OUTDOOR & LABORATORY CORROSION STUDIES OF ALUMINUM METAL–MATRIX COMPOSITES

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAI'I IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

MECHANICAL ENGINEERING

AUGUST 2004

By

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ACKNOWLEDGMENTS

The author wishes to express his gratitude for the significant contributions to this work made by Dr. Lloyd H. Hihara. Without Dr. Hihara's continued guidance, trust and enthusiasm, this huge undertaking would never have been possible. The author would also like to express his gratitude to Dr. Hihara, Alex Niemi, Ryan Sugamoto, Ben Respicio and Justin Wade for their help in fabricating and setting up the corrosion test sites on Oahu. Thanks also go to Chester Tonokawa and Arielle Shirland of HECO for their help with test site maintenance. The author would like to thank Thanigai Arasu Govindaraju for preparing the Al6061-T6 standard specimens used in the outdoor and immersion experiments in addition to Dr. Kent Ross, Dr. Hongbo Ding, Raghu Srinivasan and Dr. Ralph Adler for their contributions to this project. Initial funding for this project was provided from the Concurrent Technologies Corporation (CTC) through the sponsorship of the U.S. Army Industrial Ecology Center under Contract DAAE30-98-C-1050 as part of the National Defense Center for Environmental Excellence program. The author is grateful to the former technical liaison contacts Mr. Brian Deforce and Mr. Robert Mason at CTC. Current funding is provided form the Pacific Rim Corrosion Research Program (PRCRP) through the sponsorship of the U.S. Army TACOM-ARDEC under contract DAAE30-03-C-1071. The author is grateful to the program manager Mr. Bob Zanowicz, and for the support of Dr. Joseph Argento, Mr. John Theis and Mr. Donald Skelton. Finally, the author would like to thank the thesis committee consisting
of Dr. Lloyd H. Hihara, Dr. Bruce E. Liebert and Dr. Marcelo Kobayashi for their time, patience and valuable contributions.
Eight aluminum metal-matrix composites (MMCs) containing SiC, B₄C or Al₂O₃ reinforcing particulate with volume fractions ranging from 5% to 50% were studied in both outdoor and laboratory experiments. Corrosion rates were determined and compared to those of monolithic Al6061-T6 under the same conditions. All of the metal-matrix composites corroded at much higher rates than Al6061-T6 both in the field experiments and in controlled laboratory experiments. Corrosion rates of MMCs increased as the volume fraction of the reinforcing particulate increased. The observed increase in corrosion rates of MMCs with higher volume fractions of SiC, B₄C or Al₂O₃ may be due to galvanic corrosion resulting from an increase in the number of cathodic sites as well as the formation of micro-crevices at the particulate-matrix interface. In SiC/Al MMCs, the purity and hence the resistivity of the SiC used seems to have an effect on the corrosion rate. In most of the field and laboratory experiments, Al6092-T6/SiC/50p showed higher corrosion rates than Al6092-T6/SiC/50p (Gr.). Anodic polarization of the MMCs in deaerated 3.15 wt.% sodium chloride (NaCl) and 0.5M sodium sulfate (Na₂SO₄) solutions show that the pitting potentials and passive current densities of all eight MMCs are similar having values close to those of Al6061-T6.
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For almost 25 years, the engineering and design community have been using aluminum metal-matrix composites (MMC) in an attempt to reduce structural weight and dramatically improve performance. MMC is a general term that encompasses discontinuously reinforced aluminum (DRA) composites. Of particular interest are MMCs consisting of an aluminum matrix reinforced with ceramic particles such as silicon carbide (SiC), boron carbide (B₄C) or aluminum oxide (Al₂O₃) in varying volume loadings. Al6092 is a matrix formulation manufactured by DWA Aluminum Composites in California. Table 1.1 indicates that Al6061 and Al6092 contain similar quantities of magnesium (Mg) and silicon (Si) alloying elements. Magnesium silicide (Mg₂Si) second-phase intermetallic particles serve to strengthen the aluminum matrix through precipitation hardening during the heat treatment process.

<table>
<thead>
<tr>
<th>Table 1.1: Comparison of Al6061-T6 and Al6092-T6</th>
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<tr>
<td>Maximum Amounts Specified (Wt.%):</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Si       Fe       Cu       Mn       Mg       Cr       Zn       Ti</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Al6061 [1]   0.40 - 0.8 0.7 0.15 - 0.40 0.15 0.8 - 1.2 0.04 - 0.35 0.25 0.15</td>
</tr>
<tr>
<td>Al6092 [2]   0.75 0.09 0.83 - 1.05 - - 0.05</td>
</tr>
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Volume loadings of 15 to 25% are suitable for structural applications, and loadings of 30 to 55% for CTE and thermal-management applications. Current applications include the use of 6092/SiC/17.5p DRA for extruded Fan Exit Guide Vanes (FEGV’s) for Pratt & Whitney’s high by-pass gas turbine engines on the Boeing 777 and thin gage sheet for both F-16 ventral fins and fuel access covers [2]. Other applications include 2009/SiC/15p aircraft hydraulic components for the F-18 E/F, 6092/SiC/17.5p brake fins for Walt Disney World thrill rides, and Global Positioning System (GPS) satellite electronic packaging chip carriers produced from 6063/SiC/50p forgings [2]. Other potential applications for DRA include sporting goods such as golf equipment, bicycle frames and components, and spent nuclear fuel containers utilizing Boron Carbide (B$_4$C) particle reinforcement in lieu of SiC [2]. Despite the many benefits of MMC technology, metal-matrix composites suffer from preferential corrosion because of their nonhomogeneous composition and structure. In particular, aluminum alloy matrix materials are very susceptible to corrosion when the dispersoid is a noble phase, such as SiC [3]. Table 1.2 shows the resistivities of the aluminum and ceramics used.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Purity (%)</th>
<th>Resistivity (Ω-cm)</th>
<th>Reference</th>
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<tr>
<td>SiC (black)</td>
<td>97.0</td>
<td>10$^0$</td>
<td>[4]</td>
</tr>
<tr>
<td>SiC (green)</td>
<td>99.3</td>
<td>10$^6$</td>
<td>[4]</td>
</tr>
<tr>
<td>B$_4$C</td>
<td>99.5</td>
<td>10$^1$</td>
<td>[4]</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>99.7</td>
<td>$&gt;10^{14}$</td>
<td>[5]</td>
</tr>
<tr>
<td>Al6061-T6</td>
<td>98.0</td>
<td>$4 \times 10^{-6}$</td>
<td>[6]</td>
</tr>
</tbody>
</table>
The MMCs selected for this corrosion project were manufactured by DWA Aluminum Composites using 6092 aluminum powder in combination with different volume fractions of SiC, B₄C and Al₂O₃ particulate. The aluminum powder and ceramic particulate were homogeneously blended and vacuum-hot-pressed into cylindrical billets. In this case, each billet was manufactured with the same processing and thermomechanical history. In addition, after pressing, each billet underwent the same T6 heat treatment. The billets, ranging from 3.56 inches to 3.75 inches in diameter, were cut into 0.1 inch thick wafers using an electric discharge machining (EDM) technique. Each wafer was then abrasive grit blasted to remove the recast layer. The eight aluminum metal matrix composites selected included Al6092-T6/SiC (black) with 5, 10, 20, 40 and 50% volume fractions in addition to Al6092-T6/SiC/50p (green), Al6092-T6/B₄C/20p and Al6092-T6/Al₂O₃/20p. Metallographic specimens of each MMC were prepared by setting 0.25 inch diameter disks in Buehler Epo-Thin low viscosity epoxy. The specimens were polished in a multi-step process using a Buehler Ecomet 6 variable speed polisher. The face of each specimen was ground flat with 320 grit silicon carbide paper and then reground with a 30 micron Ultra-Prep diamond grinding disk. Subsequent refinement of the MMC surface included polishing with 9, 3, 1, 0.25 and 0.05 micron Metadi Supreme polycrystalline diamond suspensions. The images shown in Figures 1.1 through 1.8 were captured using a Nikon Epiphot optical microscope in conjunction with Buehler Omnimet software. It is clear from the metallographic images that the SiC, B₄C and Al₂O₃ particles are irregular in shape and randomly distributed. Also, it is apparent that the average particulate size
increases as the volume fraction of the MMC increases. This is intentional and necessary in order to achieve the higher volume fractions.

Figure 1.1: Microstructure of Al6092-T6/SiC/5p

Figure 1.2: Microstructure of Al6092-T6/SiC/10p
Figure 1.3: Microstructure of Al6092-T6/SiC/20p

Figure 1.4: Microstructure of Al6092-T6/SiC/40p
Figure 1.5: Microstructure of Al6092-T6/SiC/50p

Figure 1.6: Microstructure of Al6092-T6/SiC/50p (Gr.)
Figures A.1 through A.8 in Appendix A show the eight MMCs at a lower magnification thereby revealing the macroscopic uniformity of the microstructure.
Due to the wide availability of aluminum MMCs compared to other more exotic metal composites, corrosion research has focused on aluminum MMCs containing boron, graphite, SiC, Al₂O₃ and mica [7]. In the late 1960s literature on the corrosion of MMCs began to appear. Initially the focus was on boron monofilament/aluminum (B_{MF}/Al) MMCs [8] but by the early 1970s the research had expanded to include graphite fiber/aluminum (Gr/Al) MMCs [7]. It wasn’t until the end of the 1970s that research on the corrosion of alumina fiber/aluminum (Al₂O₃/Al) and magnesium MMCs was published [9-12]. Corrosion literature pertaining to silicon carbide/aluminum (SiC/Al) MMCs [7] became available in the early 1980s along with literature on lead, depleted uranium and stainless steel MMCs. The reinforcement particles used can be classified as insulators in the case of boron and Al₂O₃, semiconductors in the case of SiC and conductors in the case of graphite [13]. The emphasis of much of the corrosion literature has been the study of galvanic corrosion between the MMC’s matrix and reinforcement. Evidence has shown that galvanic corrosion occurs in B/Al and SiC/Al MMCs. For SiC/Al MMCs in aqueous solutions, hydrogen evolution (proton reduction) and oxygen reduction can occur on the SiC particles which act as an inert electrode [14]. The pitting potential (E_{PI}) of SiC/Al MMCs is very similar to that of the monolithic matrix material suggesting that the pitting resistance of the passive layer on the aluminum is unaffected by the addition of silicon carbide particles [14]. Alumina (Al₂O₃) has a resistivity of
about $10^{14}$ Ω-cm [15] indicating little or no galvanic corrosion between the aluminum matrix and the Al$_2$O$_3$ particulate. However, in accelerated corrosion tests of Al$_2$O$_3$/Al (2% Li) MMCs in environments containing chlorides, the corrosion rate of the alumina/Al MMC was in most cases slightly higher than that of 6061-T6 aluminum [16]. Literature discussing the corrosion of aluminum reinforced with boron filaments (BFs) indicates that corrosion rates increase with an increase in the content of BFs due to an escalation in the number of aluminum-boride cathodic sites [17]. Boron/aluminum MMCs experience severe corrosion in chloride environments and are significantly less corrosion resistant than unreinforced aluminum alloys [18]. Few studies have been conducted in which various MMCs with a wide range of particulate type and volume fraction have been exposed to diverse real-world environmental conditions. Oxidizing or halide containing environments can induce pitting of the matrix metal of MMCs exposed to those environments [14]. The presence of noble reinforcing particles can accelerate pitting of the MMC matrix due to galvanic effects [14] and discontinuous SiC/Al MMCs are susceptible to localized corrosion in the form of mild to moderate pitting exposed in splash/spray and marine atmospheric environments [18]. Corrosion rates of SiC/Al MMCs immersed in real seawater are much higher than those observed in atmospheric testing [18]. Corrosion rates of SiC/Al MMCs immersed in seawater are generally higher than those for unreinforced aluminum alloys in the same solutions [18]. Discontinuous SiC/Al MMCs corrode at the particle matrix interface due to crevices that form in those regions [19-21]. The crevices are preferential sites for pitting [18].
CHAPTER 3
OUTDOOR EXPERIMENT

3.1 Introduction

Atmospheric corrosion is an electrochemical process involving a metal, corrosion products, a surface electrolyte, and the atmosphere [22]. On the basis of all the testing, outdoor atmospheres have been broadly classified into three qualitative categories: rural, industrial, and marine [23]. For the purpose of this corrosion study, rural and agricultural classifications are used interchangeably. In addition, two more outdoor classifications, namely wet and dry were identified. All of these atmospheric climates can be found on the island of Oahu therefore six test sites were selected with the intent of exposing the MMC specimens to these diverse atmospheric conditions. Test site selection was primarily dependent on three criteria; each of the five outdoor atmospheric classifications needed to be represented, each site had to be reasonably accessible, and each site had to be sufficiently secure to reduce the risk of vandalism or theft. Figure 3.1 shows the location of six atmospheric test sites on the island of Oahu. Test sites are located at the Lyon Arboretum in Manoa Valley (A), on Coconut Island in Kanehoe Bay (B), Campbell Industrial Park (C), Kahuku (D), Ewa Nui (E), and Waipahu (H). The Lyon Arboretum and Coconut Island sites are on University of Hawai’i property and the remaining sites are on Hawaiian Electric Company (HECO) property. Once the test sites were selected, racks were designed to hold the MMC specimens in addition to holding weather and atmospheric monitoring equipment. Test site maintenance which includes changing
chloride candles, downloading weather data, photographing and/or retrieving specimens is performed on a monthly basis.

![Figure 3.1: Location of atmospheric corrosion test sites on Oahu](image)

3.2 Materials

Test racks were designed and constructed using 316 stainless steel and TREX®. TREX® is a “wood-like” composite made from recycled wood chips and recycled polyethylene. Racks on HECO property had to be non-conductive and therefore were constructed entirely from TREX®. Test racks on UH property comprised of TREX® slats on a stainless steel frame. Two test racks on Coconut Island were secured to a concrete slab with stainless steel bolts, but the remaining test racks were anchored with four 83 lb concrete blocks such that they can withstand winds up to 100 miles per hour. In addition,
all test racks, with the exception of the Lyon Arboretum racks due to test site limitations, were oriented such that they face North East in an attempt to expose the specimens to the predominantly North Easterly trade winds. Dimensioned drawings of those racks are provided in Figures B.1 through B.4 in Appendix B. Test racks, equipment, specimens and test site locations are shown in Figures B.5 through B.12 in Appendix B. Standard exposure angles are either 30 or 45 degrees from the horizontal (the higher angle usually recommended for paints and other organic systems), and the lower edge of individual specimens should be not less than 0.8m (30 in.) from the ground [24]. For this corrosion study, the specimens were exposed at 30 degrees to the horizontal and each specimen was secured with three NYLON 6/6 (Polyamide) insulators as shown in Figure 3.2.
3.3 Procedure

Each MMC disk was stamped with an alphanumeric code using a Telisis Benchmark 320 pin stamping system. The disks were washed in acetone followed by ultrasonic cleaning in deionized water. After drying, each specimen was weighed on a Mettler AE163 electronic balance. The weight of each specimen was measured in grams to four decimal places. Ten sets of each of the eight MMCs were exposed at the six test sites resulting in a total of 480 specimens included in the field study. Figure 3.3 shows a typical arrangement of the MMC specimens on a test rack at Coconut Island.

Figure 3.3: Typical arrangement of MMCs at test sites
The eight MMCs are arranged in eight columns of ten rows where each column contains the same type of MMC. Specimens were placed on the rack with the alphanumeric code on the underside (facing down). Table 3.1 shows the exposure schedule at each test site. At the time of writing, rows 1 through 6 at all six test sites had been retrieved and rows 7 through 9 had been retrieved from the Lyon Arboretum and Coconut Island sites. Rows 7 through 9 at the remaining four sites are scheduled to be retrieved at the end of June, 2004. Once the MMC specimens were recovered from the field, they were scanned or photographed in the uncleaned state. The majority of the disks were then cleaned in a solution of phosphoric acid (H₃PO₄), chromium trioxide (CrO₃) and ultrapure (18.1 MΩ-cm) water as described in ISO 8407:1991(E).

Table 3.1: Metal-matrix composite exposure intervals at each test site

<table>
<thead>
<tr>
<th>MMC Exposure Intervals</th>
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<tbody>
<tr>
<td>Row number</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>1, 2, 3</td>
</tr>
<tr>
<td>4, 5, 6</td>
</tr>
<tr>
<td>7, 8, 9</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

The specimens were immersed for 10 minutes at a temperature between 90°C and 100°C. They were then ultrasonically cleaned for 30 minutes in deionized water. After oven drying at 70°F for 20 to 30 minutes the specimens were reweighed on the same Mettler balance to determine weight loss. The initial and final weights were used along with the
surface area of each specimen to calculate the average weight loss and thus the average corrosion rate for each MMC. The average corrosion rate defined in (1) is given in grams per meter squared per day (gmd).

\[ \text{Average Corrosion Rate (gmd)} = \frac{\text{Initial Wt.}(g) - \text{Final Wt.}(g)}{\text{Surface Area} \ (m^2) \times \text{Exposure (days)}} \] (1)

Figure 3.4 shows an Al6092-T6/SiC/40p specimen that was exposed at the Lyon Arboretum test site for 90 days. The specimen is shown before and after cleaning.

Figure 3.4: Al6092-T6/SiC/40p MMC exposed for 90 days – before and after cleaning.

In addition to the MMCs at each test site, ten Al6061-T6 specimens were also exposed at each site for the same durations in order to obtain a baseline corrosion rate of aluminum.
in its monolithic form. The Al6061-T6 coupons measuring 2 inches by 2 inches by 0.125 inches were stamped, cleaned and weighed in the same manner as the eight metal matrix composites.

3.4 Results

Average corrosion rates for the 90 day, 180 day and 360 day exposures are provided in Figures 3.5, 3.6, and 3.7. Data for 360 day exposure corrosion rates has been collected for two of the test sites, namely Manoa and Coconut Island. Figure 3.7 compares average corrosion rates over 90, 180 and 360 day exposures for those sites.

Figure 3.5: Average corrosion rates of MMCs and Al6061-T6 after 90 day exposure
Average Corrosion Rates of MMCs and Al6061-T6 after 180 Day Exposure

- A: Manoa
- B: Coconut Is.
- C: CIP
- D: Kahuku
- E: Waipahu
- F: Ewa Nui
- G: Anodized
- H: Al6092-T6/Al2O3
- I: Al6092-T6/SiC
- J: Al6092-T6/AL2O3
- K: Al6092-T6/SiC
- L: Al6061-T6

Figure 3.6: Average corrosion rates of MMCs and Al6061-T6 after 180 day exposure

Average Corrosion Rates of MMCs and Al6061-T6 after 90, 180 and 360 Day Exposures

- AR6092-T6/SiC/5p
- AR6092-T6/SiC/10p
- AR6092-T6/SiC/20p
- AR6092-T6/SiC/40p
- AR6092-T6/SiC/50p
- AR6092-T6/SiC/50p(Gr)
- AR6092-T6/SiC/20p(Gr)
- AR6061-T6/SiC/20p
- AR6061-T6/SiC/20p(Gr)
- AR6061-T6+SIC/20p
- AR6061-T6+SIC/20p(Gr)

Figure 3.7: Average corrosion rates of MMCs and Al6061-T6 after 360 day exposure
3.5 Discussion

Some trends are clearly visible from the corrosion data obtained. Corrosion rate of an MMC generally increases with an increase in volume fraction of the reinforcement. At the end of the 90 day exposure, Al6092-T6/SiC/50p at Coconut Island was the worst performing MMC having a corrosion rate more than 80 times that of Al6061-T6 at the same site exposed for the same duration. Even the best performing MMC, Al6092-T6/SiC/10p at the Ewa Nui test site had a corrosion rate almost 10 times greater than Al6061-T6 at the same site. Three of the eight MMCs have the same twenty percent volume fraction of reinforcement but Al6092/B₄C/20p generally appears to corrode at a higher rate than either SiC or Al₂O₃ reinforced aluminum. This is likely due to the resistivity of the reinforcements since boron carbide is generally considered to be a conductor, silicon carbide a semi-conductor and aluminum oxide an insulator. Corrosion rates for all of the MMCs at the Manoa (Lyon Arboretum) and Coconut Island test sites were comparable for the 90, 180 and 360 day exposures despite significant differences in atmospheric and weather conditions at the two sites. The data collected for the 360 day exposure only included two test sites, namely Manoa and Coconut Island, but Figure 3.7 shows some convergence of the corrosion rates of the MMCs at those sites. Not only are the corrosion rates of each MMC diminishing throughout the year, but the differences between the MMCs are becoming less obvious to the extent that one MMC has no clear corrosion advantage over another. After one year, the difference between the worst performing MMC at the Manoa site compared to Al6061-T6 at the same site had decreased by almost seventy five percent i.e. from 138 times to less than 39 times the
corrosion rate. The same was true at the Coconut Island site where the corrosion rate of the worst performing MMC was initially more than 80 times greater than that of Al6061-T6. After one year the difference had been reduced by more than two thirds to a corrosion rate that was 28 times greater than monolithic aluminum. This decreasing trend could be due to the undercutting and subsequent elimination of cathodic reinforcement particles (SiC, B₄C or Al₂O₃) and/or iron-rich intermetallics in the aluminum matrix. Undercutting of the reinforcing particulate or intermetallics is caused by the dissolution of the surrounding aluminum matrix. As the MMC corrodes the cathodic site may be left in relief. Eventually the particle can be sufficiently undercut that it falls or is washed off the surface of the composite.
4.1 Introduction

In order to correlate the corrosion rates of different MMCs at different test sites, it is necessary to understand the environment in which the specimens are exposed. Standard ASTM or ISO methods for measuring atmospheric chloride or sulfur dioxide concentrations can be found in the literature. However, standards for weather monitoring in terms of corrosion testing are hard to find, but at the very least, a quality weather station should be installed at each site as near to the specimens as possible [24]. The accurate monitoring of temperature, humidity, rainfall and chloride deposition rates is essential for any outdoor corrosion study since these variables have the greatest effect on corrosion rates.

4.2 Materials

Weather and atmospheric conditions at each test site were monitored and logged continuously with N.I.S.T. (National Institute of Standards and Technology) certified Davis Vantage Pro weather stations and data loggers. Time of wetness (TOW) of the specimens was determined using Davis leaf wetness sensors also at 30 degrees to the horizontal. The leaf wetness sensor uses a scale from 0 to 15 to represent wetness. A value of 0 indicates that the sensor is completely dry whereas a value of 15 indicates that the sensor is completely wet. Chloride (Cl⁻) deposition rates were measured using the
wet candle method as described in ASTM G 140-96 and ISO 9225:1992(E). Initially, sulfur dioxide (SO2) concentrations were measured with sulfation plates as described in ASTM G91-97 and ISO 9225:1992(E). The sulfation plates (two per site per month) were manufactured and analyzed by an Industrial Hygiene Accredited Laboratory (AIHA), but after collecting data for three months it became clear that there was a problem with some or all aspects of the process. It was decided that accurate SO2 monitoring would require a different approach or technique and therefore SO2 monitoring by the sulfation plate method was stopped. Figures B.11 and B.12 in Appendix B show the weather and atmospheric monitoring equipment used at each test site.

4.3 Procedure

A Davis Vantage Pro weather station at each test site measures and records independent weather variables such as temperature, humidity, atmospheric pressure, rainfall, wind speed, wind direction, leaf wetness and UV. Other dependent variables such as dew point, evapotranspiration and heat index are calculated in real time. Some of the parameters such as temperature are averaged for each 30 minute period, whereas others, such as rainfall, are totaled. In all, more than thirty data points are written to an internal data logger every half an hour. The data stored at each site is downloaded once a month. Chloride candles are exposed in the field for approximately thirty days and then brought back to the lab for analysis. The gauze wick is soaked in the remaining ultrapure water and 100mL of that solution is poured into a beaker. 2mL of 5M sodium nitrate (NaNO3) is added to the beaker which serves as an ionic strength adjustor (ISA). Chloride candle
analysis is performed in the lab with an Orion 290A ISE/pH meter and an ion (Cl\(^-\)) selective electrode (9617BN). Figure B.13 in Appendix B shows a calibration curve generated with solutions of known Cl\(^-\) concentration. Actual and measured concentrations are shown. The Cl\(^-\) deposition rates for the Manoa test site are maximum theoretical rates since Cl\(^-\) ions were only detected for the months of November in 2003 and March in 2004. The values shown were calculated using Cl\(^-\) concentrations just below the lower limit of detection possible with an Orion 290A ISE/pH meter and an ion (Cl\(^-\)) selective electrode (9617BN). The lowest concentration of Cl\(^-\) detectable with an Orion 290A ISE/pH meter and an ion (Cl\(^-\)) selective electrode (9617BN) is 1.0 \(\times\) 10\(^{-4}\)M therefore a concentration of 9.0 \(\times\) 10\(^{-5}\)M was assumed for those months when no Cl\(^-\) ions were detected.

4.4 Results

Tables 4.2, 4.3 and 4.4 show the weather and atmospheric data collected at each of the sites during 90, 180 and 360 day exposures. Values in the TOW columns represent the percentage of the total exposure time when the leaf wetness sensor showed a value of 15 indicating that the specimens were completely wet. The data shows that Manoa and Coconut Island are very different sites in terms of temperature, humidity, rainfall, time of wetness and chloride deposition rates. However, Figure 3.7 shows that corrosion rates of MMCs exposed at those two sites for one year are very similar.
Table 4.2: Weather and atmospheric data for 90 day exposure at corrosion test sites

<table>
<thead>
<tr>
<th>Test Site</th>
<th>Avg. Temp (°F)</th>
<th>Avg. Humidity (%RH)</th>
<th>Rain (inches)</th>
<th>TOW (% of exposure time)</th>
<th>Avg. Cl Deposition Rate (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manoa</td>
<td>72.0</td>
<td>82.9</td>
<td>62.0</td>
<td>28.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Coconut Is.</td>
<td>77.5</td>
<td>73.7</td>
<td>8.6</td>
<td>12.4</td>
<td>64.6</td>
</tr>
<tr>
<td>Campbell</td>
<td>82.7</td>
<td>60.6</td>
<td>4.1</td>
<td>4.0</td>
<td>17.3</td>
</tr>
<tr>
<td>Kahuku</td>
<td>80.3</td>
<td>71.8</td>
<td>20.1</td>
<td>8.8</td>
<td>47.0</td>
</tr>
<tr>
<td>Waipahu</td>
<td>81.3</td>
<td>63.8</td>
<td>11.6</td>
<td>1.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Eva Nui</td>
<td>80.6</td>
<td>64.0</td>
<td>2.2</td>
<td>1.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 4.3: Weather and atmospheric data for 180 day exposure at corrosion test sites

<table>
<thead>
<tr>
<th>Test Site</th>
<th>Avg. Temp (°F)</th>
<th>Avg. Humidity (%RH)</th>
<th>Rain (inches)</th>
<th>TOW (% of exposure time)</th>
<th>Avg. Cl Deposition Rate (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manoa</td>
<td>73.3</td>
<td>83.1</td>
<td>140.9</td>
<td>26.1</td>
<td>7.0</td>
</tr>
<tr>
<td>Coconut Is.</td>
<td>78.4</td>
<td>74.9</td>
<td>25.6</td>
<td>8.2</td>
<td>58.3</td>
</tr>
<tr>
<td>Campbell</td>
<td>81.0</td>
<td>63.2</td>
<td>17.9</td>
<td>5.3</td>
<td>24.4</td>
</tr>
<tr>
<td>Kahuku</td>
<td>78.1</td>
<td>73.4</td>
<td>52.0</td>
<td>13.6</td>
<td>89.9</td>
</tr>
<tr>
<td>Waipahu</td>
<td>79.4</td>
<td>66.9</td>
<td>31.1</td>
<td>6.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Eva Nui</td>
<td>78.6</td>
<td>67.4</td>
<td>32.5</td>
<td>6.1</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 4.4: Weather and atmospheric data for 360 day exposure at corrosion test sites

<table>
<thead>
<tr>
<th>Test Site</th>
<th>Avg. Temp (°F)</th>
<th>Avg. Humidity (%RH)</th>
<th>Rain (inches)</th>
<th>TOW (% of exposure time)</th>
<th>Avg. Cl Deposition Rate (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manoa</td>
<td>72.3</td>
<td>85.0</td>
<td>333.9</td>
<td>31.4</td>
<td>5.9</td>
</tr>
<tr>
<td>Coconut Is.</td>
<td>76.8</td>
<td>76.2</td>
<td>101.8</td>
<td>14.9</td>
<td>93.4</td>
</tr>
</tbody>
</table>
Leaf wetness sensors, in addition to providing data indicating the percentage of the total exposure time at each test site when specimens are completely wet, may also provide an insight into how the specimens transition for the wet to the dry state. Figure 4.1 shows the time of wetness (TOW) of the leaf wetness sensor at the Lyon Arboretum during the 90 day exposure period. In contrast, Figure 4.2 shows the time of wetness (TOW) of the leaf wetness sensor at the Coconut Island test site during the same 90 day exposure.

Figure 4.1: Time of wetness (TOW) of leaf wetness sensor at Manoa test site
4.5 Discussion

It should be noted that the Manoa test site had seven times the rainfall of the Coconut Island test site in the same 90 day period. The average temperature and humidity in Manoa for that period were lower and higher respectively. However, the percentage of the exposure time when the leaf wetness sensor was completely wet was only greater by a factor of about 2.3. Figure 4.1 indicates that the leaf wetness sensor and therefore the specimens in Manoa were for the most part either wet or dry and the figure implies a rapid transition between those states. In contrast, Figure 4.2 implies a more gradual transition between the wet and dry states of the specimens at the Coconut Island site. The marked difference in Cl deposition rates at the Manoa and Coconut Island test sites,
i.e. 6.5 compared to 64.6 mg/m²/day respectively, may explain the difference seen in the two figures. It is possible that salt on the leaf wetness sensor, and thus on the specimens, may delay or retard the transition from the wet to the dry state. The weather data shown in the tables above have to a great extent validated the test site selection process. The atmospheric conditions at each site vary considerably in terms of humidity, rainfall, time of wetness, Cl⁻ deposition rates and wind. However, temperature variations are limited by the negligible differences in test site elevation. The Manoa site has the highest elevation at 520 feet above sea level whereas the Coconut Island site has the lowest elevation at only ten feet above sea level. Accurately and tediously correlating the atmospheric and weather data with the corrosion rates observed will provide a less simplistic analysis of metal-matrix composite performance in different environmental conditions.
CHAPTER 5
HUMIDITY CHAMBER EXPERIMENT

5.1 Introduction
Correlating the corrosion rates of MMCs to real-world environmental conditions is a complex undertaking due to the multitude of weather and atmospheric variables that the MMCs may be exposed to. Humidity chamber experiments are more easily controlled having only three adjustable parameters. At the start of the experiment the electrolyte determines which ions if any are on the surface of the MMC. Once the experiment has started the only other variables are temperature and humidity which are easily controlled.

5.2 Materials
A tile cutting saw with diamond blade was used to cut 1 inch by 1 inch squares from the MMC disks manufactured by DWA Aluminum Composites. Acrylic holders capable of holding three specimens of the same type in the vertical position with minimal specimen-holder contact were designed and manufactured.

5.3 Procedure
Each specimen was stamped with an identification number, washed in acetone and ultrasonically cleaned in deionized water. After drying, each specimen was weighed on a Mettler AE163 electronic balance. The weight of each specimen was measured in grams to four decimal places. The specimens were placed in the holders then immersed for one
minute in beakers containing one of four electrolytes. All of the eight MMC types were immersed in ASTM sea water, 3.15 wt% sodium chloride (NaCl) and 0.5M sodium sulfate (Na₂SO₄) solutions. In addition, the following MMCs, Al6092/SiC/20p, Al6092/B₄C/20p and Al6092/Al₂O₃/20p were immersed in real sea water obtained from the Waikiki Aquarium resulting in twenty seven holders and eighty one specimens. Table C.1 in Appendix C lists the major ionic constituents found in different types of seawater and more specifically, in the seawater used for this experiment. It should be noted that the chloride (Cl⁻) ion content of 3.15 wt.% NaCl solution, Waikiki Aquarium seawater and ASTM seawater is 19,108, 19,582 and 20,488 ppm respectively. After immersion, each set of three specimens was immediately placed inside a humidity chamber. The temperature and humidity inside the chamber was maintained at 30°C and 85% (RH) respectively for 90 days.

Figure 5.1: MMC specimens after 90 day exposure in humidity chamber
Atmospheric conditions inside the chamber were controlled via an Electro-tech model 514 automatic humidity controller, a Cole Parmer model 2186-20 Digi-sense temperature controller and an Evenflo humidifier containing ultrapure water. After 90 days the specimens were removed from the chamber and scanned or photographed in the uncleaned state. Figure 5.1 shows the specimens after they were removed from the humidity chamber. The majority of the exposed coupons were then cleaned in a solution of phosphoric acid (H₃PO₄), chromium trioxide (CrO₃) and ultrapure (18.1 MΩ-cm) water as described in ISO 8407:1991(E). The specimens were immersed for 10 minutes at a temperature between 90°C and 100°C. They were then ultrasonically cleaned for 30 minutes in deionized water. After oven drying at 70°F for 20 to 30 minutes the specimens were reweighed on the same Mettler balance to determine weight loss.

5.4 Results

As shown in equation (1), the initial and final weights were used along with the surface area and exposure time of each specimen to calculate the average weight loss and thus the average corrosion rate for each MMC. Figure 5.2 shows the corrosion rates for each of the MMCs exposed to the different electrolytes. The average corrosion rate is given in grams per meter squared per day (gmd).
5.5 Discussion

As in the field study, the corrosion rates were generally found to increase with an increase in the volume fraction of the particulate reinforcement. The corrosion rates of the specimens dipped in ASTM sea water, 3.15 wt.% NaCl and real sea water were similar. Of the three MMCs having a volume fraction of 20 percent, Al6092-T6/Al₂O₃/20p had a consistently lower corrosion rate than the B₄C reinforced aluminum. This may be due to the much greater resistivity of Al₂O₃ compared to B₄C. This explanation is further reinforced by the corrosion rates of the three MMCs dipped in ASTM sea water. Of the three, the highest corrosion rate was the SiC MMC followed by
B₄C and Al₂O₃ MMCs. This trend follows the respective resistivities of \(10^0\), \(10^1\) and \(10^{14}\) as shown in Table 1.2. The corrosion rate for Al6092-T6/SiC/50p was consistently greater than that of Al6092-T6/SiC/50p (Gr.) which contains a higher purity SiC reinforcement.
CHAPTER 6
IMMERSION EXPERIMENT

6.1 Introduction
Immersion experiments in aerated solutions containing aggressive ions provide some of the most hostile environments for aluminum alloys and aluminum MMCs. Corrosion rates may be many times higher when compared to MMCs exposed at corrosion test sites.

6.2 Materials
As in the humidity chamber experiment, a tile cutting saw with diamond blade was used to cut 1 inch by 1 inch squares from the MMC disks manufactured by DWA Aluminum Composites. Al6061-T6 coupons measuring 2.0 inches by 2.0 inches were cut with a low-speed saw. Acrylic holders capable of holding three specimens of the same type in the vertical position with minimal specimen-holder contact were designed and manufactured.

6.3 Procedure
Each specimen was stamped with an identification number, washed in acetone and ultrasonically cleaned in deionized water. After drying, each specimen was weighed on a Mettler AE163 electronic balance. The weight of each specimen was measured in grams to four decimal places. The specimens were placed in the holders then placed in 250ml beakers. The pH of the five electrolytes to be used in the immersion experiment was
measured with an Orion 290A ISE/pH meter and an Orion pH triode 9107BN electrode. 200mL of solution was added to each beaker and the beakers were covered to reduce evaporation while still allowing oxygen to diffuse into the electrolyte. All of the eight MMC types and the Al6061-T6 coupons were immersed in ASTM sea water, 3.15 wt% sodium chloride (NaCl) and 0.5M sodium sulfate (Na2SO4) solutions. In addition, the following MMCs, Al6092/SiC/20p, Al6092/B4C/20p and Al6092/Al2O3/20p were immersed in ultrapure (18.1 MΩ-cm) water and real sea water obtained from the Waikiki Aquarium. Three Al6061-T6 coupons were immersed in real sea water. Table C.1 in Appendix C lists the major ionic constituents found in different types of seawater and more specifically, in the seawater used for this experiment.

Figure 6.1: MMC in electrolyte after 90 day immersion
The aquariums used contained thirty four beakers and one hundred and two specimens. After arranging the beakers in two aquariums, deionized water was added to within 0.5 inches of the tops of the beakers. The aquariums were covered and the water was maintained at 30°C with an electric submersible aquarium heater in an effort to maintain the temperature of the solutions in the beakers. After 90 days the beakers were removed and the pH of the solution in each beaker was re-measured with the same Orion 290A ISE/pH meter and an Orion pH triode 9107BN electrode. Figure 6.1 shows three MMC coupons in a beaker at the end of the 90 day immersion. Initial and final pH data is provided in Table C.2 and Table C.3 in Appendix C. The specimens were removed from the beakers, dried and scanned or photographed in the uncleaned state. The majority of the exposed coupons were then cleaned in a solution of phosphoric acid (H₃PO₄), chromium trioxide (CrO₃) and ultrapure (18.1 MΩ-cm) water as described in ISO 8407:1991(E). The specimens were immersed for 10 minutes at a temperature between 90°C and 100°C. They were then ultrasonically cleaned for 30 minutes in deionized water. After oven drying at 70°F for 20 to 30 minutes the specimens were reweighed on the same Mettler balance to determine weight loss.

6.4 Results

As shown in equation (1), the initial and final weights were used along with the surface area and exposure time of each specimen to calculate the average weight loss and thus the average corrosion rate for each MMC and the Al6061-T6 coupons. Figure 6.2 shows the average corrosion rates for each of the MMCs and Al6061-T6 immersed in the different
electrolytes. The average corrosion rate is given in grams per meter squared per day (gmd).

![Average Corrosion Rates of MMCs and Al6061-T6 after 90 Day Immersion](image)

**Figure 6.2:** Corrosion rates of MMCs and Al6061-T6 after 90 day immersion

Five MMC specimens were selected for Energy Dispersive X-ray Analysis (EDXA) after the 90 day immersion experiment to determine the composition of the corrosion products on the surface of each coupon. The five MMCs selected included Al6092/SiC/20p immersed in 3.15 wt% NaCl, ASTM sea water and real sea water. Also, Al6092-T6/B4C/20p and Al6092-T6/Al2O3/20p immersed in ASTM sea water. Figures 6.3, 6.4 and 6.5 show the data collected from a 600 micron by 400 micron area from the three Al6092/SiC/20p MMC specimens.
Figure 6.3: EDXA of Al6092-T6/SiC/20p immersed in 3.15 wt.% NaCl

Figure 6.4: EDXA of Al6092-T6/SiC/20p immersed in ASTM sea water
EDXA results for the B₄C and Al₂O₃ MMCs are shown in Figures C.1 and C.2 in Appendix C.

6.5 Discussion

The data in Figure 6.2 shows an increase in corrosion rate with a corresponding increase in the volume fraction of the particulate reinforcement. As in the humidity chamber experiment, the corrosion rates of the three MMCs having reinforcement volume fractions of 20 percent exhibit corrosion behavior that may be partly explained by the relative resistivities of the reinforcement material. Of the three 20p MMCs in most of the solutions, the highest corrosion rates were observed in the B₄C MMC followed by SiC and Al₂O₃ MMCs. This trend maintains Al₂O₃ as the best performer and follows the
respective resistivities of $10^1, 10^0$ and $10^{14}$ as shown in Table 1.2. The corrosion rates of all of the MMCs in 3.15 wt.% NaCl are markedly higher than corresponding rates in ASTM sea water or real sea water. In each case where the specimen was immersed in either ASTM sea water or real sea water, EDXA analysis indicated the presence of magnesium hydroxide ($\text{Mg(OH)}_2$) and not calcium carbonate ($\text{CaCO}_3$) as expected. It is suggested that the $\text{Mg(OH)}_2$ covered the cathodic sites on the composite thereby reducing the rate of corrosion in both ASTM and real sea water. Figures C.1 and C.2 in Appendix C show EDXA results of Al6092-T6/B4C/20p and Al6092-T6/Al2O3/20p after immersion in 3.15 wt.% NaCl. In both cases there are no peaks to suggest the presence of either magnesium or calcium. This is expected since 3.15 wt.% NaCl solution shouldn’t contain either element. However, the result may help to confirm that sea water is the source of the magnesium rather than the 6092 matrix material which does contain small amounts of magnesium as shown in Table 1.1. Real sea water and ASTM sea water have natural corrosion inhibitors in addition to providing some form of solution buffering. Both ASTM sea water and real sea water became more neutral over the 90 day immersion experiment. ASTM sea water had an initial pH of 8.2 and the real sea water had an initial pH close to 7.8 but after the experiment was completed the pH of both solutions was close to 7.5. The other three solutions became more alkaline ending with pH ranges of 7.4 to 8.7. Since all of the solutions were aerated in the sense that oxygen was allowed, both proton reduction (hydrogen evolution) and oxygen reduction could take place on cathodic sites. For MMCs in 0.5M $\text{Na}_2\text{SO}_4$, 3.15 wt.% NaCl or ultrapure water, the higher corrosion rates and hence increase in hydrogen evolution and/or oxygen
reduction could result in the consumption of $\text{H}^+$ ions and the production of $\text{OH}^-$ ions.

Both reactions could shift the pH of the solutions in the alkaline direction.
CHAPTER 7
POLARIZATION EXPERIMENTS

7.1 Introduction
A complete set of anodic polarization experiments for the eight MMCs and Al6061-T6 in this study required fifty four individual polarizations employing thirty eight electrodes.

7.2 Materials
Four 1cm by 1cm squares were cut from the eight types of MMC disks manufactured by DWA Aluminum Composites using a low-speed saw and high concentration diamond blade. Six 1cm by 1cm squares were also cut from Al6061-T6 coupons. Once the MMCs and aluminum were cut, the corners were radiused to reduce stress concentrations and the backs of the electrodes were sanded using 320 grit silicon carbide paper. The specimens were cleaned in acetone and dried. A 0.0325 inch copper wire approximately 12 inches in length was attached to the back of each MMC and aluminum electrode with silver conductive epoxy (MG Chemicals 8331-14g) and cured in an oven at 70°C for 20 minutes. Once cured, the copper wire was threaded through the center of a 9 inch long glass tube having on O.D. of 9/32 inch. The back face and sides of each electrode was coated with Loctite 0151 Hysol® epoxi-patch adhesive (manufactured by Loctite Corp.) in addition to being bonded and sealed to the glass rod such that the front face was the only part of the MMC or aluminum exposed to the atmosphere. The electrode was cured in an oven at 70°C for two hours. The face of each electrode was ground flat with 320
grit silicon carbide paper followed by 600 grit silicon carbide paper. After grinding with 600 grit silicon carbide paper, each electrode was viewed under an optical microscope to check for crevices between the edges of the electrode face and the surrounding epoxy. In addition, the resistance between the face of the electrode and the end of the copper wire was measured to ensure good conductivity. Resistances ranging from $0.5\Omega$ to $1.0\Omega$ were found to be ideal.

![Figure 7.1: MMC polarization electrodes ready for final polishing](image)

Subsequent refinement of the MMC or aluminum electrode surface included polishing with 1, 0.3 and 0.05 micron deagglomerated alpha alumina polish until a "mirror-like" finish was achieved. The electrodes were polished on Buehler Ecomet 6 variable speed
polishers using Buehler microcloth polishing wheels. Figure 7.1 shows two electrodes after grinding with 320 grit silicon carbide paper.

7.3 Procedure

Polarization experiments for the MMCs were conducted using a Princeton Applied Research Potentiostat/Galvanostat Model 273A controlled with DOS based software. Polarization experiments for the Al6061-T6 were conducted using a Princeton Applied Research Potentiostat/Galvanostat Model 283 controlled with Windows® based software. All of the anodic polarization experiments were run in either deaerated 3.15 wt.% sodium chloride (NaCl) solution or deaerated 0.5M sodium sulfate (NaSO₄) solution. In both cases the cell was deaerated with nitrogen (N₂) gas that was 99.999% pure. A typical polarization cell set up is shown in Figure 7.2. The cell contained a working electrode, a platinum counter electrode, a glass luggin probe that provided connectivity to a calomel reference electrode, a gas dispersion tube and a thermometer. The jacketed cell was connected to a Fisher Scientific model 9100 Isotemp refrigerated circulator that maintained the electrolyte inside the cell at 30°C. For each of the polarization experiments, the cell was filled with electrolyte and allowed to reach operating temperature while the working electrode was repolished with 0.05 micron alumina polish. The electrode was rinsed in ultrapure water and placed in a beaker of ultrapure water to prevent the oxide layer from drying out. The electrode was then placed in the cell and electrolyte was drawn through the luggin probe to the reference electrode.
Nitrogen gas was bubbled into the cell to deaerate the electrolyte, and the potential between the working electrode and the reference electrode was monitored for one hour. After an hour the cell was completely deaerated and the open circuit potential (OCP) had been reached. The electrode was then polarized at a scan rate of 1mV/sec from the open circuit potential to $-0.5V_{SCE}$ in 3.15 wt.% NaCl to obtain pitting potentials, and from the open circuit potential to $1.0V_{SCE}$ in 0.5M Na$_2$SO$_4$ to obtain passive current densities.

7.4 Results

Figure 7.3 represents twenty seven experiments and provides data obtained from anodic polarizations in deaerated 3.15 wt.% sodium chloride (NaCl) solution. Figure 7.4 also
represents twenty seven experiments and provides data obtained from anodic polarizations in deaerated 0.5M sodium sulfate (Na₂SO₄) solution.

![Graph](image)

**Figure 7.3:** Anodic polarization in deaerated 3.15 wt.% sodium chloride solution

It should be noted that each curve in the above figures is an average curve obtained from three experiments conducted with two electrodes per MMC or Al6061-T6 per solution. The first electrode was polarized once whereas the second electrode was polarized twice. The electrode to be polarized a second time was removed from the cell and reground on 600 grit silicon carbide paper before being reused for the third experiment. It was repolished using 1, 0.3 and 0.05 micron deagglomerated alpha alumina polish until a "mirror-like" finish was achieved.
Table D.1 in Appendix D provides the pitting potentials and passive current densities for the eight MMCs and Al6061-T6 in both solutions. In addition, plots with data error bars for each of the MMCs and Al6061-T6 in both solutions are shown in Figures D.1 through D.9 in Appendix D.

7.5 Discussion

The polarization experiments reveal the negligible differences in open circuit potential, pitting potential or passive current densities between most of the metal-matrix composites. The one exception is the anodic polarization of Al6092-T6/B₄C/20p in deaerated 0.5M sodium sulfate solution which exhibits odd behavior requiring further
study. However, generally, the differences during polarization between the metal-matrix composites and Al6061-T6 in either solution aren’t sufficient to explain the differences in corrosion rates.
Corrosion of aluminum-based MMCs may initiate due to galvanic coupling between the reinforcing phase and the matrix, selective corrosion at the reinforcement/matrix interface or matrix defects formed during the manufacturing process [25]. Fabrication of MMCs can lead to the formation of intermetallic particles due to reactions between the particulate and matrix or the precipitation of compounds [26]. The outdoor, humidity chamber and immersion experiments all indicate that corrosion rates of aluminum MMCs increases as the volume fraction of the reinforcing particulate increases. This is most likely due to an increase in the galvanic-corrosion rate between the noble SiC, B₄C or Al₂O₃ particles and the aluminum matrix. Figure 8.1 shows a theoretical increase in the galvanic current (Log $I_{GALV}$) as the area fraction of the reinforcement increases [26]. Generic cathodic curves for the noble particulate intersect the anodic curve for Al6061-T6 at higher currents as the area fraction increases resulting in an increase in $I_{GALV}$. That increase translates directly into higher dissolution rates of the aluminum matrix yielding higher corrosion rates. The cathode limited galvanic current between the matrix and particulate can be expressed as a function of the area fraction and hence volume fraction of the reinforcement [26].

$$i_{GALV} = i_c \left( \frac{X_c}{1 - X_c} \right)$$ (2)
In equation (2), $i_{\text{GALV}}$ is the dissolution current density of the matrix; $i_c$ is the current density of the cathode; $X_c$ is the area fraction of the cathode; and $1-X_c$ is the area fraction of the anode.

![Generic polarization plot for Al6061-T6 and a noble particulate with increasing volume fraction](image)

**Figure 8.1:** Generic polarization plot for Al6061-T6 and a noble particulate with increasing volume fraction

The magnitude of the galvanic current between the matrix and particulate is also affected by the resistivity of the particles. The outdoor, humidity chamber and immersion experiments reveal a difference in the corrosion rates of Al6061-T6/B₄C/20p,
Al6061-T6/SiC/20p and Al6061-T6/Al₂O₃/20p. Table 1.2 shows the resistivities of the reinforcing particles used in the MMCs that were tested. Since the area fractions of those particular MMCs are approximately the same, the difference in corrosion rates may be explained by the difference in the resistivities of the particulate. The higher the resistivity of the particulate, the larger the ohmic losses through the reinforcement resulting in a reduction in galvanic corrosion [26].

Figure 8.2: Generic polarization plot for Al6061-T6 and Al₂O₃, SiC and B₄C particulate
Figure 8.2 shows theoretical cathodic curves for $\text{Al}_2\text{O}_3$, SiC and B$_4$C intersecting the anodic curve for Al6061-T6. As the resistivity ($\rho$) of the noble particulate decreases, the galvanic current increases. Line C-D in Figure 8.2 represents the ohmic loss between B$_4$C and SiC at a fixed current value. In addition to the influence that volume fraction and particle resistivity have on corrosion, the microstructure of each MMC may also have a significant effect. One of the MMCs manufactured for this study showed inconsistencies in processing. Large voids can clearly be seen in the matrix of the Al6092-T6/SiC/50p (Gr.) MMC shown in Figure 8.3. It is unclear at this time if the presence of such voids had a major effect on corrosion rates. Specimens with manufacturing voids retrieved from test sites showed an increase in weight after cleaning. The increase in weight could be due to corrosion products remaining in the voids.

Figure 8.3: Large voids in Al6092-T6/SiC/50p (Gr.) MMC
It is thought that the interface between the particulate and the matrix is one of the primary initiation sites for corrosion due to the formation of micro-crevices between the two phases. If this is the case, the corrosion rates of higher volume fraction MMCs may be exacerbated by an increase in the number of interfaces and therefore the number of micro-crevices. Iron-rich intermetallic particles may also provide initiation sites for corrosion. Corrosion may also be affected by differences in particle size, shape and distribution. Figures 1.7, 1.8 and 1.3 show that Al6092/B₄C/20p and Al6092/Al₂O₃/20p MMCs have a similar appearance, whereas the particles in the Al6092/SiC/20p MMC exhibit more variety in terms of size, shape and distribution.
Figure A.1: Metallographic image of Al6092-T6/SiC/5p

Figure A.2: Metallographic image of Al6092-T6/SiC/10p
Figure A.3: Metallographic image of Al6092-T6/SiC/20p

Figure A.4: Metallographic image of Al6092-T6/SiC/40p
Figure A.5: Metallographic image of Al6092-T6/SiC/50p

Figure A.6: Metallographic image of Al6092-T6/SiC/50p (Gr.)
Figure A.7: Metallographic image of Al6092-T6/B$_4$C/20p

Figure A.8: Metallographic image of Al6092-T6/Al$_2$O$_3$/20p
Figure B.1: Typical dimensions of 316 stainless steel test rack used at Manoa (Lyon Arboretum) and Coconut Island test sites
Figure B.2: Typical dimensions of TREX® test rack used at Hawaiian Electric Company (HECO) test sites
Figure B.3: Typical dimensions and front view of TREX® test rack used at Hawaiian Electric Company (HECO) test sites. Arrangement and dimensions are similar for stainless steel racks.
Figure B.4: Arrangement of metal-matrix composite disks (at left) on test racks at all six atmospheric corrosion test sites
Figure B.5: Manoa (Lyon Arboretum) test site – wet

Figure B.6: Coconut Island test site - marine
Figure B.7: Campbell Industrial Park test site - industrial

Figure B.8: Kahuku test site - marine
Figure B.9: Waipahu test site – dry, light industrial

Figure B.10: Ewa Nui test site - agricultural
Figure B.11: Chloride candle and leaf wetness sensor

Figure B.12: Davis Vantage Pro weather station
Figure B.13: Calibration curve for chloride candle measurements using an Orion 290A ISE/pH meter and an ion (Cl-) selective electrode (9617BN)
Table C.1: Comparison of the major ionic constituents of different types of seawater

<table>
<thead>
<tr>
<th>Ion</th>
<th>Waikiki* (ppm)</th>
<th>Coconut island* (ppm)</th>
<th>ASTM* (ppm)</th>
<th>IAPSO (ppm)</th>
<th>The Oceans, Prentice-Hall, Inc., Newyork,1942 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium, Ca++</td>
<td>429.50</td>
<td>365.77</td>
<td>516.66</td>
<td>432</td>
<td>400.1</td>
</tr>
<tr>
<td>Magnesium, Mg++</td>
<td>1513.58</td>
<td>1319.84</td>
<td>1731.6</td>
<td>1348</td>
<td>1272</td>
</tr>
<tr>
<td>Sodium, Na+</td>
<td>10461.5</td>
<td>9113.82</td>
<td>10118</td>
<td>11266</td>
<td>10556.1</td>
</tr>
<tr>
<td>Potassium, K+</td>
<td>356.13</td>
<td>323.24</td>
<td>396.74</td>
<td>411</td>
<td>380</td>
</tr>
<tr>
<td>Chloride, Cl-</td>
<td>19581.5</td>
<td>17074.23</td>
<td>20488</td>
<td>19900</td>
<td>18980</td>
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<tr>
<td>Sulfate, SO₄⁻</td>
<td>2663.46</td>
<td>2294.38</td>
<td>2596.6</td>
<td>N/A</td>
<td>2649</td>
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<tr>
<td>Bromine, Br</td>
<td>61.10</td>
<td>54.34</td>
<td>141.57</td>
<td>N/A</td>
<td>64.6</td>
</tr>
</tbody>
</table>

* Analysis performed by Dr. Huebert, Dept. of Oceanography, University of Hawai‘i at Manoa.

It should be noted that a 3.15 wt.% NaCl solution theoretically contains 19,107.9 ppm of the chloride (Cl⁻) ion.
Table C.2: Initial pH values of electrolytes used in immersion experiment

<table>
<thead>
<tr>
<th>pH of electrolytes at start of 90 day immersion experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM Sea Water</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>8.204</td>
</tr>
<tr>
<td>T = 20.6 °C</td>
</tr>
</tbody>
</table>

Table C.3: Final pH values of electrolytes used in immersion experiment

<table>
<thead>
<tr>
<th>pH of electrolytes after 90 day immersion experiment (T = 29.1°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>ASTm Sea Water</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Al6092-T6/SiC/5p</td>
</tr>
<tr>
<td>Al6092-T6/SiC/10p</td>
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<td>Al6092-T6/SiC/20p</td>
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<td>Al6092-T6/SiC/40p</td>
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<tr>
<td>Al6092-T6/SiC/50p</td>
</tr>
<tr>
<td>Al6092-T6/SiC/50p (Gr.)</td>
</tr>
<tr>
<td>Al6092-T6/B₄C/20p</td>
</tr>
<tr>
<td>Al6092-T6/Al₂O₃/20p</td>
</tr>
<tr>
<td>Al6061-T6</td>
</tr>
</tbody>
</table>
Figure C.1: EDXA of Al6092-T6/B₄C/20p immersed in 3.15 wt.% NaCl

Figure C.2: EDXA of Al6092-T6/Al₂O₃/20p immersed in 3.15 wt.% NaCl
Table D.1: Pitting potentials and passive current densities for MMCs and Al6061-T6 in 3.15 wt.% NaCl and 0.5M Na₂SO₄

<table>
<thead>
<tr>
<th>Material</th>
<th>Eₚithmetic (V SCE)</th>
<th>i₀ (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al6092-T6/SiC/5p</td>
<td>-0.727</td>
<td>-5.267</td>
</tr>
<tr>
<td>Al6092-T6/SiC/10p</td>
<td>-0.712</td>
<td>-5.319</td>
</tr>
<tr>
<td>Al6092-T6/SiC/20p</td>
<td>-0.712</td>
<td>-5.347</td>
</tr>
<tr>
<td>Al6092-T6/SiC/40p</td>
<td>-0.712</td>
<td>-5.331</td>
</tr>
<tr>
<td>Al6092-T6/SiC/50p</td>
<td>-0.712</td>
<td>-4.684</td>
</tr>
<tr>
<td>Al6092-T6/SiC/50p (Gr.)</td>
<td>-0.712</td>
<td>-5.198</td>
</tr>
<tr>
<td>Al6092-T6/B₄C/20p</td>
<td>-0.727</td>
<td>-3.606</td>
</tr>
<tr>
<td>Al6092-T6/Al₂O₃/20p</td>
<td>-0.681</td>
<td>-5.222</td>
</tr>
<tr>
<td>Al6061-T6</td>
<td>-0.732</td>
<td>-5.378</td>
</tr>
</tbody>
</table>

Figure D.1: Anodic polarization of Al6092-T6/SiC/5p at 30°C with scan rate of 1mV/sec
Figure D.2: Anodic polarization of Al6092-T6/SiC/10p at 30°C with scan rate of 1mV/sec

Figure D.3: Anodic polarization of Al6092-T6/SiC/20p at 30°C with scan rate of 1mV/sec
Figure D.4: Anodic polarization of Al6092-T6/SiC/40p at 30°C with scan rate of 1mV/sec

Figure D.5: Anodic polarization of Al6092-T6/SiC/50p at 30°C with scan rate of 1mV/sec
Figure D.6: Anodic polarization of Al6092-T6/SiC/50p (Gr.) at 30°C with scan rate of 1 mV/sec

Figure D.7: Anodic polarization of Al6092-T6/B₄C/20p at 30°C with scan rate of 1 mV/sec
Figure D.8: Anodic polarization of Al6092-T6/Al₂O₃/20p at 30°C with scan rate of 1mV/sec

Figure D.9: Anodic polarization of Al6061-T6 at 30°C with scan rate of 1mV/sec
REFERENCES


2. DWA Aluminum Composites, [www.dwa-dra.com](http://www.dwa-dra.com), 2004.


