CATHODIC PROTECTION OF ALUMINUM COMPONENTS OF ARMOURED AMPHIBIOUS VEHICLES IN MARINE ENVIRONMENT

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ABSTRACT

CATHODIC PROTECTION OF ALUMINUM COMPONENTS OF ARMOURED AMPHIBIOUS VEHICLES IN MARINE ENVIRONMENT

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Usually, hull of amphibious vehicles which are constructed from aluminum alloys, working in both land and seawater, need to be protected against corrosion. Although aluminum alloys are considered as good choice for corrosion resistance, long term service life observations reveals that even aluminum alloys are corroded in Cl^- containing environments. Cathodic protection is one of the common methods to protect structures that are immersed in electrolyte. The materials that are used in the construction of this vehicle were subjected to polarization tests to characterize electrochemical properties. Furthermore, salt spray fog tests were applied to observe corrosion resistance of the metals. Alternate immersion tests were applied to both sacrificial anodes attached and unattached specimens to observe the benefits of protection. Finally, cathodic protection applications to the vehicle were simulated with the help of the COMSOL software.

Keywords: corrosion, aluminum, cathodic protection, sacrificial anode, computer modeling, polarization tests

ÖZ

ZIRHLI AMFİBİK ARAÇLARDA ALUMİNYUM PARÇALARIN DENİZ SUYUNDA KATODİK KORUMA UYGULAMASI

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Çoğunlukla aluminyum alaşımlarından gövdeye sahip, kara ve denizde çalışma özelliği olan amfibik araçların korozyondan korunmaları gerekmektedir. Aluminyumun korozyona karşı olan direnci bilinmesine karşın uzun dönem araçlarda yapılan gözlemler göstermiştir ki aluminyum da özellikle Cl^- içeren ortamlarda korozyona uğramaktadır. Bir elektrolit içersindeki yapıların korozyondan korunması için katodik koruma uygulaması sıklıkla kullanılan yöntemlerden birisidr. Bu kapsamda araçta kullanılan aluminyum alaşımları polarizasyon testlerine tabi tutulmuş ve elektrokimyasal özellikleri incelenmiştir. Ayrıca bu alaşımların korozyon direncini görebilmek adına bir çeşit hızlandırılmış korozyon testi olan tuz sisi testi uygulanmıştır. Katodik korumanın etkisini görebilmek adına ise hem kurban anotlu hem de kurban anotsuz test plakaları döngüsel daldırma testlerine tabi tutulmuştur. Son olarak araç modeli üzerinde katodik koruma simulasyonu COMSOL yazılımı kullanılarak yapılmıştır.

Anahtar Kelimeler: korozyon, aluminyum, katodik koruma, kurban anot, bilgisayar modellemesi, polarizasyon testleri



To my family

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CHAPTER 1

INTRODUCTION

Aluminum is one of the most preferred metal for the production of military land vehicles due to its superior properties like high corrosion resistance, low density and relatively good mechanical properties etc. which are given in more detail in the following section [1]. Although, they provide good resistance to atmospheric corrosion, their seawater corrosion resistance due to alloy itself or due to the galvanic couples formed in the electrolyte may cause severe corrosion related problems. As known, corrosion related losses are important burden on county's economy. Usually the life expectancy of the military land vehicles is around 30 years. This makes the corrosion protection far more important for those vehicles and especially for amphibious military vehicles.

An amphibious vehicle as given in Figure 1 can travel both on land and at sea or river. This makes matters more complicated in terms of corrosion protection but at the same time it reveals the fact that corrosion protection is a design issue that must be tackled from various aspects taking into account changing service conditions during the useful lifetime of the vehicle.

In this study, our aim was to design, optimize and validate a cathodic protection system, which is one of the most common corrosion protection methods employed for structures in direct contact with electrolytes such as seawater and soil. The efforts were concentrated on amphibious military vehicles that are working in seawater in the present case.



Figure 1. Photograph of an amphibious military vehicle [2]

In the simplest sense, cathodic protection is making a structure cathode of a corrosion cell. By making the structure cathode, cathodic protection protects the desired structure from corrosion in the electrolyte. In other words, it is called cathodic protection once the structure which is to be protected is acting as an anode in the corrosive environment (electron provider or oxidized) is converted into a cathode (taking electron, or reduced) by means of attaching an electrochemically more active metal or the electron source to the structure. In this way, even if the structure is unpainted and uncoated, corrosion of the structure is stopped and the structure is protected from corrosion if there are sufficient numbers of such electron sources or anodes more or less evenly distributed on the structure. In situations where paint/coating is applied, cathodic protection will act as a safety valve against the possibility of scratches on the paint/coating, and corrosion protection of the relatively anodic areas of material will thus be achieved [3].

Although cathodic protection is widely used in water, oil or chemical tanks, ships, and pipelines, its application to military vehicles is relatively restricted. To name a few examples, AAAV – The Advanced Amphibious Assault Vehicle was designed for the use of USMC (United States Marine Corps). AAAV is one of the vehicles

that features a cathodic protection system with ample testing and validation activities reported in open source literature [4]. The hull structure of this vehicle was constructed from 2519 series aluminum alloy. There is no wide information about the corrosion behavior of this alloy in seawater. To this end, USMC has conducted various tests on this alloy to observe its corrosion characteristics. Those tests were comprised of two stages. In the first stage, corrosion resistance of the 2519 alloy was investigated by alternating immersion tests. In the second stage, various sacrificial anodes were attached to 2519 specimen and the efficiency of these anodes together with prevalent corrosion mechanisms on unprotected specimen were recorded. The Figure 2 given below represents the alternate immersion tests of the stage one.

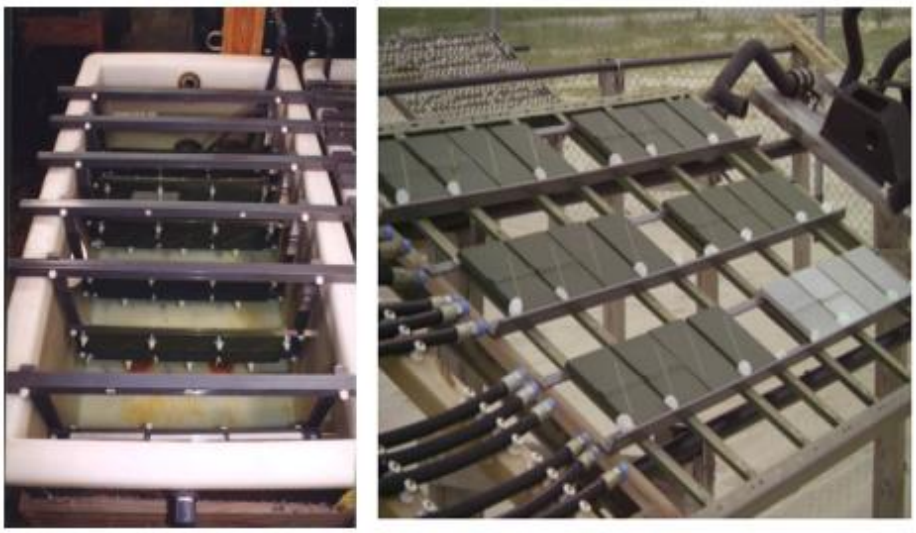


Figure 2. Photograph of US NAVY AAAV vehicle corrosion tests stage 1

Figure 3 given below shows the results of the stage 2. There are three different cases represented. Blisters around the scribe were observed on the specimen that is subjected to alternating immersion test without cathodic protection. However, cathodically protected specimen subjected to alternating immersion test is free of blisters or any other corrosion related problem. Alternate immersion test shows the efficacy of applying cathodic protection even in a cyclically changing environment (with wet-dry cycles) such as experienced by amphibious military vehicles.

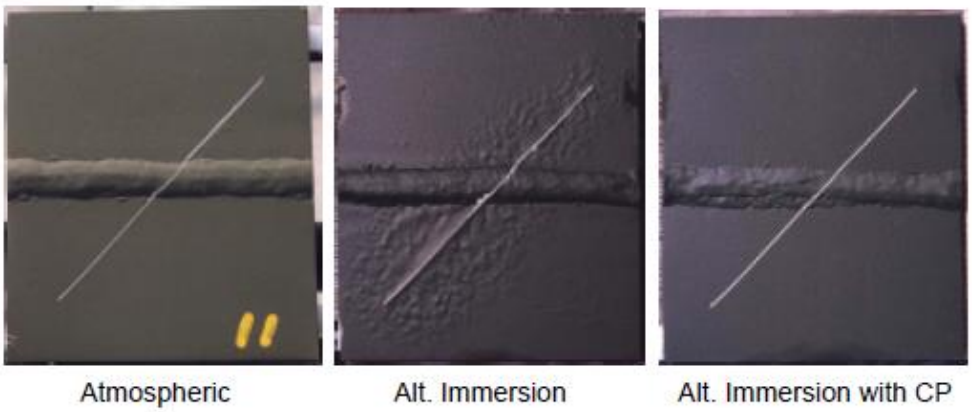


Figure 3. Photographs of US NAVY AAAV corrosion tests stage 2

The cathodic protection of AAAB – Armored Amphibious Assault Bridge Vehicle of FNSS Defense Systems Inc. was investigated in this study. This vehicle was designed and built for Turkish Armed Forces to be used in rivers and lakes. Hull of the vehicle was produced from 5000 series aluminum alloys due to their superior corrosion protection, good weldability and also relatively good mechanical properties. However, the vehicle was also required to be operated near seaside and hence, a need was arisen for corrosion protection in seawater environment. This operation environment resulted in corrosion of the vehicles at a higher rate than expected in fresh water conditions. It was not possible to adopt modifications on the vehicles that comprise improvements in coating quality by simply taking into account the characteristics of the environment. Because the design process was frozen, the vehicles were already produced and they were in service. Therefore, for additional corrosion protection in seawater, adopting a cathodic protection system was deemed the more appropriate solution. To this end, various 5000 series aluminum alloys used in manufacture of the vehicle hull were electrochemically characterized, test coupons simulating the operating environment were prepared, accelerated corrosion tests on these coupons were conducted, the performance of the vehicle after cathodic protection was monitored, cathodic protection simulations were performed using Comsol Multiphysics software package, and finally real life observations were compared with the results of the model.

CHAPTER 2

LITERATURE REVIEW

2.1 Aluminum Alloys and Their General Behaviors

Aluminum is the most widely produced nonferrous alloy in the world and its consumption is increasing continuously since it has various distinctive properties such as:

- Low density
- Thermal and electrical conductivity
- Corrosion resistance
- Lots of alloying options
- Variety of semi-products

One of the impressive properties of aluminum is its low density. Its density is 2700 kgm^{-3} where steel has nearly three times higher density. If one takes into account the specific strength (that is strength/density), aluminum alloys gain a considerable advantage over steel in many structural applications. For this reason, there are lots of applications that employ aluminum due to its lightweight. For example, transportation industry has been using aluminum since the early 1900s [5].

Since the end of the 19^{th} century, its use has been increasing due to its lightness, relative corrosion resistance and other superior properties such as heat conductivity. With the help of these advantages, one of the first applications for aluminum alloys was a kitchenware product. Nowadays its use is not restricted to kitchenware, but they are very widely used as heat exchangers in cars, refrigerators, air conditioning, etc. In 1900s, aluminum alloys even began to replace copper in some applications due to their better electrical conductivity.

19^{th} century chemists observed that aluminum has good resistance to atmospheric corrosion; they also found that aluminum has a very good corrosion resistance while

it is directly in contact with water. Aluminum and its alloys, 1000, 3000, 5000, 6000 and 8000 series have very good resistance to corrosion in marine, urban and industrial atmospheres. This property provides also long service life, minimal maintenance, and long lasting initial appearance. Also surface treatments like anodizing enhance the corrosion resistance of aluminum and provide cosmetically better-looking finish.

There are 8 different series of aluminum with unique properties. For example 5000 series aluminum has good corrosion resistance and they are weldable. However, 2000 series is considered non-weldable and their corrosion resistance is lower although they have better mechanical properties.

Many aluminum alloys can be produced by rolling, extrusion and casting with different range of semi-products, which provides ease for designers and manufacturers [5]. Aluminum alloys mostly contain copper, manganese, silicon, magnesium, and zinc. Alloys of the aluminum are described by four digit notations where the first digit indicates the main alloying element. To get the desired mechanical properties and improve the other properties such as corrosion resistance, these alloys need to go through a thermal processing, namely tempering or aging.

Tempering process is categorized into three basic groups and symbolized by three different capital letters, namely, F, O and H according to EN 515 standard. For example, if the aluminum is used as wrought, then the letter F is used and it means that the mechanical properties are not guaranteed. Letter O is used for annealed alloys and if it is strain hardened, then the letter H is used [6].

Strain hardening of aluminum is designated by 2 or 3 digits. The first digit coming after letter H describes the basic process that is applied to alloy.

- H1X: Strained hardened only
- H2X: Strain hardened and partially annealed
- H3X: Strain hardened and stabilized by a low-temperature heat treatment

The second digit represents the degree of strain hardening. Hard temper is indicated by the number 8 while quarter hard indicated by letter 2 and letters 4 and 6 are used for half and three-quarters hard temper respectively.

2000, 6000, and 7000 series aluminum alloys are age-hardenable alloys. With the application of the below processes those alloys may have the maximum mechanical properties.

- Heating the alloy to a specific temperature, termed as solutionizing temperature, in order to dissolve alloying elements.
- Quenching the alloy rapidly.
- Aging the alloy. There are two types of aging; if it is performed at 20 ^{o}C (i.e. room temperature), this process is called natural aging, and if it is performed at elevated temperatures, around 100-200 ^{o}C, then this process is called artificial aging.

Letter T is used to designate age hardenable alloys. Letter T is followed by one to five digits as defined in standard EN 515. Some of the most common temper designations are given below.

- T1: Natural aging
- T3: Solution heat treatment, strain hardening and natural aging
- T351: Solution heat treatment, controlled stretching, and natural aging
- T4: Solution heat treatment, and natural aging
- T5: Artificial aging, and extrusion
- T6: Solution heat treatment, and artificial aging
- T8: Solution heat treatment, strain hardening, and artificial aging

1000 series aluminum is commercial purity alloys. Refined alloys such as 1199 alloy have purity more than 99.90 percent. Refined 1000 series alloys are used to manufacture condensers, lightning devices, and decorative applications. 1050 alloy has level of purity more than 99.50 percent.

2000 series alloys have copper as the main alloying element and have some amount of magnesium and silicon to achieve formation of desired precipitates during aging.

T6 tempers of this alloy provide good mechanical strength. T4 tempers have low crack propagation rate. Their heat resistance is good and ease of machining is another advantageous property of this alloy.

3000 series alloys have manganese as the main alloying element. Manganese improves the mechanical property of the aluminum. 3003 is the most common alloy. Addition of 0.20 % copper even increases its mechanical properties further. This alloy is preferred for its good atmospheric corrosion resistance and because of this extensively used in construction sector as cover panels for buildings.

Main alloying element of 5000 series aluminum is magnesium. These alloys provide relatively good mechanical properties. As the amount of magnesium increases, mechanical properties increase further. 5000 series aluminum alloys cannot be heat-treated but mechanical properties can be enhanced through solid solution strengthening. These alloys have good weldability and they also provide superior corrosion resistance whether used in welded fabrications or standalone components. Alloys 5086 and 5083 have become popular in marine applications due to their superior marine environment corrosion resistance. Those alloys have magnesium about 3.5 to 5 % and also some amount of manganese and chromium. These alloying elements provide further increase in mechanical properties.

6000 series of aluminum alloys contain magnesium and silicon as main alloying elements. These alloys also have good atmospheric corrosion resistance. They have good mechanical properties and this property can be even improved with the addition of silicon. They provide good cold formability and they have good surface appearance after anodizing. Their weldability is considered good although they suffer considerable loss in fatigue strength in the weld area compared to 5000 series welded joints.

7000 series alloys are divided into two, as alloys with copper and without copper.

- 7000 series without copper: 7020 is the most common alloy that is widely used in the fields of transportation, mechanics industry, and armaments. T5 or

T6 conditions provide mechanical strength in the order of 360 – 400 MPa. These alloys can be arc welded with a suitable filler metal. However, these alloys are prone to exfoliation corrosion in the heat-affected zone. This behavior of the alloy limits its use after welding. These alloys have satisfactory corrosion resistance unless welded.

- 7000 series with copper: Copper is added to aluminum-zinc-magnesium system. T73 or T76 tempered alloys can resist very aggressive environments however this process results in about 20 % drop in mechanical properties. 7075 is the most common alloy of this series and they are preferred by the field of aerospace, mechanics, sport and leisure. 7049 alloy is the most common aluminum alloy with the best mechanical properties in T6 temper.

7000 series have superior mechanical properties however their corrosion properties are not as good as 5000 series. Thus, these alloys are generally coated with 1000 or 6000 series aluminum alloys. This process is called as Alclad process. This process provides cathodic protection to the 7000 series aluminum. It is also common to deliver these alloys in overaged T7 temper condition, which has improved corrosion characteristics compared to T6 temper.

8000 series alloys are most commonly used as foils. Addition of iron and silicon improves mechanical properties of aluminum and provides very good formability.

Although all alloys have some specific properties, furthermore, all aluminum alloys can be considered to have good corrosion resistance. For vehicles that are working in the marine environment, aluminum alloys are good choices due to their low densities and superior corrosion behaviors of certain grades. Under normal atmospheric conditions a noncoherent passive oxide layer is formed on the surface of the alloy and this provides corrosion resistance [7].

2.2 Corrosion Behavior of Aluminum

With the most common definition, corrosion is a deterioration of a material due to exposure to its environment. This phenomenon can be observed only if the existence of the following 4 elements of corrosion is satisfied; namely, anode, cathode,

aqueous environment, and a metallic conductor between anode and cathode. If any of these elements is missing, then there will be no corrosion observed [8].

During the corrosion process, there are two reactions:

- Oxidation of metal, which means loss of electrons by the corroding metal. Anodic current, $i_{a,}$ flows in the direction from metal to solution due to this reaction. This reaction occurs on the anode and is designated by (-) sign.

$$M \rightarrow M^{n+} + ne^{-} \quad (1)$$

- Reduction of an ion, results in the flow of cathodic current, i_k, in the direction of solution to metal. This reaction occurs on the cathode and designated by the (+) sign.

$$X^{n-} \rightarrow X + ne^{-} \quad (2)$$

For a given natural corrosion system, i.e. there is no external generator connected, both anodic and cathodic reactions take place simultaneously and anodic and cathodic currents are at local equilibrium, so that net anodic and net cathodic currents are equal:

$$\sum i_a = \sum i_k \quad (3)$$

When metal is immersed in an aqueous solution without any power unit connection, this system is called an open circuit cell. That means there is no current transfer from metal to the solution and solution to the metal.

Corrosion of aluminum was an old subject and studied very deeply by many other scientists [9], [10]. As all metals, aluminum is oxidized in aqueous media, and gives electron. Oxidation reaction is given below as:

$$Al \rightarrow Al^{+3} + 3e^{-} \quad (4)$$

This reaction is balanced by reduction reaction. Most of the time aluminum is subjected to media such as fresh water, seawater or atmospheric moisture, where pH is almost neutral. In such a media, there are only two favorable reactions as reduction.

- One of the favorable reactions is reduction of H^+ protons that are produced from the dissociation of water molecules as given below.

$$H_2O \rightarrow H^+ + OH^- \quad (5)$$

$$3H^+ + 3e^- \rightarrow \frac{3}{2}H_2 \quad (6)$$

- Or reduction of oxygen that is dissolved in water.

If the media is alkaline:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (7)$$

If the media is acidic:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (8)$$

Corrosion of aluminum is the result of these two reactions; reduction and oxidation. Thus, total corrosion reaction of aluminum is as follows.

$$Al \rightarrow Al^{+3} + 3e^- \quad (9)$$

$$3H^+ + 3e^- \rightarrow \frac{3}{2}H_2 \quad (10)$$

$$Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2}H_2 \quad (11)$$

or

$$Al + 3H_2O \rightarrow Al(OH)_3 + \frac{3}{2}H_2 \quad (12)$$

Corrosion of aluminum yields alumina, $Al(OH)_3$, which is insoluble in water and has gelatinous look.

Polarization curves are very powerful diagrams to study corrosion. Details regarding how these diagrams are drawn will be explained in detail in the following sections, but a schematic diagram is given in Figure 4. The intersection point of blue and red

lines in the figure gives the corrosion potential, E_{corr} and corrosion current density, i_{corr}.

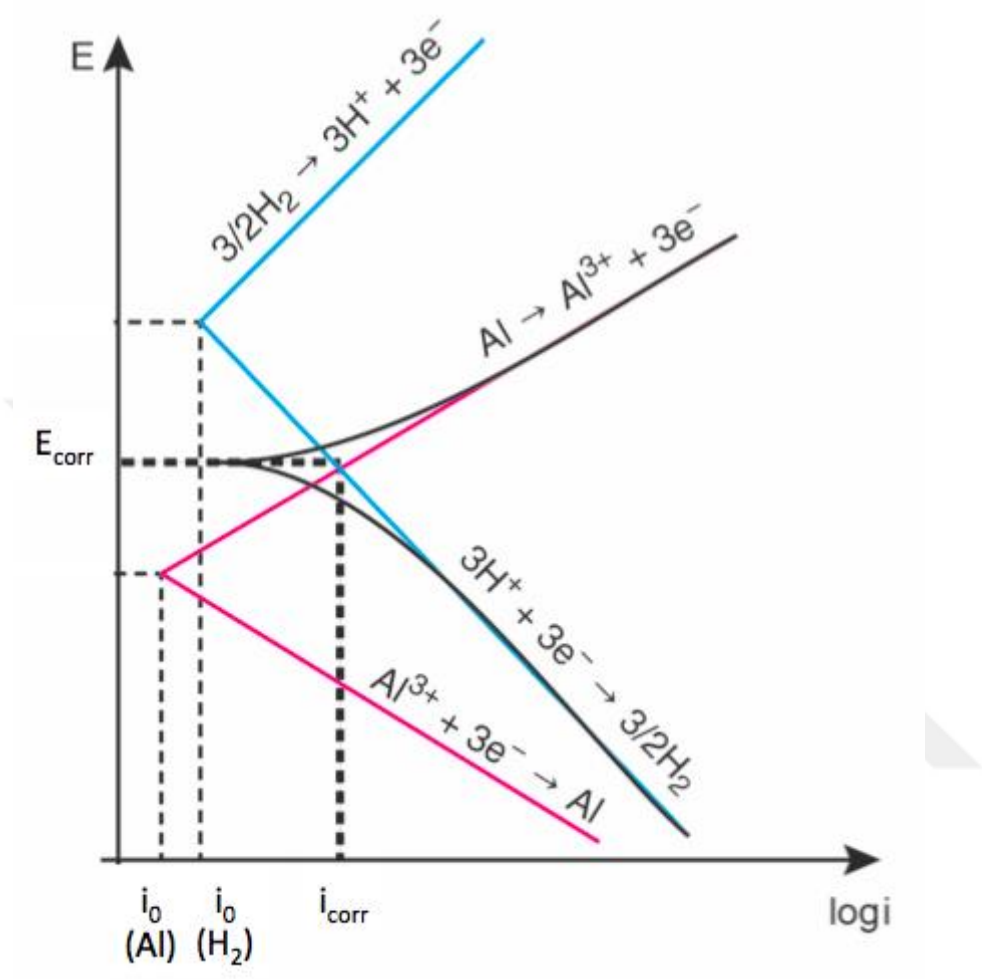


Figure 4. Representative polarization plot reproduced from [5]

Polarization curves provide corrosion potentials and currents. Since this test method is not complicated, scientists commonly use this method for characterizing corrosion behavior of almost all metals including aluminum alloys. However, it is observed that there are some limitations for aluminum while using this method.

The main reason can be explained with the help of the Pourbaix diagrams and Faraday's law. As discussed, Faraday's law gives corrosion current when the mass loss and decrease in thickness is uniform through the surface. Such uniform thickness

decrease can only be achieved by uniform corrosion. However, this is the only case for aluminum when the environment is too acidic or alkaline. Most of the time aluminum alloys are subjected to seawater or natural water, and as Pourbaix diagrams suggest, when the environment is neutral then the corrosion type of aluminum will be pitting corrosion. The oxide film on the surface of aluminum has a major effect on the corrosion behavior of the aluminum. What is more, different aluminum alloys have different corrosion potentials. However, those potentials are not useful to compare their affinity to corrosion. For example, 2000 series aluminum has potential of -650mV while 5000 series has -850 mV. For most of other metals, it is expected that the metal with more electronegative potential has higher affinity to corrode. However, due to structure of oxide film on the aluminum, those potentials do not help in discussing and making an inference regarding corrosion affinity, as such, in this example 5000 series has superior resistance to corrosion compared to 2000 series [11].

Measuring the potential of aluminum, as a metal alone, is not possible due to the rapid reaction between aluminum and the solution in which aluminum is immersed. Within 1 ms or even less time aluminum surface will become oxidized. The measured value represents not the potential of the aluminum metal but the mixed potential of oxide layer and metal [12].

Furthermore, concept of corrosion potential of steel and aluminum should be differentiated. As the corrosion potential of steel is detected, that means, corrosion has already been started. Corrosion of steel once started propagates very quickly. On the other hand, in the case of aluminum, there is always a large number of pits with small depth around intermetallic particles present as second phase constituents.

However, measurement of potential does not give any information regarding the propagation of pits. Thus, measurement of corrosion current density of aluminum should be considered as resulting from uniform corrosion, although it will progress as pitting. This measurement does not provide any information about the size, depth, location, density or diameter of pits [5].

Mass loss or corrosion rate can be calculated by using Faraday's law and polarization curves if the corrosion type is homogenous. Faraday's law relates mass loss with current density and exposure time as:

$$m = \frac{1}{96500}\frac{A}{n}it \tag{13}$$

Where;

m: mass

A: Atomic mass of a metal ($A_{aluminum}$: 27)

n: valence atom number ($n_{aluminum}$: 3)

i: current density (i_{corr}), Ampere

t: time, seconds

However, most of the time aluminum shows localized corrosion, not homogenous corrosion. Hence, one must be careful in using Faraday's law as it tends to under-predict decrease in section thickness for alloys with pitting tendency such as aluminum and austenitic stainless steels.

Pourbaix diagrams, on the other hand, show the corrosion, passivation and immunity sites for a given metal in electrochemical equilibrium conditions. Figure 5 given below represents the Pourbaix diagram for pure aluminum, at 25 ^{o}C, in chemically pure water.

The Pourbaix diagram of aluminum, presented in figure indicates that Al_2O_3, is the stable phase between about pH 4 and 9. This oxide film is considered to be responsible for the successful use of aluminum in many structural applications.

This diagram also predicts the amphoteric nature of aluminum, with corrosion under highly acidic and highly alkaline conditions and protection by an oxide film between about pH 4 and 9 for potentials higher than -2000mV [13].

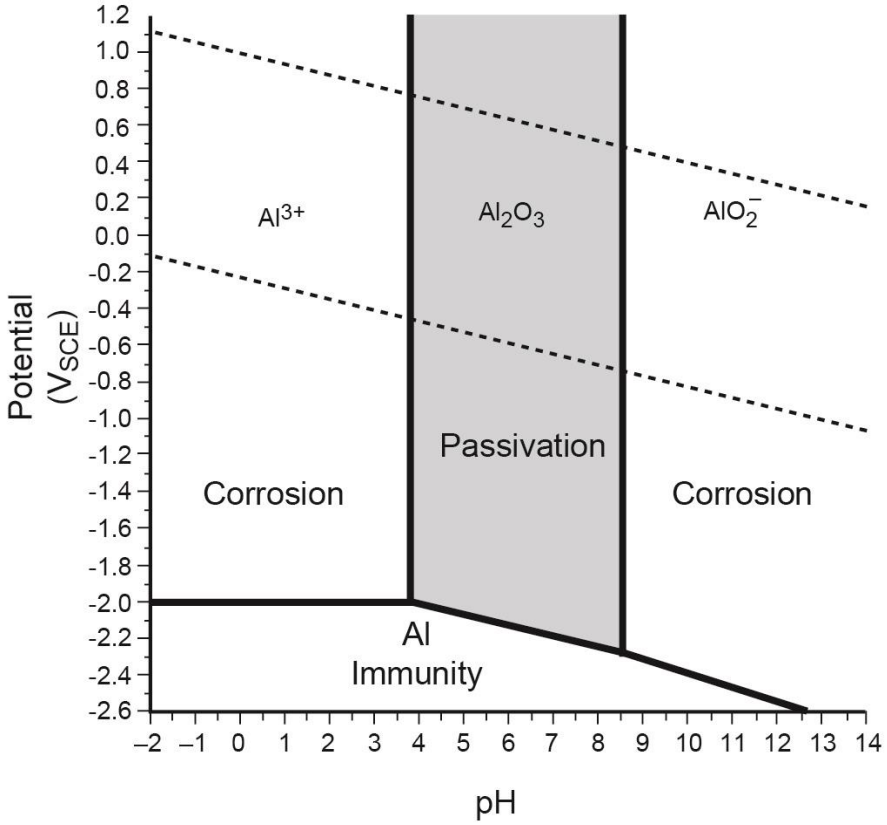


Figure 5. Aluminum Pourbaix diagram reproduced from [14]

There are defined regions on the pH vs Potential (V) diagrams. However, using these diagrams may lead to some mistakes. Reasons are given below;

- Applicable when the solution is ideal, i.e. H-O-Al system. Effects of constituents like chloride are not taken into consideration.
- Metal shall be pure, not an alloy
- Drawn only with the thermodynamic data, ignoring kinetic factors, i.e. time dependency.

To get rid of such unknowns, modified E-pH plots are drawn for a given alloy. For example, E-pH diagram of 5086 alloy was redrawn experimentally in an electrolyte containing chloride as in

Figure 6. [5]

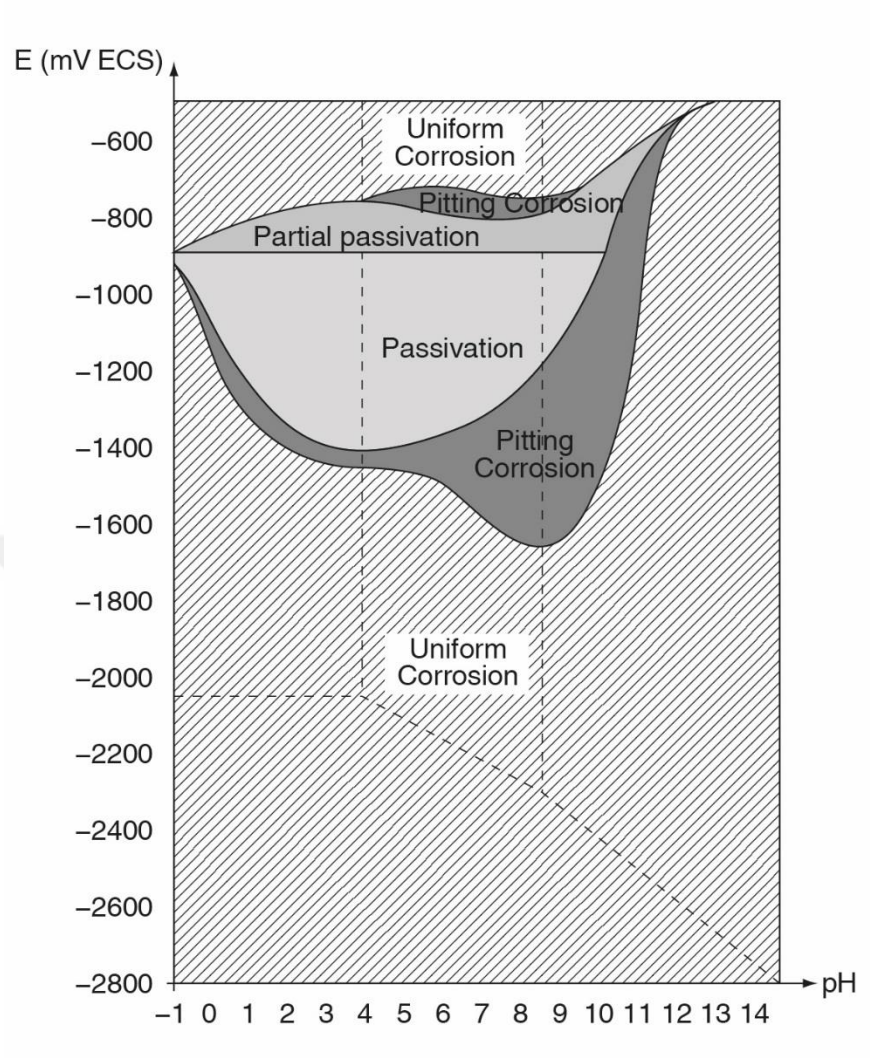


Figure 6. Modified E-pH diagram for Al 5086 alloy[15]

2.2.1 Pitting Corrosion of Aluminum

Some metals especially those, which have good passive behaviors like stainless steels, aluminum alloys and nickel alloys mostly, suffer from pitting corrosion. These alloys are very resistant to corrosion due to the very thin oxide film that spontaneously forms on their surface. Although this layer works very well in atmospheric condition, it is very weak to dissolved oxygen and chlorine containing aqueous environments. These ions easily break the passive oxide layer [16].

Although aluminum alloys show better corrosion resistance in fresh water, they are not very resistant in sea water as in the other environments due to halide ions, especially Cl^-. Halide ions may break the passive layer at certain points and may cause localized corrosion of the alloy [7]. This type of corrosion is called pitting corrosion. Chemical composition, presence and distribution of micro and macro defects and electrolyte properties are important parameters that affect the severity of the corrosion.

Pitting is a highly localized type of corrosion in the presence of aggressive chloride ions. Pits are initiated at weak sites in the oxide by chloride attack and propagate according to the reactions [17]:

- Oxidation at the anode (bottom of the pit):

$$2Al \rightarrow 2Al^{3+} + 3e^- \tag{14}$$

- Reduction at the cathode:
  - Reduction of water

$$\frac{2}{3}O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \tag{15}$$

  - Reduction of H^+

$$6H^+ + 6e^- \rightarrow 3H_2 \tag{16}$$

Local OH^- formation and H^+ consumption in the cavity lead to formation of alkaline environment. Thus corrosion of aluminum continues at the tip accordingly;

$$2Al + 3H_2O + \frac{3}{2}O_2 \rightarrow 2Al(OH)_3 \tag{17}$$

As the amount of the Al^{3+} ions increases inside the cavity, those ions attract the negatively charged Cl^- ions from the solution and form aluminum chlorides to neutralize the solution.

Aluminum chlorides hydrolysis accordingly, and decreases pH below 3. Solution inside the cavity becomes very aggressive. This increases the depth of the pit.

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (18)$$

As amount of Al^{3+} increases, they tend to diffuse through the pit's opening and precipitate as $Al(OH)_3$. Furthermore, hydrogen gas which is formed due to the reduction of H^+ pushes the aluminum hydroxide that is formed inside the cavity and accumulates them on top of the pit [17]. Accumulated corrosion products narrow the pits opening that restrict the ion exchange. This mechanism is schemed in below Figure 7. Recent studies show that pitting of aluminum is not a continuous process, once pit is formed on the surface, its deepening slows down or even stops as the time passes [5].

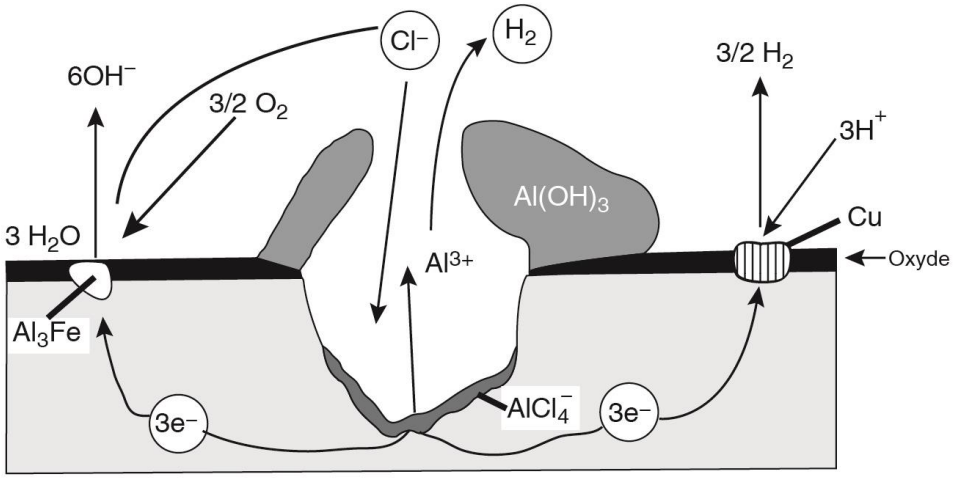


Figure 7. Representative illustration of pitting corrosion of aluminum, reproduced from [5]

The reduction reaction will cause local increase in alkalinity around cathodic particles. As previously mentioned, aluminum oxide is not stable in such environment, and aluminum around the particles will dissolve (and form alkaline

pits). The active aluminum component of the particles will also dissolve selectively, thereby enriching the particle surface with Fe and increasing its cathodic activity. Etching of the aluminum matrix around the particles may detach the particles from the surface, which may repassivate the alkaline pits. This may also reduce the driving force for the acidic pits causing repassivation of some in the long run [17].

There are many studies related to pitting corrosion of aluminum in seawater. Those tests, especially the long run tests show that the pitting corrosion rate will decrease with time. Below Table 1 gives the pitting depth after 5 and 10 years. It can be observed from the table that 5000 and 6000 series aluminum alloys have less amount off pit depth and for all alloys maximum pit depth is mostly below 1.5 mm after 10 years, and there is no proportional relationship between pit depths after 5 and 10 year [18, 19].

Table 1. Pitting depth of different aluminum alloys after 5 and 10 years

	Maximum pitting depth (μm)	
Alloy	5 years	10 years
1199	90	-
1100 H14	<50	1000
3003 H14	<50	250
	130	1170
	330	530
5052 H34	<50	120
5083	<50	150
5086 H112	500	
5154	375	
6061 T4	50	350
	80	100

2.3 Polarization

When two different metal pieces are put in an electrolyte, then a driving voltage will be required to overcome ohmic and non-ohmic resistances. Ohmic resistances are mostly due to electrode size, shape or electrolyte resistivity. On the other hand, non-ohmic resistances are observed near anode and cathode on the electrode/electrolyte surfaces. This phenomena is called as polarization, or overpotential [20].

There are three types of polarization, namely, activation polarization, concentration polarization, ohmic and pseudo-ohmic polarizations.

- Activation polarization depends on the specific reactions that take place and also current density. There is a Tafel relation between activation polarization and current density. Below equation gives this relation where η is the activation polarization, i is the current density, and a and b are constants. a and b depend on the electrode reactions.

$$\eta = a + b\ logi \tag{19}$$

- Sometimes reaction products may agglomerate around the electrode/electrolyte interface. This may alter the properties of the electrolyte and results in concentration polarization. This is minimum for the flowing electrolytes.
- Sometimes during the reactions, electrode surface may change as time passes. These changes may yield ohmic and pseudo-ohmic polarization, which is very important for the corrosion protection concept. Ohmic polarization may be due to a change in the resistivity of the interface. Pseudo-ohmic resistivty is due to the formation of the passive film on the surface. Both of them are time dependent phenomena.

2.3.1 Electrochemical Polarization Measurement Methods

There are two methods to get polarization behavior of the metals. First one is galvanostatic and the second one is potantiostatic [21]. The first method, which is

galvanostatic, provides current density versus potential diagrams. With this method one can get full cathodic polarization curve however; one cannot get the full anodic polarization curve. Only active and transpassive parts of the anodic curve can be observed. Since this method does not provide pitting potential or passivation potential, it is not a good choice for corrosion measurements when pitting is present.

The second and more widely used method is potentiostatic polarization method. Since the first method has some weaknesses, this method was developed and it allows getting the full curve of potential versus current density diagram including passivation and pitting potentials. There are two ways to conduct this experiment.

- The first method is potentiostatic method. Potential is gradually increased step by step in this method. Direct current is used for potential.
- The second method is potentiodynamic method. Potential is continuously raised at a constant speed. Potentiostat is used for potential.

2.4 Corrosion Control of Aluminum

Corrosion protection is very important for engineering applications. Unprotected structures may fail before the end of the service life. Failed parts or sometimes whole system may need to be changed. To overcome such unnecessary economic losses, metallic parts of the system should be protected against corrosion carefully. There are lots of ways of corrosion protection.

i. Material selection: In the case of aluminum alloys, using more noble alloying elements like Mn or Mg instead of Si, Fe, and Cu.
ii. Cathodic protection application
    a. Sacrificial anodes
    b. Impressed current
iii. Coatings/plating
iv. Alteration of environment: Use of inhibitors
v. Improvement of design of the system

Aluminum forms galvanic couple with uncoated steel and stainless steel and also with many other engineering materials. Such couplings should also be avoided

especially on fastener applications. Aluminum must be isolated from the system if there is a risk of galvanic coupling.

Sometimes it is easier to change the environment instead of the material itself. Use of inhibitors may be very effective with regard to the application. They decrease the corrosion rate of the metal for the environment in question.

One of the easiest ways to control corrosion is using coatings that act as barriers for the corrosive medium. These coatings can be inorganic, organic or metallic. Furthermore, coating the metal with another alloy that is more active in the galvanic series (such as plating steel with zinc) results in cathodic protection in the areas having openings of the coating. These deficiencies of the coating can always be experienced during service life of a component and therefore, the barrier effect of coating can be easily lost. Cathodically protective coatings can help overcome these deficiencies by supplying additional protection via anodic reactions taking place at the coating and cathodic reactions taking place at the bare metal surface.

2.5 Cathodic Protection

Cathodic protection (CP) is one of the corrosion protection methods that are applied to metal structures. As mentioned previously, it is achieved by making the structure cathode of the system simply by attaching a more active or more electronegative metal and ensuring that electrical connection remains throughout the protection period or lifetime of the part.

This method is only applicable in an electrolytic media, not in open atmospheric conditions. Also electrical contact is needed between anode and cathode for protection. Thus, all constituents of cathodic protection need to exist for corrosion protection, otherwise it will not work. Constituents of cathodic protection are given below;

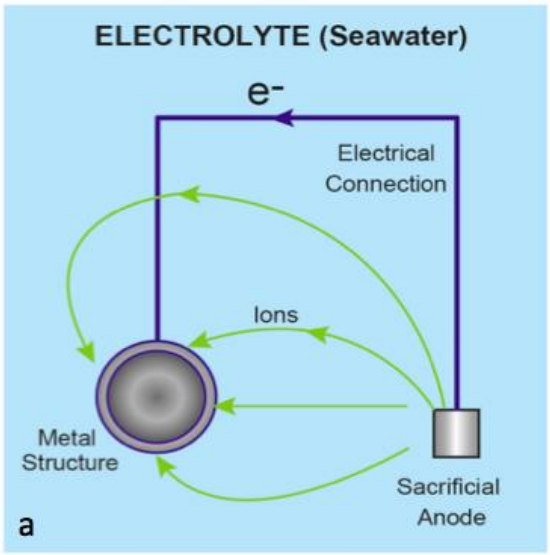
- Cathode, the protected structure
- Anode, less noble metal or electron provider metal
- Electrolyte, media that allows flow of ions

- Metallic path between anode and cathode, providing flow of electrons

As given in Figure 8, current flow can be achieved by two different methods.

- by galvanic anodes and
- by impressed current

Both systems protect the structure; the only difference is electron source. In the case of galvanic anode cathodic protection, less noble or more active metal is attached to the metal, thus the anode itself is an electron provider. On the other hand, impressed current cathodic protection (ICCP) provides electron to the system with the help of the attached external power supply. Electron flow is created by attaching the positive pole to the anode and negative pole to the cathode. ICCP does not require an active metal, instead they require insoluble materials like graphite, silicon cast iron or activated titanium [22].



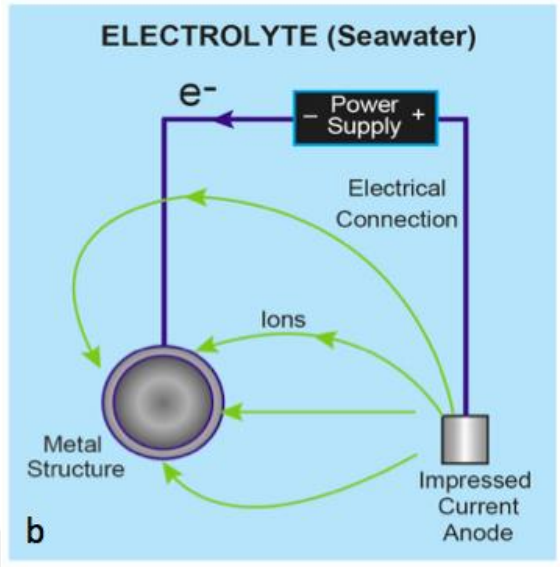


Figure 8. Cathodic protection by (a) sacrificial anode and (b) impressed current methods

2.6 Cathodic Protection of Aluminum

Compared to steel structures, aluminum is more difficult to protect since its protection potential is much more electronegative, below -800 mV SCE. Studies revealed that the surface structure of an aluminum alloy plays very important role for both corrosion and cathodic protection. Cathodic protection mechanism of an aluminum alloy immersed in seawater (chloride containing environment), schematically described in Figure 9, can be summarized as below [8]:

1. Cathodic intermetallic particles which are located on the surface of the aluminum alloy are good places for hydrogen evolution and oxygen reduction as given below.

$$2H^+ + 2e^- \rightarrow H_2 \quad (20)$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (21)$$

or,

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (22)$$

2. Due to the reactions given in step 1, pH increases around the intermetallic particles that result in the protective film breakdown. Since the protective layer on the surface no longer exists, aluminum matrix starts to corrode.

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2 \quad (23)$$

3. In the mean time, iron-rich intermetallic particles will be detached from the surface due to the corrosion of the matrix. The surface underneath the particle will be covered by calcareous deposits and insulates the surface from the electrolyte.

$$Ca^+ + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \quad (24)$$

or,

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (25)$$

4. When the intermetallic particle is removed from the surface, the increase in alkalinity, and therefore protective film breakdown will be stopped and aluminum surface becomes resistant to its environment.

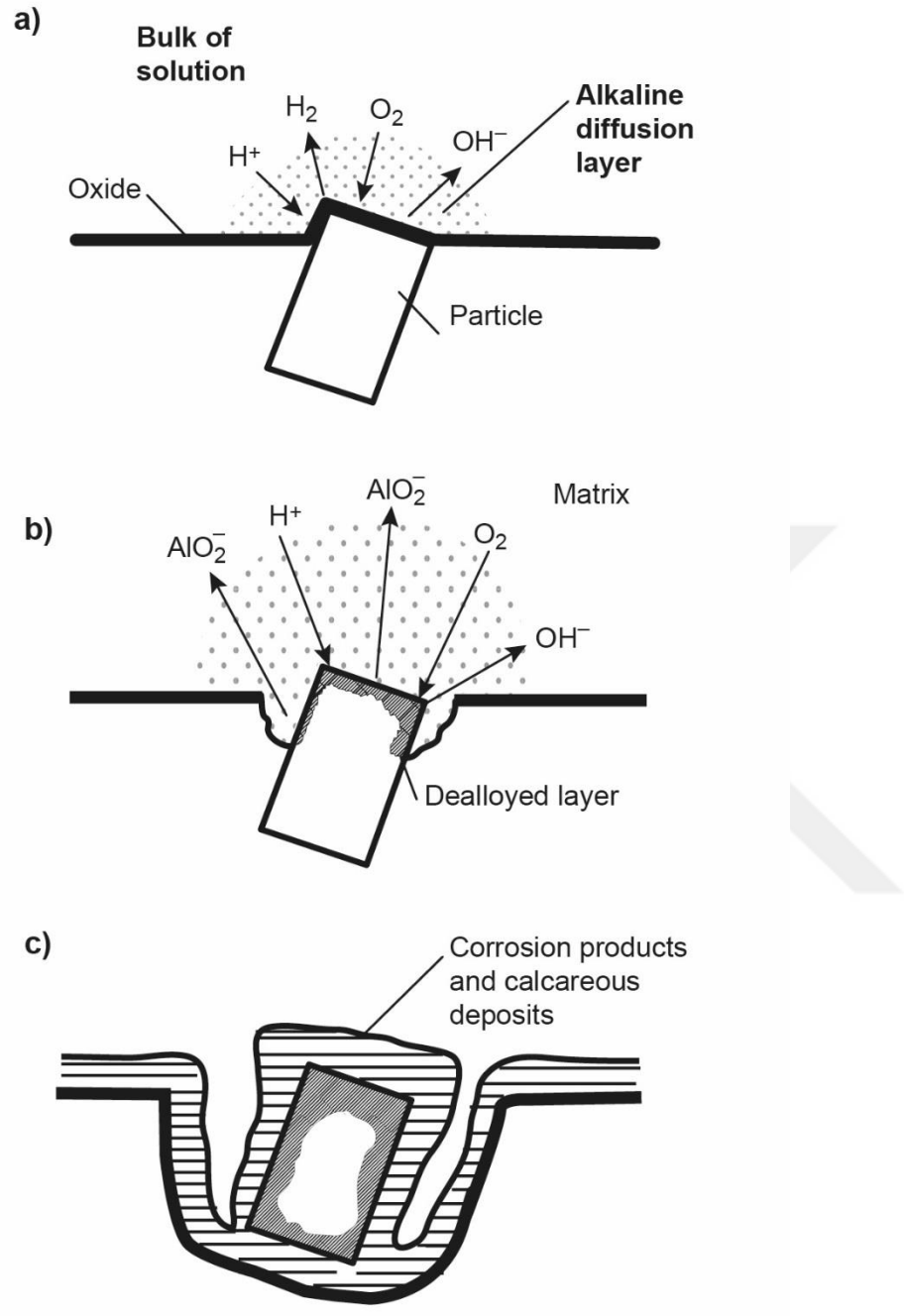


Figure 9. Cathodic protection mechanism of aluminum, reproduced from [8]

There is also one more benefit of cathodic protection of aluminum. Especially 5000 and 6000 series aluminum alloys are very resistant to corrosion even in seawater. From this point of view cathodic protection can be thought unnecessary. However, all aluminum alloys including 5000 and 6000 series must be protected in seawater

especially for the structures that are produced not only from aluminum but also with many other metals. With the help of cathodic protection those structures can also be protected from galvanic corrosion that can be the case when two dissimilar metals are coupled together.

To apply cathodic protection in seawater to aluminum structures, first of all one should select the proper protection method: impressed current system or galvanic anodes [23, 24].

An impressed current technique can be employed only in the presence of electric source. Its advantage is it can be monitored easily. However, its investment and maintenance costs are far more expensive than the galvanic anode technique.

Galvanic anode technique is more applicable in seawater applications since it does not require electrical power unit and does not require maintenance. Uniform corrosion distribution can be achieved by using homogenously distributed anodes and this will lead to weight increase in the total structure. This is the main drawback of this system.

Then, protection potential should be selected. Pourbaix diagrams are used to decide protection criteria for most of the metals. According to Pourbaix diagram, aluminum should be protected with highly electronegative potential, i.e. more negative then -1750 mV with respect to SCE. However, such potentials are very dangerous for aluminum due to the high cathodic corrosion risk. Cathodic protection of aluminum is not like protection of steel. Here, on aluminum the main target is to protect aluminum from pitting corrosion, even some amount of uniform corrosion can be accepted [25].

Conveniently, at least -100 mV potential difference relative to the structure to be protected is required by the attached anode [5]. Representative 100 mV shift is given in Figure 10. Furthermore, it is possible to protect aluminum from corrosion by passivity by setting potential between -800 mV to -1000 mV range. This can be achieved easily by using anodes made of zinc or a special aluminum alloy called Hydral that contains indium or tin. Magnesium anodes are not preferred for the

protection of aluminum since they decrease the potential even further and cause cathodic corrosion of aluminum [8, 26].

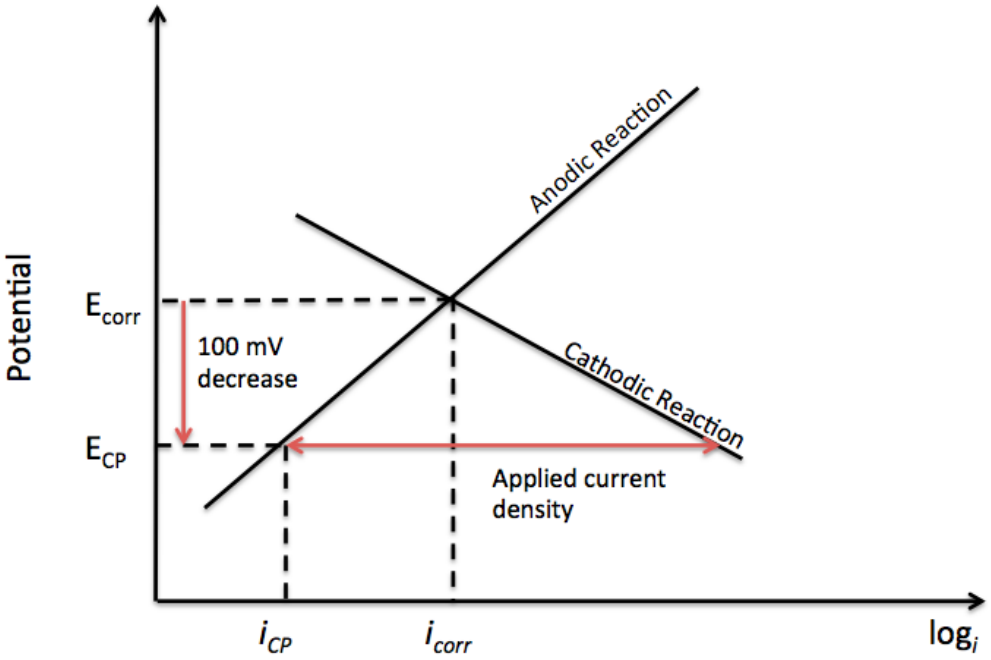


Figure 10. Representative 100mV decrease scheme

Following the selection of proper protection potential, current demand of the system should be calculated. To this end, total bare surface area to be protected and current density is needed. By multiplying total bare surface area and current density, one can get the current required for the protection of the structure [13].

After selecting either Al-In or Zinc galvanic anodes, total number of anodes can be calculated also. Number of anodes depends on the total current demand and current output of a single anode. Total anode requirement can be found by dividing these two.

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Test Materials

In this study, Al 5083, Al 5059 and Al 7020 aluminum alloys have been investigated. The compositions of these alloys are given in Table 2.

Table 2. Compositions of the alloys used in the experiments

Alloy	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Zn %	Ti %	Al %
Al 5083	0.40	0.40	0.10	0.40-1.0	4.0-4.9	0.05-0.25	0.25	0.15	Balance
Al 5059	0.45	0.50	0.25	0.6-1.2	5.0-6.0	0.25	0.40-0.9	0.2	Balance
Al 7020	0.35	0.40	0.20	0.05-0.50	1.0-1.4	0.10-0.35	4.0-5.0	-	Balance

Both polarization and alternating immersion corrosion tests were completed in substitute seawater prepared according to ASTM D1141 standard having composition as given in Table 3 [27].

Table 3. Composition of the substitute seawater

Compound	**Concentration g/L**
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003

The artificial sea water was prepared by dissolving 245.34 g of sodium chloride and 40.94 g anhydrous sodium sulfate in 8 to 9 L of water and then adding 200 mL of Stock solution of No.1, Table 4, and 100 mL of Stock No.2, Table 5, and diluted to 10 L as defined in standard. Final pH of the solution was set to 8.2 by adding 0.1N NaOH. Stock solutions that were used are prepared by adding salts given below accordingly and diluting to 7L.

Table 4. Stock solution No.1 as given in ASTM D1141

Component	Amount
$MgCl_2.6H_2O$	3889.0 g
$CaCl_2$ (anhydrous)	405.6 g
$SrCl_2.6H_2O$	14.8 g

Table 5. Stock solution No.2 as given in ASTM D1141

Component	Amount
KCl	486.2 g
$NaHCO_3$	140.7 g
KBr	70.4 g
H_3BO_3	19.0 g
NaF	2.1 g

For polarization tests 230 mL and for alternating immersion tests 5 L of seawater were used for each experiment. Fresh solutions were used for each run of the test.

3.2 Instruments and Test Apparatus

The test setup given in
Figure 11 was used to conduct polarization tests of materials given in Table 2. For the polarization tests Gamry Reference 3000 potentiostat were used with Gamry Framework software. Three-necked glass vessel having 230 ml volume, standard calomel reference electrode, and graphite counter electrode were used for the tests.

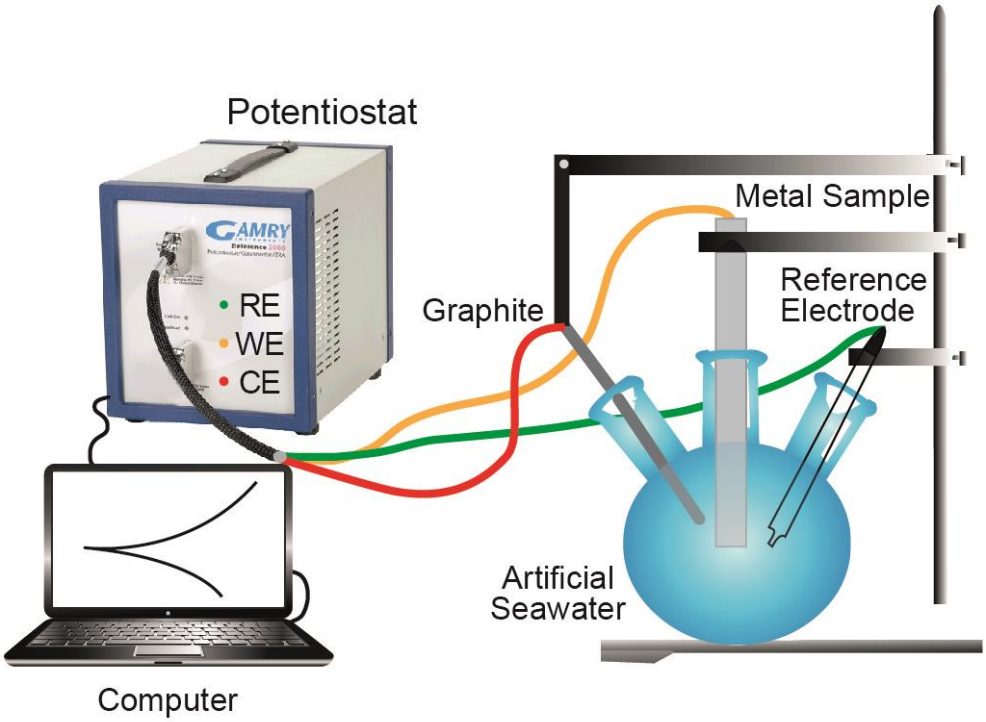


Figure 11. Polarization test setup

The auxiliary, working and reference electrodes were placed in the cell separately. The reference electrode, which was a saturated calomel electrode, was placed just adjacent to the working electrode, and care was given so that there was no more than 2 mm space between them.

Weiss SC-1000 type salt spray test chamber was used for salt spray fog corrosion tests as shown in Figure 12. All test panels were placed into a chamber that conforms to ASTM B117 standard. Throughout the tests, the apparatus in the chamber continuously sprayed salt fog with a nominal composition of 5 wt% NaCl and 95 wt% H_2O onto the panels attached to wooden racks [28].



Figure 12. Weiss SC 1000 Salt Spray Test Chamber

Alternate immersion tests were conducted using the instrument given in Figure 13. All test panels were continuously held in artificial seawater for two hours and then held in the air for the same period of time in an alternating manner, throughout the test period with the help of this instrument.



Figure 13. Alternate Immersion Test Chamber

3.3 Preparation of Specimens

Four different types of alloys are used in this study. All specimens used for polarization tests have rectangular cross section and their surface areas are given in Table 6.

Table 6. Specimens subjected to polarization test and their surface areas

Specimen	Surface area
Al 5083	36 mm^2
Al 5059	40 mm^2
Al 7020	60 mm^2

All surfaces of specimens were covered by epoxy, which is an insulating material that does not conduct electricity, except the bottom part, which was exposed to the electrolyte and allowed to conduct ions through the electrolyte. The top part, left outside the solution, was connected to the system with a copper wire and allowed to conduct electricity through this wire and between the anode and cathode of the cell.

Before the experiments, the surfaces of the specimens which were in contact with the electrolyte were grounded with 200 and 600 grit emery papers and then cleaned with distilled water and alcohol.

Test panels that were used for the alternating immersion and salt spray tests were 100 mm long and 150 mm wide. All panel surfaces were cleaned and then chemical conversion coatings were applied. Following the chemical treatments all panels were coated with epoxy primer that were produced according to MIL-DTL-53022 and then coated with polyurethane topcoat that was produced according to MIL-DTL-53039. These paints are specialized military coatings used specifically for land systems and they are commonly referred to as Chemical Agent Resistant Coating, or in short CARC paints. All panels were left at room temperature for seven days for full curing [29, 30].

For the salt spray tests, all panels were scribed with a scribing tool, which had a 1 mm tip, as defined in ASTM B117. Figure 14 shows the scribed and unscribed test panels together with the scribing tool. The scribed line, which is shown with dashed lines is the main testing surface, provides bare metal surface susceptible to corrosion. Painted areas are assumed isolated from the corrosive environment, hence those surfaces are not examined.

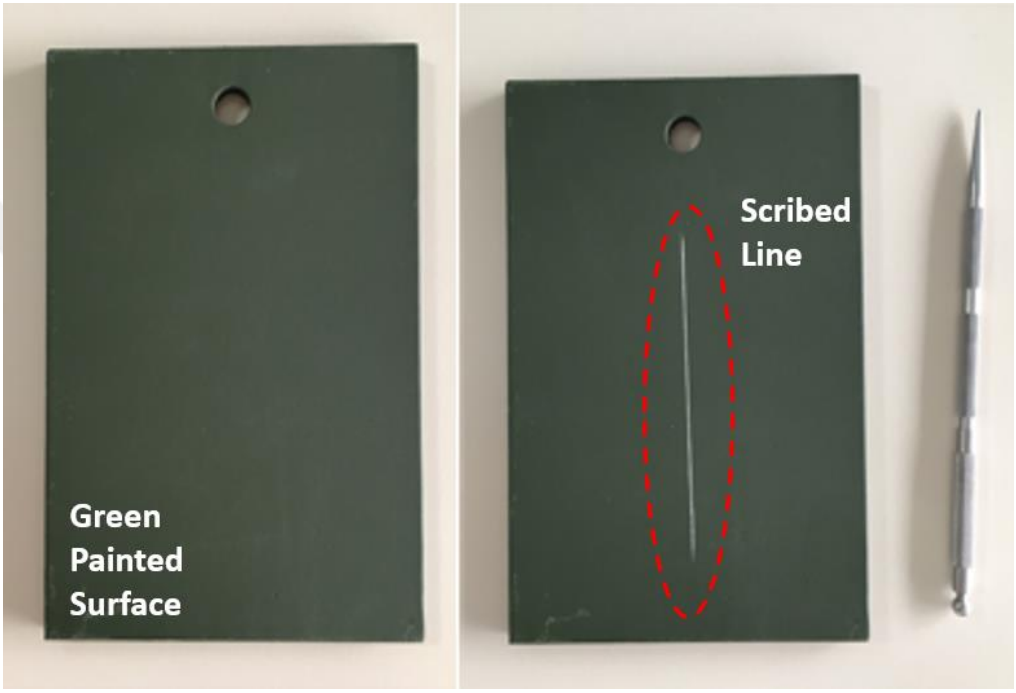


Figure 14. Scribed and unscribed test panels used as salt spray test specimens before the tests together with the scribing tool

Alternate immersion tests were conducted with two different types of plates. Both types of panels were prepared similar to salt spray test specimens as defined in previous paragraph, but one of the sets had Al-Zn-In sacrificial anodes attached to their surfaces while the other did not [19]. Those anodes were connected to the surfaces with copper cables and polyurethane sealant was applied to prevent entrapment of electrolyte between the sacrificial anode and the test plate. Figure 15 shows the scribed and anode attached specimens. Electrical conduction between anodes and metal panels were tested and verified before the tests.

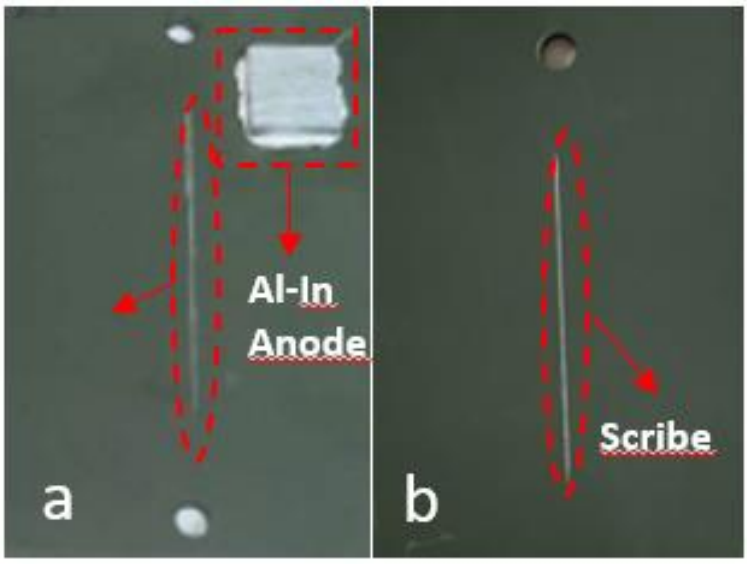


Figure 15. Alternate immersion test plates before the test, a) Scribed and anode attached, b) Only scribed, no anode attachment

3.4 Electrochemical Measurements

Potentiometric polarization measurements were conducted with the polarization cell that was described in section 3.2. 230 mL of substitute seawater was added and electrodes were placed into the chamber. All measurements were conducted at room temperature and saturated calomel reference electrode was used as a reference electrode. Fresh substitute seawater was used for each specimen.

A corrosion phenomenon is the result of two electrochemical reactions. First reaction is the oxidation of the metal and this is called anodic reaction. The other reaction is the reduction of O_2 or H^+ and this is called cathodic reaction. A schematic representative polarization plot is given in

Figure 16 which depicts current curves belonging to these two reactions.

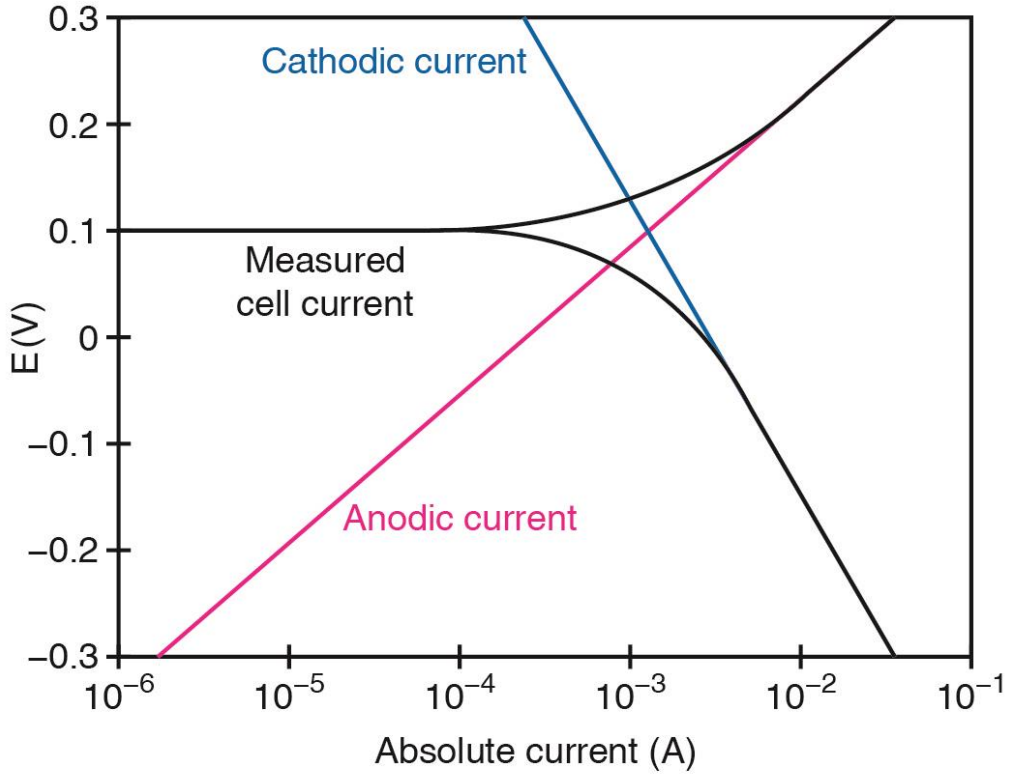


Figure 16. Representative anodic and cathodic polarization curves

Three electrodes, namely, working electrode (test metals given in Table 1), standard calomel reference electrode and graphite counter electrode were connected to GAMRY Reference 3000 potentiostat and potential controlled polarization tests were conducted. Tafel constants, β_A and β_C, were obtained from the resultant Tafel curves. Also corrosion potential, E_{corr}, was obtained. However, to get corrosion current, i_{corr}, Tafel and Buttler-Volmer equations should be used. Those equations are given below accordingly. All the computations to get Tafel constants, corrosion potential and current were done with the help of the GAMRY Echem Analyst Software. Tafel equation is given as:

$$I = I_0 e^{\frac{2.3(E-E_0)}{\beta}} \tag{26}$$

In this equation I is the reaction current, I_0 is the exchange current, E is the electrode potential, E_0 is the equilibrium potential and β is the Tafel constant.

Since Tafel equation gives only one specific reaction, i.e. anode or cathode, these two equations are combined to get full definition of corrosion. This equation is called Butler-Volmer equation, and is given as:

$$I = i_{corr}(e^{\frac{2.3(E-E_{corr})}{\beta_a}} - e^{\frac{2.3(E-E_{corr})}{\beta_c}}) \quad (27)$$

Where, i_{corr} and E_{corr} are corrosion current and corrosion potential, respectively, and β_a and β_c are the anodic and cathodic Tafel constants, respectively.

3.5 Salt Spray Tests

The salt spray test is an accelerated corrosion test that is used to evaluate material and coating corrosion resistance for comparison purposes. Test panels were prepared as described in section 3.3. and tested for 336 and 1000 hours. During this period all panels were controlled every week and corrosion initiation and propagation were investigated. The degree of corrosion, c, was evaluated according to ISO 4628-8 and explained as below [31].

$$c = \frac{A_C - A_I}{2} - \frac{1}{l} \quad (28)$$

Where,

c: Degree of corrosion

A_C: Area of corrosion, including the scribed area

A_I: Scribed area

l: Scribe length

3.6 Alternate Immersion Test

Amphibious vehicles are continuously subjected to both environments alternatingly, such as seawater and atmosphere. Such change of environments, to a first approximation, is simulated on test panels by alternate immersion test. Alternate immersion tests were conducted in order to evaluate the effectiveness of the galvanic

anodes on aluminum surfaces. To this end, two sets of aluminum test plates were prepared. Sacrificial anodes that were produced according to TS9234 standard was attached to first group while the second group had no anodes attached [32].

Both groups of plates were tested according to the following cycle for 336 hours: During this period samples were subjected to cyclic changes of the environment i.e. two-hour immersion followed by two-hour air dry. During this period all plates were checked every two days to observe corrosion formation. At the end of the test all plates were subjected to corrosion rating according to ISO 4628-8 as defined in previous section.

3.7 Cathodic Protection Modeling

Structures that are immersed in an electrolyte shall be protected from the corrosion in any of the ways that were described previously. As far as aluminum structures are concerned, they are very susceptible to corrosion in seawater. All surfaces should be coated with any appropriate coating to prevent corrosion. However, coatings may be easily removed from the structure due to wear, abrasion, impact or any kind of other external factors. Once the metal is exposed to seawater, oxide layer of the aluminum is broken easily and corrosion reactions get started.

This is a very common problem for amphibious military vehicles that operate in both seawater and on land. Due to rough working conditions, coatings of the vehicle can be harmed on various locations. Those areas that are not coated anymore are called holiday. During land operations, deficiencies on coatings (termed as holidays), to a certain extent, are not problematic either due to enhanced corrosion resistance provided by metallic coatings anodic to substrate and/or slower corrosion reactions of aluminum in atmospheric conditions. However, those areas must be protected in seawater operations, otherwise aluminum will start to corrode.

Cathodic protection is one of the best alternatives to protect those areas from corrosion. Cathodic protection is a very common method for ships, pipelines, or similar immersed structures; however, it is not often applied to moving structures like military vehicles. Instead of impressed current systems, sacrificial anode

protection system was selected in military vehicles to avoid many issues related to electronic systems such as sensors attached to the vehicle that may be harmed due to impressed current interference etc.

To this end, one of the vehicles that is designed and produced by FNSS Defense Systems was chosen for application of cathodic protection using sacrificial anodes. Before the application of the cathodic protection to the vehicle, it was modeled using COMSOL electrochemistry and cathodic protection module [33]. First of all, polarization test results of the aluminum were introduced into the COMSOL software for modeling purposes. Then 3D CAD model of the hull as shown in

Figure 17. 3D CAD model of the hull of the vehicle

was introduced to the program. The electrolyte, in this case seawater, was created to cover the hull structure.

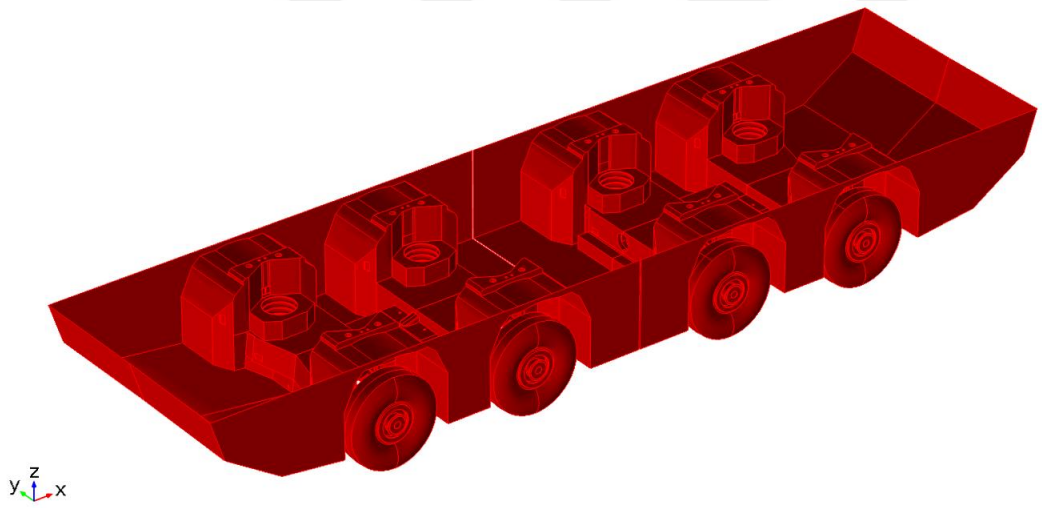


Figure 17. 3D CAD model of the hull of the vehicle

For cathodic protection modeling of a vehicle first of all it is necessary to define the electrolyte, for our case it is seawater. Also cathodic surfaces i.e. the vehicle itself, and anode surfaces, i.e. Al-In anode shall be defined to the program. Finally polarization data must be incorporated into the software.

Cathodic protection of structures can be modeled via implementing boundary conditions to governing equation and solving numerically by any appropriate method such as finite element analysis (FEM) for a defined domain gives the potential an current density distributions on the surface of this given domain [35].

During the corrosion reactions there is no loss or gain of electrical current as given in below equation, where i_x, i_y, and i_z are the components of the electrical current vector.

$$\frac{\partial i_x}{\partial x} + \frac{\partial i_y}{\partial y} + \frac{\partial i_z}{\partial z} = 0 \tag{29}$$

The electrical current is directly related with the first derivative of the electrical potential, Φ. In this equation σ represents the conductivity of the electrolyte.

$$i = -\sigma\left(\frac{\partial \Phi}{\partial x} + \frac{\partial \Phi}{\partial y} + \frac{\partial \Phi}{\partial y}\right) \tag{30}$$

Combination of these equations yields below equation.

$$-\sigma\left(-\frac{\partial}{\partial x}\left(\frac{\partial \Phi}{\partial x}\right) - \frac{\partial}{\partial y}\left(\frac{\partial \Phi}{\partial y}\right) - \frac{\partial}{\partial z}\left(\frac{\partial \Phi}{\partial z}\right)\right) = 0 \tag{31}$$

Conductivity may be functional or constant. Assuming that it is constant, then above equation become a Laplace equation, which is a governing equation for cathodic protection modeling.

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0 \tag{32}$$

There are three different boundary conditions are defined for cathodic protection modeling.

- 1st or Dirichlet type used for the regions where potential has fixed values. In this equation C is a constant value. Voltage sources are boundary conditions for this Dirichlet type. In this boundary condition electrical potential has a defined value. Defined values of voltage can be used to model impressed current type cathodic protection systems where voltage is always constant.

$$\Phi = C_1 \tag{33}$$

- 2nd or Neumann type equation is used for electrical sources where C is a constant value. In this boundary condition electrical current or current density is the dependent variable, and taking derivative of this variable yields a defined value. If surface is painted, then the constant C is equal to 0.

$$i = \frac{\partial \Phi}{\partial n} = C_2 \tag{33}$$

- 3rd or Cauchy type is the polarization response. Electrical current or current density of a corroded surface is determined from the material polarization response. In this equation *f* represents a functional relationship. In the Tafel region the polarization relationship between current and potential is not represented by one analytical solution.

$$i = f(\Phi) \tag{34}$$

Those boundary conditions are used to solve governing equation for the potential and current density at all points on the exposed surface. Any computer method, which can be used to solve the governing equations, can be used to predict electrochemical behavior. Here in this project COMSOL multyphysics was used to evaluate cathodic protection of an amphibious vehicle.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Polarization Tests

Polarization tests are one of the most common corrosion test for materials. From this test one can get lots of electrochemical behavior of the material i.e. anodic Tafel constant (β_A), cathodic Tafel constant (β_C), corrosion potential (E_{corr}), and corrosion current (i_{corr}) values were obtained.

It should be noted that, all potential measurements hereon are conducted with respect to standard calomel reference electrode (SCE).

All samples were subjected to potentiometric polarization tests for 3 times. The polarization tests were conducted for three different aluminum alloys; Al 5083, 5059, and 7020. Tests were repeated for three times for each alloy and each run the electrolyte, viz. artificial sea water, was refreshed with new batch. Also all specimens were grinded with 600 grit emery paper after each test cycle to remove oxide film layer that is formed on the surface due to polarization test. The average was taken to minimize the error, because surface compositions might be affected by grinding and this may cause recording different corrosion potential and corrosion current each time.

Before starting polarization tests specimens were subjected to SEM to observe surface intermetallic compounds. It is known that those intermetallic compounds are the initiation sites for pitting corrosion. Below Figure 18 show the aluminum matrix as gray and surface intermetallic compounds as white spots.

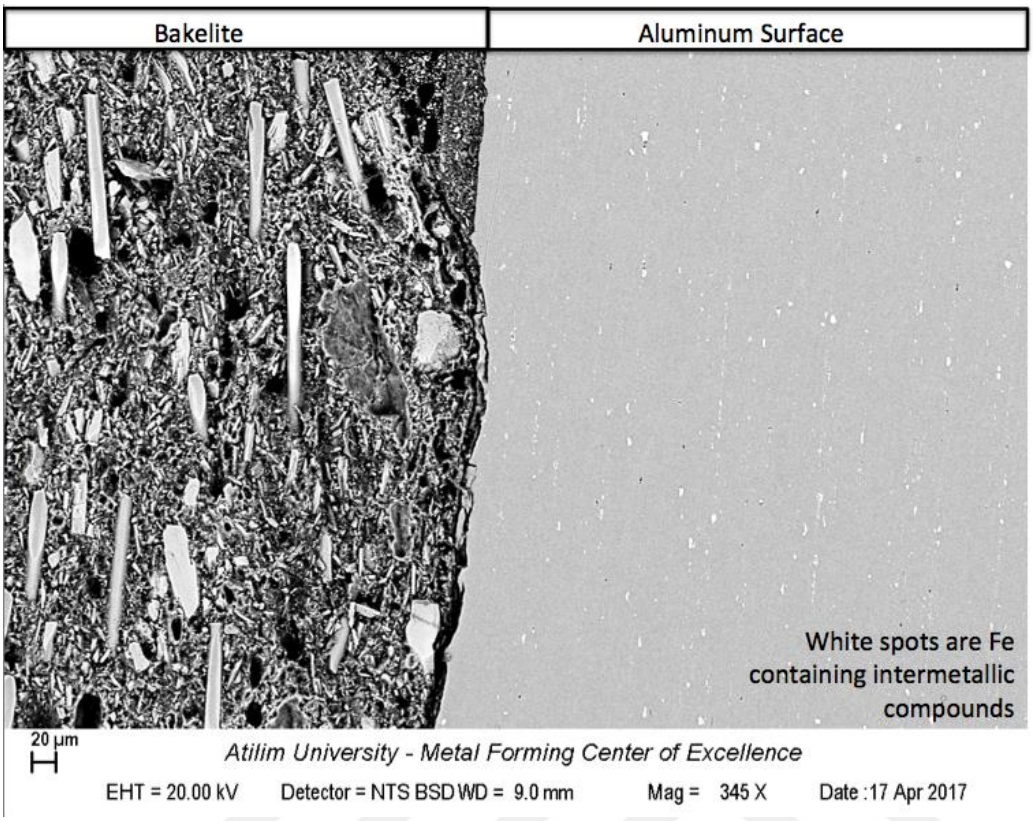
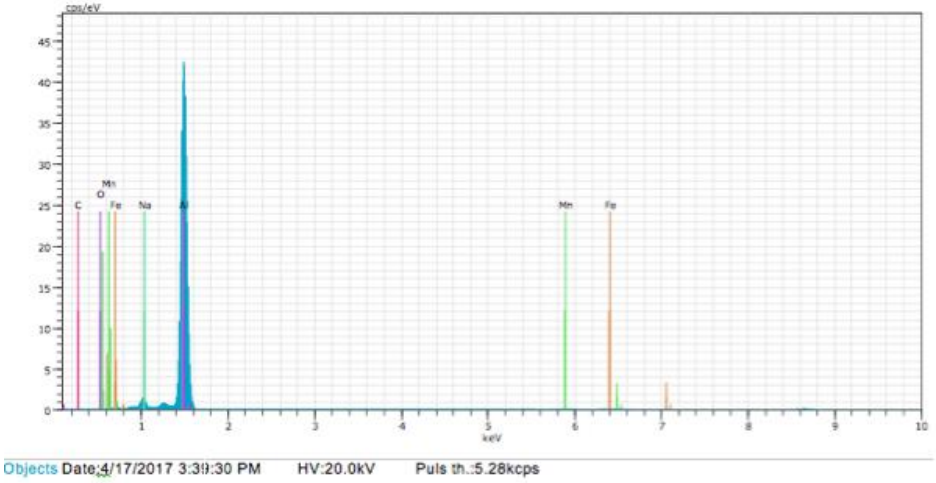


Figure 18. SEM image of Al5059 that shows aluminum matrix and surface intermetallic compounds

Those white spots were also investigated more to be sure that they are Fe containing intermetallic compound. Below Figure 19 and Figure 20 EDS result proves that they contain reasonable amount of iron while the matrix gives no indications of iron.

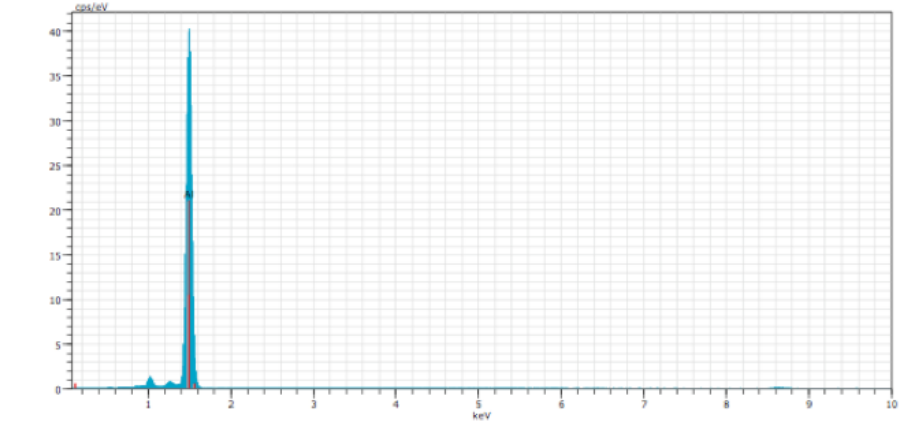


Objects Date:4/17/2017 3:39:30 PM HV:20.0kV Puls th.:5.28kcps

Spectrum: Objects

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Aluminium	K-series	82.13	85.67	79.49	3.9
Iron	K-series	1.57	1.64	0.73	0.1
Sodium	K-series	3.52	3.67	3.99	0.3
Oxygen	K-series	3.57	3.73	5.83	0.8
Carbon	K-series	4.43	4.62	9.64	0.9
Manganese	K-series	0.65	0.67	0.31	0.1
	Total:	95.87	100.00	100.00	

Figure 19. EDS results of surface intermetallic of Al5059



Objects Date:4/17/2017 3:55:39 PM HV:20.0kV Puls th.:4.96kcps

Spectrum: Objects

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Aluminium	K-series	75.85	100.00	100.00	3.6
	Total:	75.85	100.00	100.00	

Figure 20. EDS result of Al matrix of Al5059

After polarization tests surfaces of the specimens were evaluated by Huvitz microscope to observe pitting formation. Although pitting formations can be observed from the images as dark spots, they cannot differentiated from the background clearly due to the coarse grinding process. Below, Figure 21 show the surface of Al5059 specimen after the polarization test. Other specimens have also similar images with Al5059.

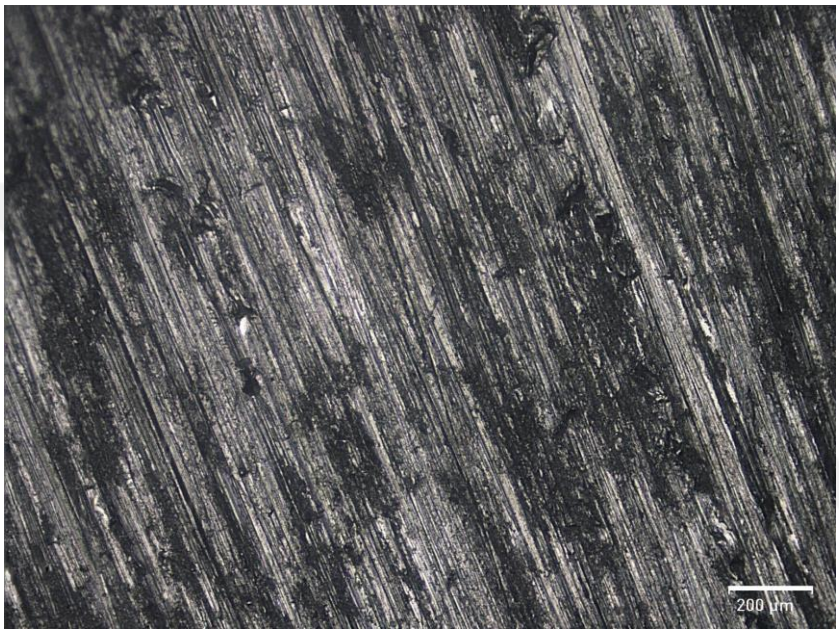


Figure 21. Microstructure of Al5059 alloy, 200X magnification, after polarization tests

Al5083

The results of three polarization tests conducted on Al5083 alloy. As it can be seen from Figure 22 test results are nearly similar but there are some expected shifts due to different surface compositions of the specimen. Tafel plots were superimposed on each curve to determine Tafel slopes for each test. All test results together with their averages are tabulated in

Table 7.

Table 7 Polarization test results of Al5083

	β_a (mV)	β_c (mV)	E_{corr} (mV)	i_{corr} (nA/cm^2)
Exp 1	172	250	-852	145
Exp 2	136	208	-848	115
Exp 3	161	202	-870	98
Mean	156,3	220	-856,7	119,3
Standard Deviation	18,5	26,2	11,7	23,8
Max	172	250	-848	145
Min	136	202	-870	98

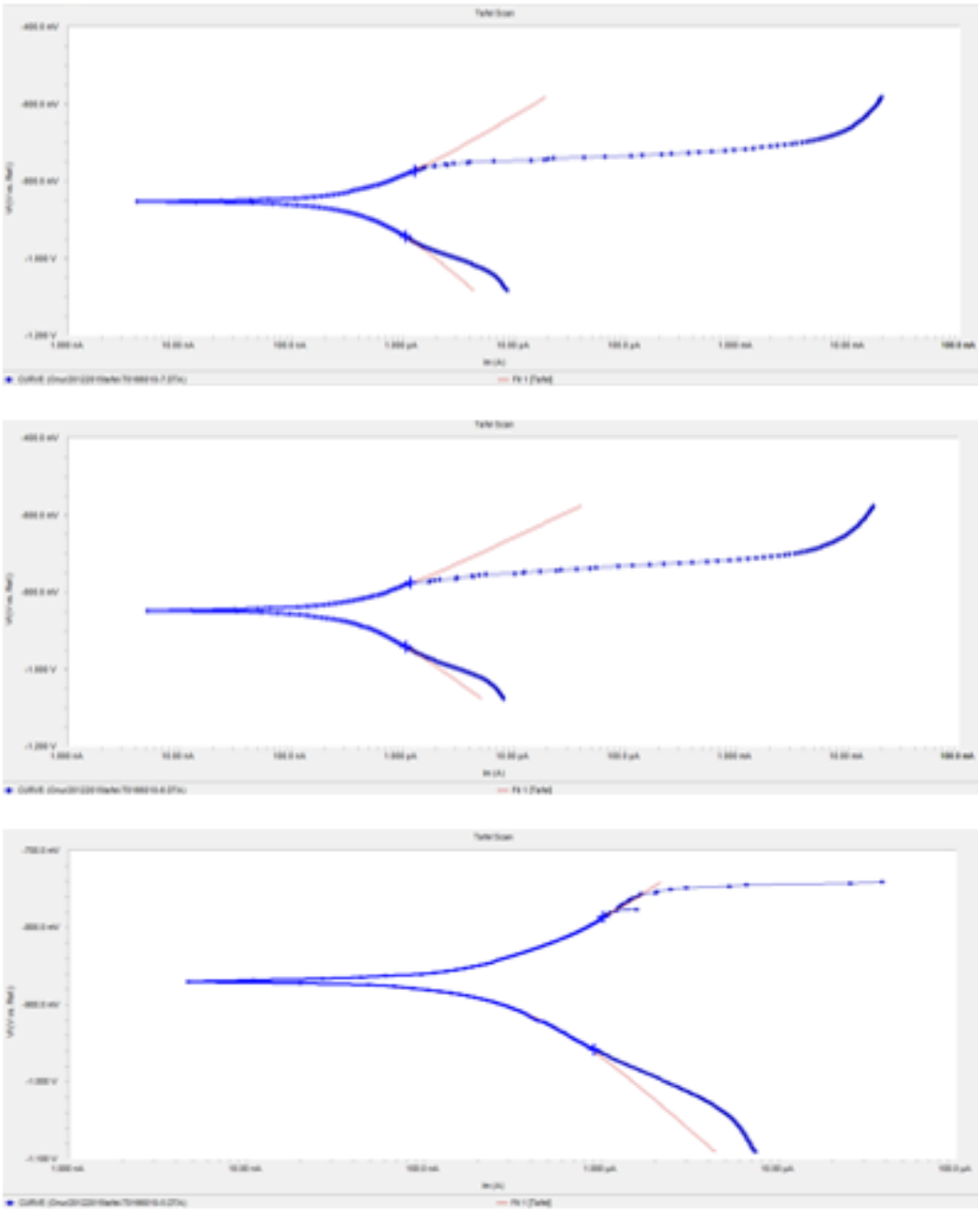


Figure 22. Tafel fit to Al5083 alloy, Experiments 1-3 from top to bottom

Al5059

Al5059 shows behavior similar to Al5083. Test results show some deviations due to similar reasons given in previous sample. Figure 23 shows the Tafel plots. All test results are given in Table 8.

Table 8 Polarization test results of Al5059

	β_a (mV)	β_c (mV)	E_{corr} (mV)	i_{corr} (nA/cm^2)
Exp 1	164	227	-931	228
Exp 2	159	148	-954	152
Exp 3	441	94	-979	282
Mean	254,7	156,3	-954,7	220,7
Standard Deviation	161,4	66,9	24,0	65,3
Max	441	227	-931	282
Min	159	94	-979	152

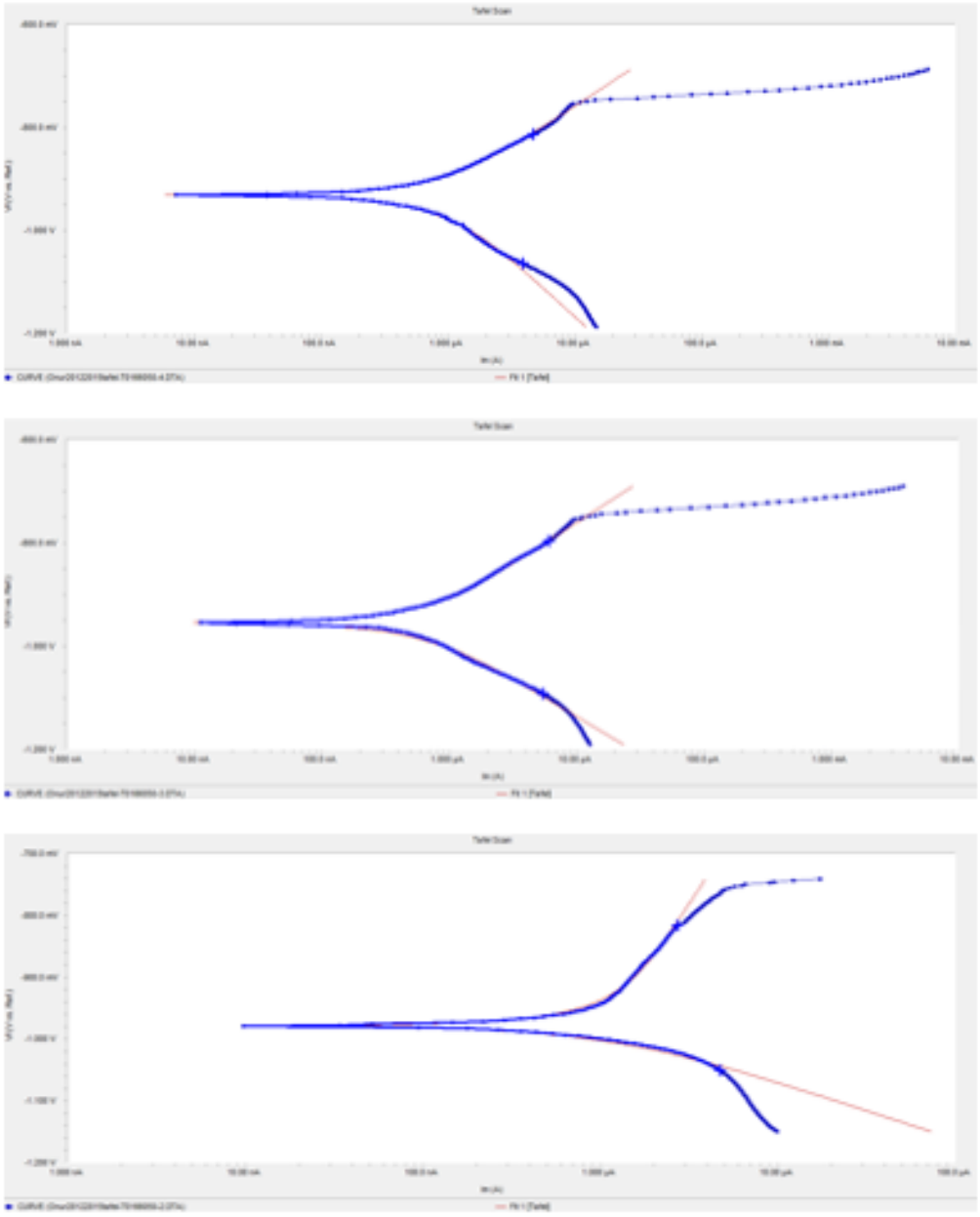


Figure 23. Tafel fit to Al5059 alloy, Experiments 1-3 from top to bottom

Al7020

Test results of Al7020 alloy also shows similar behavior compared to all previously given alloys tested. Table 9 gives all the test results. Figure 24 shows the Tafel fits to anodic and cathodic polarization curves.

Table 9 Polarization test results of Al7020

	β_a (mV)	β_c (mV)	E_{corr} (mV)	i_{corr} (nA/cm^2)
Exp 1	52	49	-818	42
Exp 2	119	108	-843	116
Exp 3	115	97	-849	64
Mean	95,3	84,7	-836,7	74
Standard Deviation	37,6	31,4	16,4	38
Max	119	108	-818	116
Min	52	49	-849	42

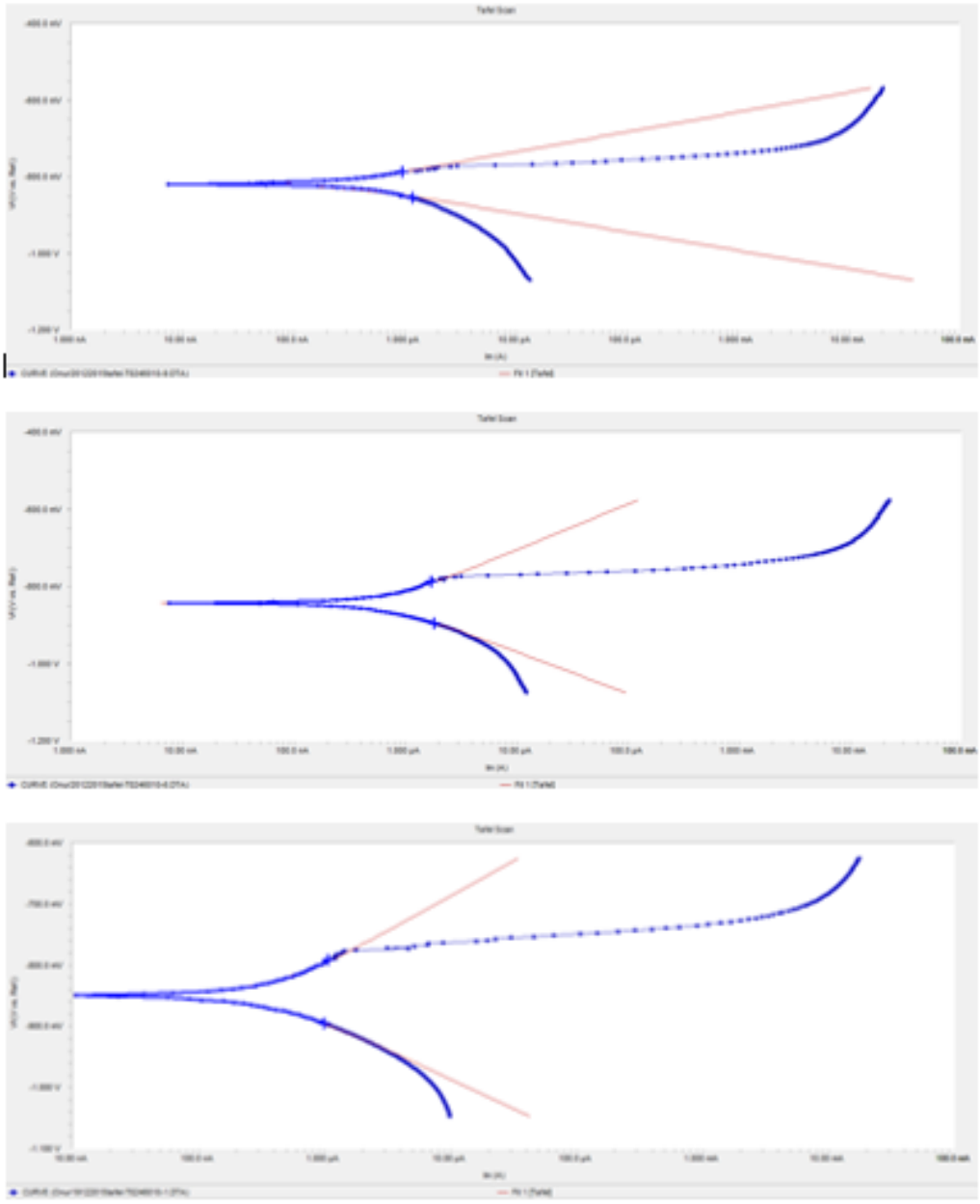


Figure 24. Tafel fits of Al7020, Experiments 1-3 from top to bottom

The mean values of experimentally determined parameters that are going to be used in cathodic protection model are collected for three alloys and given in Table 10.

Table 10 Polarization test results of all alloys

	β_a (mV)	β_c (mV)	E_{corr} (mV)	i_{corr} (nA/cm^2)
Al5083	156,3	220	-856,7	119,3
Al5059	254,7	156,3	-954,7	220,7
Al7020	95,3	84,7	-836,7	74

4.2 Salt Spray Tests

All test panels were subjected to 336 hours and 1000 hours of salt spray test. At the end of 336 hours of test, corrosion formation was not detected on the scribed surfaces. After 500 hours of testing, very small amount of corrosion products were detected on the surface but not enough to rate. Test results were recorded and photographs of specimen surfaces after 1000 hours of testing are given below in Table 11.

Table 11. Salt spray test results of the specimens

Dates/h	**Al5083**	**Al5059**	**Al7020**	**Results**
22.09.2016 24hours				- No corrosion formation - No blister formation - No Paint Adhesion defects
06.10.2016 360 hours				- No corrosion formation - No blister formation - No Paint Adhesion defects
13.10.2016 528 hours				- No corrosion formation - No blister formation - No Paint Adhesion defects

Dates/h	Al5083	Al5059	Al7020	Results
20.10.2016 696 hours				- No corrosion formation - No blister formation - No Paint Adhesion defects
02.11.2016 1008 hours				- Some corrosion formation - No blister formation - No Paint Adhesion defects

4.3 Alternate Immersion Test Results

First group of alternate immersion test was prepared without anode attached. Test results were recorded in the middle of the test that is after 168 hour, and at the end of the test, that is, after 336 hours.

In the first group shown in Figure 25 there is no corrosion or paint defect observed neither at the mid-test evaluation not at the end with respect to ISO 4628-8. The same case also happened for the second group given in Figure 26 samples with

anodes attached. Mid-term evaluations and final evaluations according to ISO 4628-8 were all OK.

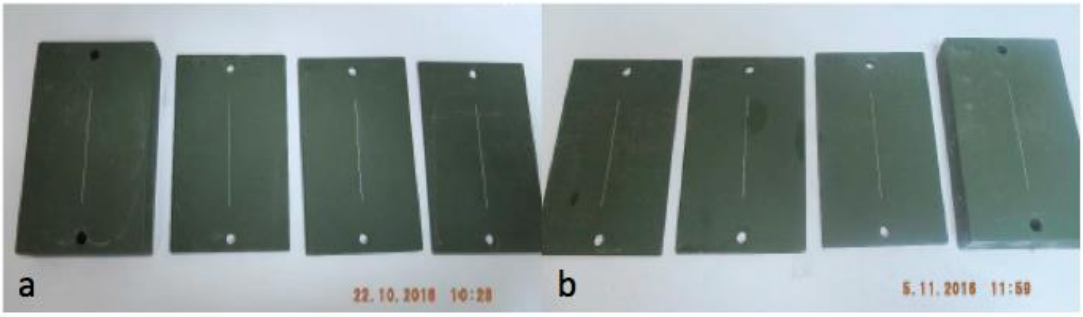


Figure 25. Group 1 specimens – without anode attached a) before the tests b) after the test

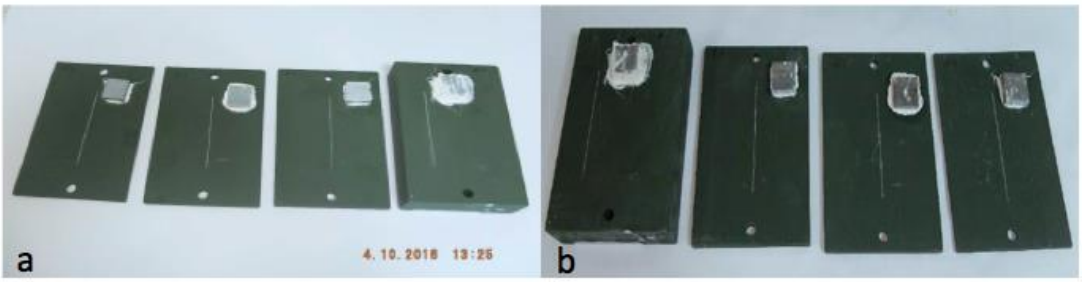


Figure 26. Group 2 specimens – with anode attached a) before the tests b) after the test

Although all test results are acceptable with respect to ISO 4628-8, this does not mean that there is no corrosion formed on the surfaces of the specimens. To this end, detailed microstructural analysis was conducted to the specimens with the help of the SEM and optical microscope.

Among 3 specimens only Al5059 alloy gives the promising images. Thus, all microstructural analysis is belonging to this alloy.

Under optical microscope, corrosion products and pitting sites were observed from both protected and unprotected specimens. White areas on the images refer to a

corrosion product, that is aluminum oxide, and black spots are the pits formed during the test period. Microscopic images show that although both specimens were corroded, the unprotected one corroded the most. There is much more dense white corrosion layer on the surface on unprotected specimen as given in

Figure 28 then the protected specimen as given in Figure 27. The reason why protected one also corroded is, during the alternate immersion test, specimens were subjected to immersion and drying period without immersion. During the drying period cathodic protection stops since there is no presence of electrolyte. During this period aluminum was corroded even there was an anode attached to its surface.

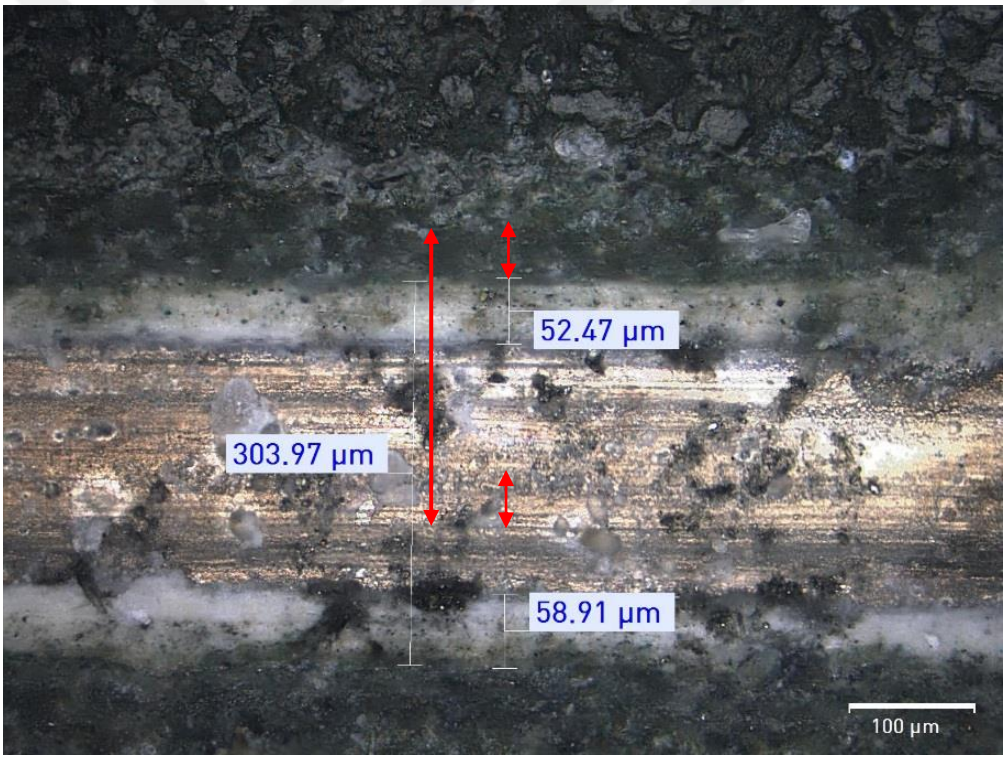


Figure 27. Al5059, 500x magnification with protection



Figure 28. Al5059, 500x magnification, without protection

Scanning Electron Microscope (SEM) analysis also performed for the Al5059 alloy. Purpose of using SEM is to get images with higher magnifications and observe oxide film thickness formed on the scribe of both protected and unprotected specimens. And also to get images of Chemical compositions were identified using energy-dispersive X-ray spectroscopy (EDS).

Specimens were also subjected to SEM to differentiate corrosion layer thickness of protected and unprotected samples. Specimens were prepared from the alternate immersion test panels as shown in below Figure 29.

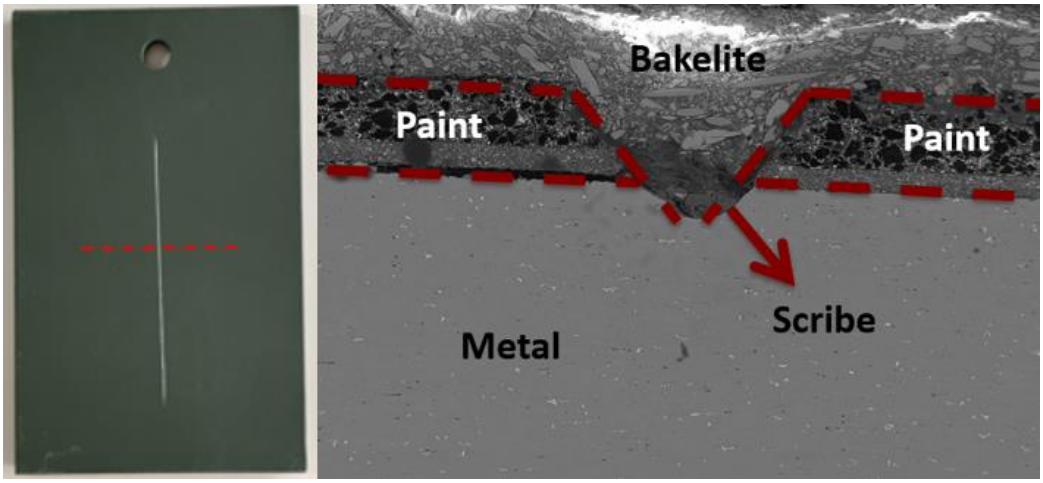


Figure 29. SEM specimen preparation

From the samples that were examined, it was observed that there is a noteworthy thickness difference. There is thicker layer of aluminum oxide formed on the surface of unprotected specimen. This difference can be noticed from Figure 30 and Figure 31.

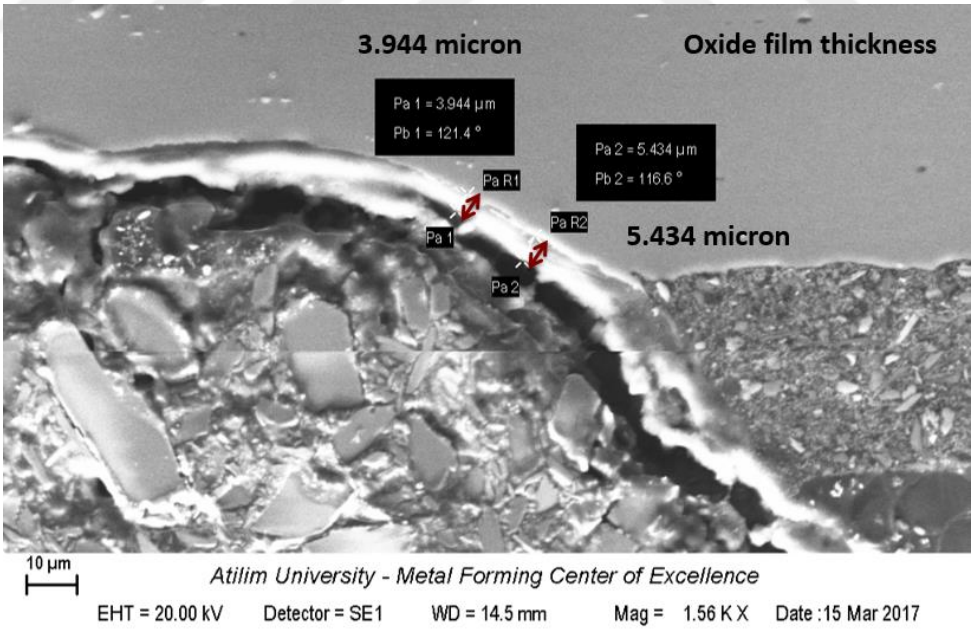


Figure 30. SEM image of protected sample, oxide film thickness

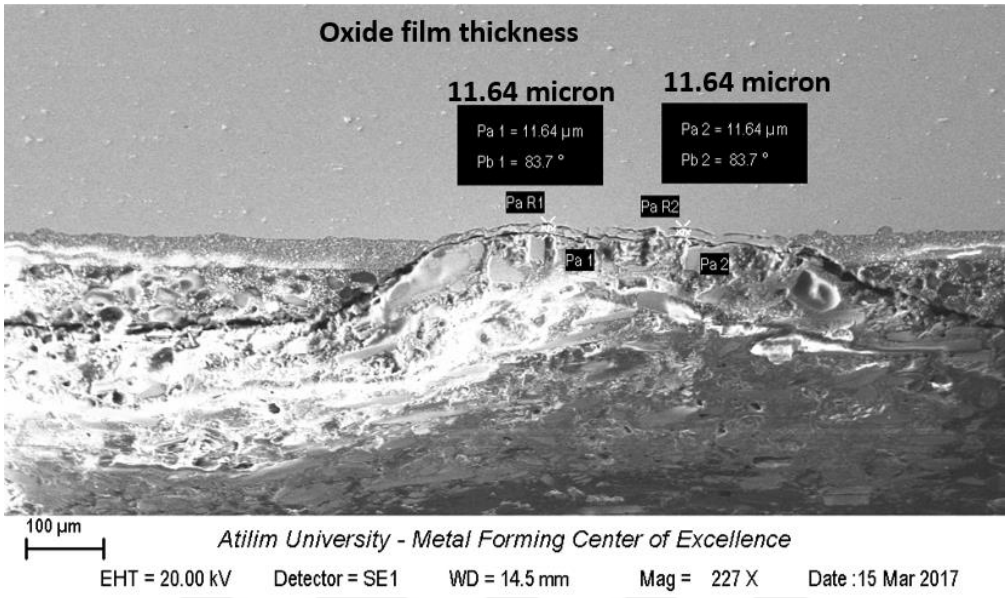
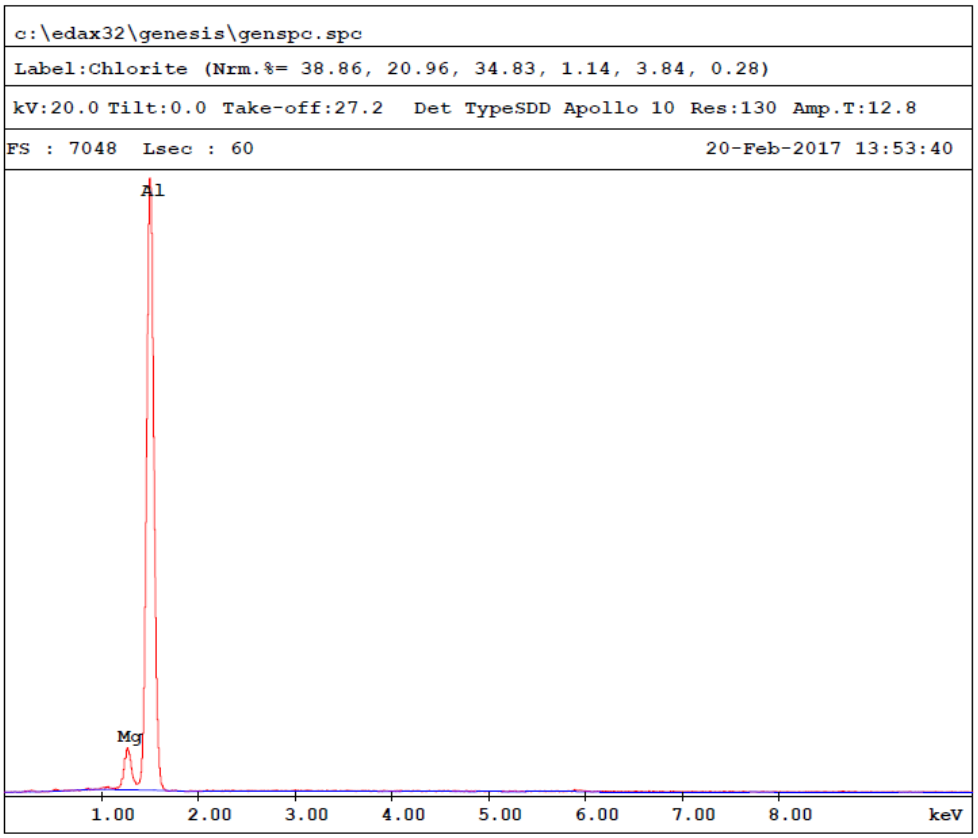


Figure 31. SEM image of unprotected sample, oxide film thickness

This result also proves that although aluminum has good corrosion resistance, cathodic protection makes it better.

EDS results also conform that unprotected Al5059 specimen has higher amount of oxygen than protected one and as expected there is no oxygen detected from the bare aluminum surface. Bare surface of aluminum, protected and unprotected specimens EDS results are given in below Figure 32, Figure 33, and Figure 34 respectively.



Element	Wt %	At %	K-Ratio	Z	A	F
MgK	5.69	6.28	0.0557	1.0286	0.9099	1.0457
AlK	94.31	93.72	0.8198	0.9983	0.8708	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
MgK	51.38	3.68	1.93	13.95
AlK	746.60	3.10	0.47	240.84

Figure 32. EDS result of bare Al5059 alloy

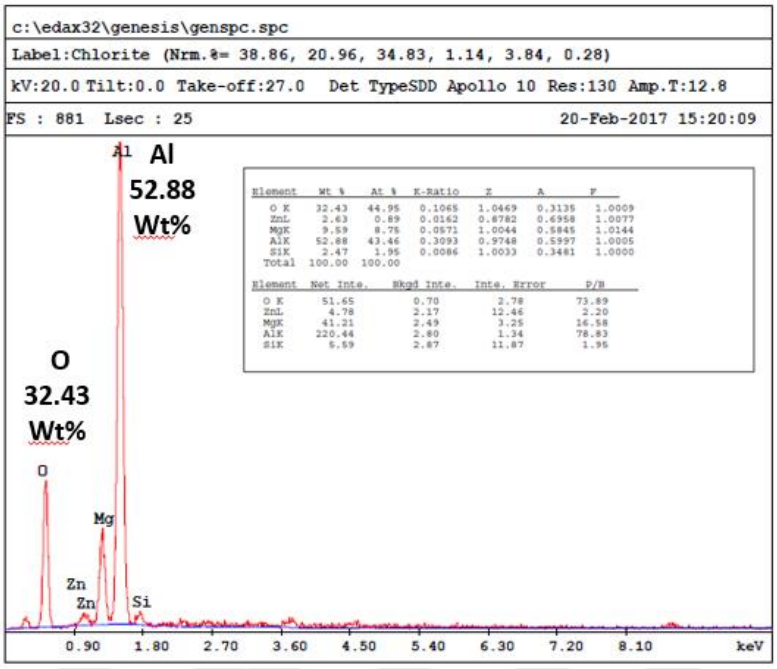


Figure 33. EDS result of Al5059 sample with cathodic protection

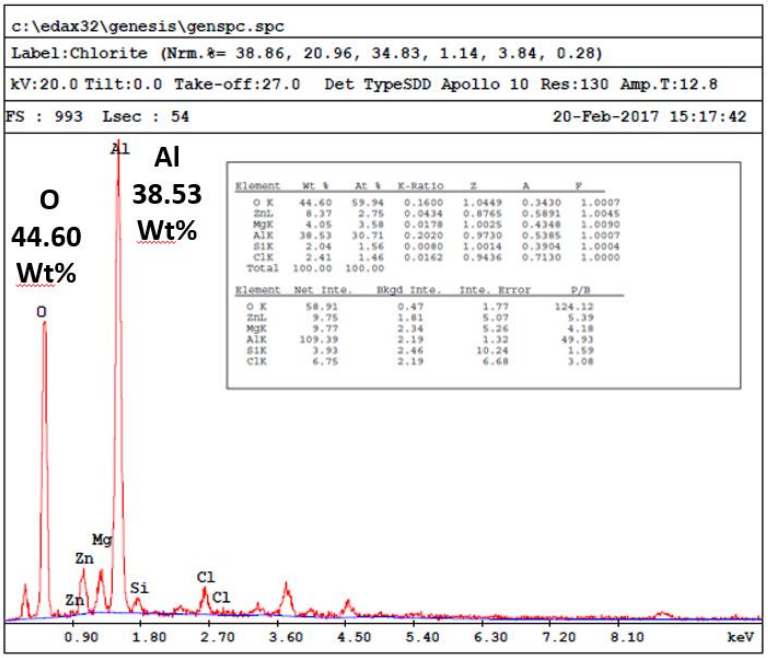


Figure 34. EDS result of Al5059 sample without cathodic protection

From Figure 33 and Figure 34 one can observe that there are some irrelevant elements other than aluminum and magnesium inspected from the EDS. Those elements are interrupted most probably from the artificial seawater since EDS photographs were took after the alternate immersion test.

4.4 Cathodic Protection Modeling

Assuming that there is only uniform corrosion on the vehicle surface, there is no galvanic coupling, electrolyte conductivity is constant and lastly -1000 mV potential difference with respect to SCE reference electrode is enough to protect aluminum surfaces from the corrosion, modeling of the hull were completed. It can be observed from

Figure 35 with the 32 anodes attached on the selected part of the vehicle, it can be protected from the corrosion since the potential difference is around 1000mV and this value is enough for protection of the aluminum from the corrosion in seawater. This represents the case that whole vehicle was uncoated.

Normally the outer surfaces of the hull are covered with organic paint to cut off the contact with seawater. For a vehicle that is perfectly coated no potential difference is expected, thus, there will be no corrosion on the surface of vehicle.

However, due to reasons such as collision, vibration, removal of the paint can be observed in some painted areas. Taking these situations into account, the modeling was done. In order to be more realistic, a circular outer surface of the hull near to the bumper was considered to be uncoated while the rest was coated to simulate possible damaged area. The simulations were run again with the same anode configuration. It was observed as given in Figure 36 that damaged sites on the aluminum hull could be protected without being overprotected with the help of Al-In anodes.

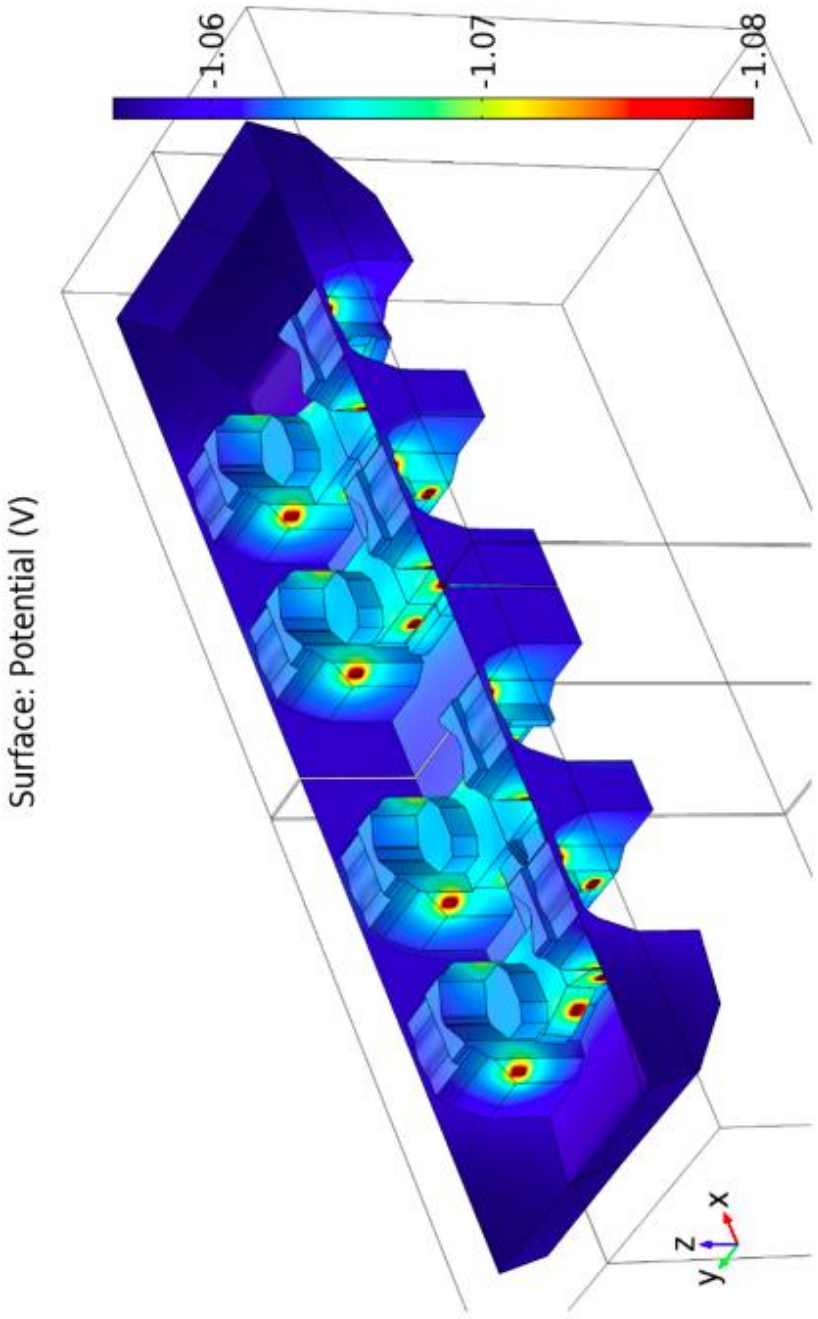


Figure 35. Cathodic protection model of the vehicle assuming all surfaces are uncoated

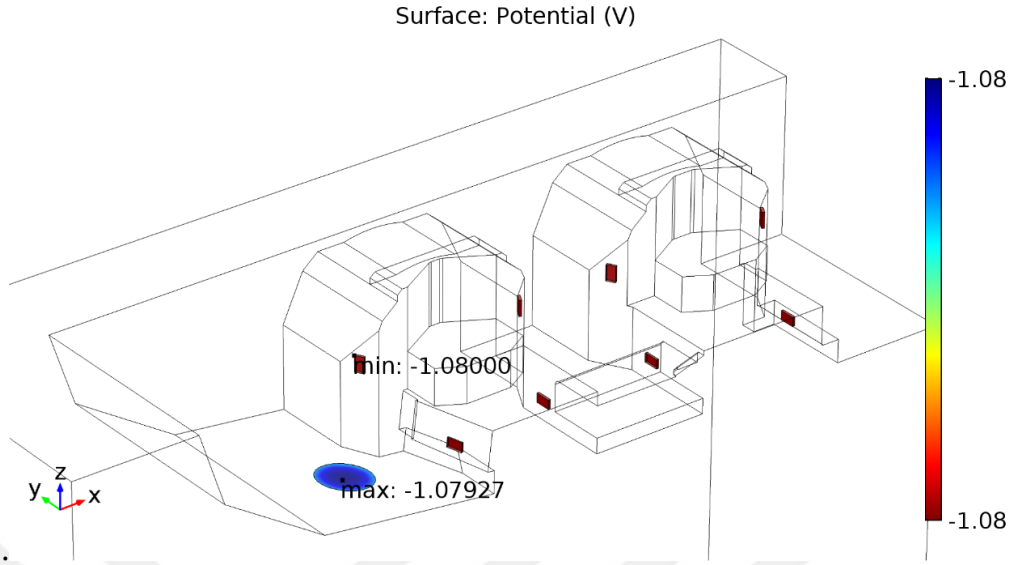


Figure 36. Cathodic protection model of ¼ of vehicle having circular damaged paint area.

CONCLUSION

The corrosion behaviors of 5083, 5059 and 7020 aluminum alloys were investigated and the results were used to employ cathodic protection model.

Polarization tests were conducted in synthetic seawater, at pH 8.2 to determine the parameters required to perform cathodic protection model of armoured amphibious vehicles in marine environment. Although aluminum does not polarize like steel due to the presence of a passive layer, but damages observed in Cl^- containing environments, like seawater, was considered important. The alloys showed differences in potansiostatic polarization test results probably due to the differences in surface intermetallics. The concentration and composition of intermetallics which work as initiation sites for corrosion altered the results of polarization tests.

All scribed specimens of 5083, 5059, and 7020 aluminum alloys showed no ratable corrosion formation around scribes after 1000 hours of salt spray in 5 wt% NaCl. There were only some white corrosion products near the scribed line after 500 hours of testing. Paint around the scribe remained without any defects like blister.

All three alloys showed good corrosion resistance to synthetic seawater under alternating corrosion resistance test conditions. Although they possessed good corrosion resistance, Al-In sacrificial anodes made their corrosion resistance even better and prevented corrosion propagation inside the pittings.

Experimentally measured electrochemical data were used to simulate cathodic protection of aluminum hull structure. The homogenous distribution of current at potentials lower than -1000 mV with respect to SCE was achieved over the entire structure by configuring 32 Al-In anodes in seawater. The presence of these anodes was found to protect local paint deficient parts without overprotection. Modeling of aluminum structure may be advantageous to observe potential changes over the structure by changing the location of the anodes.

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