normal load and stylus tip radius. Dividing the applied normal force on the stylus by the projected area of the scratch contact, scratch hardness number could be calculated. However, it based on assumption that the hemispherically-tipped stylus produces a groove whose leading surface has a radius of curvature *r,* the tip radius of the stylus. The estimated area of the contact surface is therefore a semi-circle, whose diameter is the final scratch width. The critical load is demarcated at the onset of the coating loss, which is associated with the appearance of the metallic substrate inside the scratch channel. This measurement was accomplished with the help of an optical microscope. The tester was also qualified to gain the frictional coefficient at the critical load(Ruckh et al., 2008). The scratch hardness HS_p was estimated following the specification of ASTM G171-03 norm:

$$HS_P = \frac{8P}{\pi w^2} \qquad \text{Eq. (1)}$$

Where HS_p, P and w are the scratch hardness number, normal force and the scratch width, respectively.

3.6 Microhardness

Vickers microhardness testing machine (Mitutoyo-AVK C200-Akashi Corporation, Kanagawa, Japan) is employed to identify the microhardness of the samples by the indentation-strength method at room temperature. Five samples require indentation at dwell time of 15s and an applied load of 98.07 mN. Based on microhardness, it able to determine the average value of the mechanical properties of these five samples.

3.7 Corrosion Studies

Potentiodynamic polarization measurements were carried out in a single compartment cell. The cell consist of standard three-electrode arrangement. Those three electrode known as working electrode (sample), reference electrode (SCE) and counter electrode (platinum electrode). The sample surface area uncovered to the cell solution was $1cm^2$. Experiment was conducted in Artificial seawater and applicable to all samples. Experimental data was collected by potentiostat Bio-Logic SP-150 monitored by a PC computer and EC-Lab software. It also assist to evaluate experimental data. Potentiodynamic polarization curves were recorded in the potential range −2000 to +2000mV versus SCE reference electrode at a scan rate of $1mVs^{-1}$, after allowing a steady-state potential to develop. Similar experiment were performed under identical testing parameter to verify data consistency and reproducibility.

The electrolyte corrosion study was artificial seawater in the room temperature. According to the Burkhoder's formulation B, the compositions of the simulated seawater were as follows (per litre):23.476 g NaCl+3.917 g Na_2SO_4+ 0.192 g $NaHCO_3$+ 0.664 g KCl+0.096 g KBr+10.61 g $MgCl_2.6H_2O$+ 1.469 g $CaCl_2.6H_2O$+0.026 g H_3BO_3+ 0.04 g $SrCl_2.6H_2O$+0.41 g $MgSO_4.7H_2O$+ 0.1 g NH_4Cl+ 0.1 g $CaSO_4$+ 0.05 g K_2HPO_4+0.5 g tri-sodium citrate+ 3.5 g sodium lactate+ 1 g yeast extract. The pH is control in between 7.5 ± 0.1 using a 5 M NaOH solution(Yuan, Liang, Zhao, & Pehkonen, 2013).

Tafel plot will indicate the corrosion current (I_{corr} / µA cm^{-2}), corrosion potentials (E_{corr} / V$_{SCE}$) and polarization resistance (R_p / Ω cm^{-2}). The corrosion protection efficiency (*P.E.*) was also estimated using the following equation (Yu *et al.*, 2014):

$$P.E.(\%) = \frac{I_{corr}^{0} - I_{corr}^{c}}{I_{corr}^{0}} \times 100 \qquad \text{Eq. (3)}$$

Where I_{Corr}^{0} is the corrosion current of the bare series 5 and I_{Corr}^{c} is the corrosion current of the coated sample.

Moreover, *CR* was calculated by the following formula:

$$CR(mmyear^{-1}) = \frac{0.13 I_{corr}(E.W.)}{d} \qquad \text{Eq. (4)}$$

where *E.W.*, *d*, and I_{corr} are equivalent weight of the corroding species in g, density of the corroding species in g cm^{-3}, and corrosion current in A cm^{-2}.

3.8 Surface Wettability

The surface wettability will provide information of hydrophilicity of samples. It was examined by measuring the contact angles of sessile droplets of deionized water deposited on each samples surface. A video-based optical contact angle measuring system (OCA 15EC, Data Physics Instruments GmbH, Germany) was utilized to examine the optical wettability. A constant liquid volume of 5 µl was used for the contact angle evaluations of all the specimens. Drop velocity of 2 µl s^{-1} at a temperature of 26±1 °C also were keep constant for all applied sample. The droplet width "*d*" and height "*h*" were measured to determine the contact angle "θ" as follows(Elias, Oshida, Lima, & Muller, 2008).

$$\theta(°) = 2\tan^{-1}\left(\frac{2h}{d}\right) \qquad \text{Eq. (5)}$$

CHAPTER 4: RESULT AND DISCUSSION

4.1 XRD Analysis

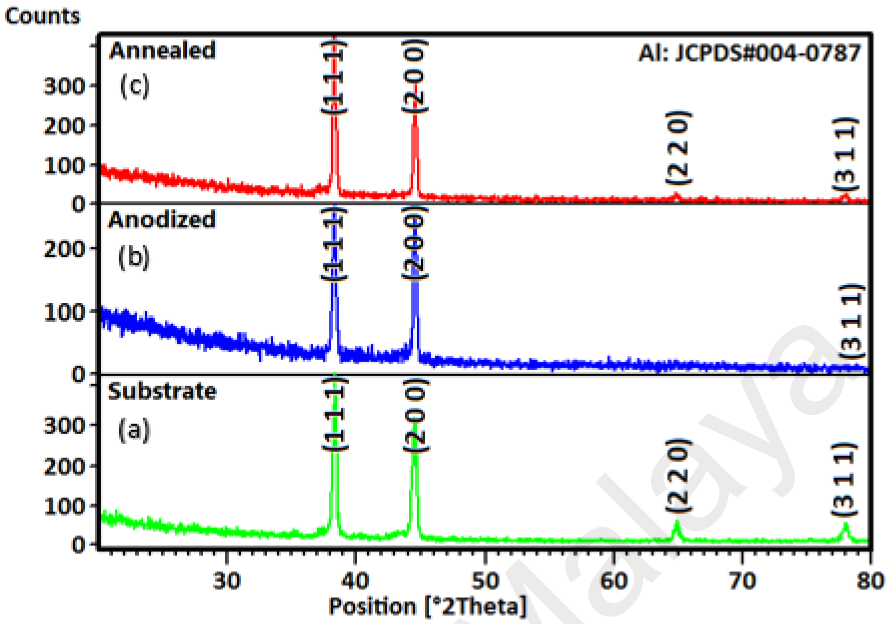


Figure 4.1: XRD profiles of the (a) substrate, (b) anodized sample and (c) annealed sample 450 degree C for 1.5 hour

Figure 4.1 display the XRD profile of substrate (AA 5052), anodized sample and annealed sample at 450˚C. As can be seen in fig 4.1 (a), XRD reflection of substrate illustrated at diffraction peak of Al: JCPDS#004-0787 located at 2θ = 38.1˚, 44.5˚, 64.8˚ and 78.2˚. It representing the plane of (111), (200), (220) and (311) respectively. This peak indicating that Al 5052 have FCC structure. Sharp peaks also indicate high crystallinity of Al 5052 substrate. After 1.0h anodization, the samples is also put under XRD. Thus, through XRD, we only able to see three peaks at fig 4.1 (b) located at 2θ = 38.1˚, 44.5˚ and 78.2˚. The peak appear at almost same angle. Due to very thin and irregular arrangement, the peak eventually is reflecting the Al 5052 rather than nanoporous layer itself. However, loss of intensity as peak number of pure substrate is more than 300 count numbers but for anodized peak is detected less than 300 count numbers indicating the nanoporous layer is successfully build.

Then, the sample was annealed at 450˚C for 1.5 hour, produced peak located at 2θ = 38.1˚, 44.5˚, 64.8˚ and 78.2˚. It representing the plane of (111), (200), (220) and (311). The nanoporous layer is properly arranged their formation to more compact cell structure arrangement. Their peak intensity also better compare to anodized sample. Even though there are nanoporous layer fabricated on the substrate, it able to reveal their crystallinity and comparable to the pure AA 5052 substrate as both able to produce 4 peak during XRD test.

Based on XRD result, we can conclude that anodized layer successfully fabricated after anodization. Along the XRD test, it is found that aluminium is the main phase of either after anodization or annealing.

4.2 Microstructural Study of Nanoporous Array after Anodization

Figure 4.2 and figure 4.3 FESEM images of AA5052 top view before and after anodization. Before anodization, we could found that there are uniform rough surface area with minor line tracing probably arise from polishing and cleaning activities. No pores are present. AA 5052 was being well blended without any indication of defect and impurities found. No protective coating also observed along the samples. However, based on 100,000x magnification using secondary electron, we could found nanoporous layer after anodization process. These pores of approximately 5-10nm diameter was eventually distributed evenly at the whole sample surface. Some of the nanoporous layer have length about 50nm.

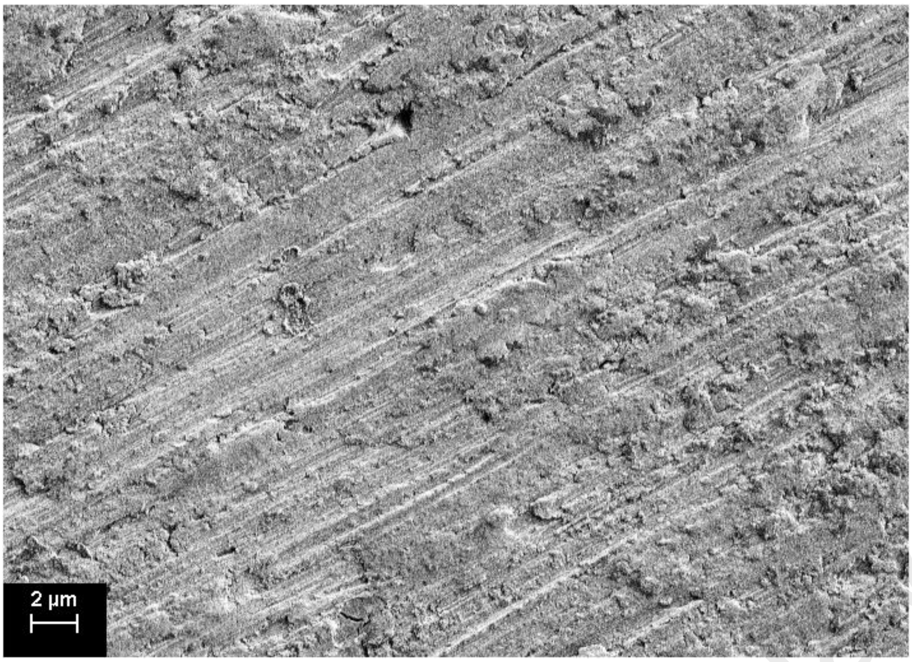


Figure 4.2: Top view of bare AA5052 substrate

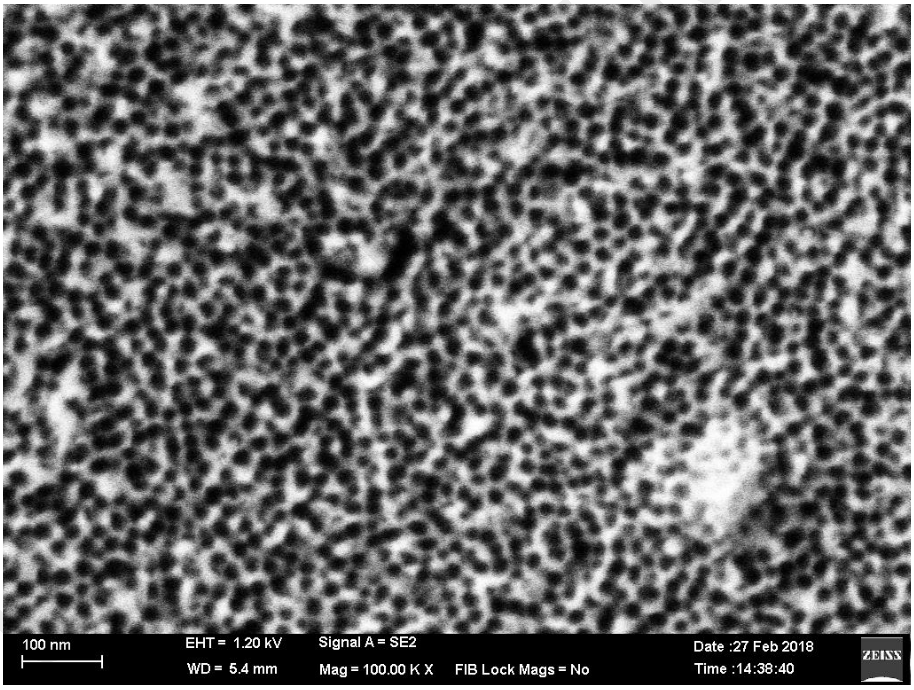


Figure 4.3: Top view of anodized AA5052

Further observation then conducted at site view of nanoporous layer. Thickness of anodization layer is quite significance.

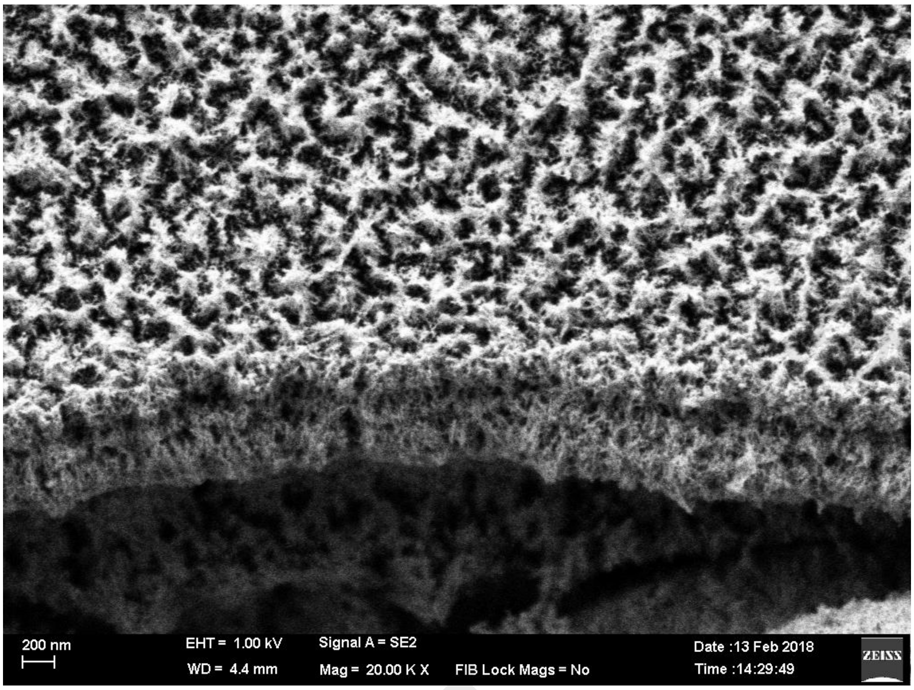
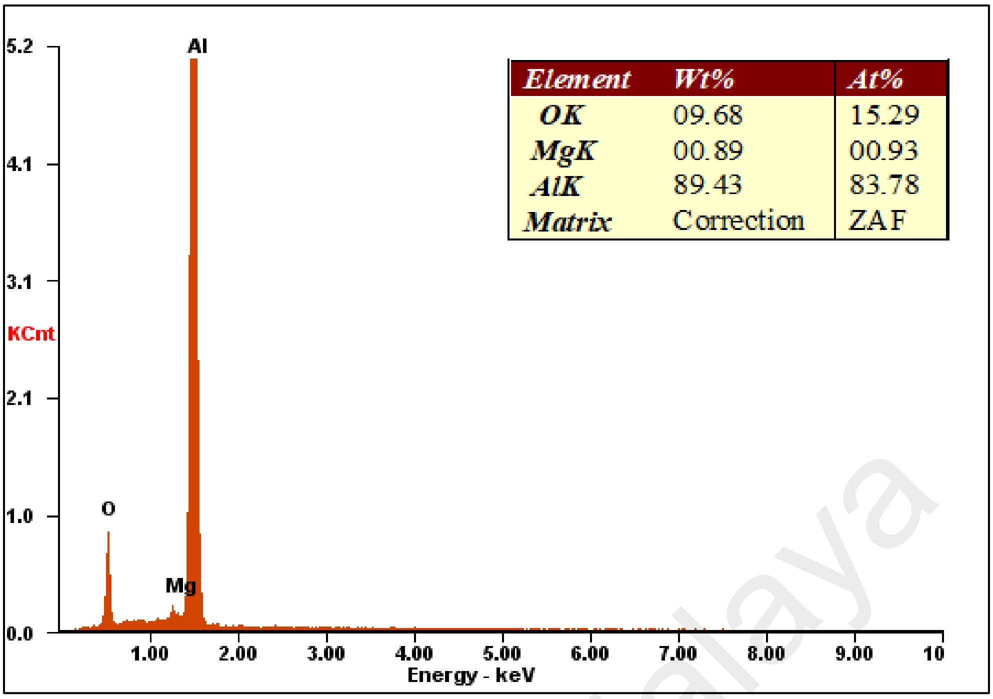


Figure 4.4: Cross section images of Al_2O_3 nanoporous array anodized at 60 minutes at 12V

As per figure 4.4, it is estimated of at least 500nm thickness had distribute evenly at the whole aluminium substrate area. It is quite good achievement where most of researcher were able to produce between 150nm – 300nm. This is contributed by appropriately choose the parameter and condition of anodization process. Most of previous study recommending to conduct anodization at 30˚C. Lower temperature will hindering the growth of nanoporous layer while higher temperature will cause blocking effect as per discussed in literature. Good nanoporous formation also contributed by the voltage supply as well as concentration and type of electrolyte use. This nanoporous layer basically will improve corrosion protection and will discuss further in next parts.

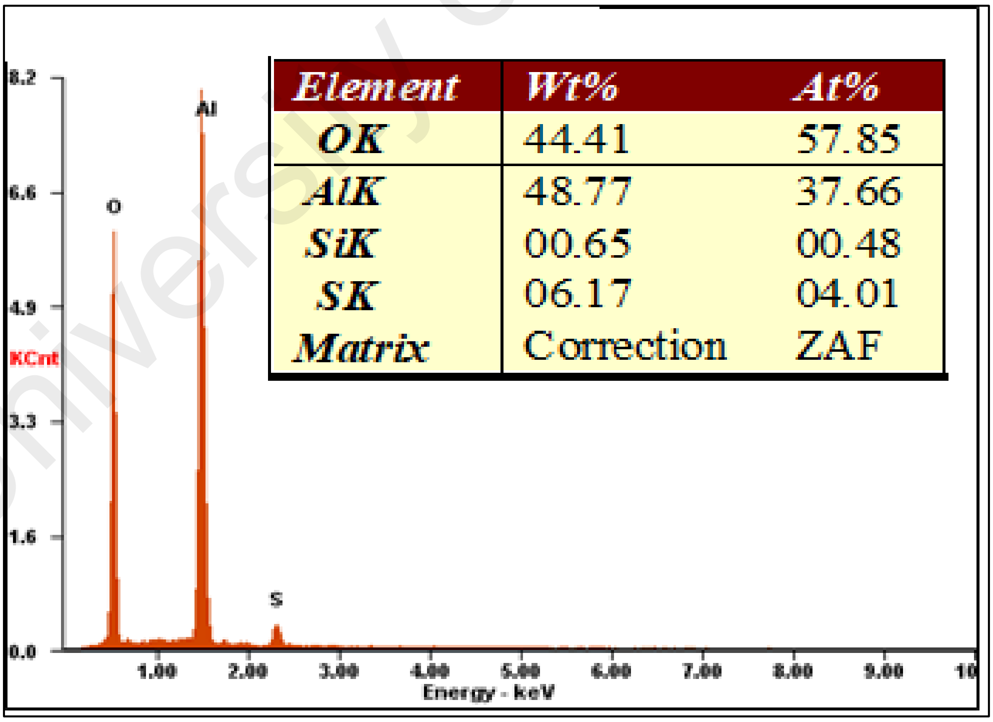
On the other hand, high aluminium content at the surface of sample is confirm through EDX testing as per figure 4.4 (a). 89.43% of aluminium is present. AA5052 also verified through EDX where magnesium of 0.89% was found while no other alloying element was found. On top of that, 9.68% oxygen also present in the aluminium substrate before anodization. Oxygen content basically the an oxide layer which naturally produce to prevent AA 5052 from corrosion. We could say that AA sample is purely aluminium 5 series and it production is almost perfect since no other element were capture by EDX. Meanwhile, after anodization, percentage of aluminium was drop tremendously as illustrated in figure 4.4(b). This is because aluminium had react during anodization and becoming aluminium ions. It react with oxygen which present in electrolyte and forming aluminium oxide layer which also known as anodization layer.

Due to that, we could see number of oxygen increase from 9.68% to 44.81%. Amount of Sulphur found also quite significance. This is by product of anodization process since the electrolyte use was 15% H_2SO_4. We could conclude that after anodization, the peak produce is belong to nanoporous layer which produce due to interaction of electrolyte and electrode inside control environment.



Element	Wt%	At%
OK	09.68	15.29
MgK	00.89	00.93
AlK	89.43	83.78
Matrix	Correction	ZAF

Figure 4.5: EDS for pure AA5052 substrate



Element	Wt%	At%
OK	44.41	57.85
AlK	48.77	37.66
SiK	00.65	00.48
SK	06.17	04.01
Matrix	Correction	ZAF

Figure 4.6: EDS for Al_2O_3 nanoporous array after anodization

4.3 Adhesion Strength of Al_2O_3 Nanoporous Array and Heat Treated Al_2O_3Nanoporous Alloy

Scratch test use indenter in order der to measure the adhesion strength of anodized layer and substrate. Result of the test found that nanoporous layer at anodized sample fail after travel at 412.75µm. It travel much shorter distance compare to annealed sample which fail at 575.11µm. Optical microscopy in figure 4.7 and figure 4.8 use to measure and confirm the indenter distance travel before failure. Failure point is identify based on delamination occur observed at each sample. In this case annealed sample able to travel 39% higher compare to anodized sample.

Base on methodology, the load were increased gradually 9.2 mN s^{-1}. In other word, the longer distance travel, the higher load applied. Since failure distance of annealed sample is higher, it directly indicate that it also has higher failure load compare to anodized sample. Based on table 4.1, anneal sample failure load is 1,990.24mN while 1,250.45mN. In term of percentage nanoporous layer at anneal sample can hold 37% higher load compare to anodized sample. This test clearly indicating that mechanical properties of nanoporous layer was improved by annealing process for 1.5 hours at 450˚ C. Failure load and failure distance data also test us that the equipment test is reliable with acceptable deviation of 2% since their percentage ratio is almost similar.

Table 4.1: Summary of adhesion test for anodized and annealing AA 5052 samples

Sample	Anodized AA5052	Annealing AA 5052
Failure Distance (µm)	412.75	575.11
Failure Load (mN)	1250.45	1990.24
Friction (µm)	~989.00	~1380.00
Coefficient of Friction	~0.79	~0.69
Scratch Hardness ($\frac{8P}{\pi w^2}$)	9.68 MN/m²	15.32 MN/m²

Annealing at 450˚C eventually bind the nanoporous layer to aluminum substrate. It improve the surface energy between nanoporous layer and aluminum alloy substrate. Based on methodology, we could find scratch hardness number of these samples. Scratch hardness of anneal sample is 18% higher than anodization sample due to increase of nanoporous size. Nanoporous in anodization sample is align closely which make them have more resistance to scratch. The summary of adhesion strength and scratch test could be refer at figure 4.7, figure 4.8 and table 4.1.

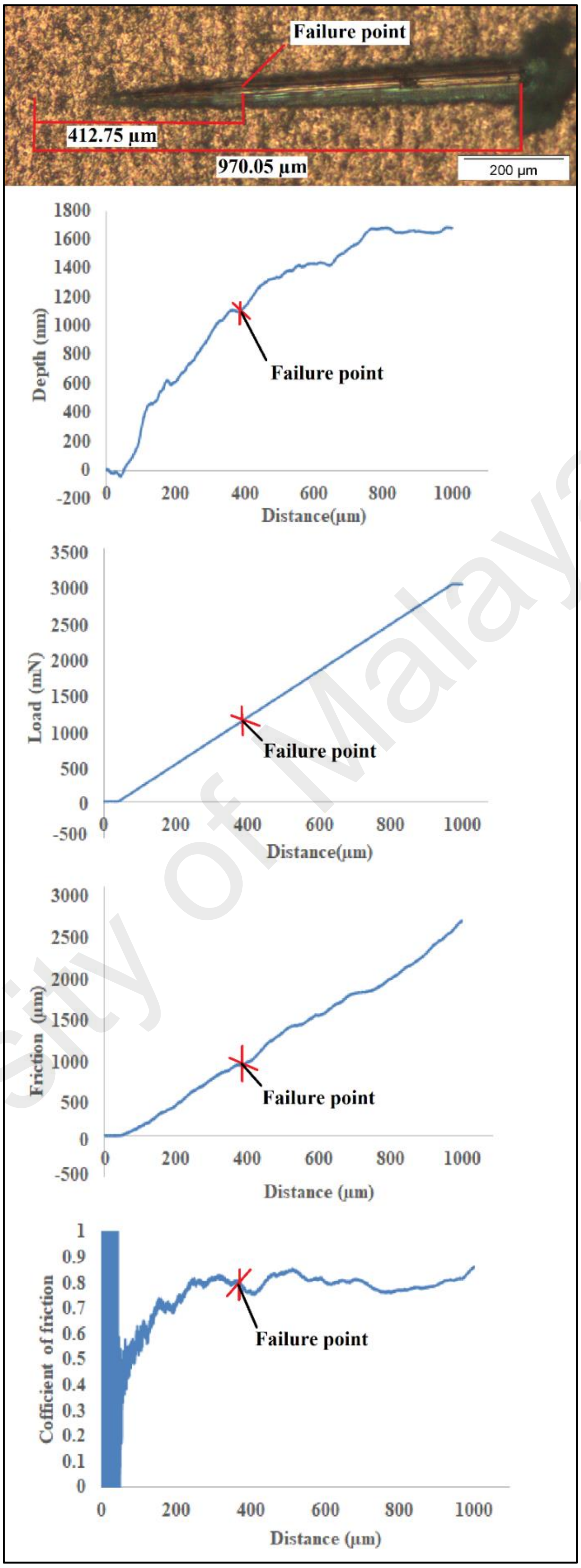


Figure 4.7: Scratch test data for anodized sample

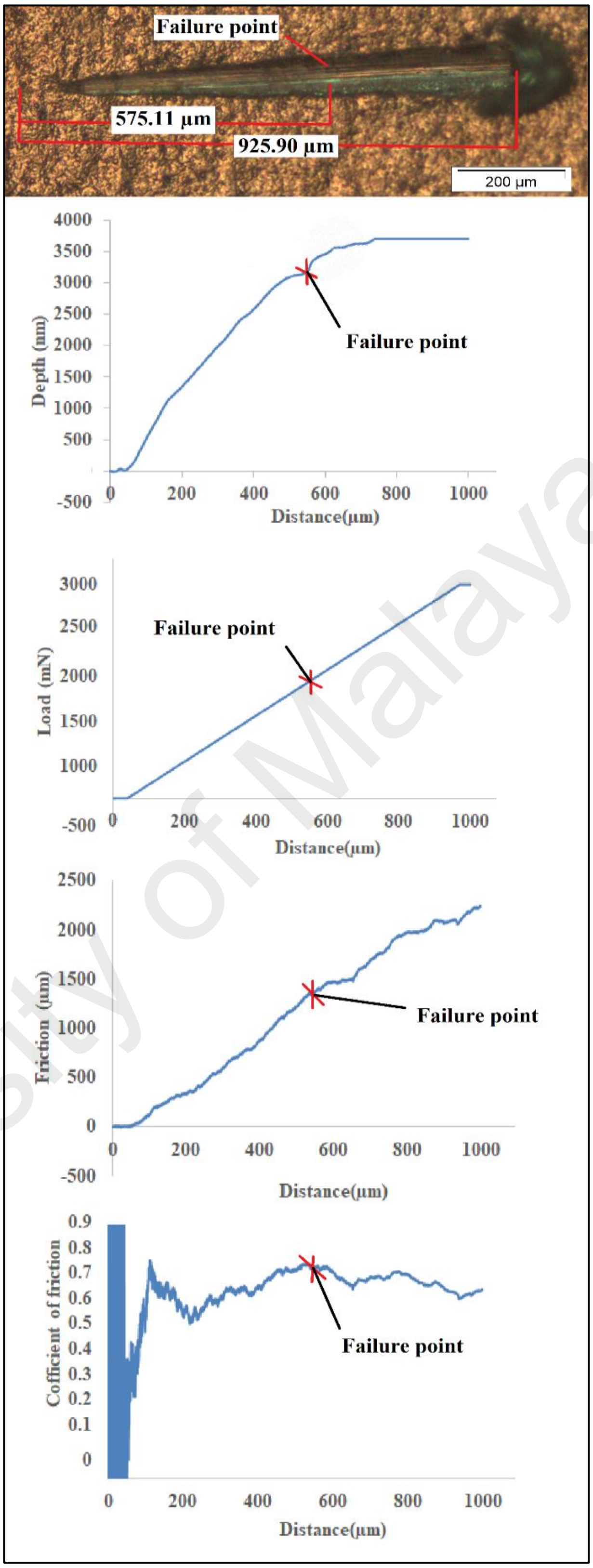


Figure 4.8: Scratch test data for annealed sample

4.4 Vickers Microhardness

Main objectives of Vickers Microhardness test is to verify the quality of nanoporous layer produce after anodizing and annealing. The substrate of AA 5052 produce 50.5 HV. After anodizing, their hardness increase to 85.3. The increase in hardness show the effect of nanoporous which contribute to the enhancement of mechanical properties of substrate. However, high hardness will lead to brittle effect.

Thus, in order to improve nanoporous structure, annealing is conducted in order to reduce the hardness. It occur because sufficient temperature during annealing resulting residual stress to release and binding nanoporous to substrate become better. After heat treated at 450˚C for 1 hour, their hardness decrease to 60.7HV. Even though it has lower hardness, the nanoporous layer is well blending with the substrate and their mechanical properties in term of ductility and adhesive strength proven to be improved. On top of that, sensitization effect also is minimum since the hardness recorded by anneal sample is higher than substrate. Figure 4.9 is the summary of the Vickers Microhardness conducted for AA 5052 substrate, anodizing sample and annealing sample.

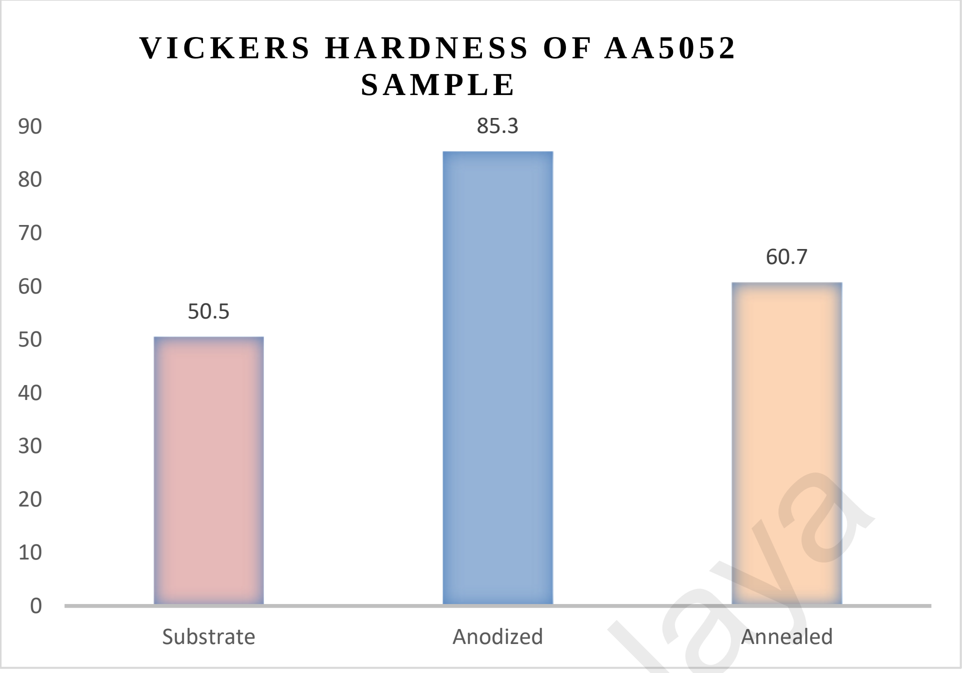


Figure 4.9: Data of Vickers hardness test for AA5052 samples

4.5 Effectiveness of Corrosion Protection

In general, corrosion will occur by anodic reaction (metal A is oxidized and releasing electron) and cathodic reaction (metal B is reduce and removing electron). The rate of both reaction is then measured.

In this study, all sample (bare substrate, anodized sample and annealed sample) were tested in artificial sea water in order to study their corrosion susceptibility. Result of bare substrate of AA5052 becoming the reference. Based on testing, data of E_{corr}, I_{corr}, sample density and sample weight were recorded. On top of that, corrosion rate and corrosion efficiency also calculated. All the observation and calculated result was tabulated in table 4.2.

Table 4.2: Corrosion data for AA5052 samples

AA 5052	Substrate	Anodized	Heat treated
E_{corr} (V_{SCE})	-725.063	-725.345	-796.711
I_{corr}, (µA/cm^2)	9.441	5.657	1.116
Sample Weight (g)	1.87	2	2
Density (g/cm³)	2.68	3.95	3.95
E.W (g)	9	17	17
Corrosion Rate	4.12 x 10^{-6}	3.16 x 10^{-6}	0.624 x 10^{-6}
P.E (%)	-	40.08	88.17

E_{corr} basically is tell information on tendency of materials to corrode. The more positive the E_{corr} value thus, it is susceptible to corrosion (anodic behaviour). The presence of nanoporous layer slightly assist to reduce anodic behaviour of AA5052 substrate. However, the anodic behaviour of aluminium is further improved when substrate of anodized being annealed at 450˚C for 1.5 hour. Meanwhile, I_{corr} provide information on effectiveness of corrosion protection. The lower the I_{corr}, will lead to less attack from corrosion agent which then reduce the corrosion rate. Base on table 4.2, I_{corr} of substrate is 9.441 µA/cm^2. This value is very much higher compare to anodized and annealed sample which is 5.657 µA/cm^2 and 1.116 µA/cm^2.

Result in table 4.2 was verified by polarization plots in figure xxx. Polarization curve clearly draw that annealed sample demonstrate very stable nanoporous layer. It indicate by lowest I_{corr} values among the other samples. However, anodized nanoporous itself sufficient to produce tremendous improvement on AA502 substrate corrosion resistance properties.

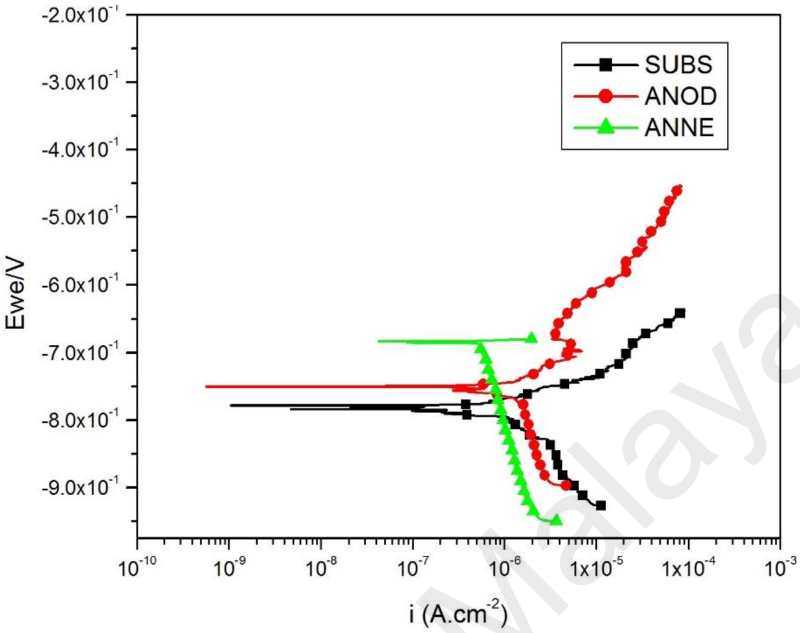


Figure 4.10: Polarization curve for AA5052 substrate

Base on result, corrosion rate is reduced significantly. AA5052 bare substrate undergoes rate corrosion as much as 4.12 x 10^{-6}. The presence of nanoporous layer able to reduce to 3.16 x 10^{-6}. Through heat treatment and annealing process, properties of nanoporous is enhanced, corrosion rate is further reduce to 0.624 x 10^{-6}.

This is an argument where anodizing and annealing process assisting aluminium alloy in improving surface energy and surface area of substrate through emergence of nanoporous layer which directly reduce their corrosion tendency. The great difference corrosion rate between anodized layer and annealed layer could be related to homogenization effect. Anodized specimen which treated with sodium benzoate (to promote homogeneity in nanoporous) found had better level of polarization resistance (Huang, Li, Xiao, Huang, & Ren, 2016). Thus, through this study, homogeneity effect actually contributed by annealing process. It is proven that anodized samples has higher corrosion rate compare to anneal samples.

4.6 Surface Wettability

Water contact angle (WCA) is indicator to differentiate degree of wettability. Large contact angle associated to the poor capacity of surface to be coated by liquid. This project compare the pure Aluminium 5052 substrate wettability characteristic to mechanism of wettability of surface treated aluminium.

Poor wettability is observed when a drop of ionized water interact with pure aluminium, WCA observed is at 92˚. Presence of nanoporous layer after anodization had tremendously improve wettability where interaction of deionized water and anodized aluminium 5052 had produce 35.9˚ WCA. Aluminium 5052 becoming almost perfect hydrophilic characteristic where WCA becoming 13˚ after heat treated at 450˚C. This is contributed by formation of higher ordered of crystalline nanoporous. On top of that, it due to the size of nanopores after annealing is much smaller, deeper and thicker after anodization. These two factor mainly modify the state of interaction between aluminium oxide layer, anodized aluminium and deionized water becoming better. Illustration of wettability test is summarize in figure 4.11.

This pattern basically applicable to other series of AA. This finding is parallel to Rodriques *et al.* study where nanoporous enhancement basically increase the nanoporous layer and the turn the aluminium alloy into superhydrophilic. During at anodization of AA 6016 in H_2SO_4 electrolyte, it produce 45˚ before being enhance by second step anodization and produce 20˚ WCA (Rodriques, Alves, Cavaleiro, & Carvalho, 2017). All in all, intermetallic precipitate that growth have great impact to wettability of the samples. In this case Al_2O_3 nanoporous had affect wettability of AA 5052 anodized and heat treated samples.

Some researcher might question on how wettability is related to corrosion. Obviously most researcher looking for hydrophobic property rather than hydrophilic in order to reduce corrosion rate. Basically, the hydrophilicity is referring to nanoporous layer, not the aluminium alloy. Ability to have good adhesiveness with fluid (water or oil) might extend the application of AA5052 as engineering materials either in automotive, aeronautic or semiconductor.

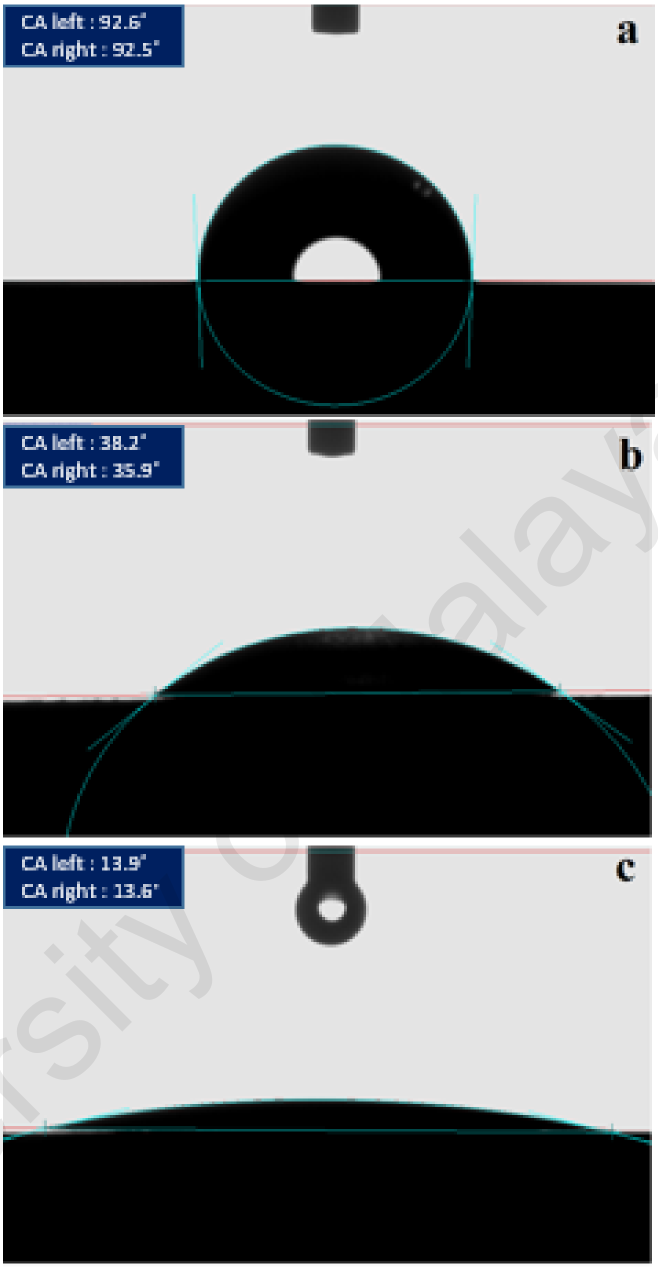


Figure 4.11: Wettability of (a) bare AA 5052 substrate, (b) anodized sample and (c) heat treated sample

CHAPTER 5: CONCLUSION

In this work nanoporous layer of Al_2O_3 was successfully developed through anodization method. 15% wt of $H_2SO_4$of electrolyte was used at 12V for 1 hour. Through FESEM, we found 500nm nanoporous layer thickness was evenly distributed on the substrate. Then, nanoporous layer was enhanced through heat treatment process at 450˚C for 1.5 hour.

The property of nanoporous layer was investigate through characterization, adhesive test, hardness test, corrosion study and wettability study. Nanoporous of at least 10 nm was observed through FESEM after anodization process. On the other hand, adhesive strength of nanoporous layer were improved through heat treatment process where critical load from 1250.45 mN for anodized sample reached to 1990.24 mN for heat treated sample. It directly tells that surface energy of nanoporous and substrate increase during heat treatment.

On top of that, this study show that hardness could be improved through anodization. HV value for anodize sample are 85.3HV compare to 50.5 for pure substrate The ductility of anodized AA5052 then improved also through heat treatment where it optimized to 60.7. Corrosion behaviour of AA5052 also becoming better after anodizing and subsequent process of heat treatment. Nanoporous after anodized providing 40.08% efficiency of corrosion while heat treatment process provide more than double efficiency which is 88.17%. The wettability of AA5052 also improving after anodization and heat treatment where the contact angle reduce from 93˚ to 33˚ and finally to only 13˚.

All in all, this work achieve their objective to fabricate nanoporous layer on AA5052 through anodization process. Their properties also improving after surface treatment compare to bare substrate.

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