CORRELATION STUDIES BETWEEN OUTDOOR EXPOSURE AND
ACCELERATED LABORATORY CORROSION TESTS FOR GALVANIC
AND NON-GALVANIC CERAMIC-ALUMINUM COUPLES

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This dissertation is dedicated to Deepika, my wife.

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Abstract

The objective of this research was to develop test protocols to analyze the corrosion between aluminum and ceramics in accelerated and natural-exposure corrosion tests. The focus was on correlating outdoor exposure corrosion behavior from a variety of microclimates with a series of accelerated laboratory corrosion tests for both galvanic and non-galvanic ceramic-aluminum (Al) couples. Electrolytes with varying amounts of chloride contents (0, 10, 100, 1000, 10000, and 20000 ppm chlorides) were used in the accelerated tests to improve correlation with field results. In addition, the outdoor exposure test data were used to adjust the duration of the accelerated corrosion tests so that the corrosion damage accumulated in the accelerated tests could better represent the corrosion damage accumulated in the field.

The galvanic ceramic-Al couples were those consisting of Al coupled to titanium diboride (TiB_2) and boron carbide (B_4C) ceramics which have resistivities of 10^{-5} and 10^1 ohm-cm, respectively. The non-galvanic couples consisted of Al coupled to silicon carbide (SiC), silicon nitride (Si_3N_4), and aluminum nitride (AlN) ceramics which have resistivities of 10^7 , 10^{14} , and 10^{15} ohm-cm, respectively.

Ceramics and 6061-T6 Al coupons were coupled together using 6061-T6 C-clamps. Outdoor experiments for 3, 6, and 12- month exposure periods were conducted at eight different test sites, to determine corrosion behavior for various climate and environmental conditions (i.e., rain forest, alpine, marine, volcanic, industrial, agricultural, and arid). Accelerated laboratory experiments include controlled humidity-chamber experiments and cyclic corrosion test chamber (CCTC) experiments following modified GM9540P using different chloride-containing solutions. Corrosion rates were

determined at the ceramic-Al interface for the outdoor and accelerated laboratory experiments using weight loss data. Polarization experiments were conducted on 6061-T6 Al to study the governing corrosion mechanisms in different chloride solutions. Zero-resistant ammeter (ZRA) studies were conducted between 6061-T6 Al and the conductive ceramics (TiB_2) inside a humidity chamber by spraying different chloride solutions in intervals of 24 hours for 5 days to simulate rain and the steady-state galvanic corrosion rates (i_{Galv}) were observed.

Keywords: Aluminum, ceramic-aluminum couples, galvanic corrosion, crevice corrosion, accelerated corrosion tests.

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CHAPTER 1

INTRODUCTION

1.1 Purpose of the Research

Today, many components and equipment are comprised of a material system rather than a single type of material. To reduce weight and increase performance, more and more advanced systems and machines are being developed using alloys, composites, polymers, and ceramics.

Traditional ceramics such as tableware, pottery, tiles, bricks, and porcelains have been used for decorative purposes for years. Advanced ceramics such as silicates, oxides, and non-oxide ceramics have unique physical properties such as a very wide range of electrical resistivities, good thermal conductivity, low density, high temperature strength, excellent wear resistance, and good corrosion resistance [1]. Some of the superior properties of advanced ceramics paved the way for their use in many technical applications which includes mechanical, automotive, aerospace, electronic, and structural. One major drawback of advanced ceramics, however, is their brittleness [1, 2, and 3]. Though ceramics are in many ways superior to metals and polymers, their brittleness and high cost limit their use as a standalone material; however, combinations with metals and other materials lead to unique and enhanced properties of ceramic-metal systems [4 and 5].

Ceramic-metal interfaces have become more prevalent with the increase in use of ceramic-metal systems. Ceramic-metal applications include hybrid ceramic/metal armor systems, metal-matrix composites (MMC), heat sinks in high-temperature electronics, and re-entry shields for space vehicles.

A system of dissimilar materials, however, can lead to potential corrosion problem. Contact between metallic and ceramic components can lead to crevice and/or galvanic corrosion in a corrosive environment. If the ceramics are electrically conductive, they are usually noble and act as a cathode in a galvanic couple. The metallic component, which usually has a lower electrochemical potential, is more active and acts as the anode. The result is that the metallic component corrodes at an accelerated rate due to galvanic and crevice corrosion. If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion. Hence, in order to take advantage of material systems, compatibility issues must be thoroughly understood.

In this research, experiments were conducted to study the compatibility between 6061-T6 aluminum (Al) and different non-oxide ceramics which were titanium diboride (TiB_2), boron carbide (B_4C), silicon carbide (SiC), silicon nitride (Si_3N_4), and aluminum nitride (AlN). With respect to electrical resistivity, the borides have metallic characteristics, carbides exhibit semiconductor characteristics, and nitrides behave as insulators [6, 7].

1.2 Research Objective

The main objective of this research was to correlate outdoor exposure corrosion-rate data from a variety of microclimates to a series of accelerated laboratory corrosion tests for both galvanic and non-galvanic ceramic-aluminum couples. Accelerated corrosion tests were modified to better predict corrosion behavior in the field. Various electrolytes were used in the accelerated corrosion tests. The outdoor exposure test data were used to adjust the duration of the accelerated corrosion tests so that the corrosion damage accumulated in the accelerated tests could better represent the corrosion damage accumulated in the field.

1.3 Method of Investigation

Electrochemical experiments: Potentiodynamic polarization and zero-resistant ammeter (ZRA) electrochemical experiments were conducted on 6061-T6 Al and TiB₂ electrodes in simulated and real seawaters. Polarization experiments were used to identify the governing corrosion mechanisms, and ZRA experiments were used to determine the steady-state galvanic corrosion rates (i_{Galv}) between 6061-T6 Al and TiB₂. The results from polarization and ZRA experiments conducted in the simulated fresh water and seawaters were correlated with the results obtained from immersion experiments.

Outdoor Experiments: Ceramics and 6061-T6 Al coupons were coupled together using 6061-T6Al C-clamps. Outdoor experiments were conducted at eight different test sites, to determine the corrosion behavior of the couples for various climate and

environmental conditions (i.e., rain forest, alpine, marine, volcanic, industrial, agricultural, and arid) for durations of approximately 3, 6, and 12 months. Statistical analysis was conducted to study the relationship between the atmospheric weather parameters such as humidity, temperature, rainfall, time of wetness (TOW), and chloride deposition rate. The correlation between corrosion rates and atmospheric weather parameters were studied using statistical analysis. The ingress of environmental constituents across the interface was analyzed using scanning electron microscope (SEM) and energy dispersive-X-ray analysis (EDXA). Raman analysis was conducted on the un-cleaned 6061-T6 Al coupons coupled to various ceramics and exposed at Kilauea, Coconut Island, and Mānoa for 12 months. The anions concentrations (chlorides and sulfates) in the corrosion product from the above samples were analyzed using ion chromatography technique.

Accelerated indoor experiments: Controlled humidity-chamber experiments were conducted on couples treated with simulated fresh water (i.e., sodium sulfate (Na_2SO_4)) and seawater (sodium chloride (NaCl), simulated, and real seawaters) to determine the effect of electrolyte type on the corrosion behavior. The couples were treated with electrolytes for one minute and kept inside a humidity chamber at 30°C with 90% relative humidity for both 21-day and 90-day exposures. Experiments were also conducted inside a cyclic corrosion test chamber (CCTC). The ceramic-Al couples inside the CCTC experiments were treated with solutions containing various amounts of chlorides and subjected to a modified GM9540P standard procedure for 2 and 24 cycles. Galvanic corrosion rates between the conductive TiB_2 ceramic and 6061-T6 Al samples were

recorded using a ZRA inside a humidity chamber and the samples were sprayed with different chloride solutions at 24-hour intervals for 5 days to simulate rain.

Corrosion rates were determined at the ceramic-Al interface for the outdoor and accelerated laboratory experiments using weight loss data. The corroded area fraction at the ceramic-6061-T6 Al interface from the outdoor exposure experiments and humidity chamber experiments were quantified using a Video Image Enhanced Evaluation of Weathering (VIEEW) surface analyzer. Average penetration rates were calculated from the area fraction and mass loss.

1.4 Principal Results

Galvanic corrosion rates from ZRA experiments were much higher in the 3.15 wt% NaCl when compared to 0.5 M Na₂SO₄ solution. During the ZRA experiments, the growth of calcareous deposits on the TiB₂ cathode limited the galvanic-corrosion rate between the 6061-T6 Al and TiB₂ electrodes in the seawaters. Galvanic corrosion rates predicted using polarization curves were in agreement to the ZRA experiments for the 3.15 wt % NaCl and 0.5 M Na₂SO₄ solutions. In immersion experiments, corrosion rates were more severe in chloride-containing environments than in chloride-free environments. Higher corrosion rates were observed in 3.15 wt% NaCl when compared to seawaters which was likely caused by calcareous deposit, as observed in the ZRA experiments.

For exposure in the outdoor test sites, a trend of higher corrosion rates were observed for 6061-T6 Al when coupled to the more conductive TiB₂ and B₄C ceramics as compared to when coupled to the much less-conductive SiC, Si₃N₄, and AlN ceramics.

The statistical analysis showed a strong positive relationship between the weather parameters TOW, humidity and rainfall; whereas, these three weather parameters showed a strong negative relationship with the temperature. The two important parameters that affected the corrosion rate of the couples were TOW and chloride deposition rate. The corrosion mechanisms at Kilauea differed significantly from the other test sites. Results from SEM/EDXA, raman analysis and ion chromatography analysis showed deposition of sulfur compounds on the samples at Kilauea test site.

In the accelerated corrosion tests such as CCTC and humidity ZRA, the high-concentration chloride treatments were too aggressive and did not produce corrosion trends observed at the outdoor test sites. Results from low-concentration chloride treatments in the accelerated corrosion tests had a better correlation with the outdoor results. The duration of the accelerated tests also altered the corrosion mechanism of the galvanic couples (i.e., Al couple to conductive ceramics) that resulted in different trends when compared to outdoor data. For long exposure accelerated tests, the buildup of insulative alumina corrosion product at the interface can galvanically decouple a conductive ceramic from the aluminum coupon, changing the driving force for corrosion from galvanic and crevice to just crevice. Hence, for some of the longer accelerated corrosion tests using high chloride solutions, there was little difference in the corrosion rates for the galvanic and non-galvanic couples.

A comparison between the corrosion rate in gmd and the corroded area fraction quantified using VIEEW analyzer showed a good correlation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This literature review is divided into four sections. The first section covers the potential uses for the coupling of non-oxide ceramics and metals; the second section discusses the potential corrosion concerns which include corrosion behavior of Al, galvanic corrosion, and crevice corrosion associated with Al; the third and fourth sections deal with atmospheric corrosion and accelerated laboratory corrosion tests, respectively.

2.2 Potential Uses for the Coupling of Non-oxide Ceramics and Metals

Ceramics are classified into traditional ceramics and advanced ceramics based on their applications [1, 3]. Tableware, pottery, tiles, bricks and porcelains are traditional ceramics. Advanced ceramics are classified based on their physical and mechanical properties and their corresponding applications. Physical properties of ceramics include thermal, electrical, magnetic, optical, and chemical properties. Mechanical properties such as tensile strength, compressive strength, and fracture toughness are useful in some of the structural applications [1, 2]. Ceramics, unlike metals, can retain strength at high temperatures [1, 4], are used instead of metals or to shield and line metals in high temperature applications. Ceramics are used as insulators, refractory and heat sinks in high-temperature electronics, heat engines and re-entry shields for space vehicles due to

its excellent thermal properties [4, 5, 6, and 7]. The range of ceramics electrical resistivity is considerable. Ceramics that have low electrical resistivities are used as heating elements in furnaces. Ceramics which act as semiconductors are used in electronic industries as thermistors, heating elements, and in integrated chips. Ceramic with very high electrical resistivities are used as insulators for electronic packages and spark plugs in the automobile industry. Some ceramics can be used as superconductors [7].

Ceramics are very hard materials with very high wear resistance [8]. This property makes them good candidates for cutting tools, bearings, and ceramic seals [3, 7]. Ceramics are used in combination with metals to increase the strength of the matrix materials in composites [3]. Metal matrix composites (MMC) and ceramic matrix composites (CMC) are used in the automobile and aerospace industries [8].

Magnetic properties of ceramics are used in various automobile parts [9]. The electromagnetic property of the ceramics allows certain wavelengths to pass through, making them ideal for communications with airplanes, missiles, or space crafts [9]. This kind of electromagnetic window is called a radome, a cone shaped covering on the tip of a missile. Ceramics also possess some optical properties like transparency and translucency that are utilized in the fiber optic industry [7]. The chemical properties of some ceramics enable them to be used as catalysts, inert electrodes for electrometallurgy, and anticorrosive coatings. Certain ceramics are also used in nuclear applications [7, 9].

Ceramics are generally subdivided according to their chemical composition and atomic structure [1, 6]. The three major subdivisions are

1. Silicates
2. Oxide ceramics
3. Non-oxide ceramics

Non-oxide ceramics such as borides, carbides, nitrides have high strength and good oxidation resistance [10]. In this research, experiments were conducted to study the compatibilities between different non-oxide ceramics in contact with metals in corrosive environments.

2.2.1 Borides

Borides are the most commonly used advanced ceramics because of their availability and low cost [8]. The diboride studied in this research is TiB_2 . In the titanium-boron binary system, TiB_2 is the stable compound [9] and it has attractive properties such as high hardness, high melting point, excellent thermal conductivity and electrical conductivity [10]. These properties are used in a wide range of applications.

In its monolithic form TiB_2 is commonly used in armors with aluminum backing material [11]. Cho and Katz studied the strength and fracture toughness of hot-pressed TiB_2 for its application in ballistic armor protection [12]. Rajendran and Grove developed a model for the shock response of TiB_2 ceramics in armor systems under impact loading [13]. TiB_2 , with a density of 4.5 g/cm^3 , is the heaviest among the ceramics studied in this research; hence, these ceramics are widely used in tactical wheel and logistic support vehicles, combat, land, and commercial vehicles for ballistic armor protection [14].

Al matrix composites with TiB_2 reinforcements are widely used in structural

application to make use of its high specific strength and high modulus [15]. TiB_2 is chemically inert and does not readily react with the aluminum matrix to form aluminum borides or other reaction products at the interface [8, 15]; hence, TiB_2 is a good candidate for reinforcement in aluminum MMCs. Aluminum MMCs with TiB_2 reinforcements are widely studied for their improved matrix strength and other applications such as wear components, cutting tools, and structural components [15, 16, 17, 18, 19, and 20].

TiB_2 ceramics are refractory boron compounds with good thermal conductivity and a low coefficient of thermal expansion. These properties are utilized in high temperature applications such as refractory linings in heat exchangers, rocket nozzles, turbine applications, and sintered pump parts [8, 11]. TiB_2 particles are also added to Si_3N_4 and SiC ceramic matrices to manufacture ceramic matrix composites (CMCs) with increased hardness, strength, and fracture toughness — attributes that make them ideal for wear parts, high temperature heaters and heat exchanger components [21, 22, and 23].

TiB_2 ceramics have electrical resistivity similar to those of metals, and their resistance to scratching and abrasion make it useful as sliding contacts in electrical systems [14]. The electrical resistivity of TiB_2 varies from $9\ \mu\Omega\text{-cm}$ to $20\ \mu\Omega\text{-cm}$ [10, 24, and 25] which is about 6 times higher than the electrical resistivity of copper. Complex shapes of TiB_2 can be achieved using electric discharge machining (EDM) due to their low electrical resistivity [10, 26]. TiB_2 is also used as evaporation boats due to its excellent electrical conductivity and high melting point [10, 26].

TiB_2 is also highly inert and will not react with molten, non-ferrous metals such as aluminum, zinc, copper [10, 26]; hence, they are widely used as inert cathodes in the production of aluminum by the Hall-Heroult cell electrolysis method [11, 26, and 27].

2.2.2 Carbides

The two most commonly used advanced ceramic carbides are B₄C and SiC [28].

2.2.2.1 B₄C

At room temperature, B₄C is the third hardest material known after diamond and cubic boron nitride [28] and it is the hardest material to be produced in large quantity (in tons) [29]. Due to its high thermal stability, B₄C is the hardest material above 1100⁰C [30]. B₄C is used as abrasives, and cutting tools, blast nozzles for sand blasting [3, 8, and 29], and shrink fitting parts onto metal sleeves [29].

B₄C, with a density of 2.5 g/cm³, is the lightest of the five ceramics studied in this research [14]. The combination of its low density and high Young's modulus makes it an excellent component for light-weight armor system [31, 32]. B₄C ceramics backed by aluminum plates have been used successfully as personal and helicopter armors [3, 8, 28, 33, and 34].

The low specific gravity, high elastic modulus, and high hardness of MMCs with B₄C particles or B₄C whiskers make them ideal materials for structural applications, and for the automobile and aerospace industries [35, 36, 37, and 38]. B₄C containing MMCs are not commonly used for high temperature applications due to the possible reaction between the B₄C reinforcement and the metal matrix at high temperature [28, 39].

B₄C has an electrical resistivity of 10 Ω-cm, and therefore is the second most conductive ceramic in this research [14]. Its high melting point, low thermal conductivity, and high electrical conductivity make it an excellent material for high-temperature thermo-electric generators, thermo-electric converters, and high temperature

semiconductors [40, 41, and 42]. B_4C is also photo-luminescent [43].

B_4C compositions exist in the range of $B_{4.3}C$ (carbon-rich limit) to about $B_{11}C$ (boron-rich limit) [29, 44, 45, and 46]. B_4C with its high boron content are excellent neutron absorber [29]. The flexibility of synthesizing B_4C with different amounts of boron ($B_{4.3}C$ to about $B_{11}C$), long-half life decay products from nuclear reactions, very high cross section for neutron absorption and lack of producing secondary radioactive products makes B_4C a promising candidate for structural neutron absorber components [29, 44, and 47].

2.2.2.2 SiC

SiC can be synthesized into cubic β and hexagonal α crystalline forms, and are the earliest non-oxide ceramics used as advanced and technical ceramics [40, 48]. The high hardness and wear resistance of SiC make it useful as seal rings for water pumps, bearings, and pistons, and other automobile components [1, 48, and 49].

The combined mechanical properties of SiC and metal backings are also exploited in the hybrid ceramic-metal armor industry with improved ballistic performance [13, 14]. MMCs reinforced with SiC are attractive materials for automobile, aerospace and high temperature components [50, 51, 52, and 53]. SiC whiskers are also used as reinforcements to manufacture MMCs to use in structural applications [54, 55].

Excellent thermal shock resistance and high thermal conductivity of SiC make it useful as refractory linings for metals in heat exchangers, gas turbines, and turbo chargers [56, 57]. CMCs with SiC matrices are stable at very high temperature and used as rocket nozzles, radiant burners, combustor linings, re-entry shields for space shuttles, heat exchanger tubes, and brake linings for airplanes [49, 58].

2.2.3 Nitrides

Si_3N_4 and AlN , the two nitrides studied in this research, are electrical insulators with resistivities of 10^{14} and 10^{15} $\Omega\text{-cm}$, respectively [14]. Nitrides are generally considered as structural ceramics due to their high mechanical strength, corrosion resistance, and high temperature stability [59].

Si_3N_4 is used as tile armors for lead and steel projectiles. The ability of Si_3N_4 to withstand multiple hits from the projectiles and low cost are attractive features of $\text{Si}_3\text{N}_4/\text{Al}$ [14]. Si_3N_4 can be synthesized in two crystalline forms (α and β) with β as the more stable form in high temperature applications [59]. Some applications of Si_3N_4 are ceramic seals, bearings, check valves, chemical-plants components, gas turbine, and turbo charger components [1, 49, 60, 61, and 62]. The thermo-mechanical and dielectric properties of Si_3N_4 make it ideal for radome and space shuttle thermal lining applications [63, 64, and 65]. Si_3N_4 ceramics are used in electronic industry as insulators [66]. The dielectric property of Si_3N_4 makes it useful for microelectronic applications [63, 66, and 67].

AlN has not only the highest thermal conductivity among the ceramics tested in this research but also has low thermal expansion, high tensile strength and high ductility [14]. These properties are useful in heat sink and thermo-mechanical applications [68, 69]. AlN is used as insulators in electronic packages because of its high thermal conductivity and high electrical resistivity [1]. AlN is also used as piezoelectric materials in surface-acoustic-wave device applications [70, 71].

Summary: Ceramic-metal interfaces have become more prevalent with the increase in use of hybrid systems.

Figures 1 through 8 show some of these ceramics applications.

Figure 1. Automobile spark plug with metal-ceramic joints manufactured by Delphi Automotive Systems, Flint, MI.

Figure 2. Ceramic nut and bolt for high temperature applications manufactured by Coors Ceramics Golden, CO.

Figure 3. Gas turbine engine rotor with Si_3N_4 blades mounted in a metal disk manufactured by Solar Turbines, Inc., San Diego, CA.

Figure 4. Si_3N_4 air turbine starter attached to a metal shaft manufactured by Allied Signal Ceramic Components, Torrance, CA.

Figure 5. SiC water-pump seals in automobile industry manufactured by Saint/Gobain/Carborundum Structural Ceramics, Buffalo, NY.

Figure 6. Electrical insulators manufactured by Rauschert Industries, Inc., Madisonville, TN.

Figure 7. Si_3N_4 parts for aerospace and high temperature applications manufactured by AlliedSignal Ceramic Components, Torrance, CA.

Figure 8. Ceramic radomes manufactured by Ceradyne, Inc., Costa Mesa, CA.

2.3 Potential Corrosion Concerns

Corrosion behavior of Al and potential corrosion concerns of Al when coupled to ceramics such as galvanic and crevice corrosion are discussed in this section.

2.3.1 Corrosion Behavior of Al

Al is the second most commonly used metal after steel and lead the table in the consumption of non-ferrous metals (approximately 25 million tons per year) for various technical applications [72]. The properties of Al alloys which attribute to their world wide use are: lightness, thermal conductivity, electrical conductivity, suitability for surface treatments, and corrosion resistance. The two main attractive features of Al alloys are lightness and corrosion resistance. Al alloys can also be joined to other materials with ease to enhance their combined properties with the following techniques: welding, bolting, riveting, clinching, adhesive bonding, and brazing [72].

Al is listed in the active region in the Electromotive Force (EMF) series because of the negative standard potential of $-1.66 \text{ V}_{\text{SHE}}$ (V_{SHE} -volts with respect to standard hydrogen electrode) at 25°C for the oxidation reaction $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$ [73]. The negative standard potential of Al due to its negative free energy ($-\Delta G$) value of -440 Kcal/mol makes Al alloys unstable in the presence of moisture [72]. In spite of having a thermodynamic tendency to corrode, Al and its alloys are good corrosion resistant materials when exposed to the atmosphere and to many aqueous electrolytes because of their ability to form a chemically inert Al oxide layer called alumina on exposure; this film formation resists the dissolution of Al metal into its ions (oxidation of Al) [73, 74].

An alumina protective layer bonded to the Al surface is stable in most neutral environments [75].

2.3.2 Galvanic Corrosion

Galvanic corrosion is defined as accelerated corrosion of a metal due to electrical contact with a more noble metal in a corrosive environment [76]. The material, which usually has a lower electrochemical potential, is more active and acts as the anode where oxidation takes place. The material, which has a higher (positive) electrochemical potential, is less active or more noble and acts as the cathode where hydrogen evolution and/or oxygen reduction take place. Electrochemical potential here refers to corrosion potential (E_{Corr}) or open circuit potential (OCP) in the same electrolyte and same conditions and they are not the equilibrium potential of the respective materials. Al alloys mostly become anodic when coupled to other materials because they are more active than many of the other materials in the galvanic series [77]. The three conditions for a galvanic couple to exist are

1. At least two different conductive materials must be involved
2. The materials must be in electrical contact so that current can flow between them
3. A corrosive medium or electrolyte

If any one of these three conditions is removed, galvanic corrosion will not occur [78].

In this study, when Al coupons are coupled to different ceramics for certain applications, Al acts as anode and conductive or semi-conductive ceramics become cathode and form a galvanic cell. At the anode, Al^{3+} ions and electrons are generated (equation 1) as a result of oxidation in the galvanic cell. These electrons are consumed at the cathode surface

(more noble metal) either by hydrogen evolution (equation 2), oxygen reduction (equation 3), or both. Hydrogen evolution takes place if the cell is deaerated. The H^+ protons are formed as a result of water dissociation ($H_2O \leftrightarrow H^+ + OH^-$). Oxygen reduction and/or hydrogen evolution take place if the cell is aerated.

Anodic reaction:

Cathodic reaction:

The flow of electrons causes a current flow in the electric conductor equal in magnitude to the ionic current flowing in the opposite direction in the electrolyte (Figure 9). Lack of electrolyte or an electrolyte void of charge carriers ceases the ionic current, thus limiting galvanic corrosion.

According to Faraday's law (equation 4), the amount of current flowing between the anode and the cathode is directly proportional to the amount of anodic material (Al in this case) that is dissolved [79].

$$M = (At. \text{ Wt.} \times I \times t) / (n \times F) \quad (4)$$

$M \equiv$ mass of Al dissolved to produce galvanic current (g)

At. wt. $\equiv$ atomic weight of Al (g)

$I \equiv$ current generated (Amperes)

$t \equiv$ time (sec)

$n \equiv$ moles of electrons per moles of Al reacted

$F \equiv$ Faraday's constant = 96487 (Ampere sec/moles of electrons)

Figure 9. Electrolytic cell showing flow of ionic and electric current.

The fundamental relationship involved in galvanic corrosion is described by Kirchhoff's Second law [73].

$$\sum E = \sum IR \quad (5)$$

From Kirchhoff's law the galvanic current (I_{Galv}) between the anode and the cathode is determined using equation 6.

$$I_{Galv} = (E_c - E_a) / (\sum R) \quad (6)$$

where E_c and E_a are the open circuit potentials of the cathode and the anode materials.

The summation of the resistance term ($\sum R$) is given in equation 7 [80].

$$\sum R = R_a + R_c + R_s + R_m \quad (7)$$

R_a and R_c are the resistance of the anode and the cathode materials, respectively. R_s is the resistance of the solution between the anode and the cathode. The metal resistance (R_m) from the anode surface to the cathode surface through a metallic path is normally negligible if the anode and the cathode are in direct electrical contact. Any factors affecting the "E" and "R" parameters can influence the I_{Galv} (equation 6) between the electrodes. Theoretically, lesser the $\sum R$ term in equation 6, higher the I_G flowing between

the electrodes. An increase in I_G implies a higher corrosion rate (Faraday's law). Some of the factors that affect the galvanic corrosion are summarized in Figure 10 [78].

Figure 10 . Factors affecting galvanic corrosion [78].

The galvanic effect of two dissimilar materials can be predicted using polarization experiments. Anodic and cathodic polarization curves for materials A and B in the same electrolyte are plotted together in Figure 11. The corrosion potential (E_{corr}) values in the Figure 11 represent the open circuit potentials (OCP) of the respective materials. Anodic curves and cathodic curves are obtained by polarizing the materials from the OCP in the positive and negative directions, respectively. The dotted lines along the polarization curves are the extrapolated Tafel plots to determine the corrosion current (I_{corr}). When materials A and B are electrically connected, the potential difference between the materials causes a current flow between them which is measured using an ammeter. This

measured current is equal to the “ I_{measured} ” value at the intersection of the anodic curve of material B and the cathodic curve of material A. The measured current between the electrodes is higher than the I_{corr} value of the material B. This increase in current due to galvanic effect causes corrosion rate of the active material to increase when electrically coupled to a noble material in a corrosive environment. Another important factor in the galvanic couple is IR loss. Current flowing between the two electrically connected materials experiences a voltage loss which is given by the Ohm’s Law: $E=IR$. As discussed earlier conductivity of the electrolyte, distance between the metals, and resistivity of the material are the contributing factors for the resistance in the IR term. The corrosion current or I_{measured} are lesser than the maximum I_{Galv} value if the IR loss is greater.

Figure 11. Hypothetical polarization curves

2.3.3 Crevice Corrosion

If the ceramic is an insulator, only crevice corrosion is a concern at the Al/ceramic interface. Localized corrosion taking place within a crevice formed as a result of holes, gasket surfaces, over lapping zones from riveting, bolting or welding for various applications is termed as crevice corrosion [72]. Crevice as wide as 1/8th of an inch is not subjected to crevice corrosion whereas an opening as small as a few thousands of an inch or less is sufficient for the liquid to enter and initiate crevice corrosion [81].

The potential-pH diagram (Pourbaix diagram) for the Al-water system at 25°C [82] shows that Al tends to form a protective aluminum oxide ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) film in the 4-9 pH range (Figure 12). However if a crevice is present, the solution becomes acidified and makes the passive films unstable inside the crevice.

Figure 12. Potential –Ph diagram for Al-water system at 25 °C.

Alkire and Siitari [83, 84] showed the relationship between pH and current distribution inside the crevice. The experiments were conducted with aluminum system with pre-designed crevices in aerated dilute chloride solutions. Initially the corrosion was

uniform throughout the sample due to the anodic reaction of aluminum. The anodic reaction was balanced by the cathodic reaction (oxygen reduction and/or hydrogen evolution). Over a period of time the transportation of oxygen inside the crevice was restricted; hence the anodic reaction inside the crevice was balanced by oxygen reduction outside the crevice. The Al^{3+} ions from the anodic reaction combine with H_2O to form $\text{Al}(\text{OH})_3$ (equation 8) [74] inside the crevice which leaves the crevice with excess H^+ ions. Acidification within the crevice accelerates the corrosion rate by breaking down passivity.

Herbet and Alkine [85] modelled the influence of various parameters such as pH, chloride concentration, and dissolved Al inside the crevice. The initiation of crevice corrosion due to the acidification process was excluded and they concluded that the metal ions (Al^3) in the crevice was above a critical chloride concentration limit (0.0005-0.025N) which in turn broke down the passive layer.

Reising [86] conducted electrochemical experiments to measure corrosion potentials, charge transfer resistances, and capacitances for 6061 Al alloy in chloride solutions. The main reason for the crevice corrosion mechanism highlighted by Reising was due to the acidification process and the subsequent migration of chloride ions into the crevice for charge neutrality [86].

Alavis and Cottis [87] determined the pH values inside the crevice using a palladium/hydrogen diffusion electrode and showed that the pH values were acidic near the mouth of the crevice and alkaline in the deeper part of the crevice. Although they didn't explain the chemistry behind this phenomenon, the pH gradient was believed to be

the reason for the passive layer breakdown and they also found that the activity of chlorides in the crevice was not that different from the bulk solution.

Fotnanna and Greene [75] proposed a crevice corrosion mechanism which was widely accepted. The following five steps summarizes their model (Figure 13):

1. Initially normal anodic and cathodic reaction takes place both inside the crevice and outside the crevice.
2. Over a period of time oxygen is depleted in the crevice, resulting in only anodic reaction inside the crevice and oxygen reduction (cathodic reaction) takes place outside the crevice.
3. Chloride ions are migrated towards the crevice which has excess Al^{3+} ions to maintain charge neutrality.
4. High levels of chloride ions and acidic solution breaks down passivity and accelerates corrosion in the crevice.
5. Corrosion is accelerated in the crevice even in the chloride-free solution due to the acidic nature of the crevice.

Figure 13. Crevice corrosion mechanism

Summary: If the ceramics are electrically conductive both galvanic and crevice corrosion are concerns. If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion. The result is that the Al component corrodes at an accelerated rate due to galvanic and crevice corrosion.

2.4 Atmospheric Corrosion

Metals degrade when exposed to the atmosphere by reacting with the environment to return to their oxide state (lower energy level) and this oxidation process is termed as atmospheric corrosion [72]. Atmospheric corrosion is a complex process which involves chemical, electrochemical, and physical changes to the metal exposed [88]. It is an important form of corrosion because many structures and systems are used in natural environments. In general, the environment is categorized as rural, urban, industrial, and marine based on the corrosion rates of exposed samples and atmospheric conditions [89]

Al upon exposure to the environment corrodes relatively slowly when compared to other metals due to its ability to form a thin layer of protective alumina film. The corrosion rate of Al increases in marine and industrial areas. The chloride ions in the marine atmosphere and sulfur ions in the industrial environment contribute to the higher corrosion rates when compared to other environments. The factors that affect the corrosion rates other than chlorides and sulfur ions are rainfall, temperature, humidity, and time of wetness [90].

Blucher et al. [91] studied the influence of chloride and sulfate ions by conducting experiments in NaCl, Na₂SO₄, AlCl₃.6H₂O and MgCl₂.6H₂O solutions. Corrosion rates were aggressive in the sodium chloride solution because the sodium ion

enhanced the development of alkaline region in the cathodic sites which dissolved the passive alumina layer. The corrosivity decreased in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution followed by $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 solutions. Although $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ had chlorides in the solution corrosion rates were lower due to the inability of Mg^{2+} to maintain the pH in the alkaline region. The corrosion rates were the least in Na_2SO_4 solution due to the inability of sulfate ions to initiate pitting of aluminum as compared to chlorides. Experiments conducted with carbon dioxide which occurs naturally in the atmosphere showed no effect on the corrosion rate of atmospheric corrosion of Al [72].

Oesch and Faller [92] exposed Al to air pollutants such as sulfur dioxide, nitrogen dioxide, and ozone in the laboratory under humid conditions. The corroded samples were investigated using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis, and ion chromatography for identifying the anions. The corrosion rates were strongly influenced by ozone followed sulfur dioxide and nitrogen dioxide.

Corvo and Mendoza [93] exposed non-ferrous metals at three different test site (coastal, urban-industrial and rural) for 18 months both indoors and outdoors. The statistical model performed using STATISTICA Release 4.5 following a stepwise multiple regression analysis showed corrosion rates had strong dependence on chloride deposition rate and rainfall. Other parameter that had significant effect on corrosion rate was time of wetness for the samples exposed outside where the temperature was between $25\text{-}35^\circ\text{C}$.

As mentioned above atmospheric corrosion depends on various environmental factors but most of the atmospheric corrosion models are predicted using the empirical kinetic formula (equation 9) which takes time as the only function [94]:

$$M = Kt^n \quad (9)$$

where “M” is the mass loss per unit area and “t” is the exposure time. The empirical coefficient like proportionality constant (K) and exponent (n) usually takes care of other environmental factors. This kind of model is usually good in predicting the corrosion rate over a period time for various atmospheric conditions. Natesan et al. [95] mapped India by exposing mild steel, galvanized iron and Al at 10 different test sites. The k and n values were obtained using linear regression and the 10 different test sites were ranked based on their corrosivity index.

Summary: The time dependant models may often estimate the corrosion rates inaccurately if the concerned environments are different from the environment in which the model was calibrated. In this study, the measured corrosion rates of Al in the galvanic and non-galvanic couples for three different exposure periods from eight different environments will be used to understand the environmental parameters that affect the corrosion rates which includes rainfall, humidity, temperature, chloride ion deposition rate, and time of wetness.

2.5 Accelerated Laboratory Experiments

Laboratory experiments are divided into following categories: electrochemical experiments, immersion tests, simulated atmospheric tests, and environmentally aggressive tests [96]. In this study, accelerated laboratory experiments refer to humidity

chamber experiments and cyclic wet/dry exposure tests conducted on galvanic and non-galvanic couples.

Standardized accelerated laboratory corrosion experiments are used to screen materials and components; the results from this indoor corrosive environments are used to evaluate their performance in the field. A correlation between laboratory tests and outdoor exposure tests should exist in order to validate the accelerated laboratory corrosion tests. Often the accelerated laboratory corrosion tests are too aggressive and do not represent the actual performance in the field.

The most widely used standardized corrosion test is the salt spray ASTM B117 method [97]. The main 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” [98]. In order to reproduce data that correlated well with the outdoor field data, series of modifications are developed over the years. The next generation of accelerated corrosion tests are cyclic test which gives more realistic and better correlation with outdoor exposure data than the conventional salt-spray tests [99]. The dry-off cycle is added to the test methods and this modification is included in the ASTM G85 standard test [100]. More variables like humidity, temperature, and varying salt solutions added to the wet/dry cycles simulate the environmental conditions more precisely [99].

Harrison, Tickel, and Barraclough [101, 102] showed the continuous spraying of sodium chloride solution resulted in inaccurate prediction of corrosion products for steel in industrial environments. The reason for the unreliable results in the accelerated tests was due to the absence of ammonium and sulfate ions which were found in the industrial

environments. The correlation improved with the mixed-solution of 3.5% ammonium sulfate and 0.25% sodium chloride with wet/dry cycle. Timmins [103] suggested a dilute mixture of the above solution (0.35% ammonium sulfate and 0.05% sodium chloride) for spraying and the cabinet was sprayed with the dilute mixed-solution intermittently for the first one hour and dried at 35° C for the next one hour followed by natural cooling.

Lyon et al. [104] conducted accelerated atmospheric corrosion testing on Al wires centrally reinforced with galvanized steel. Lyon et al. following Timmins wet/dry cycle [103] and had two sets of experiments with varying salt concentration. Timmins high-sulfate mixed-solution (0.35% ammonium sulfate and 0.05% sodium chloride) did not reproduce the corrosion products as found in the industrial environments whereas a high-chloride mixed-solution (0.05% ammonium sulfate and 0.35% sodium chloride) was successful in replicating the corrosion products found in the outdoor experiments.

Lyon et al. [105] compared the cabinet results with the atmospheric exposure results in another study and concluded that wet/dry cycle test was a better representative of outdoor conditions than the continuous salt-spray test for the following reasons:

1. Thin layer of moisture was maintained at the surface which enhanced a steady state corrosion
2. Concentration of salt particles increase as the surface film dried out during the dry-off cycle which in turn increased the corrosion rate
3. Corrosion process was arrested after humidity dropped below the critical value which was required to maintain the moisture level
4. Corrosion rate increased after the next wetting cycle

Summary: The corrosion behavior of a material or a component is evaluated by service history, field tests, or accelerated corrosion tests. The service history predicts the system's life more accurately followed by field tests and accelerated laboratory tests. But time and budget constraints make service history and field tests almost impossible for material selection and evaluation. Accelerated tests can be a valuable tool if proper study has been conducted and showed better correlation with the field exposure tests. It is also important to know whether to follow the existing standard tests or devise new test methods. If the accelerated tests are used solely as a proving test existing standardized tests can be used although they are not a good representation of the atmospheric attack provided the standardized tests can be reproducible. In order to model a test for various environments, new test methods should be devised considering all the environmental parameters.

Overall Summary: Al alloys are predominantly used in many technical applications due to its light weight. Al alloys also exhibit excellent corrosion resistance on exposure to environments due to its tendency to form a protective oxide layer. But the corrosion concerns remain in the form of galvanic and crevice corrosion when Al alloys are used in conjunction with ceramics for various applications. The literature information on the electrochemistry and corrosion behavior of conductive ceramics is limited to high temperature acidic environments. Very little work has been done on the corrosion behavior of ceramics in neutral solutions at room temperature [106, 107, and 108]. An extensive literature search was conducted for previous works on the corrosion at the ceramic/metal interfaces. Unfortunately, there has been no reported work in this area.

Limited literature sources exist on the correlation between accelerated laboratory corrosion tests and outdoor tests for uncoupled materials.

In this study, electrochemical experiments will be conducted with the Al and conductive ceramics samples to identify the governing corrosion mechanisms in near neutral solutions. A data base of corrosion rates for the galvanic and non-galvanic couples will be developed for various environments by taking advantage of Hawai'i's diverse climatic conditions. A series of modified accelerated corrosion tests for galvanic and non-galvanic couples will be correlated with outdoor data to better understand the operating corrosion mechanism in field exposure, and to develop new accelerated tests that better predict outdoor corrosion behavior.

CHAPTER 3

MATERIALS

3.1 Ceramics

The ceramics used in this research were manufactured by Ceradyne, Inc., California. Ceramics with a wide range of electrical resistivities were selected to study their effect on galvanic corrosion: TiB_2 (10^{-5} ohm-cm), B_4C (10^1 ohm-cm), SiC (10^7 ohm-cm), Si_3N_4 (10^{14} ohm-cm), and AlN (10^{15} ohm-cm). For the outdoor and laboratory corrosion experiments, the ceramics were cut into 1 inch x 1 inch tiles by Ceradyne, Inc. The thicknesses of the ceramic tiles were 0.25 inches (TiB_2 and B_4C), 0.24 inches (SiC), and 0.2 inches (Si_3N_4 and AlN). All of the ceramics were hot pressed. Table 1 shows the material properties of the ceramics [14].

Table 1. Ceramic Properties

Property	TiB_2	B_4C	SiC	Si_3N_4	AlN
Purity (%)	>98.5	99.5	98.5	>98.5	>99.5
Density (g/cm^3)	4.5	2.5	3.2	3.1	3.26
Electrical resistivity ($\Omega\text{-cm}$)	10^{-5}	10^1	10^7	10^{14}	10^{15}

The surface roughness of the above mentioned ceramics were measured using a Sheffield Profilometer Model QEI-2. The average values of the measured arithmetic

roughness heights (R_a) of the ceramics along the grinding marks and across the grinding marks are listed in Table 2. AlN was found to be the roughest ceramic among those tested.

Table 2. Average surface roughness (R_a) of the ceramics in micro inches

Materials	X- direction	Y-direction	Average
TiB ₂	10.88	13.36	12.12
B ₄ C	6.48	12.48	9.48
SiC	9.44	22.4	15.92
Si ₃ N ₄	9.28	21.92	15.6
AlN	42.32	47.04	44.67
6061-T6 Al	13.33	26.33	19.83

X-along the grinding marks; Y-across the grinding marks

3.2 Al Alloy

The 6061-T6 Al alloy was coupled to these ceramics which were cut into 2 inch x 2 inch tiles from 0.125 inch thick sheets. The composition 6061-T6 Al alloy with an electrical resistivity of $4 \times 10^{-6} \Omega\text{-cm}$ [109] is shown in Table 3.

Table 3. Composition of 6061-T6 Al [110]

Material	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
6061-T6 Al	0.4-0.8	0.7	0.15- 0.4	0.15	0.8-1.2	0.04- 0.35	0.25	0.15

3.3. Couple Holder

C-clamp holders machined from 6061-T6 Al were used to couple 6061-T6 Al coupons to the ceramic tiles (Figure 14). A 6061-T6 Al bolt (5/16-18 X 1 in.) was used in the C-clamp to hold the 6061-T6 Al coupon and ceramic tile in place. The 6061-T6 Al bolts were manufactured by Non-Ferrous fastener Inc., CA. The holders and bolts were made of the same alloy as the Al in the couple to eliminate contamination. The front and side views of the holder are shown in Figure 14 and the 3-dimensional view of the holder is shown in Figure 15.

Figure 14. Front and side view of the holder

Figure 16. Couple holder, couple, and bolt in place

The C-clamps were torqued from 10 to 50 in-lbs in increments of 10 in-lbs to measure deflection of the arms. For reproducibility, at each torque level, the clamp was torqued and re-torqued six times resulting in six deflection measurements. The preload on the bolt was estimated from the deflection values. Using the torque, preload, and bolt diameter values, the torque factor K was determined. The average K based on 30 measurements was determined to be 0.052 with a standard deviation of 0.004. The bolts of the C-clamp were torqued to 35 in-lbs resulting in approximately 2000 lbs force preload that secured the ceramic and 6061-T6 Al specimens together.

Figure 17. A typical ceramic/6061-T6 Al couple.

3.4 Electrolytes

Electrolytes used in the immersion and humidity chamber experiments were 3.15 wt% NaCl, 0.5 M Na₂SO₄, ASTM seawater, real seawater, and 18.1 MΩ-cm water. Electrolytes were classified into two major groups: chloride-free and marine-type.

Chloride-free electrolytes

18.1 MΩ-cm water

0.5 M Na₂SO₄

Marine-type electrolytes

3.15 wt% NaCl

ASTM seawater

Real seawater

The 18.1 MΩ-cm water was dispensed using the Barnstead/Thermolyne NANOpure® Diamond™ Life Science (UV/UF) Ultrapure water system. The 3.15 wt% NaCl and 0.5 M Na₂SO₄ solutions were prepared from reagent-grade chemicals and

18.1 M Ω -cm water. The ASTM seawater was prepared using ASTM D-1141-52 sea salt.

Table 4 shows the standard composition of the ASTM sea salts in weight percent [111].

The density of ASTM seawater equals 1.025 (g/cm³) at 15°C.

Table 4. Composition of ASTM sea salt

Salts	Wt%
Nacl	58.490
Mgcl ₂ 6h ₂ o	26.460
Na ₂ so ₄	9.750
Cacl ₂	2.765
Kcl	1.645
Nahco ₃	0.477
Kbr	0.238
H ₃ bo ₃	0.071
Srcl ₂ .6h ₂ o	0.095
Naf	0.007

Real seawater was obtained from the Waikiki Aquarium. Seawater was also collected from the Coconut Island shore within 25 feet of the test racks. The Coconut Island, Waikiki- Aquarium, and ASTM seawaters were tested for their ionic constituents. Table 5 shows the major ionic constituents of the seawaters, which are also compared to other data in the literature. The 3.15 wt% NaCl solution contains 19,108 parts per million (ppm) of chloride ion (Cl⁻), a ratio that is similar to the real seawater and the ASTM seawater.

Table 5. The major ionic constituents of different types of seawater

Ions	Waikiki* (ppm)	Coconut island* (ppm)	Astm seawater* (ppm)	Iapso (ppm)	The oceans, Prentice- hall,inc., Newyork,1942 (ppm)
Calcium, Ca^{++}	429.50	365.77	516.66	432	400.1
Magnesium, Mg^{++}	1513.58	1319.84	1731.60	1348	1272
Sodium, Na^{+}	10461.5	9113.82	10118	11266	10556.1
Potassium, K^{+}	356.13	323.24	396.74	411	380
Chloride, Cl^{-}	19581.5	17074.23	20488	19900	18980
Sulfate, So_4^{--}	2663.46	2294.38	2596.6	2712	2649
Bromide, Br^{-}	61.10	54.34	141.57	67	64.6

*Analysis performed by Dr.Huebert, Dept. of Oceanography, University of Hawai'i .

Various amounts of chloride solutions were used in the CCTC and humidity chamber-ZRA experiments and the details are given in the respective chapters.

3.5 Electrode Fabrication

The 6061-T6 Al and TiB₂ electrodes were fabricated in the laboratory. Al coupons with a thickness of 0.3175 cm were cut into 1 cm x 1 cm squares using an IsometTM low speed saw. The four corners of each Al square were rounded off to reduce any stress concentration in the epoxy surface surrounding the corners. One of the faces was sanded using 320-grit SiC paper. The Al squares were then cleaned in acetone and cleaned ultrasonically in 18.1 MΩ-cm water for 20 minutes. A 10-in. copper wire was attached to the ground face of each Al square with silver conductive epoxy (MG Chemicals 8331-14g) and cured in an oven at 70°C for 20 minutes. An 8-in. glass tube was slid over the copper wire. The end of the glass tube that contacted the Al square was covered with 0151 Hysol epoxi-patch adhesive. The adhesive was applied in a manner such that Al was bonded to the glass tube leaving a surface area of 1 cm x 1 cm exposed. The 0151 Hysol epoxi-patch adhesive was cured at 70°C for 2 hours. The electrodes were ground using a Buehler Ecomet® 6 variable speed grinder-polisher. The surface area that was exposed was ground flat with 180-grit SiC paper followed by 320-grit, and 600-grit SiC papers. The electrodes were then examined under an optical microscope to detect and avoid any crevices around the edges of the exposed area and the epoxy surface. Electrodes were then successively polished to a mirror-like finish using Buehler micro-cloth and slurries of 1 micron alpha alumina, 0.3 micron alpha alumina, and 0.05 micron gamma alumina powder. Figure 18 shows a typical ground and polished 6061-T6 Al electrode. The TiB₂ squares were cut into 1 cm x cm squares with a thickness of 1 mm by Ceradyne, Inc. The procedure described above was followed to fabricate each TiB₂ electrode.

Figure 18. A typical ground and polished 6061-T6 Al electrode.

CHAPTER 4

ELECTROCHEMICAL EXPERIMENTS

4.1 Introduction

Electrochemical experiments were conducted using the potentiodynamic polarization and ZRA techniques to study how TiB_2 affects the corrosion of 6061-T6 Al by galvanic interaction in various electrolytes. The rate of corrosion can be measured conveniently using the electrochemical techniques as most of the corrosion phenomena have an electrochemical nature [112].

4.2 Potentiodynamic Polarization

Anodic and cathodic polarization of 6061-T6 Al and cathodic polarization of TiB_2 electrodes were conducted with a Model 273A potentiostat/galvanostat. Electrodes were prepared as discussed in section 3.5. Polarization experiments were conducted in 3.15 wt% NaCl, 0.5 M Na_2SO_4 , ASTM seawater and real seawater. The material with the more negative corrosion potential (E_{Corr}) or open-circuit potential (OCP) is the anode, and the material with the more positive OCP is the cathode. In this study, TiB_2 was the cathode. Each polarization experiment was performed three times in aerated and deaerated conditions in the aforementioned solutions. A platinum electrode was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The specimens were stabilized at the OCP for 1 hour before scanning in either

the anodic or cathodic direction at the rate of 1 mV/sec. Some of the experiments were conducted at slower scan rates, and all scan rates are specified next to the respective figures.

The rate of galvanic corrosion was predicted using polarization curves of the individual materials. Polarization curves were generated as a function of potential and plotted with the average logarithm of three current density values. The i_{Galv} and E_{Galv} values correspond to the intersection of anodic curve of 6061-T6 Al and cathodic curve of TiB_2 . Figure 19 shows the schematic diagram of the polarization setup.

Figure 19. The schematic diagram of the polarization setup.

4.3 ZRA Technique

The change in galvanic corrosion rate over a period of time was measured using the ZRA technique. Short-circuit current between the two electrically connected materials is related to the rate of the mass loss of the active metal due to the galvanic effect [113].

Figure 20 shows the general circuit diagram of a commercial ZRA instrument [114]. The potential difference between the electrodes are maintained at zero and the galvanic current (I_{Galv}) or the true short circuit current between the electrodes is derived from the voltage output of the operational amplifier and the feedback resistance [114]. This short-circuit current can also be measured using a potentiostat by setting the control potential to zero volts.

Figure 20. Schematic of a ZRA circuit [114].

The 6061-T6 Al and TiB_2 electrodes were fabricated with a surface area of 1 cm^2 (See section 3.5). The ZRA experiments were conducted in a three-electrode setup in 3.15 wt% NaCl, 0.5 M Na_2SO_4 , ASTM seawater, and real seawater electrolytes. The magnitude of the galvanic corrosion current (I_{Galv}) depends on the area ratio of the electrodes. The measured I_{Galv} was the normalized current density (i_{Galv}) since the area ratio of the anode and the cathode was one in this case. A saturated calomel electrode (SCE) was used as a reference electrode to measure the galvanic potential (E_{Galv}). The i_{Galv} and the E_{Galv} values of the couple were measured using a ZA100 ZRA and an

EM002 Electrometer, respectively, both of which were manufactured by Intertech Systems Inc., CA.

Measured i_{Galv} and E_{Galv} values were recorded in VOLT101 data loggers manufactured by Madge Tech, Inc., NH. The electrical connection between 6061-T6 Al and TiB_2 electrodes immersed in an electrolytic cell was made through a ZRA to measure i_{Galv} . The SCE inside a reference cell was connected electrically to a 6061-T6 Al electrode through an electrometer to measure E_{Galv} . Ionic contact between the electrolytic cell and the reference cell was made by a luggin probe. Simultaneous measurements of i_{Galv} and E_{Galv} help to determine the changes in corrosion reaction kinetics [115]. Figure 21 shows the schematic diagram of the ZRA connections. Figure 22 shows a typical ZRA set up. Resistance through the electrolyte was minimized by placing the electrodes 1-2 cm apart with the exposed electrode areas facing each other. The tip of the luggin probe was placed close to the exposed area of the 6061-T6 Al electrode (insert in Figure 22). The i_{Galv} and corresponding E_{Galv} for each experiment were recorded with data loggers every 15 seconds from 0 to 120 hours (5 days) to achieve steady state values.

Figure 21. ZRA connections.

Figure 22. Typical ZRA setup.

4.4 Cell Conditions

The electrolytic cell was a jacketed vessel in which the temperature was maintained at 30°C using a Fisher Scientific Isotemp refrigerated circulator 9500. The cell was aerated by sparging compressed air through a fritted glass dispersion tube at volumetric rate of 320-370 ml/minute at 1 atmospheric pressure. The natural convection in the cell was kept relatively constant for each experiment by maintaining a uniform gas dispersion rate. The deaerated condition was achieved by sparging the cell with nitrogen gas with a purity of at least 99.999.

Electrodes from polarization and ZRA experiments were analyzed with a Hitachi S-3400N Scanning Electron Microscopy (SEM) and Oxford Instruments Energy Dispersive X-ray Analysis (EDXA).

4.5 Results and Discussion

Results from the polarization experiments were compared with the corresponding ZRA experiments to understand the behavior of the 6061-T6 Al and TiB₂ couple in various electrolytes and two different conditions. Unless otherwise specified, steady state values of i_{Galv} and E_{Galv} refer to the values obtained by ZRA experiments.

4.5.1 Effect of 0.5 M Na₂SO₄

The anodic behavior of 6061-T6 Al and the cathodic behavior of TiB₂ in aerated and deaerated 0.5 M Na₂SO₄ were studied using potentiodynamic polarization experiments. Figure 23 shows the polarization curves in aerated and deaerated 0.5 M Na₂SO₄. In the polarization experiments, the i_{Galv} values were very low due to the passivation of 6061-T6 Al. The 6061-T6 Al passivates in both aerated and deaerated 0.5 M Na₂SO₄. Interestingly, the i_{Galv} value was slightly higher in the deaerated solution as compared to the aerated solution. However, since the maximum dissolution rate of the 6061-T6 Al is limited to its passive current density, the corrosion rates in the aerated and deaerated solutions should be similar.

Each curve is an average of at least 3 experiments.

Figure 23. Polarization diagrams of 6061-T6 Al and TiB₂ in aerated (Ae) and deaerated (De) 0.5 M Na₂SO₄ solution at 30° C. Scan rate = 1mV/s.

Figures 24 and 25 show the steady state i_{Galv} and E_{Galv} values of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 0.5 M Na_2SO_4 from the ZRA experiments. As shown in the polarization experiments, the steady state i_{Galv} values of 6061-T6 Al coupled to TiB_2 in deaerated 0.5 M Na_2SO_4 were slightly higher than the steady state i_{Galv} values in their corresponding aerated 0.5 M Na_2SO_4 . Though the steady-state i_{Galv} values were similar in the aerated and deaerated solutions, the steady-state E_{Galv} value was more positive in the aerated condition due to oxygen reduction as the cathodic reaction. In the deaerated solution, hydrogen evolution was the cathodic reaction.

Figure 24. Average i_{Galv} ($\mu\text{A}/\text{cm}^2$) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 0.5 M Na_2SO_4 at 30°C.

Figure 25. Average E_{Galv} (V_{SCE}) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 0.5 M Na_2SO_4 at 30°C.

4.5.2 Effect of 3.15 Wt% NaCl

The anodic behavior of 6061-T6 Al in aerated and deaerated 3.15 wt% NaCl was shown in Figure 26. In the deaerated condition, 6061-T6 Al tends to passivate initially with a fairly constant current. This passive layer breaks down at the pitting potential due to the presence of aggressive Cl^- ions in the solution, thus increasing the current rapidly. In the aerated condition, 6061-T6 Al pits immediately. The anodic curves of 6061-T6 Al were plotted with the cathodic curves of TiB_2 in aerated and deaerated 3.15 wt% NaCl to determine the i_{Galv} and E_{Galv} values (Figure 26).

In the polarization experiments, the i_{Galv} value in the deaerated condition was lower than the i_{Galv} value in the aerated condition. In the deaerated condition, the cathodic

curve of TiB_2 (due to hydrogen evolution) intersected the anodic curve of 6061-T6 Al in the passive regime. In the aerated condition, the cathodic curve of TiB_2 (due to oxygen reduction) intersected the anodic curve of 6061-T6 Al in the pitting regime of 6061-T6 Al.

Figures 27 and 28 show the steady state i_{Galv} and E_{galv} values of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 3.15 wt% NaCl obtained from ZRA experiments. The steady state i_{Galv} values of 6061-T6 Al coupled to TiB_2 in aerated 3.15 wt% NaCl were significantly higher than the steady state i_{Galv} values in deaerated 3.15 wt% NaCl. The E_{Galv} values predicted by the polarization experiments were in agreement to those observed in the ZRA experiments. In the aerated condition, steady-state E_{Galv} values were in the pitting potential range; whereas, the steady-state E_{Galv} value shifted in the negative direction for the deaerated condition.

Each curve is an average of at least 3 experiments.

Figure 26. Polarization diagrams of 6061-T6 Al and TiB₂ in aerated (Ae) and deaerated (De) 3.15 wt% NaCl solution at 30° C. Scan rate = 1mV/s.

Figure 27. Average i_{Galv} ($\mu\text{A}/\text{cm}^2$) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 3.15 wt% NaCl at 30°C.

Figure 28. Average E_{Galv} (V_{SCE}) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated 3.15 wt% NaCl at 30°C.

4.5.3 Effect of Seawaters

The passive current densities of 6061-T6 Al in deaerated seawaters were higher than the passive current density in deaerated 3.15 wt% NaCl (Figures 29 and 30). This could be due to the alkaline nature of seawaters where the aluminum oxide layer was less stable when compared to near-neutral solutions. The pH values of ASTM seawater and real seawater were 8.2 and 7.9, respectively.

As determined by the polarization diagrams, the i_{Galv} values in aerated seawaters were similar to that in 3.15 wt% NaCl. The OCP of 6061-T6 Al in aerated seawaters was in the pitting potential range of aluminum (Figures 29 and 30). In the aerated condition, Al electrode pitted spontaneously in aerated chloride-containing solutions. Since the galvanic corrosion in aerated chloride-containing solutions is under cathodic control, the i_{Galv} values in aerated seawaters were similar to that in 3.15 wt% NaCl.

Each curve is an average of at least 3 experiments.

Figure 29. Polarization diagrams of 6061-T6 Al and TiB₂ in aerated (Ae) and deaerated (De) ASTM seawater 30° C. Scan rate = 1mV/s.

Each curve is an average of at least 3 experiments.

Figure 30. Polarization diagrams of 6061-T6 Al and TiB₂ in aerated (Ae) and deaerated (De) real seawater 30° C. Scan rate = 1mV/s.

In the ZRA experiments, however, the i_{Galv} values in aerated seawaters diminished with time. The effect was pronounced in real seawater. Figures 31 and 32 show the steady state i_{Galv} and E_{Galv} values of 6061-T6 Al coupled to TiB_2 in aerated and deaerated real seawaters. Figures 33 and 34 show the same for ASTM seawater.

Figure 31. Average i_{Galv} ($\mu\text{A}/\text{cm}^2$) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated real seawater at 30°C.

Figure 32. Average E_{Galv} (V_{SCE}) profiles of 6061-T6 Al coupled to TiB₂ in aerated and deaerated real seawater at 30°C.

Figure 33. Average i_{Galv} (μA/cm²) profiles of 6061-T6 Al coupled to TiB₂ in aerated and deaerated ASTM seawater at 30°C.

Figure 34. Average E_{Galv} (V_{SCE}) profiles of 6061-T6 Al coupled to TiB_2 in aerated and deaerated ASTM seawater at 30°C.

The difference in corrosion rates could be due to the presence of other ions in seawater, though Cl^- concentrations of seawaters are comparable to the 3.15 wt% NaCl. Calcium and magnesium ions present in the seawater electrolytes possibly react with the hydroxyl ions (OH^-) ions (generated on the cathode as a result of oxygen reduction in the aerated condition) to form calcium carbonate and magnesium hydroxide films on the cathodic sites of TiB_2 surface [116, 117].

This film formation could have lowered the corrosion rate in seawaters by stifling oxygen reduction at the cathodic sites in aerated condition.

Dissolved carbon-di-oxide (CO_2) in aqueous systems reacts to form carbonic acid (H_2CO_3) via the following reaction:

Carbonic acid dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) according to the following equations

The equilibrium constant K_{a1} for the dissociation of carbonic acid into bicarbonate is 4.47×10^{-7} and the equilibrium constant K_{a2} for the dissociation of bicarbonate into carbonate is 4.65×10^{-7} [118]. Since these equations are functions of the proton concentration, H^+ , it is customary to use pH instead of H^+ concentration. The $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values are 6.35 and 10.35, respectively. The Figure A1 in the Appendix A shows a graphical summary of the relative concentrations of the three carbonate species (H_2CO_3 , HCO_3^- , and CO_3^{2-}) in the pH range of 0 to 14. As mentioned earlier, the pH values of ASTM seawater and real seawater were 8.2 and 7.9, respectively. At these pH values the relative concentration HCO_3^- is higher than the other carbonate species. The bicarbonate and hydroxyl ions generated on the cathode as a result of oxygen reduction in the aerated condition reacts with calcium ions present in the seawater to form calcium carbonate (equation 11)

A similar trend was observed for the i_{Galv} plots in the deaerated ASTM seawater and real seawater. Hydroxyl ions may have generated on the cathode by the hydrogen evolution reaction in alkaline solutions as shown in equation 3. As a result, calcium carbonate and magnesium hydroxide films may have precipitated on the TiB_2 cathode in the deaerated condition.

The polarization results in aerated seawaters were similar to those in 3.15 wt% NaCl; whereas, the galvanic corrosion rates in seawaters were different from 3.15 wt% NaCl solution based on the steady-state values from ZRA experiments. The steady state i_{Galv} values from the ZRA experiments were recorded after 120 hours; whereas, the polarization experiments were run for 1 to 2 hours to obtain the i_{Galv} value. The ZRA i_{Galv} values at the initial period were comparable with the polarization i_{Galv} values. This suggested that a calcareous film may have precipitated on cathodic TiB_2 sites over time.

Cathodic polarization experiments with of TiB_2 electrodes were run at slower scan rates to see if the current density decreased as a result of calcareous film growth. The cathodic curve of TiB_2 shifted to lower current densities with slow scan rates in aerated polarization experiments (Figure 35). SEM and EDXA results on the TiB_2 electrode after the cathodic polarization experiment (scan rate: 0.02 mV/s) showed deposits of calcium carbonate (Figure 36) which were confirmed by the EDXA results (Table 6).

Figure 35. Cathodic polarization of TiB_2 in aerated real seawater at 30°C

Figure 36. SEM results on the TiB_2 cathode scanned at 0.02mV/sec .

Table 6. EDAX results on the TiB₂ cathode scanned at 0.02mV/sec

Sites	Carbon	Oxygen	Calcium
CaCO ₃	20	60	20
Site 1	38	48	15
Site 2	24	55	16
Site 3	22	64	19

The cathodic polarization of TiB₂ at slower scan rates took about 4 to 5 hours. The ZRA results showed that it took about 10 hours for the i_{Galv} values to attenuate. The i_{Galv} values between 6061-T6 Al and TiB₂ electrodes were again monitored through ZRA for 5 days. A similar trend of a steep rise in the current density for the first 10 hours followed by a decrease (Figure 37) was observed. After 5 days, the TiB₂ electrode was replaced with a virgin TiB₂ electrode and the current density immediately increased (Figure 37). This suggests that the decrease in current density was due to the formation of calcareous film on the TiB₂ electrode, thus stifling the cathodic reactions (Figure 38 and Table 7).

Figure 37. ZRA results with two different TiB_2 electrodes.

Figure 38. SEM results for the TiB_2 electrode coupled in the ZRA experiment for 5 days.

Table 7. EDXA results for the TiB_2 electrode coupled in the ZRA experiment for 5 Days.

Sites	Carbon	Oxygen	Magnesium	Aluminum	Silicon
Site 1	8.04	63.38	14.61	2.87	11.11
Site 2	6.04	69.33	12.89	2.86	8.88

The anodic polarization of 6061-T6 Al and cathodic polarization of TiB_2 electrodes which were previously coupled together for 5 days in a ZRA experiment were conducted at 1mV/sec scan rate. This experiment was conducted to see the change in the i_{Galv} value using anodic and cathodic polarization curves. The i_{Galv} value from the electrodes coupled together in the ZRA experiment decreased significantly when compared to the i_{Galv} value of virgin TiB_2 and 6061-T6 Al electrodes (Figure 39).

A- i_{Galv} value based on virgin 6061-T6 Al and TiB_2 electrodes.

B- i_{Galv} value based on 6061-T6 Al and TiB_2 electrodes which were previously coupled together for 5 days in a ZRA experiment.

* Results from one experiment

Figure 39. Polarization diagrams of 6061-T6 Al and TiB_2 in aerated real seawater at 30° C Scan rate = 1mV/s.

4.6 Conclusion

In deaerated and aerated chloride-free solutions and in deaerated chloride-containing solutions, i_{Galv} was limited to the passive current density of 6061-T6 Al. In aerated chloride-containing solutions, i_{Galv} was primarily limited by oxygen reduction on TiB_2 since 6061-T6 Al was in the pitting regime.

The galvanic corrosion rates predicted by the polarization experiments in aerated simulated seawater (3.15wt% NaCl) were in agreement to those in aerated real seawater and ASTM seawater, but the results from ZRA experiments show that the i_{Galv} values diminished with time in the aerated seawaters. The steady-state i_{Galv} value was approximately 10^{-6} A/cm^2 in real seawater and approximately 10^{-5} A/cm^2 in ASTM seawater as compared to the steady-state i_{Galv} value of 10^{-4} A/cm^2 in aerated 3.15 wt% NaCl. The calcareous deposits on the TiB_2 cathode in aerated real seawater explained the lower corrosion rates in seawater as compared to the corrosion rate in simulated seawater (3.15 wt% NaCl solution).

The discrepancies in i_{Galv} values from polarization and ZRA experiments suggest that polarization experiments are good at predicting the kinetics of galvanic corrosion whereas ZRA experiments are more useful in determining the changes in i_{Galv} over a period of time.

CHAPTER 5

IMMERSION EXPERIMENTS

5.1 Introduction

In the immersion experiments, TiB₂/6061-T6 Al specimens were soaked in the chloride-free solutions and marine type solutions for 90 days at 30°C. The ionic compositions of each solution are discussed in Chapter 3.

5.2 Procedure

Each 6061-T6 Al coupon was pin stamped with an assigned alphanumeric code for identification using a Telesis Benchmark 320 marking system. The 6061-T6 Al coupons and TiB₂ ceramics were first cleaned in acetone, followed by an ultrasonic cleaning in 18.1 MΩ-cm water for 20 minutes after which they were dried at room temperature. The 6061-T6 Al coupons were weighed in grams to four decimal places. Couple holders and bolts were cleaned ultrasonically in a dilute solution of Liqui-nox® liquid detergent and rinsed in deionized water.

Assembled specimens were individually placed in 250 ml beakers. The beakers were distributed and glued to the bottom of four 30 in. x 12.5 in. x 12.5 in. glass tanks (aquariums) using silicone sealant. Three uncoupled monolithic 6061-T6 Al coupons in each acrylic holder were placed in 600 ml beaker and a total of five 600 ml beakers were glued to the bottom of the glass tank.

The solutions were then added to each beaker. Approximately 170-180 ml of each solution was poured into 250 ml beakers and 470-500 ml of each solution was poured into 600 ml beakers so that the specimens were completely immersed inside the solution. Each glass tank was maintained at 30°C in a de-ionized water bath using an automatic aquarium heater. One aquarium pump was installed inside each glass tank to circulate the water in the bath. This setup maintained a uniform temperature in the water bath that in turn kept the solutions inside the beakers at a constant temperature. Each beaker was partially covered to keep the evaporation of the solution to a minimum. The partial covering of each beaker also ensured maintenance of an aerated condition. Figure 40 shows the immersion setup with couples immersed in different solutions inside the beakers.

Figure 40. Immersion setup.

5.3 Results and Discussion

In the immersion experiments, the specimens were completely immersed in the solutions, resulting in galvanic corrosion even on the backside and not limited to the interface alone due to the ionic path. The corrosion rate given in grams per meter squared per day (gmd) was normalized to the entire 6061-T6 Al surface area where corrosion was observed (equation 15).

$$\text{Corrosion rate} = \frac{\text{mass loss of 6061-T6 Al in the couple}}{\text{area of interface} \times \text{exposure time}} \quad (15)$$

Figure 41 shows the corrosion rates of uncoupled monolithic 6061-T6 Al and 6061-T6 Al coupled to different ceramics in the five different solutions. Corrosion rates of the uncoupled monolithic 6061-T6 Al coupons were significantly lower than those of the coupled coupons in all the solutions. The lower corrosion rates of the uncoupled 6061-T6 Al was due to the absence of galvanic and/or crevice corrosion.

Figure 41. Corrosion rates of 6061T6 Al coupled to TiB₂ in immersion cell

The corrosion rates were the lowest in 18.1 MΩ-cm water for all the couples.

Ultrapure water with a very high resistivity (18.1 MΩ-cm) could have limited the ionic current in the solution, stifling I_{Galv} according to Ohms law.

The corrosion rates were lower in 0.5 M Na₂SO₄ solution than in 3.15 wt% NaCl but were significantly higher than the corrosion rate of 6061-T6 Al in 18.1 MΩ-cm water. As shown in the electrochemical experiments, in a chloride-free solution such as 0.5 M Na₂SO₄, the i_{Galv} value was limited to the passive current density of 6061-T6 Al; and in a chloride-containing solution such as 3.15 wt% NaCl, the i_{Galv} value was in the pitting potential range.

The corrosion rates of 6061-T6 Al coupled to TiB₂ ceramics and immersed in 3.15% NaCl were higher than the corrosion rate in the seawaters, though Cl⁻

concentrations of marine-type solutions are comparable. Lower corrosion rates in the seawaters could be due to the formation of calcareous deposits on the cathodic sites seawaters as shown in the electrochemical experiments.

The final pH values of the solutions after the couples were retrieved from the immersion cells are listed in Table 8. The values in parenthesis show the change in pH value from the initial value.

Table 8. The pH values of the solutions used in the immersion experiments after 90 days

6061-T6Al coupled to	3.15 wt% NaCl	0.5M Na ₂ SO ₄	ASTM seawater	Real seawater	18.1 MΩ- cm water
TiB ₂	8.3 (+1.6)*	8.4 (+1.4)*	6.2 (-2.0)*	4.9 (-3.0*)	7.5 (-0.5)*

* Change in pH value from initial pH

The pH values of the solutions after the experiment became more alkaline in the case of 3.15 wt% NaCl, 0.5 M Na₂SO₄, and 18.1 MΩ-cm water. The pH values of the real seawater and ASTM seawater became more acidic. The pH value of the real seawater can also change due to biological activity over a period of time [119]. These pH values were measured after the couples were retrieved and represent the pH value of the bulk electrolyte rather than the pH value inside the crevice. A similar increase in pH values in 3.15 wt% NaCl, 0.5 M Na₂SO₄, and 18.1 MΩ-cm water and a decrease in pH values in seawater were observed in a different study in which Al metal-matrix composites were immersed in the same types of solutions [120].

A considerable amount of corrosion was observed on the backside of the 6061-T6 Al coupons, where the G-10 fiberglass pad had made contact with the 6061-T6 Al

coupon. The worst case was observed when 6061-T6 Al was coupled to TiB_2 and immersed in real and ASTM seawater. Figure 42 shows the backside of the 6061-T6 Al coupons coupled to TiB_2 and immersed in real seawater. This result could be due to the formation of crevices at the interface between the G-10 fiberglass pad and the 6061-T6 Al coupons and exacerbated by galvanic corrosion due to the TiB_2 coupon coupled to the other side of the specimen. The resulting pH values of these seawater solutions after corrosion had taken place were more acidic than the other seawater solutions.

Figure 42. The backside of 6061-T6 Al coupons coupled to TiB_2 and immersed in real seawater. The region shows crevice corrosion under G-10 fiberglass pad.

5.4 Conclusion

Corrosion rates of the 6061-T6 Al coupons from the couples were significantly higher than the corrosion rates of the uncoupled monolithic 6061-T6 Al coupons. The corrosion rates were more severe in chloride-containing environments than in chloride-free environments. The results were in agreement with polarization experiments where

the i_{Galv} values in aerated chloride free solution is limited to the passive region of the 6061-T6 Al's anodic curve. The corrosion rates in seawater were generally lower when compared to 3.15 wt% NaCl which has similar Cl^- concentration to seawaters due to calcareous deposition on the TiB_2 cathode.

CHAPTER 6

OUTDOOR EXPERIMENTS

6.1 Outdoor Experiments

Atmospheric corrosion is an important form of corrosion because many structures and systems are used in natural environments. Hawai'i's climate, one of the most spatially diverse on earth, makes Hawai'i a premier site to study corrosion in natural environments.

6.2 Site Description

Eight test sites were selected on two different islands (Oahu and Hawai'i) with diverse climatic conditions to expose the galvanic and non-galvanic couples (Figure 43 and 44). The geographic coordinates of the test sites are listed in Appendix B.

Figure 43. Location of atmospheric test sites on Oahu

Figure 44. Location of atmospheric test sites on Hawai'i

The two marine test sites at Coconut Island in Kaneohe Bay (Figure 45) and Kahuku (Figure 46) are located approximately 25 feet and 0.5 miles from the shoreline, respectively with high chloride (Cl^-) deposition rates. The industrial site at Campbell Industrial Park (CIP) is situated amidst oil refineries and power plants (Figure 47). The volcano site at Kilauea (Figure 48) on the island of Hawai'i is located in the path of the volcanic plume and near the ocean. This site is characterized by severe acid rain, with measurements as low as pH 3. The tropical rain forest at Mānoa (Figure 49) is located at an elevation of 520 feet above sea level with high rainfall, and high humidity. The alpine site at Mauna Loa (Figure 50) is located on the island of Hawai'i at an elevation of approximately 11,140 feet above sea level. This test site is characterized by high solar radiation and low temperatures. The agricultural site at Ewa Nui (Figure 51) and the dry

site at Waipahu (Figure 52) on the Island of Oahu have low levels of Cl^- deposition rates, low humidity, and low rainfall.

Test Racks. Test racks were designed and built by George Hawthorn of the Hawai'i Corrosion Lab (HCL). Trex®, a wood composite made of recycled wood chips and polyethylene, is an excellent material for outdoor exposure because it resists moisture, insects, and sunlight and withstands harsh weather conditions. These wood composite slats were painted white and secured to the stainless steel frame at 30° to the horizontal. Racks were designed so that the distance between the specimens and ground was at least 30 inch. Test racks face the northeast (except Mānoa test site), exposing the specimens to the northeast trade winds. Winds prevailing over Oahu are predominantly in the northeast direction.

Figure 45. Coconut Island.

Figure 46. Kahuku

Figure 47. Campbell Industrial Park

Figure 48. Kilauea.

Figure 49. Mānoa.

Figure 50. Mauna Loa.

Figure 51. Ewa Nui.

Figure 52. Waipahu.

6.3 Weather Monitoring

The weather and the atmospheric conditions at test sites are important factors because they influence the corrosion behavior of the specimens exposed. Atmospheric parameters such as ambient temperature, relative humidity, rainfall were collected and recorded by either a Davis Vantage Pro® weather station or Campbell Scientific Inc. weather equipments. The time of wetness (TOW) at the test sites were recorded using a model 237 leaf wetness sensor from Campbell Scientific. The TOW is defined by the ISO 9223:1992(E) as follows: “The period during which a metallic surface is covered by adsorptive and/or liquid films of electrolyte that are capable of causing atmospheric corrosion”.

The TOW was recorded as a function of voltage and the voltage output ranges from 0-25 mV. The specimens were completely wet if the voltage output was above 20 mV. The voltage output was reported as TOW number ranging from 0-15 where a TOW number above 12 was considered to be wet. The schematics and working procedure of model 237 leaf wetness sensors are discussed in detail in Appendix C. The Chloride candles were installed to measure the Cl^- concentration in the atmosphere using the ASTM G 140-96 and ISO 9225:1992(E) wet candle method.

6.4 Weather Analysis

The relationship between the weather parameters was determined using the Pearson correlation coefficient (r). Pearson r ranges from ± 1 where a positive value represents a direct relation and a negative value represents an inverse relation (Table 9). Pearson r analysis was also conducted to understand the relationship between the corrosion rate and the weather parameters

Table 9. Interpretation of Pearson Correlations

+0.7 to +1.0	High degree of positive correlation
+0.3 to +0.7	Moderate degree of positive correlation
-0.3 to +0.3	Low degree of correlation or no correlation
-0.7 to -0.3	Moderate degree of negative correlation
-0.7 to -1.0	High degree of negative correlation

6.5 Ingress of Corrosive Species

The un-cleaned 6061-T6 Al coupons coupled to various ceramics at seven different test sites (excluding Mauna Loa) for the 3 exposure periods were analyzed using a Hitachi S-3400N scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) (Oxford Instruments) to study the ingress of the environmental constituents across the interface. Seven different positions were selected across the interface at regular intervals (P1 to P7) to capture SEM images and elemental analyses using EDXA and the Point & ID method of the INCA software. Figure 53 shows a 6061-T6 Al coupon that was coupled to TiB_2 at Coconut Island and exposed for 6 months with the different positions across the interface.

Figure 53. The 6061-T6 Al coupon coupled to TiB_2 at Coconut Island (exposed for 6 months).

6.7 Raman spectroscopy

Raman analysis were conducted on the un-cleaned 6061-T6 Al coupons coupled to various ceramics that were exposed at Kilauea, Coconut Island, and Mānoa test sites

for 12 months using a Nicolet Almega XR dispersive Raman Spectrometer (Thermo Scientific Corp.). The Raman spectra was collected at three different positions for each samples (at the interface, outside the interface and on the backside) using a 50X magnification objective. A green Nd:YAG laser source with 532 nm wavelength excitation was used to operate the instrument and the laser power was maintained approximately less than 1 mW. The accumulation time was 300 seconds

6.8 Ion chromatography analysis

The interface, outside the interface and the backside area of the un-cleaned 6061-T6 Al coupons coupled to various ceramics that were exposed at Kilauea, Coconut Island, and Mānoa test sites for 12 months were cleaned using a cotton swab dipped in 18.1 MΩ-cm water. The cotton swabs were again washed with 18.1 MΩ-cm water to make 20 ml solution that contained the corrosion product from the un-cleaned samples. The solution samples were then analyzed by the ion chromatography technique using a Dionex model DX-120 Ion Chromatograph where the ionic components were separated, identified, and quantified. The anion analysis was performed following the Environmental Protection Agency (EPA) method 300.1, 1997. For anions (sulfates and chlorides), a pH10 bicarbonate eluent was pumped through the Dionex IonPac AS14A column at 1.0 mL/min. The samples were injected into the respective eluent stream by a Dionex model AS40 autosampler using Dionex 0.5mL filtercap vials. A conductivity detector monitors the conductance of the sample ions as they emerge from the columns and the chromatographic data was collected and processed using Dionex's PeakNet 5.1

software. The analysis was performed by Mr. Joseph Lichwa of Water Resources Research Center, University of Hawai'i at Mānoa.

6.9 Cleaning procedures

The corroded 6061-T6 Al coupons from the outdoor and accelerated laboratory experiments were cleaned using a 2% chromium tri-oxide and 5% phosphoric acid solution according to International Standard ISO 8407: 1991 (E) C.1.1.

Corrosion Rate Determination. The corrosion rate of the interface region of the coupled 6061-T6 Al coupons was calculated by estimating the mass loss in the interface region ($\Delta M_{\text{interface}}$) by first determining the total mass loss of the specimen (ΔM_{total}) from weight-loss data, and subtracting from that an estimated mass loss outside of the interface region ($\Delta M_{\text{outside interface}}$), which is subjected only to general corrosion: $\Delta M_{\text{interface}} = \Delta M_{\text{total}} - \Delta M_{\text{outside interface}}$. The mass loss outside of the interface region was estimated from uncoupled 6061-T6 Al coupons that were exposed along side the coupled coupons at each test site. Since the surface area on the outside region of the interface was less than that of the uncoupled coupons, the mass loss outside of the interface had to be adjusted:

$$\Delta M_{\text{outside interface}} = \Delta M_{\text{uncoupled 6061-T6 Al}} \times (a_{\text{outside of interface}} / a_{\text{total coupon area}})$$

equation (16)

where $\Delta M_{\text{uncoupled 6061-T6 Al}}$ is the mass loss of uncoupled 6061-T6 Al and $\frac{a_{\text{region outside interface}}}{a_{\text{total coupon area}}}$

is the area fraction of the region outside of the interface. The corrosion rate at the interface region given in grams per meter squared per day (gmd) was then calculated by

dividing the mass loss at the interface region ($\Delta M_{\text{interface}}$) by the area of the interface and exposure time (equation 17).

$$\text{Corrosion rate at the interface region} = \frac{\left[\text{mass loss of 6061-T6 Al in the couple} \right] - \left[\text{estimated mass loss of 6061-T6 Al outside the interface region} \right]}{\text{area of interface} \times \text{exposure time}}$$

equation (17)

6.10 Results and Discussion

The atmospheric weather parameters such as average temperature, average humidity, total rainfall, average chloride deposition rate and average TOW for the three exposure periods at seven different test sites were tabulated in Table 10, 11, and 12. The exposure periods for the test sites at HECO facilities (Kahuku, Campbell, Ewa Nui, and Waipahu) were 3-, 7-, and 13- months instead of 3-, 6-, and 12- months. The chloride deposition rate was below detection limit at Mānoa for the three exposure periods. The TOW was an average number on a scale of 0-15 where TOW 0 was completely dry and TOW 15 was completely wet. Hence, the higher TOW number corresponded to wetter samples at the respective test sites.

Table 10. Weather Data for 3-month exposure

Test Sites	Average Temperature (°F)	Average Humidity (%RH)	Total Rainfall (Inches)	Average Cl ⁻ deposition rate (mg/m ² /day)	Average TOW
Coconut Island	73.90	79.27	25.86	93.20	3.58
Mānoa	70.23	86.73	119.35	----**	7.15
Kilauea	65.66	81.7	24.25	38.40	5.70
Kahuku	78.62	71.50	4.42	67.42	1.55
Campbell	80.96	63.63	0.20	15.58	0.47
Waipahu	80.60	60.67	0.22	15.48	0.85
Ewa Nui	80.19	60.73	0.20	15.59	0.85

**below detection limit

Table 11. Weather Data for 6/7-month exposure

Test Sites	Average Temperature (°F)	Average Humidity (%RH)	Total Rainfall (inches)	Average Cl ⁻ deposition rate (mg/m ² /day)	Average TOW
Coconut Island	75.62	78.23	36.51	79.30	3.11
Mānoa	71.25	86.87	210.55	----**	7.17
Kilauea	66.31	78.22	31.11	31.19	4.56
Kahuku	77.61	72.51	23.76	76.66	2.20
Campbell	79.75	62.60	7.93	17.40	0.88
Ewa Nui	77.9	65.77	11.46	16.24	1.84
Waipahu	78.69	65.34	12.98	13.72	1.94

**below detection limit

Table 12. Weather Data for 12/13-month exposure

Test Sites	Average Temperature (°F)	Average Humidity (%RH)	Total Rainfall (inches)	Average Cl ⁻ deposition rate (mg/m ² /day)	Average TOW
Coconut Island	77.07	77.57	66.24	74.50	2.87
Mānoa	71.70	86.33	281.80	----**	6.75
Kilauea	67.71	78.20	90.01	26.45	4.29
Kahuku	76.24	72.09	31.65	73.07	2.43
Campbell	78.21	61.57	12.21	16.24	0.77
Ewa Nui	76.03	66.67	16.57	14.54	1.83
Waipahu	76.86	66.09	17.86	11.54	1.89

**below detection limit

The diversity of the micro-climates represented by the test sites was confirmed by the weather data monitored for the three exposure periods at the test sites (Tables 10, 11, and 12). Coconut Island, Kahuku, and Kilauea are the marine test sites with the highest chloride deposition rate for the three exposure periods. Mānoa test site with a high rainfall and TOW is the rainforest environment. Campbell, Ewa Nui, and Waipahu are the drier test sites based on their total rainfall and TOW data for the three exposure periods.

Weather parameters were plotted against each other to determine Pearson r. Figures 54 through 57 shows the plot of humidity against rainfall, temperature, TOW, chloride deposition rate for 3-month exposure. Similar plots were made to determine the Pearson r value to see the relationship between two weather parameters and the values are tabulated in Tables 13, 14, and 15 for 3, 6/7, 12/13 months of exposure, respectively.

Figure 54. Humidity Vs Rainfall (3 months).

Figure 55. Humidity Vs Temp. (3 months).

Figure 56. Humidity Vs TOW (3 months).

Figure 57. Humidity Vs Chloride (3 months).

Table 13. Pearson r values between weather parameters for 3-month exposure

	Humidity	Rainfall	TOW	Chloride	Temp
Humidity	1	0.78	0.95	0.24	-0.89
Rainfall		1	0.86	-0.28	-0.61
TOW			1	-0.031	-0.93
Chloride				1	-0.11
Temp					1

Table 14. Pearson r values between weather parameters for 6/7-month exposure

	Humidity	Rainfall	TOW	Chloride	Temp
Humidity	1	0.64	0.94	0.11	-0.76
Rainfall		1	0.8	-0.36	-0.45
TOW			1	-0.24	-0.79
Chloride				1	0.09
Temp					1

Table 15. Pearson r values between weather parameters for 12/13-month exposure

	Humidity	Rainfall	TOW	Chloride	Temp
Humidity	1	0.87	0.95	0.08	-0.67
Rainfall		1	0.95	-0.32	-0.57
TOW			1	-0.22	-0.74
Chloride				1	0.26
Temp					1

The statistical analyses of the atmospheric weather parameters based on the Pearson r values showed a strong relationship between humidity, rainfall, and TOW. Test sites with high rainfall (Mānoa, Kilauea, Coconut Island, and Kahuku) resulted in high TOW and humidity data. The relatively higher humidity observed at Mānoa were due to higher rainfall when compared to other test sites.

However humidity, rainfall, and TOW showed a negative relationship with temperature. The Campbell, Waipahu, and Ewa Nui were the drier test sites with less rainfall and they have the lowest TOW and humidity data for the three exposure periods when compared to other test sites. The Campbell, Waipahu, and Ewa Nui test sites also recorded higher temperatures hence temperature was inversely related to rainfall, TOW and humidity.

There was no correlation between chloride deposition rate and other parameters. The Coconut Island, Kilauea, and Kahuku test sites facing the north-east trade winds recorded the highest amount of chloride deposition rate due to their closeness to the

ocean, whereas; Mānoa which recorded high rainfall, TOW, and humidity had no chloride deposition. The chloride deposition rate at the drier test sites (Campbell, Waipahu, and Ewa Nui) were the lowest when compared to marine test sites. The chloride deposition rate was dependent on proximity to the ocean and wind direction.

Corrosion rates at the interface region were estimated using equations 16 and 17 for the outdoor experiments for the three exposure periods. The corrosion rate at the interface for the 6061-T6 Al coupled to five different ceramics and exposed at the 7 different test sites for the 3 exposure periods are shown in Figures 58, 59, and 60. The corrosion rate of uncoupled 6061-T6 Al for the same exposure period were also shown.

* Electrical resistivity of ceramics (Ω -cm)

Figure 58. Corrosion rate based on the interface area for 3-month exposure.

* Electrical resistivity of ceramics ($\Omega\text{-cm}$)

Figure 59. Corrosion rate based on the interface area for 6/7-month exposure.

* Electrical resistivity of ceramics (Ω -cm)

Figure 60. Corrosion rate based on the interface area for 12/13-month exposure.

Due to the absence of crevice and/or galvanic effects, the corrosion rates of uncoupled 6061-T6 Al coupons were significantly lower than those of coupled 6061-T6 Al coupons. Due to the galvanic effects by the relatively conductive TiB_2 and B_4C ceramics, high corrosion rates were observed in the coupled 6061-T6 Al coupons exposed at the outdoor tests sites. Corrosion rates of the 6061-T6 Al coupons in the non-galvanic couples with SiC , AlN , or Si_3N_4 were lower.

The highest corrosion rates were recorded when 6061-T6 Al coupons were coupled to B_4C , which was the second most conductive ceramic. Electrochemical experiments (ZRA) were conducted with $\text{B}_4\text{C}/6061\text{-T6}$ Al couples and compared with the results of $\text{TiB}_2/6061\text{-T6}$ Al couples. The $\text{B}_4\text{C}/6061\text{-T6}$ Al and $\text{TiB}_2/6061\text{-T6}$ Al couples were connected to a ZRA with a thin insulating layer in between them and immersed in 3.15 wt% NaCl (exposed to air condition). The dimensions of the couples were similar to the outdoor exposure couples (Figure 61). The i_{Galv} value between B_4C and 6061-T6 Al coupons were higher than that between TiB_2 and 6061-T6 Al coupons in 3.15 wt% NaCl (Figure 62). This result could be due to B_4C being more catalytic to oxygen reduction and/or hydrogen evolution than TiB_2 . The cathodic polarization of B_4C and TiB_2 electrodes were conducted (one cm^2 exposure area) in aerated 3.15 wt% NaCl at 25°C and plotted with the anodic curve of 6061-T6 Al electrode under the same condition (Figure 63). The i_{Galv} values for the $\text{B}_4\text{C}/6061\text{-T6}$ Al and $\text{TiB}_2/6061\text{-T6}$ Al couples were almost the same. These results show that the galvanic current between B_4C and 6061-T6 Al couple was almost equal to the galvanic current between TiB_2 and 6061-T6 Al. Notice, however, if the galvanic potential increases, i_{Galv} would be higher for the $\text{B}_4\text{C}/6061\text{-T6}$ Al couple compared to the $\text{TiB}_2/6061\text{-T6}$ Al couple.

Figure 61. The B_4C /6061-T6 Al couple connected to ZRA.

Figure 62. The i_{Galv} profile of B_4C /6061-T6 Al and TiB_2 /6061-T6 Al couple in open-to-air 3.15 wt% NaCl solution.

Figure 63. Polarization diagrams of 6061-T6 Al, TiB₂, and B₄C in aerated 3.15 wt% NaCl at 30° C. Scan rate = 1mV/s. Each curve is an average of 3 experiments.

The higher galvanic current between B₄C and 6061-T6 Al could be caused by the photo-electrochemical properties of B₄C, which is a semi-conductor. Ding and Hihara conducted cathodic polarization experiments with monolithic B₄C and B₄C reinforced aluminum metal matrix composites in air-exposed 0.5 M Na₂SO₄ solution in the dark and under illumination [121]. The cathodic curve of both the materials shifted to higher current values under illumination due to photo-electrochemical properties of B₄C (Figure 64).

Figure 64. Cathodic polarization diagrams of a monolithic B₄C electrode and an Al/B₄C MMC in air-exposed 0.5 M Na₂SO₄ solution both in the dark and under illumination [120].

Kilauea. The highest corrosion rate for each type of couple was observed at Kilauea, possibly due to the high sulfur dioxide content in the air leading to acid rain for 3 and 6 months of exposure. Some of the corrosion rates calculated from Kilauea after 3 month exposures showed negative values (Figure 65). This result was due to the higher mass loss of uncoupled 6061-T6 Al as compared to the mass loss of 6061-T6 Al coupled to various ceramics (Figure 66). This higher mass loss of uncoupled 6061-T6 Al used in equation 16 and 17 resulted in the negative value for the corrosion rate at the interface areas.

Figure 65. Corrosion rate of 6061-T6 Al coupled to various ceramics at Kilauea based on the interface area.

Figure 66. The total mass loss of 6061-T6 Al coupled to various ceramics at Kilauea.

Figure 67 shows the SEM pictures of 6061-T6 Al coupled to TiB_2 and exposed for 12 months at Kilauea. SEM pictures were taken across the interface at seven different positions (P1 to P7) where P1 and P7 positions are outside the interface area. The corrosion product build up was uniform across the interface. The EDXA analysis for oxygen and aluminum for the three exposure periods showed relatively uniform aluminum oxide layer formation (Al_2O_3) from P1 to P7 (Figures 68, 69 and 70). This result showed that the composition of the corrosion products on the outside and in the interface regions of the 6061-T6 Al coupons were uniform.

Figure 67. Build up of aluminum oxide layer at the 6061-T6 Al interface coupled to TiB_2 for 12 months at Kilauea.

Figure 68. Oxygen and aluminum profile across the 6061-T6 Al coupled to various ceramics at Kilauea (3- month exposure).

Figure 69. Oxygen and aluminum profile across the 6061-T6 Al coupled to various ceramics at Kilauea (6- month exposure).

Figure 70. Oxygen and aluminum profile across the 6061-T6 Al coupled to various ceramics at Kilauea (12- month exposure).

Sulfur compounds from the volcanic ash deposited on the 6061-T6 Al samples at the Kilauea site were also identified using SEM/EDXA analysis. Atomic percentage of sulfur across the 6061-T6 Al coupon that had been coupled to different ceramics at the Kilauea site showed decreasing amounts in the interface regions (Figures 71). The ceramics appeared to hinder the ingress of sulfur compounds into the interface region.

Figure 71. Ingress of sulfur across the 6061-T6 Al interface at Kilauea (3 exposure periods).

Raman spectra were obtained from two different locations on the interface, outside the interface, and on the backside of the 6061-T6 Al coupled to different ceramics after 12- month exposure (Figures 72 to 76). Spectral peak was identified for sulfate ions (980 cm^{-1}) on the outside area and as well as on the backside. Sulfate ion spectral peaks were missing in the interface regions for all the samples with exceptions to 6061-T6 Al coupled to SiC and Si_3N_4 .

Figure 72. Raman spectra from different areas on the 6061-T6 Al coupled to SiC (12-month Kilauea exposure).

Figure 73. Raman spectra from different areas on the 6061-T6 Al coupled to B_4C (12-month Kilauea exposure).

Figure 74. Raman spectra from different areas on the 6061-T6 Al coupled to TiB_2 (12-month Kilauea exposure).

Figure 75. Raman spectra from different areas on the 6061-T6 Al coupled to Si_3N_4 (12-month Kilauea exposure).

Figure 76. Raman spectra from different areas on the 6061-T6 Al coupled to AlN (12-month Kilauea exposure).

Ion chromatography analysis was performed to detect sulfate ions in the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Kilauea for 12 months. Figure 77 shows a trend of increasing amounts of sulfate ion concentration from the interface to outside to the backside area.

Figure 77. Ion chromatography analysis for sulfate ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Kilauea for 12 months.

Ion chromatography analysis was also performed to detect the chloride ions in the corrosion products. Figure 78 shows a trend of high chlorides at the interface when compared to outside and backside area for the corrosion products obtained from 6061-T6 Al coupled to various ceramics and exposed for 12 months at Kilauea. Chlorides trapped inside the aluminum oxide layer were difficult to identify using EDXA analysis whereas ion chromatography analysis was able to identify the chlorides in the corrosion product after dissolving in 18.1 MΩ-cm water.

Figure 78. Ion chromatography analysis for chloride ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Kilauea for 12 months.

The deposition of sulfur compounds from the aggressive environments led to more corrosion on the backside as well as on the outside of the interface. The ceramic coupons may have shielded the interface from the corrosive atmosphere resulting in lower overall mass loss for the coupled coupons when compared to the corrosion rates of uncoupled 6061-T6 Al. Corrosion rates of uncoupled 6061-T6 Al were the highest at Kilauea test site for 3, 6, and 12 months of exposure (Figure 79). These results indicate that the corrosion mechanism of the coupled samples differed significantly from the coupled samples from other test sites.

Figure 79. Corrosion rates of uncoupled 6061-T6 Al at 8 different test sites for 3-, 6-, and 12- month exposures.

Coconut Island: A decreasing trend in the corrosion rates was observed after 3 months of exposure at Coconut Island (Figure 80). The wetness of the samples decreased over the three exposure periods as showed by the TOW histogram (Figure 81). Coconut Island is a marine test site with high chloride deposition rate and the average TOW data showed a moderately wet atmosphere.

Figure 80. Corrosion trend at Coconut Island.

Figure 81. TOW histogram at Coconut Island test site.

The buildup of insulative aluminum oxide corrosion product at the interface could have increased the ohmic loss (IR) and restricted the I_{Galv} flowing between the 6061-T6 Al and conductive ceramics. As the exposure period increases, galvanic action could be eliminated due to electrical decoupling, resulting in the corrosion of 6061-T6 Al in the interface changing from crevice corrosion enhanced by galvanic action to just crevice corrosion. The electrical resistance between TiB_2 and 6061-T6 Al couple increased from one ohm to 450 Kilo-Ohms after being exposed at the Coconut Island test site for 29 months. This showed that TiB_2 and 6061-T6 Al galvanically decoupled over a period of time. Figure 82 show the build up of aluminum oxide layer at the interface of 6061-T6 Al coupled to TiB_2 after 12 months of exposure. Figure 83 shows aluminum and oxygen concentrations across the interface. A build up of thick aluminum oxide layer build up was evident from the trend of higher oxygen concentration in the interface.

Figure 82. Build up of aluminum oxide layer at the 6061-T6 Al interface coupled to TiB_2 for 6 months.

Figure 83. Oxygen and aluminum profile across the 6061-T6 Al coupled to various ceramics at Coconut Island (12- month exposure).

Raman analysis on the un-cleaned 6061-T6 Al coupons coupled to various ceramics and exposed at Coconut Island for 12 months showed no sulfate peaks as in the Kilauea test site case (Figure 84). Ion chromatography analysis for sulfate ions showed very little sulfate ion concentration (Figure 85). Chloride concentrations from the corrosion products after 12 months of exposure at Coconut Island showed a trend of high chloride content at the interface when compared to outside and backside area (Figure 86). This chloride ion concentration trend was similar to the Kilauea test site.

Figure 84. Raman spectra from different areas on the 6061-T6 Al coupled to Al (12-month coconut Island exposure).

Figure 85. Ion chromatography analysis for sulfate ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Coconut Island for 12 months.

Figure 86. Ion chromatography analysis for chloride ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Coconut Island for 12 months.

Mānoa: There was no consistent decreasing trend in corrosion rate at Mānoa (Figure 87) after 3 months. The TOW was consistent throughout the three exposure periods (Figure 88). Due to high levels of rainfall, the TOW histogram showed that the samples were wet for close to 50% of the exposure time at Mānoa for the three exposure periods. More corrosion products were build at the center of the interface for conductive ceramics like B_4C and TiB_2 (Figure 89) when compared to 6061-T6 Al coupled to less conductive samples like SiC, Si_3N_4 , and AlN (Figure 90).

Figure 87. Corrosion trend at Mānoa.

Figure 88. TOW histogram at Mānoa test site.

Figure 89. Build up of aluminum oxide layer at the 6061-T6 Al interface (P4) coupled to TiB₂ and B₄C at Mānoa for 12 months.

Figure 90. Build up of aluminum oxide layer at the 6061-T6 Al interface (P4) coupled to SiC, Si₃N₄, and AlN at Mānoa for 12 months.

Raman analysis on the un-cleaned 6061-T6 Al coupons coupled to various ceramics and exposed at Mānoa for 12 months showed no sulfate peaks similar to the Coconut Island test site case (Figure 91). Ion chromatography analysis for sulfate ions showed very little sulfate ion concentration (Figure 92). Chloride concentrations from the corrosion products after 12 months of exposure at Mānoa were negligible when compared to Coconut Island and Kilauea test sites (Figure 93).

Figure 91. Raman spectra from different areas on the 6061-T6 Al coupled to Al (12-month Mānoa exposure).

Figure 92. Ion chromatography analysis for sulfate ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Mānoa for 12 months.

Figure 93. Ion chromatography analysis for chloride ions on the corrosion products obtained from 6061-T6 Al coupons coupled to various ceramics at Mānoa for 12 months.

Kahuku. Figure 94 shows a general decreasing trend in the corrosion rate of 6061-T6 Al coupled to various ceramics over three exposure periods at Kahuku. The average TOW was higher than other drier test sites, and the TOW histogram data showed less dry days at Kahuku for three exposure periods when compared to Ewa Nui, Waipahu and Campbell test sites (Figure 95).

Figure 94. Corrosion trend at Kahuku test site.

Figure 95. TOW histogram at Kahuku test site.

Campbell Industrial Park. The corrosion rates at Campbell industrial park was relatively lower than the marine test sites (Coconut Island, Kahuku, and Kilauea) and the rainforest test site (Mānoa). Figure 96 shows the corrosion rate trend at Campbell industrial park for the three exposure period. The weather parameters at Campbell were similar to Ewa Nui and Waipahu. The TOW histogram (Figure 97) showed the samples were dry for more than 80% of the time for three exposure periods.

Figure 96. Corrosion trend at Campbell Industrial Park.

Figure 97. TOW histogram at Campbell Industrial Park.

Sulfur compounds deposited on the 6061-T6 Al samples at the Campbell Industrial Park test site were identified using SEM/EDXA analysis. Atomic percentage of sulfur across the interface of 6061-T6 Al coupled to different ceramics at the Campbell Industrial Park at regular intervals (P1 through P7) showed a decrease of sulfur compounds at the interface (Figures 98, 99 and 100). The ceramics hindered the ingress of sulfur compounds inside of the interface.

Figure 98. Ingress of sulfur across the 6061-T6 Al interface (3-month exposure).

Figure 99. Ingress of sulfur across the 6061-T6 Al interface (7-month exposure).

Figure 100. Ingress of sulfur across the 6061-T6 Al interface (13-month exposure).

Ewa Nui and Waipahu. The corrosion rates of 6061-T6 Al coupled to various ceramics at Ewa Nui and Waipahu test sites were relatively lower when compared to other test sites. Figures 101 and 102 show the corrosion trend of 6061-T6 Al coupled to various ceramics for the three exposure periods for Ewa Nui and Waipahu test sites, respectively. Ewa Nui and Waipahu test sites are the driest test site with less rainfall and chloride deposition rate. Figures 103 and 104 show the TOW histogram for Ewa Nui and Waipahu test sites, respectively. The couples at these test sites were dry for more than 80% of their exposure time for all of the three exposure periods. The weather parameters for these two test sites were similar (Tables 10, 11, and 12).

Figure 101. Corrosion trend at Ewa Nui test site.

Figure 102. Corrosion trend at Waipahu test site.

Figure 103. TOW histogram at Ewa Nui test site.

Figure 104. TOW histogram at Waipahu test site.

Figure 105 compares aluminum and oxygen concentration across the interface of the 6061-T6 Al coupled to various ceramics and exposed for 12 months at Ewa Nui and Waipahu test sites. The atomic percentage of oxygen was less than 60% for most cases due to lack of aluminum oxide layer build up across the interface. The aluminum oxide corrosion product was less evident on the 6061-T6 Al samples at the drier test sites.

Figure 105. The ingress of atomic aluminum and oxygen across the interface of the 6061-T6 Al coupled to various ceramics and exposed for 12 months at Ewa Nui and Waipahu test sites.

Red dirt and sand particles were deposited on the 6061-T6 Al samples at the Ewa Nui test site and EDXA analysis showed higher amounts of silicon on the samples when compared to the Waipahu test sites. The amount of silicon compounds decreased inside the interface (position 3, 4, and 5) for both the test sites (Figure 106).

Figure 106. The ingress of atomic silicon across the interface of the 6061-T6 Al coupled to various ceramics at Ewa Nui and Waipahu test sites and exposed for 3 exposure periods.

Mauna Loa: The corrosion rate for each type of couple at Mauna Loa was the lowest when compared to other test sites. The 6061-T6 Al coupons coupled to various ceramics and the uncoupled 6061-T6 Al coupons looked almost pristine even after 12 months of exposure. Figure 107 shows the 6061-T6 Al/TiB₂ couple after 12 months of exposure. Figure 108 shows the un-cleaned 6061-T6 Al coupons coupled to TiB₂ for 12 months. The mass loss of the exposed couple was negligible after chemical cleaning. As mentioned earlier, Mauna Loa test site is located on the island of Hawai‘i at an elevation of approximately 11,140 feet above sea level with no chlorides and very little moisture. The weather data for this data is unavailable.

Figure 107. The 6061-T6 Al/TiB₂ couple after 12 months of exposure at Mauna Loa.

Figure 108. The un-cleaned 6061-T6 Al coupons coupled to TiB₂ for 12 months at Mauna Loa.

The relationship between the corrosion rate and the weather parameters were determined using the Pearson correlation coefficient (r). Corrosion rate data from Kilauea test sites were excluded from the analysis since the corrosion mechanisms at Kilauea differed significantly from the other test sites as discussed above. Corrosion rate data from Mauna Loa test sites were also excluded due to the unavailability of weather data.

The Pearson r values between the weather parameters and the corrosion rates of 6061-T6 Al coupled to different ceramics at six different test sites (i.e., Coconut Island, Mānoa, Kahuku, Waipahu, Campbell, and Ewa Nui) are shown in Tables 16 through 20.

Table 16. Pearson r values for the corrosion rate of 6061-T6 Al coupled to TiB_2

	3 months	6 months	12 months
Temp	-0.45	-0.921	-0.883
Hum	0.607	0.971	0.662
Rain	0.139	0.818	0.679
Cl	0.845	0.14	-0.174
TOW	0.326	0.885	0.758

Table 17. Pearson r values for the corrosion rate of 6061-T6 Al coupled to B_4C

	3 months	6 months	12 months
Temp	-0.84	-0.891	-0.602
Hum	0.904	0.919	0.846
Rain	0.599	0.832	0.809
Cl	0.523	0.046	-0.053
TOW	0.737	0.855	0.796

Table 18. Pearson r values for the corrosion rate of 6061-T6 Al coupled to SiC

	3 months	6 months	12 months
Temp	0.698	-0.473	-0.043
Hum	-0.68	0.502	0.244
Rain	-0.87	0.448	0.338
Cl	0.403	-0.07	-0.216
TOW	-0.78	0.507	0.212

Table 19. Pearson r values for the corrosion rate of 6061-T6 Al coupled to Si₃N₄

	3 months	6 months	12 months
Temp	0.619	0.311	0.044
Hum	-0.53	-0.33	-0.171
Rain	-0.66	-0.303	-0.053
Cl	0.148	-0.107	-0.496
TOW	-0.68	-0.347	-0.047

Table 20. Pearson r values for the corrosion rate of 6061-T6 Al coupled to AlN

	3 months	6 months	12 months
Temp	0.547	0.475	0.517
Hum	-0.46	-0.488	-0.558
Rain	-0.41	-0.272	-0.282
Cl	-0.22	-0.235	-0.347
TOW	-0.52	-0.435	-0.475

The best correlation was achieved for the TOW comparison for the galvanic couples (TiB₂/6061-T6 Al and B₄C/6061-T6 Al). Similar to TOW, humidity and rainfall also showed good correlation for the galvanic couples. As shown in the weather analysis; TOW, rainfall, and humidity had a high degree of positive correlation. Correlation with TOW for the non-galvanic couples improved as the exposure time increased. Inconsistent correlation was observed with temperature.

TOW was an important weather parameter for corrosion behavior of galvanic and non-galvanic couples as both galvanic and crevice corrosion depends on the wetness of the samples. TOW is a reflection of humidity and the amount of rainfall recorded at the test sites and they all showed a high degree of positive relationship. The TOW data was

further divided into four periods i.e., Q1, Q2, Q3, and Q4 to see the effects of different wet/dry periods. The TOW number between 0 and 3 were considered to be dry period (Q1), and the intermediate periods were with the TOW number between 4 and 11 (Q2+Q3). The TOW number between 12 and 15 were wet periods (Q4). Tables 21, 22, and 23 show the overall TOW number and the Q1, Q2, Q3, and Q4 values for the 3 exposure periods at 6 test sites. Q1, Q2, Q3 and Q4 are % of exposure time.

Table 21. TOW and the Q1, Q2, Q3, and Q4 values for the 3-month exposure

Test sites	TOW	Q1	Q2+ Q3	Q4
Coconut Island	3.58	76.2	2.9	21
Mānoa	7.15	50.9	3.4	46
Kahuku	1.55	86.5	7	6.5
CIP	0.47	95.9	2.5	1.6
Ewa Nui	0.85	92.4	5.1	2.5
Waipahu	0.85	92.4	4.9	2.7

Table 22. TOW and the Q1, Q2, Q3, and Q4 values for the 6/7-month exposure

Test Sites	TOW	Q1	Q2+ Q3	Q4
Coconut Island	3.11	79.16	2.32	18.5
Mānoa	7.17	50.58	4.07	45.3
Kahuku	2.2	79.42	13.1	7.47
CIP	0.88	92.95	3.89	3.16
Ewa Nui	1.84	84.4	7.17	8.43
Waipahu	1.94	83.71	6.93	9.36

Table 23. TOW and the Q1, Q2, Q3, and Q4 values for the 12/13-month exposure

Test Sites	TOW	Q1	Q2+ Q3	Q4
Coconut Island	2.87	80.7	1.96	17.33
Mānoa	6.75	53.13	4.59	42.28
Kahuku	2.43	77.26	14.6	8.186
CIP	0.77	93.7	3.47	2.83
Ewa Nui	1.83	84.06	7.75	8.189
Waipahu	1.89	83.84	7.03	9.128

The Pearson r values between corrosion rate and Q1, Q2, Q3, and Q4 were established to determine which levels of wetness affected corrosion most significantly (Tables 24, 25 and 26). The Pearson r values for the overall TOW almost exactly mirrored the person r values for the wet period (Q4).

Table 24. The Pearson r values between TOW, Q1, Q2, Q3, Q4 and corrosion rate

3 months	TiB ₂	B ₄ C	SiC	Si ₃ N ₄	AlN
TOW	0.326	0.737	-0.782	-0.677	-0.524
Q1	-0.328	-0.714	0.796	0.710	0.529
Q2+Q3	0.158	-0.440	0.162	-0.373	-0.138
Q4	0.303	0.735	-0.789	-0.653	-0.501

Table 25. The Pearson r values between TOW, Q1, Q2, Q3, Q4 and corrosion rate

6 months	TiB ₂	B ₄ C	SiC	Si ₃ N ₄	AlN
TOW	0.885	0.855	0.507	-0.347	-0.435
Q1	-0.846	-0.796	-0.445	0.472	0.502
Q2+Q3	-0.401	-0.53	-0.548	-0.796	-0.365
Q4	0.899	0.875	0.551	-0.243	-0.379

Table 26. The Pearson r values between TOW, Q1, Q2, Q3, Q4 and corrosion rate

12 months	TiB ₂	B ₄ C	SiC	Si ₃ N ₄	AlN
TOW	0.758	0.796	0.212	-0.047	-0.475
Q1	-0.837	-0.698	-0.049	0.074	0.577
Q2+Q3	0.425	-0.619	-0.986	-0.303	-0.594
Q4	0.669	0.862	0.355	0.024	-0.367

The correlation factor for corrosion rate and chloride deposition was low (Tables 16 to 20) because corrosion rates were high at Mānoa even though the chloride deposition rate was below the detection limit (Figures 58, 59, and 60). Nevertheless, chlorides still play an important role in understanding the corrosion behavior of Al coupled to ceramics. The effects of chlorides on the correlation of accelerated laboratory corrosion tests to outdoor exposure tests for ceramics-aluminum couples are discussed in the following sections.

6.10 Conclusions

The results from the outdoor exposure tests from different environments showed that the corrosion rates were higher for the galvanic couples as compared to the non-galvanic couples. The statistical analysis showed a strong positive relationship between the weather parameters TOW, humidity and rainfall; whereas, these three weather parameters showed a strong negative relationship with the temperature. Chloride deposition rate had no correlation with TOW, humidity, rainfall, and temperature but the chloride environments affected the galvanic as well as crevice corrosion for the couples.

The two important parameters that affected the corrosion rate of the couples were TOW and chloride deposition rate. In the cases for the volcanic (Kilauea) and industrial (Campbell Industrial Park) environments that contain relatively high levels of SO_2 , the ceramic coupons had the effect of shielding and protecting the aluminum substrates to some degree: Often, the degree of corrosion would be less at the interface than on the external regions, which was in direct contrast to specimens exposed at the other test sites

CHAPTER 7

HUMIDITY CHAMBER EXPERIMENTS

7.1 Introduction

In the humidity chamber experiment, the controlled parameters are humidity, temperature, time of exposure, and the type of electrolytes used to treat the specimens. The purpose of the humidity chamber experiments was to determine how corrosion rates compared to those in the natural environments.

7.2 Procedure

The 6061-T6 Al/ceramics couples were assembled following the procedure shown in Chapter 5. In the humidity chamber experiments, assembled couples and four acrylic holders with three uncoupled monolithic 6061-T6 Al coupons in each holder were completely immersed in 3.15 wt% sodium chloride (NaCl), 0.5 M sodium sulfate (Na_2SO_4), ASTM seawater, or real seawater for 1 minute prior to placing inside the humidity chamber (Figure 109). The specimens were then aligned inside a chamber in a small rack made of acrylic plates supported by small wood-polymer composite (Trex®) pieces. The specimens were arranged with the ceramic facing up, similar to the exposure pattern in the outdoor experiments. Humidity inside the chamber was maintained at 90% RH using an Evenflo humidifier filled with 18.1 M Ω -cm water and an Electro-tech 514

automatic humidity controller. A Cole Parmer 2186-20 Digi-sense temperature controller was used to maintain the temperature inside the chamber at 30°C. Figure 109 shows the humidity chamber with specimens resting on the bolt head and ceramics facing up. The experiment was conducted for 90 and 21 days.

Figure 109. Humidity chamber setup.

7.3 Results and Discussion

The galvanic effect and the subsequent corrosion phenomenon are limited to the interface region; hence, the corrosion rate was determined at the interface only using the procedure explained in Chapter 4.

The corrosion trends from the chloride-treated specimens exposed in the humidity chamber for 90 days (Figure 110) do not resemble those from the outdoor test sites (Figure 58, 59 and 60). For the couples exposed outdoors, the corrosion rates are higher for those containing the more conductive ceramics (i.e., TiB₂, and B₄C) as compared to those containing the less conductive or insulating ceramics (i.e., SiC, Si₃N₄, and AlN).

For the couples in the humidity chamber treated with the chloride-containing electrolytes, the corrosion rates did not appear to be related to the ceramic conductivities.

* Electrical resistivity of ceramics

Figure 110. Corrosion rate for chloride- containing treatments (90-day humidity chamber experiment).

One possible hypothesis is that the much higher corrosion rates in the humidity chamber tests lead to the buildup of insulative corrosion product between the interface of the 6061-T6 Al and ceramic coupons electrically decoupling the coupons and eliminated the galvanic effect. As a result, crevice corrosion dominated, resulting in corrosion rates relatively independent of the ceramic resistivity. Hence, galvanic and non-galvanic couples could subsequently corrode at comparable rates. Accordingly, the coupons

treated with 0.5 M Na₂SO₄ (Figure 111), which was significantly less corrosive, showed similar trends to the field studies.

* Electrical resistivity of ceramics

Figure 111. Corrosion rate for 0.5 M Na₂SO₄ treatment (90-day humidity chamber experiment).

To test this hypothesis, humidity chamber experiments were conducted for a much shorter period (i.e., 21 days) to limit corrosion at the interface. The 21-day period was selected by estimating the amount of corrosion damage experienced in the 90-day long field exposure, and adjusting the duration of the humidity chamber test so that total corrosion damage would be comparable to that in the field. The 21-day period was a good compromise for the various environments. Interestingly, only the sulfate exposure (Figure 112) again showed similar trends to the outdoor tests. For the chloride-treated

couples (Figure 113), the corrosion rate of 6061-T6 Al coupled to B₄C was much higher than those coupled to the less conductive ceramics, but the corrosion rate of 6061-T6 Al coupled to TiB₂ (the most conductive ceramic) was often lower than those coupled to the non-conductive ceramics. Hence, once again, the chloride treatments could not replicate the trends in the field even though the exposure duration was reduced greatly. One possible reason is that the chloride treatments are too aggressive and do not represent the conditions at the field sites. The sulfate solution, which is free of chlorides, may better simulate rain and hence the corrosion of the specimens. Even at marine sites, chloride concentration in rain is low and hence the sulfate treatment may still be applicable to marine environments.

*Electrical resistivity of ceramics

Figure 112. Corrosion rate based on the interface area for Na₂SO₄ treatment (21-day humidity chamber experiment).

* Electrical resistivity of ceramics

Figure 113. Corrosion rate for chloride- containing treatments (21-day humidity chamber experiment).

In the absence of chlorides, corrosion may be driven more by pH gradients that developed around the crevice; whereas, in strong chloride environments, corrosion may be driven more by pitting. Hence, a low chloride concentration in the corrosive treatment medium may be the key to better simulating outdoor corrosion tests.

7.4 Conclusion

Humidity Chamber corrosion tests conducted with chloride-containing solutions were aggressive and did not always represent the outdoor exposure results; however, the humidity chamber experiments conducted with less aggressive sodium sulfate solution treatments more accurately simulate the outdoor corrosion trends.

CHAPTER 8

CYCLIC CORROSION TEST CHAMBER

EXPERIMENTS

8.1 Introduction

The CCTC experiments were conducted inside a Singleton Corporation cyclic corrosion chamber following a modified GM9540P standard. The GM9540P procedure is an accelerated corrosion test used by the automotive industry to test materials for corrosion which accounts for the various combinations of cyclic conditions (salt solution, various temperatures, humidity, and ambient environment) and they are effective in evaluating different corrosion mechanisms (general, galvanic, crevice) [122]. The cyclic test conditions, a modified version of the test and various salt solutions are described in the following “Procedure” section.

8.2 Procedure

The 6061-T6 Al/ceramics couples were assembled following the procedure described in Chapter 5. Couples and uncoupled 6061-T6 Al coupons were exposed inside the CCTC.

A typical GM9540P cyclic condition is shown in Figure 114. Each cycle is 24 hours and further sub divided equally into ambient, wet, and dry-off phases (Figure 114). In the first 8-hour phase, the chamber is maintained at 25°C and 40-50% relative humidity (RH) with four spray periods. In the second eight-hour phase, the chamber is maintained at 49°C and 100% RH. The third and the last eight-hour phase is the dry-off period where the chamber is maintained at 60°C and less than 30% RH.

Figure 114. Typical GM9540P cycle (24 hours) *Courtesy: Daniel P. Schmidt of Army Corrosion Office

The modified version accounts for the exposure of the couples which were exposed at 30° to the horizontal (similar to outdoor exposure) rather than 15° inside the chamber (Figure 115).

Figure 115. CCTC set up

The couples were sprayed with either the standard GM9540P solution or a 0.5 M Na_2SO_4 solutions with various chloride concentrations (i.e., 0, 10, 100, 1000 ppm Cl^-). The standard GM9540P solution contains 0.9% sodium chloride, 0.1% calcium chloride, and 0.25% sodium bicarbonate. The total chloride concentration in the GM9540P solution is approximately 6000 ppm. Initially, the CCTC experiments were conducted for 2 cycles with GM9540P solution or the 0.5M Na_2SO_4 solution. Each of the 24-cycle CCTC experiments was sprayed with one of the five different chloride solution (i.e., 0, 10, 100, 1000, GM9540P solution ppm Cl^-).

8.3 Results and Discussion

In the CCTC experiments, corrosion in the interface area of the 6061-T6 Al coupons was negligible when coupled to SiC, AlN, or Si_3N_4 for 2 cycles; whereas, corrosion had already initiated when coupled to B_4C for the GM9540P solution treatment

(Figure 116). If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion, which requires the development of pH gradients in the crevice regions. The 2-cycle experiment treated with the GM9540P solution was likely too short for pH gradients to develop. In contrast, if the ceramics are conductive, galvanic corrosion can progress immediately.

* Electrical resistivity of ceramics

Figure 116. Corrosion rate based on the interface area for GM95640P treatment (2-cycle CCTC).

After 24 cycles, corrosion was observed at the interfacial region of the 6061-T6 Al coupons for both the galvanic and non-galvanic couples (Figure 117). The results from the 24-cycle CCTC experiments treated with GM9540P solution (Figure 117) did not represent the outdoor corrosion trends and were comparable to 90-day chloride-

containing humidity chamber results. The GM9540P test may have been too aggressive to cause a difference between the galvanic and non-galvanic couples. When corrosion at the interface becomes extensive, the insulative alumina corrosion products can galvanically decouple a conductive ceramic from the aluminum coupon, and cause corrosion to proceed primarily as crevice corrosion for both conductive and non-conductive ceramics.

* Electrical resistivity of ceramics

Figure 117. Corrosion rate based on the interface area for GM95640P treatment (24-cycle CCTC).

The CCTC experiments were then conducted with less aggressive chloride-free 0.5 M Na₂SO₄ solutions for 2 and 24 cycles. The corrosion rates were negligible for the 6061-T6 Al samples coupled to non-conductive ceramics (Figure 118), similar to the results

obtained from the 2-cycle CCTC experiments treated with GM9540P solution. The lack of crevice corrosion at the interface for non-conductive couples during the short 2-cycle experiment may have resulted from insufficient time for pH gradients to develop in the crevice regions. In contrast, galvanic corrosion between the TiB_2 and the B_4C coupons did not show an “incubation” period as interface corrosion rates were high after only 2 cycles (Figure 118).

* Electrical resistivity of ceramics

Figure 118. Corrosion rate based on the interface area for 0.5 M Na_2SO_4 treatment (2-cycle CCTC).

After 24 cycles for the 0.5 M Na_2SO_4 solution treatment, crevice corrosion was observed (Figure 119) and showed similar trends to the field studies. The conductive ceramics induced much higher interfacial corrosion rates compared to the non-conductive

ceramics with the exception of the insulative AlN. The corrosion rates induced by AlN were comparable to those of TiB₂ and B₄C. This may have been caused by the higher surface roughness of the AlN specimen versus that of TiB₂ and B₄C. The higher surface roughness of the AlN coupons may have resulted in larger crevices at the interface inducing more crevice corrosion. Similar results where AlN induced high corrosion rates in comparison to the other ceramics were observed in immersion tests [123].

* Electrical resistivity of ceramics

Figure 119. Corrosion rate based on the interface area for 0.5 M Na₂SO₄ treatment (2-cycle CCTC).

The CCTC experiments were conducted for 24 cycles with 10, 100, 1000 ppm of chloride solutions to determine the effect of chlorides on the correlation of the CCTC experiments to outdoor exposure tests for the couples. The corrosion rate of the 24-cycle CCTC experiment for the 10 ppm Cl⁻ solution treatment (Figure 120) and 100 ppm Cl⁻

solution treatment (Figure 121) were similar to the 0.5 M Na₂SO₄ solution treatment. The corrosion rate trends from the less aggressive solution treatment were comparable to the outdoor experiments where the corrosion rates of 6061-T6 Al coupled to conductive ceramics (TiB₂ and B₄C) were higher than the corrosion rate of 6061-T6 Al coupled to non-conductive ceramics (SiC, Si₃N₄, and AlN).

* Electrical resistivity of ceramics

Figure 120. Corrosion rate based on the interface area for 10 ppm Cl⁻ solution treatment (24-cycle CCTC).

* Electrical resistivity of ceramics

Figure 121. Corrosion rate based on the interface area for 100 ppm Cl⁻ solution treatment (24-cycle CCTC).

The 24-cycle CCTC results for 1000 ppm Cl⁻ solution treatment (Figure 122) did not represent the outdoor corrosion trends and were similar to the 6000 ppm Cl⁻ solution treatment (Figure 117).

* Electrical resistivity of ceramics

Figure 122. Corrosion rate based on the interface area for 1000 ppm Cl⁻ solution treatment (24-cycle CCTC).

8.4 Conclusion

The aggressive chloride solution treatments (i.e., 1000, and 6000 ppm Cl) were comparable to results from the 90-day humidity chamber exposure with aggressive chloride treatments (i.e., 3.15 wt% NaCl, ASTM seawater, real seawater). The correlation between the outdoor experiments and CCTC experiments improved for the less aggressive chloride solution treatments (i.e., 0, 10, and 100 ppm chloride). Even at marine sites, rain which is low in chlorides (approx. 10 ppm) regularly cleanses specimens of deposited aerosol chlorides. As shown in the Humidity Chamber experiments, corrosion in more aggressive solutions is due to pitting; whereas, in less

aggressive environments, corrosion is developed around the crevice due to pH gradients.

Hence, optimal chloride concentration in the corrosive medium may be the key to simulating outdoor corrosion tests.

The duration of accelerated corrosion tests should be carefully selected so that corrosion mechanism (galvanic or/and crevice corrosion) that operate in the accelerated tests can better represent field conditions. The 2-cycle experiment was likely too short for pH gradients to develop hence the crevice corrosion for the non-galvanic couples were negligible.

CHAPTER 9

HUMIDITY CHAMBER ZRA

EXPERIMENTS

9.1 Introduction

The galvanic current between the TiB₂ and 6061-T6 Al coupons were measured inside a chamber with controlled humidity and temperature. The TiB₂/6061-T6 Al couples were subjected to spraying cycles of different solutions at 24-hour interval for 5 days to simulate rain. The galvanic current from humidity chamber ZRA experiments were used to calculate the corrosion rate in gmd using Faraday's law and the results were compared to the actual outdoor corrosion rate calculated using mass loss.

9.2 Procedure

The dimensions of the TiB₂ and 6061-T6 Al coupons were 1 in. X 1 in. and 2 in. X 2 in., respectively for the humidity ZRA experiments. The specimen dimensions were similar to the outdoor exposure specimens. In the electrochemical ZRA experiments (Chapter 4), the exposed area of TiB₂ and 6061-T6 Al electrodes were 1 cm². The electrical wires were attached to the TiB₂ and 6061-T6 Al coupons with silver conductive epoxy (MG Chemicals 8331-14g) and cured in an oven at 70°C for 20 minutes. The end of the wire connection that contacted the coupons were covered with 0151 Hysol epoxi-

patch adhesive. The 0151 Hysol epoxi-patch adhesive was cured at 70°C for 2 hours. The TiB₂ and 6061-T6 Al coupons with the wires were coupled together using the C-clamps, 6061-T6 Al bolts, and G-10 fiber glass similar to outdoor exposure couples. A thin insulating layer was inserted between the TiB₂ and 6061-T6 Al coupons to measure the galvanic current flowing between them (Figure 123).

Figure 123. Schematic diagram of ZRA connection with actual couple.

The couples were then placed inside a chamber and were maintained at 90% relative humidity (RH) and 30°C. The temperature was controlled by Digi-Sense Model – 2186 20 temperature controller, and the humidity was controlled using an Evenflo humidifier filled with 18.1 MΩ-cm water and an Electro-tech 514 automatic humidity controller. The TiB₂/6061-T6 Al couples were electrically connected to a ZA100 ZRA to measure the galvanic current. A Madgetech Volt 101 data logger was used to measure the galvanic current every 15 seconds for 5 days. The couples were sprayed with 0.5 M Na₂SO₄ solutions with various amount of NaCl (i.e., 0, 10, 100, 1000, or, 10000 ppm Cl⁻) and 3.15 wt% NaCl (≈20,000 ppm Cl⁻) every 24 hours to observe the effect of chloride concentration. In the electrochemical ZRA experiments (Chapter 4), the galvanic current between TiB₂ and 6061-T6 were in the immersed condition; whereas, in

the humidity ZRA experiments, the couples (dimensions similar to outdoor experiments) were sprayed with different solutions to simulate rain and to study galvanic corrosion under atmospheric condition. Figure 124 shows the actual couple with the electrical connections.

Figure 124. Electrical connection of a TiB_2 /6061-T6 Al couple

9.3 Results and Discussion

The galvanic current between TiB_2 and 6061-T6 couple sprayed with 0, 10, 100, 1000, and 20000 ppm Cl^- solutions are shown in Figures 125, 126, 127, 128, and 129, respectively. The galvanic currents peaked when the couples were sprayed with different solutions at 24-hour interval.

Figure 125. Galvanic currents between TiB_2 and 6061-T6 Al in humidity chamber at 90% RH and 30°C (0 ppm Cl^- treatment).

Figure 126. Galvanic currents between TiB_2 and 6061-T6 Al in humidity chamber at 90% RH and 30°C (10 ppm Cl^- treatment).

Figure 127. Galvanic currents between TiB_2 and 6061-T6 Al in humidity chamber at 90% RH and 30°C (100 ppm Cl^- treatment).

Figure 128. Galvanic currents between TiB_2 and 6061-T6 Al in humidity chamber at 90% RH and 30°C (1000 ppm Cl^- treatment).

Figure 129. Galvanic currents between TiB_2 and 6061-T6 Al in humidity chamber at 90% RH and 30°C (20000 ppm Cl^- treatment).

The short circuit current or galvanic current (I_{Galv}) between the electrically connected 6061-T6 Al and TiB_2 coupons is related to the rate of the mass loss of the active metal (6061-T6 Al) due to the galvanic effect (Faraday's law) as shown in equation 18

$$\text{Corrosion rate} = \left(\frac{\text{AW}}{n \times F} \right) \times (I \times T) \quad (18)$$

AW : Atomic weight of Al

n : number of electrons

F : Faraday constant

I : Galvanic current

T : Exposure time

The galvanic current can change with environmental conditions (equation 16); whereas, other variables such as Faraday constant, atomic weight, and numbers of electrons are constants. The corrosion rates from outdoor exposure calculated from mass loss were compared to the corrosion rate from humidity ZRA calculated from Faraday's law. An equation based on Faraday's law was developed to calculate the corrosion rate by relating the TOW from the field exposure to the galvanic current measured from the humidity ZRA (equation 16). The total exposure time was divided into wet periods (T_{wet}) and dry periods (T_{dry}).

$$\text{Corrosion rate} = \left(\frac{AW}{n \times F} \right) \times \left(\frac{(I_{ss} \times T_{\text{wet}}) + (I_{\text{min}} \times T_{\text{dry}})}{\text{Area}_{\text{Interface}} \times \text{Time}_{\text{Total}}} \right) \quad (16)$$

I_{ss} : Steady-state galvanic current values

T_{wet} : Wet period

I_{min} : Minimum current

T_{Dry} : Dry periods

$\text{Area}_{\text{interface}}$: Area of the interface

$\text{Time}_{\text{Total}}$: Total exposure period

As shown in the outdoor experiments, leaf wetness data were used to calculate the dry (T_{dry}) and wet (T_{wet}) days for the different test sites. T_{Dry} days corresponds to Q1, Q2, and Q3 values and T_{Wet} days corresponds to Q4 values from the outdoor exposure (Table 21, 22, and 23). Table 27, 28, and 29 shows the T_{Dry} and T_{Wet} days for 3, 6/7 and 12/13 month exposure periods, respectively.

Table 27. Wet and Dry days for test sites for 3- month exposure

Test Sites	T _{Dry}	T _{Wet}
Mānoa	49	41
Coconut Island	71	19
Kilauea	63	27
Kahuku	84	6
Campbell	89	1
Ewa Nui	88	2
Waipahu	88	2

Table 28. Wet and Dry days for test sites for 6/7- month exposure

Test Sites	T _{Dry}	T _{Wet}
Mānoa	98	82
Coconut Island	147	33
Kilauea	138	42
Kahuku	194	16
Campbell	203	7
Ewa Nui	192	18
Waipahu	190	20

Table 29. Wet and Dry days for test sites for 12/13- month exposure

Test Sites	T _{Dry}	T _{Wet}
Mānoa	211	154
Coconut Island	302	63
Kilauea	288	77
Kahuku	363	32
CIP	384	11
Ewa Nui	363	32
Waipahu	359	36

Leaf wetness sensors were subjected to different spray solutions inside the humidity chamber at 90% RH and 30⁰C for one day to get a better understanding of the wet/dry cycle. The leaf wetness sensor voltage output was above 22mV for 0, 10, 1000, and 20000 ppm Cl⁻ solutions treatments (Figure 130). As shown in the outdoor-experiment, TOW data, any voltage output above 20mV was considered to be wet period. Hence, galvanic corrosion during wet periods was assumed to proceed at the steady-state galvanic corrosion currents. The average galvanic current profile for different spray solutions with the steady-state current is shown in the Figure 131 and the steady-state galvanic current values (I_{ss}) in μ A are tabulated in Table 30. For dry periods, the galvanic current values were assumed to be zero.

Figure 130. The leaf wetness sensor voltage output for different solutions treatments inside the humidity chamber maintained at 90% RH and 30⁰C.

Figure 131. Average galvanic currents between TiB₂ and 6061-T6 Al in humidity chamber at 90% RH and 30⁰C for different solutions treatment.

Table 30. Steady State Galvanic currents (ISS) in μA

Solution Treatment	I_{ss} (μA)
0 PPM	21.36
10 PPM	29.38
100 PPM	41.05
1000PPM	47.51
20000 PPM	47.70

Based on these assumptions, corrosion rate in gmd were calculated from the humidity ZRA data using equation 18. The predicted corrosion rate in gmd at the seven test sites which were based on the galvanic currents measured in the humidity chamber with different solution treatment and the actual TOW data from each test site for the 3-month exposure were plotted and compared with the actual outdoor data (Figure 132).

Figure 132. Predicted corrosion rates at outdoor sites using galvanic currents for 3-month exposure.

Due to less wet days, the corrosion rates calculated from humidity ZRA were lower than the actual outdoor exposure results for drier test sites for 3-month exposure period. The correlation between the outdoor experiments and humidity ZRA experiments improved for the longer exposure periods at dry test sites (Figures 133 and 134).

Figure 133. Predicted corrosion rates at outdoor sites using galvanic currents for 6/7-month exposure.

Figure 134. Predicted corrosion rates at outdoor sites using galvanic currents for 12/13-month exposure.

9.4 Conclusion

Corrosion rates predicted using the humidity ZRA data from 0 and 10 PPM chloride treatments were the closest to the outdoor data. The 20000 and 1000 ppm chloride treatment corrosion rates were comparable, and higher than those of the less concentrated chloride treatments. This is the result of the aluminum being susceptible to pitting in Cl^- containing solutions. The anodic polarization of 6061-T6 Al in different de-aerated chloride solutions showed that the pitting potential increased with decreasing

chloride concentration, and galvanic corrosion is under anodic control in the absence of chlorides, and under cathodic control when chloride levels are high (Figure 135). Hence, there is a substantial increase in the galvanic corrosion rate from 0 ppm to 1000 ppm Cl^- , and a negligible increase from 1000 ppm to 20,000 ppm Cl^- .

Figure 135. Anodic polarization of 6061-T6 Al in de-aerated chloride solutions at 30°C. Scan rate= 1mv/s.

CHAPTER 10

ESTIMATION OF PENETRATION RATE USING THE AREA FRACTION ANALYSIS

10.1 Introduction

The corroded area fraction at the ceramic-6061-T6 Al interface from the outdoor exposure experiments and humidity chamber experiments were quantified using a Video Image Enhanced Evaluation of Weathering (VIEEW) surface analyzer. Average penetration rates were calculated from the area fraction and mass loss.

10.2 Procedure

Corroded 6061-T6 Al coupons were scanned using a VIEEW surface analyzer. VIEEW digital image analyzer from Atlas Electric Devices Company is capable of capturing digital images of samples using diffuse and direct illumination and effectively highlights the corroded area from the uncorroded area. The VIEEW software then quantifies the corroded area fraction.

The interface corrosion rates given in grams per meter squared per day (gmd) from the outdoor and humidity chamber experiments were averaged over the entire interface area. In many cases, however, the entire interface area was not corroded, and

therefore, by attributing the corrosion only to the corroded area, a better approximation of the penetration rate can be achieved. The average penetration rates were then calculated from the mass loss data and the area of the interface that was corroded. Figure 136 shows an example of a corroded area scanned using the VIEEW software, and the corresponding corroded area fraction.

The highlighted red area represents the corroded area of the scanned image.

Figure 136. VIEEW scan of the interface side of 6061-T6 Al exposed at Coconut Island for 90 days.

Corroded area fractions were used to calculate the average penetration rate in millimeters per year (mm/year) based on the average mass loss at the interface using the following formula:

$$\text{Effective corrosion rate (gmd)} = \frac{\text{Mass loss at the interface (g)}}{\text{Days exposed (days)} \times \text{Interface area (m}^2\text{)}} \times \frac{\text{Interface area}}{\text{Corroded area}} \quad (16)$$

$$= \frac{\text{Corrosion rate at the interface region}}{\text{Corroded area fraction}} \quad (17)$$

The effective corrosion rate is then converted to average penetration rate.

10.3 Results and Discussion

Figures 137 and 138 compare the corrosion rate in gmd based on the entire interface area with the penetration rate in mm/yr based on the corroded area fraction using VIEEW analysis for the 6061-T6 Al coupons at the Coconut Island site. Figures 139 and 140 compare the same for the Mānoa test site.

Figure 137. Corrosion rate based on the interface area at Coconut Island.

Figure 138. Penetration rate based on the corroded area at Coconut Island.

Figure 139. Corrosion rate based on the interface area at Mānoa.

Figure 140. Penetration rate based on the corroded area at Mānoa.

Figures 141 and 142 compare the corrosion rate in gmd based on the interface area with the penetration rate in mm/yr based on the corroded area for the 6061-T6 Al coupons coupled to ceramics and treated with 0.5 M Na₂SO₄ for the 90-day humidity chamber experiments.

Figure 141. Corrosion rate based on the interface area for Na_2SO_4 treatment (90-day humidity chamber experiment).

Figure 142. Penetration rate based on the corroded area for 0.5 M Na_2SO_4 treatment (90-day humidity chamber experiment).

The following figures compare the corrosion rate based on the interface area and penetration rate from the 90-day humidity chamber experiments for the 3.15 wt% NaCl, ASTM seawater, and real seawater treatments.

Figure 143. Corrosion rate based on the interface area for 3.15 wt% NaCl treatment (90-day humidity chamber experiment).

Figure 144. Penetration rate based on the corroded area for 3.15 wt% NaCl treatment (90-day humidity chamber experiment).

Figure 145. Corrosion rate based on the interface area for ASTM seawater treatment (90-day humidity chamber experiment).

Figure 146. Penetration rate based on the corroded area for ASTM seawater treatment (90-day humidity chamber experiment).

Figure 147. Corrosion rate based on the interface area for real seawater treatment (90-day humidity chamber experiment).

Figure 148. Penetration rate based on the corroded area for real seawater treatment (90-day humidity chamber experiment).

The penetration rate measurements based on the corroded area changed the order of severity of corrosion damage of 6061-T6 Al coupled to different ceramics when compared with the corrosion rate based on the interface area given in gmd (Figures 137 through 148). The method to calculate the penetration rate based on the corroded area (equation 17) is very sensitive to the corroded area fraction (a_{Corr}) (which is in the denominator) if a_{Corr} is very small. This sensitivity could possibly lead to errors for cases of very low a_{Corr} values. As an example, the corrosion rate of 6061-T6 Al coupled to different ceramics and treated with 0.5 M Na_2SO_4 had very low corrosion rates. The comparison of the calculated penetration rate with the corrosion rate at the interface in gmd showed very different trends (Figures 141 and 142). A comparison between the

corrosion rate in gmd and the corroded area fraction quantified using VIEEW analyzer showed a good correlation (Figures 149).

Figure 149. Corrosion rate based on the interface area and corroded area fraction at the interface for 0.5 M Na₂SO₄ treatment (90-day humidity chamber experiment).

10.4 Conclusion

The estimated penetration rates for specimens with a low area fraction of corroded interface were generally higher since the area fraction term was in the denominator.

Hence, for specimens with extremely low area fractions of corroded interface, penetration rate calculations based on the area fraction may be uncharacteristically high and in error.

Chapter 11

Conclusions

11.2 Introduction

A comprehensive test protocol was developed to study the corrosion behavior of 6061-T6 Al coupled to a variety of conducting, semi-conducting, and insulating ceramics, which were TiB_2 , B_4C , SiC , Si_3N_4 , and AlN . The environmental parameters that affected the corrosion rates of the couples were indentified. Outdoor exposure corrosion rate data from a variety of microclimates (i.e., rain forest, alpine, marine, volcanic, industrial, agricultural, and arid) were correlated with a series of accelerated laboratory corrosion tests (controlled humidity-chamber and CCTC) for both galvanic and non-galvanic ceramic-aluminum (Al) couples. A new test method (humidity-ZRA) was also developed to study galvanic corrosion under atmospheric condition.

11.2 Background

An extensive literature search was conducted for previous research on the corrosion at ceramic-metal couples. Unfortunately, there has been no reported work in this area. Ceramic-metal couples, however, have become more prevalent with the increase in use of hybrid systems which had compelled us to look at potential corrosion issues at ceramic-metal interfaces.

11.3 Electrochemical Experiments

Electrochemical experiments (polarization and ZRA) conducted on 6061-T6 Al and conductive TiB₂ ceramics identified the governing corrosion mechanisms (passivity or pitting) in different solutions. Electrochemical experiments were not conducted with other ceramics as their resistivities were too high.

Using polarization diagrams generated from experiments, galvanic corrosion rates between 6061-T6 Al and TiB₂ electrodes were predicted to be higher in aerated chloride solutions (3.15 wt% NaCl, real seawater and ASTM seawater) as compared to chloride-free 0.5 M Na₂SO₄. In polarization experiments, the rate of galvanic corrosion (galvanic current) corresponds to the intersection of the anodic polarization curve of 6061-T6 Al and the cathodic polarization curve of TiB₂. Polarization curves were generated as a function of potential and plotted with the current density values. The 6061-T6 Al pits in chloride containing solution and the anodic current increases exponentially with potential; whereas, in 0.5 M Na₂SO₄ solution (chloride-free) 6061-T6 Al passivates with a constant anodic current. The cathodic curve of TiB₂ intersected the anodic curve of 6061-T6 Al in the pitting regime in aerated chloride solutions; whereas, the cathodic curve of TiB₂ intersected the anodic curve of 6061-T6 Al in the passive regime in aerated 0.5 M Na₂SO₄ solution. This explains the higher galvanic corrosion rate in chloride solutions when compared to 0.5 M Na₂SO₄ solution.

The results from the ZRA experiments showed that the galvanic corrosion rate for the 6061-T6 Al/TiB₂ couple in 3.15 wt% NaCl and 0.5 M Na₂SO₄ solutions were in agreement with the predictions from the polarization experiments. In ZRA experiments, however, the initial galvanic current for the 6061-T6 Al/TiB₂ couple were high and

comparable in chloride solutions (3.15 wt% NaCl, real seawater and ASTM seawater), but the galvanic current diminished with time in real and ASTM seawater when compared to 3.15 Wt% NaCl solutions. The calcareous deposits on the TiB₂ cathode caused the lower corrosion rates in real and ASTM seawaters by stifling oxygen reduction at the cathodic sites as compared to the corrosion rate in the 3.15 wt% NaCl solution.

11.4 Outdoor Exposure

The diversity of the micro-climates represented by the test sites was confirmed by the weather data monitored for the three exposure periods (3, 6, and 12 months), and the statistical analysis showed a strong positive relationship between the weather parameters TOW, humidity and rainfall; whereas, these three weather parameters showed a strong negative relationship with the temperature.

Due to the galvanic effects by the relatively conductive TiB₂ and B₄C ceramics, high corrosion rates were observed in the galvanic couples (6061-T6 Al/TiB₂ and 6061-T6 Al/B₄C) exposed at the outdoor test sites for the three exposure periods at eight different test sites. Galvanic currents measured between B₄C and 6061-T6 Al using the ZRA technique were higher than those between TiB₂ and 6061-T6 Al, explaining the higher corrosion rates of 6061-T6 Al coupled to B₄C as compared to those coupled with TiB₂ in the field. The higher galvanic current between B₄C and 6061-T6 Al could be caused by the photo-electrochemical properties of semiconducting B₄C.

The outdoor chloride deposition rate and corrosion rate had a low degree of Pearson correlations (-0.3 to +0.3) due to the corrosion rate data from Manoa test site.

Corrosion rates were high in Manoa due to high wetness but chloride deposition rate was almost zero at Manoa test site. Nevertheless, the chloride environments affected the galvanic as well as crevice corrosion for the couples as shown in the accelerated laboratory experiments. The two most important parameters that affected the corrosion rate of the couples were TOW and the chloride-deposition rate.

Corrosion rates were higher in marine environments (Coconut Island and Kahuku) due to high Cl⁻ deposition, and in the rainforest environment (Mānoa) due to high wetness when compared to other dry test sites (Waipahu, Ewa Nui, and Campbell Industrial park). The corrosion mechanisms at Kilauea differed significantly from the other test sites. The ceramic coupons shielded and protected the aluminum substrate from the aggressive volcanic (Kilauea) environment that contains relatively high levels of SO₂. Often, the degree of corrosion at Kilauea would be less at the interface than on the external regions, compared to specimens exposed at the other test sites (Coconut Island, Mānoa, Kahuku, Waipahu, and Ewa Nui).

11.5 Accelerated Laboratory experiments

The existing standardized accelerated laboratory tests did not produce good representation of the corrosion in the natural environment. Therefore, new test protocols were developed to analyze the corrosion behavior of aluminum coupled to the various ceramics in the accelerated corrosion tests. The accelerated corrosion tests were modified to better simulate the corrosion behavior in the field. Electrolytes with varying amounts of chlorides (i.e., 0, 10, 100, 1000, 6000 and 20000 ppm chlorides) were used in the

accelerated tests. The duration of the accelerated corrosion tests were also adjusted to better represented the corrosion damage accumulated in the field.

The accelerated laboratory corrosion tests did not show a trend of higher corrosion rates for the galvanic couple when compared to non-galvanic couple (a trend observed at the field sites) when the couples were treated with aggressive chloride solutions (i.e., ≥ 1000 ppm NaCl, GM 9540 solution). The results from the aggressive accelerated tests showed that the corrosion rates for galvanic and non-galvanic couples were high and relatively similar. In aggressive chloride environments, corrosion is driven more by pitting and the aggressive accelerated tests had caused the conductive ceramic coupons to galvanically decouple from the aluminum coupons due to significant alumina (which is insulative) formation in the interface region, eliminating the galvanic corrosion effect. As a result, crevice corrosion can dominate, resulting in corrosion rates relatively independent of the ceramic resistivity. Hence, galvanic and non-galvanic couples could subsequently corrode at comparable rates.

The field trends that showed that corrosion rates were higher for specimens coupled to the conductive ceramics were only observed in the laboratory accelerated corrosion tests when low-concentration chloride solutions (i.e., 0 - 100 ppm NaCl solutions) were used, as these better simulate rain. Even at marine sites, rain which is low in chlorides (approx. 10 ppm) regularly cleanses specimens of deposited aerosol chlorides. Hence, optimal chloride concentration in the corrosive medium is the key to simulating outdoor corrosion tests.

If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion, which requires the development of pH gradients in the

crevice regions. Hence, the selection of the duration of accelerated corrosion tests is also important so that the corrosion mechanism (galvanic or/and crevice corrosion) that operates in the accelerated tests can better represent field conditions.

11.6 New test method

A new test method (humidity-ZRA experiments) was devised considering the two most important environmental parameters (chloride concentrations and TOW) to study the galvanic corrosion under atmospheric condition. The humidity-ZRA experiments conducted with the galvanic couples (dimensions similar to outdoor experiments) and sprayed with different solutions better simulated rain and closely predicted the outdoor data. Corrosion rates in the humidity-ZRA experiments were calculated from the galvanic current using Faraday's law and the actual TOW data from the field.

Appendix A

Carbonate Chemistry

Figure A1. The distribution of carbonate species as a fraction of total dissolved carbonate (C_T) in relation to solution pH [118].

Appendix B

Geographic Coordinates of Test Sites

Table B1. Geographic coordinates of test sites

Test Sites	Latitude	Longitude
Mānoa	21 ⁰ 19' 58'' N	157 ⁰ 48' 12'' W
Coconut Island	21 ⁰ 26' 09'' N	157 ⁰ 47' 15'' W
Campbell Industrial Park	21 ⁰ 18' 00'' N	158 ⁰ 06' 00'' W
Ewa Nui	21 ⁰ 24' 00'' N	158 ⁰ 00' 00'' W
Waipahu	21 ⁰ 42' 00'' N	157 ⁰ 54' 00'' W
Kahuku	21 ⁰ 24' 00'' N	158 ⁰ 00' 00'' W
Kilauea	22 ⁰ 12' 43'' N	159 ⁰ 24' 44'' W
Mauna Loa	19 ⁰ 32' 21'' N	155 ⁰ 34' 44'' W

Appendix C

Campbell Scientific 237 Leaf wetness Sensor*

Figure C1 shows the model 237 leaf wetness sensor. An interlaced “fingers of copper grid coated with nickel are spaced approximately 0.04 inches apart.

Figure C1. Campbell Scientific Model 237 leaf wetness sensor

Figure C2 shows the circuit for the Campbell Scientific Model 237 leaf wetness sensor.

Figure C2. The circuit for the Campbell Scientific Model 237 leaf wetness sensor.

The sensor acts as a variable resistor R_s in the circuit and it is given by the equation

$$R_s = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + \dots + \frac{1}{R_n}}$$

where $R_1, R_2 \dots R_n$ are the resistances of each droplet. As the number of droplets increases, the resistance across the sensor decreases. The sensor resistance varies from above 3 MΩ when dry to around 1 KΩ when wet. A completely dry sensor is an open circuit, and therefore has infinite resistance. A custom made data logger from MadgeTech is used as an external source to power the sensor. Once the circuit is stable, the data logger measures and records the output voltage V_s given by

$$V_s = \frac{V_x(R_2)}{R_1 + R_2 + R_s}$$

So the output voltage V_s is a function of input voltage V_x , the value of the fixed resistors R_1 and R_2 , and the resistance of the sensor R_s .

The leaf wetness sensors were painted with flat white latex paint and allowed to dry at room temperature. A total of three coats were applied to the sensors. This procedure was carried out in order to distribute water droplets evenly over the surface as recommended by Campbell Scientific.

* Instruction Manual, Model 237 Leaf Wetness Sensor, Campbell Scientific, Inc., 1988 – 1996

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