

Predicting Atmospheric Galvanic Corrosion of Aluminum using Accelerated Laboratory Electrochemical Experiments

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ABSTRACT

Aluminum (Al) alloys are the most commonly used non-ferrous metals (approximately 25 million tons per year) for various technical applications and the second most commonly used metal alloy after steel. Al alloys are also combined with other metals/materials to get specific desirable properties for particular applications. However, a system of dissimilar materials can lead to potential corrosion problems such as galvanic and/or crevice corrosion. In this work, atmospheric galvanic corrosion of aluminum (Al) alloy was predicted by combining electrochemical techniques and accelerated laboratory corrosion tests. Three different galvanic couples were analyzed where 6061-T6 Al alloy (UNS A96061) was coupled with a passivating metal (304 stainless steel or UNS S30400), noble metal (copper or UNS C11000) and a conductive polymer matrix composite (PMC) reinforced with carbon fiber. The galvanic current flowing between the anode and cathode was measured using the zero-resistance ammeter (ZRA) technique in the humidity-chamber setup. Electrolytes with varying amounts of chloride contents were used to imitate different atmospheric conditions. An equation based on Faraday's law was developed to calculate the corrosion rate in grams per meter square per day (gmd) by relating the time of wetness (TOW) from the field exposure to the galvanic current measured from the accelerated laboratory experiments. The total exposure time was divided into wet periods (T_{wet}) and dry periods (T_{dry}). Cyclic corrosion test chamber following a modified GM9540P cycle and outdoor exposure experiments are planned for the future.

Keywords: Atmospheric Corrosion, galvanic corrosion, Zero-resistance ammeter, electrochemical experiments

INTRODUCTION

Objective

Aluminum (Al) alloys are the most common non-ferrous metals used (approximately 25 million tons per year) and the second most commonly used metal alloy after steel¹. Some of the properties of Al alloys that attribute to their worldwide use include lightness, thermal conductivity, electrical conductivity, suitability for surface treatments, and corrosion resistance. Al alloys are also combined with other metals/materials to achieve desired properties for specific applications. Al alloys can be joined to other materials with ease to enhance their combined properties with the following techniques: welding, bolting, riveting, clinching, adhesive bonding, and brazing¹.

However, a system of dissimilar materials can lead to potential corrosion problems through galvanic corrosion^{2&3}. In addition to galvanic corrosion, atmospheric corrosion is vital to study as many structures and systems are used in natural environments. However, there is a vast discrepancy between accelerated laboratory corrosion tests and outdoor atmospheric corrosion tests for uncoupled samples⁴⁻⁷. The addition of galvanic couples only complicates investigations. Standardized accelerated laboratory corrosion experiments are used to screen materials and components; the results from these indoor corrosive environments are used to evaluate their performance in the field. A consistent correlation between laboratory tests and outdoor exposure tests should exist in order to validate the accelerated laboratory corrosion tests. This research aims to modify accelerated laboratory corrosion tests in combination with electrochemical techniques to predict galvanic corrosion of aluminum alloys in outdoor conditions.

Background

Al usually has a lower electrochemical potential than most metals (except magnesium); hence, Al alloys are more active and act as the anode. When coupled to a more noble/cathodic metal, the Al alloy corrodes at an accelerated rate due to galvanic and/or crevice corrosion. Contact between Al alloys and other conductive materials can lead to galvanic and/or crevice corrosion in a corrosive environment (Figure 1). According to Faraday's law (Eq.1), the amount of current flowing between the anode and the cathode is directly proportional to the amount of anodic material (Al in this case) dissolved².

$$M = \frac{At.wt.*I*t}{n*F} \quad \text{Eq.1}$$

M - mass of Al dissolved to produce galvanic current (g)

At. wt. - atomic weight of Al (g)

I - current generated (Amperes)

t - time (sec)

n - moles of electrons per moles of Al reacted

F - Faraday's constant = 96487 (Ampere sec/moles of electrons)

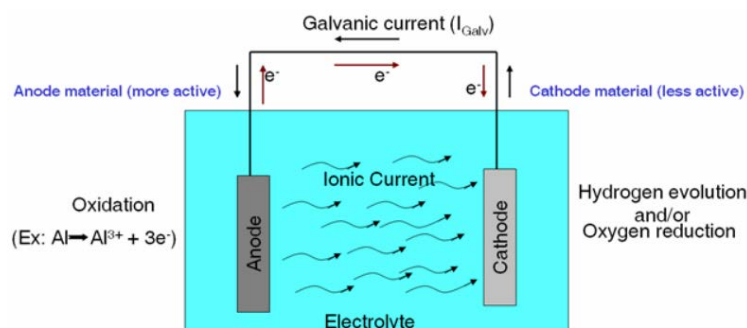


Figure 1. Electrolytic cell showing the flow of ionic and electric current

Atmospheric corrosion depends on various environmental factors, but most of the atmospheric corrosion models are predicted using the empirical kinetic formula (Eq.2), which uses time as the only function⁸⁻¹¹:

$$M = K * t^n \quad \text{Eq.2}$$

where "M" is the mass loss per unit area and "t" is the exposure time. The empirical coefficients like proportionality constant (K) and exponent (n) usually cover other environmental factors. This kind of model is usually good for predicting the corrosion rate over time for various atmospheric conditions. The time-dependent models may often estimate the corrosion rates inaccurately if the concerned environments are different from the environment in which the model was calibrated.

The most widely used standardized corrosion test is salt spray ASTM B117⁴⁻⁶. The primary purpose of this test is to simulate the actual conditions that exist in the outdoors. However, the ASTM B117 standard method states, "there is seldom a direct relation between salt spray (fog) resistance and resistance to corrosion"⁶. A series of modifications are developed over the years to reproduce data that correlated well with the outdoor field data.

The corrosion behavior of a material or a component is evaluated by service history, field tests, or accelerated corrosion tests. The service history predicts systems life accurately, followed by field tests and accelerated laboratory tests. Evaluating material's useful life by service history and field tests can take long and expensive, making them almost impossible for material selection and evaluation. Accelerated corrosion tests are valuable tools to avoid time and budget constraints to select and evaluate materials. New test methods and protocols should be developed and devised considering all the environmental parameters to model a test for various environments.

Approach

Various accelerated laboratory corrosion tests were conducted to test the corrosion behavior of the UNS A96061 alloy (hereafter referred to as Al alloy) coupled to other metals such as UNS S30400 stainless (hereafter referred to as SS), UNS C11000 (hereafter referred to as Cu), and carbon fiber reinforced PMC (hereafter referred to as CFR PMC). A Zero-resistance ammeter (ZRA) experiment was conducted in the humidity chamber for different salt solutions to determine the effect of wetness and salts concentration on the galvanic corrosion behavior of the Al alloy. Mass loss coupons were also exposed to the same conditions in the humidity chamber to measure the accelerated corrosion on the Al alloy due to galvanic corrosion. Corrosion rates were calculated by modifying Faraday's law by incorporating different galvanic current values and the corrosion samples' time of wetness (TOW).

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

Various configurations of galvanic couples were used when exposing the coupons to corrosion accelerated laboratory tests and outdoor experiments. The materials of interest included Al alloy coupled to Cu, SS, and CFR PMC. The metal samples were prepared to be 1 by 2-inch rectangles with 1/8-inch thickness. The galvanic couples have a 1-inch by 1-inch overlapping area and were separated by 1 by 1-inch thin G10 fiberglass to avoid metal to metal contact in order to be able to measure galvanic current (Figure 2). In each couple, the anode metal of interest (Al alloy) was placed on the top with the cathodic material attached to it on the bottom (Figure 2). The loggers were attached to the metal samples via copper wires and epoxy. Silver paint covered with epoxy was used to ensure substantial contact between the metal and the wire. Three of each couple with wires and without wires (for mass loss data) and three of each metal uncoupled samples were exposed at each corrosion test.

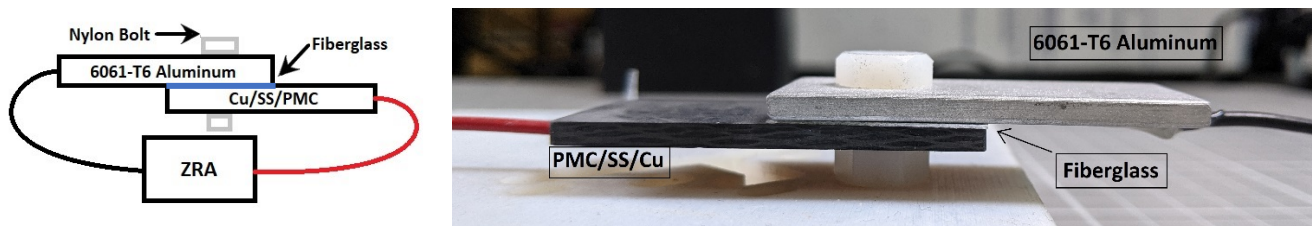


Figure 2: Galvanic Couple Configuration

Electrolytes

For the accelerated corrosion tests conducted in the humidity chamber different chloride concentration electrolyte solutions were used. Solutions used in the experiments included following solutions:

- 20,000 PPM Cl^- (3.15 wt.% NaCl)
- 10,000 PPM Cl^- (1.575 wt.% NaCl)
- 1000 PPM Cl^- (0.1575 wt.% NaCl)
- 100 PPM Cl^- (0.01575 wt.% NaCl) + 0.5 M Na_2SO_4
- 10 PPM Cl^- (0.001575 wt.% NaCl) + 0.5 M Na_2SO_4
- 0 PPM Cl^- (0 wt.% NaCl) + 0.5 M Na_2SO_4

The highest chloride content solution (3.15 wt.% NaCl) has a similar Cl^- concentration to ocean water and replicates the marine environment. For solutions with chloride concentrations less than 1000 PPM Cl^- , a 0.5 M Na_2SO_4 was used to support the electrolyte for increased ionic conductivity. The 0.5 M Na_2SO_4 chloride-free solution was used as it closely simulates fresh rainwater.

Datalogger

The galvanic current was measured by using differential voltage dataloggers and resistors. The galvanic current was calculated using Ohm's law, $R=V/I$, where measured differential Voltage and resistor were plugged into the equation. All the couples were connected to MadgeTech VoltX⁺ 12-channel DC voltage data logger with a resistor connected parallel to the circuit. The resistor size of 1 Ω was used in the humidity chamber accelerated corrosion experiment. TOW data was measured with Campbell Scientifics leaf wetness sensor (LWS)⁺ and data was recorded with Campbell Scientific CR3000 data logger⁺.

Humidity chamber

The humidity chamber coupons were exposed to a stable temperature of 30°C and relative humidity of 90% throughout the 120-hour (5 days) exposure period. The humidity chamber was equipped with an Electro-Teck system humidification system, a BriskHeat⁺ heating blanket, a fan to circulate air, and an Inkbird ITC-608T⁺ temperature and humidity controller to hold the stable conditions in the chamber throughout the experiment (Figure 3). The experiment sprayed the metal samples with an electrolyte solution for 30 seconds at the start of each cycle at 0, 24, 48, 72, and 96 hours (5 cycles). The specimens were placed at a 0-degree angle from horizontal (flat).

⁺ Trade name

Data collection

For the ZRA couples, the galvanic corrosion voltage data was measured and logged every minute. TOW (total dry and wet time) of the specimens was recorded with a leaf wetness sensor and logged every 10 minutes. Mass loss coupons were also exposed in the humidity chamber with coupon weights recorded before and after the experiment. Mass loss coupons were cleaned in the ultrasonic cleaner in Deionized water for 60 minutes. After cleaning, the weight of the coupons was recorded, and mass loss was calculated from the weight difference.

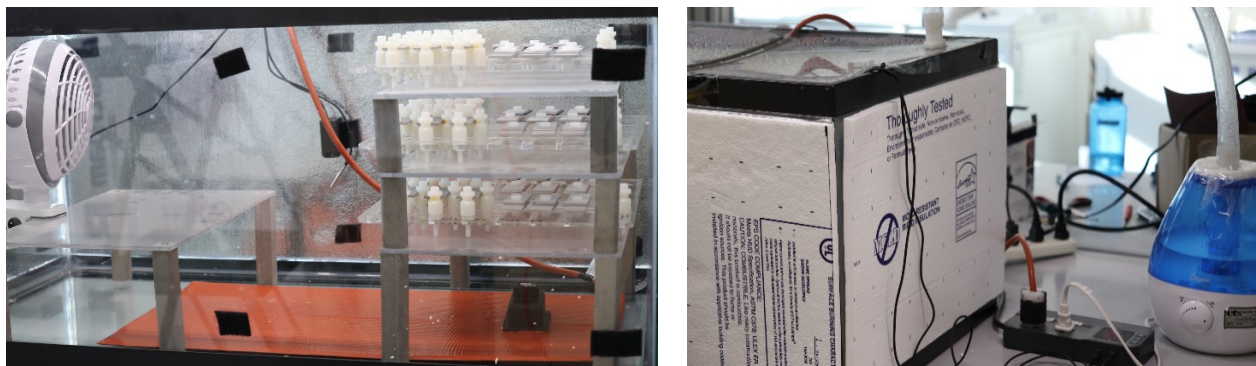


Figure 3: Humidity Chamber setup

Galvanic Corrosion Rate Study

The corrosion rate study utilized four separate equations based on Faraday's law by relating TOW to the galvanic current measured in the ZRA experiments in different exposure environments. Four separate equations (Eq. 3-6) incorporate different current density data sets retrieved from the experiment. Eq.3 contains steady-state current density (i_{ss}) that is calculated average current density of the last cycle of the experiment (last 24 hours). Eq.4 incorporates the average current density value that calculates the current density average of the whole experiment period. Eq.5 and 6 include the time of wet and dry of the coupons. All the corrosion rate study values were calculated in the units of gmd ($\text{g/m}^2/\text{day}$). Corrosion rate (in gmd) for mass loss coupons was calculated by dividing weight loss by the coupon area and the exposure period.

$$CR_1 = \frac{Aw}{n \cdot F} \cdot i_{ss} \quad \text{Eq.3}$$

$$CR_2 = \frac{Aw}{n \cdot F} \cdot i_{avg} \quad \text{Eq.4}$$

$$CR_3 = \frac{Aw}{n \cdot F} \cdot \left[\frac{i_{max} \cdot T_{wet} + i_{min} \cdot T_{dry}}{T_{total}} \right] \quad \text{Eq.5}$$

$$CR_4 = \frac{Aw}{n \cdot F} \cdot \left[\frac{i_{ss} \cdot T_{wet} + i_{min} \cdot T_{dry}}{T_{total}} \right] \quad \text{Eq.6}$$

Open Circuit Potential Measurement

Open Circuit potential was measured with respect to saturated calomel electrode (SCE), made by Koslow Scientific Testing Instruments⁺, for every electrolyte solution mentioned above (Figure 4). This helped determine and confirm which material is an anode and which is a cathode in a couple.

⁺ Trade name