CORROSION OF ALUMINUM-MATRIX COMPOSITES

by

LLOYD HIROMI HIHARA

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Abstract

The research objectives were to identify corrosion mechanisms in graphite/aluminum (G/Al) and silicon carbide/aluminum (SiC/Al) metal-matrix composites (MMCs) in simulated fresh water (0.5 M Na₂SO₄) and seawater (3.15 wt% NaCl), and to identify suitable methods for corrosion control.

Polarization diagrams were used to generate models for predicting composite corrosion behavior, and a zero-resistance ammeter (ZRA) was used to measure galvanic-corrosion rates. Localized corrosion of a G/Al MMC was studied in situ with an optical microscope. Surface analytical techniques were used to characterize composite and constituent microstructures and corrosion morphology. The following materials were examined: ultra pure Al, 6061-T6 Al, high-modulus pitch-based graphite fibers, SiC, TiB₂, Al₄C₃, and a commercial G/6061-T6 Al MMC.

Corrosion problems originating from processing and galvanic coupling between the Al matrix and reinforcement constituents were identified. The results are summarized below.

The following processing-related corrosion problems were identified: Residual microstructural chlorides, left behind during fabrication processing, in the G/Al MMC resulted in preferential dissolution and corrosion of the diffusion-bonded regions between adjacent precursor wires in six-ply plates. Aluminum carbide, which can form at graphite-Al and SiC-Al interfaces during composite fabrication, hydrolyzed at a rate of ~1%/h. This indicated that the degradation resistance of G/Al and SiC/Al MMCs would be severely compromised by the presence of Al₄C₃.

Oxygen reduction was found to be the main driving force for galvanic corrosion. The polarization diagrams indicated that galvanic corrosion would be controlled by Al passivation in aerated simulated fresh water; however, galvanic-corrosion rates (measured by the ZRA technique) were higher than predicted, which was probably due to an edge effect of the Al electrodes. Galvanic corrosion was substantial in the aerated simulated seawater, and controlled by diffusion-limited O₂ reduction occurring at noble constituents; there was excellent agreement between the predicted and measured galvanic-corrosion rates. Galvanic-corrosion rates of graphite-Al couples were predicted to be about 30 times higher than those of SiC-Al and TiB₂-Al couples in aerated simulated seawater.

Since galvanic corrosion was most severe in graphite-Al couples, the following methods were investigated in order to identify solutions which may improve the corrosion resistance of G/Al MMCs: 1) Use of pure Al matrices, 2) anodization of Al matrices, 3) electrical insulation of the graphite fibers, 4) cathodic protection, and 5) cathodic inhibition. Of these approaches, only cathodic inhibition showed promise.
The following recommendations are made in regards to developing corrosion resistant G/Al and SiC/Al MMCs. The most urgent is the elimination of residual chlorides from G/Al MMCs by developing alternative fabrication processes that do not leave behind residual halides. Precautions should be taken to avoid Al₄C₃ formation during composite manufacturing of G/Al and SiC/Al MMCs. The galvanic-corrosion rate of SiC/Al MMCs can be kept below the corrosion rate of uncoupled 6061-T6 Al by maintaining the SiC area fraction ≤ 0.3. Work on cathodic inhibition demonstrated that galvanic corrosion in G/Al MMCs can be significantly diminished by inhibiting O₂ reduction. The long-term goal is to develop modified graphite fibers (that do not catalyze O₂ reduction) which can be used in G/Al MMCs.

Thesis Supervisor: Professor Ronald M. Latanision
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EXECUTIVE SUMMARY

I Major Findings

Processing Related Corrosion Problems

1) The formation of Al₄C₃ in graphite/aluminum (G/Al) and silicon carbide/Al (SiC/Al) metal-matrix composites (MMCs) is deleterious because Al₄C₃ under goes hydrolysis. Refer to Subchapter 3.4.

2) During the fabrication of G/Al MMCs, chlorides originating from the chemical vapor deposition of TiB₂ (onto graphite fibers) were left behind primarily on precursor-wire skins and secondarily at fiber-matrix interfaces. This resulted in accelerated corrosion of the diffusion-bonded regions between adjacent precursor wires and occasional pitting in precursor interiors. Refer to Chapter 4.

Intrinsic Corrosion Problems

*Corrosion Resistance of the Matrix*

3) The corrosion resistance of G/Al and SiC/Al MMCs is unlikely to be improved by using ultra pure Al matrices (in comparison to 6061-T6 Al). Uncoupled ultra pure Al had excellent corrosion resistance because it did not pit spontaneously in aerated NaCl solutions (unlike 6061-T6 Al) due to high O₂-reduction overpotentials. Consequently, reinforcing ultra pure Al matrices with noble constituents that are catalytic to O₂ reduction (such as P100 G fibers, SiC, and TiB₂) is likely to cause those matrices to corrode at the same rate as 6061-T6 Al matrices in aerated NaCl solutions. Refer to Subchapter 3.1.

4) The P100 G fibers were oxidized and consumed during anodic polarization. This should preclude anodization of Al matrices as a method to enhance corrosion resistance of G/Al MMCs. Refer to Subchapter 3.2.

*Galvanic Corrosion*

Origin:

5) Galvanic corrosion became significant in aerated NaCl solutions where the galvanic-corrosion rate was controlled by diffusion-limited O₂ reduction. In deaerated solutions, galvanic corrosion was inconsequential. Refer to Subchapter 5.1.
6) In aerated 3.15 wt% NaCl, the galvanic-corrosion rate of 6061-T6 Al or ultra pure Al was predicted to be about 30 times greater when coupled to P100 G fibers than when coupled to SiC or TiB₂. Consequently, the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of P100 graphite was about 80 times the rate of uncoupled 6061-T6 Al; whereas, the galvanic-corrosion rate of 6061-T6 Al coupled to SiC or TiB₂ was predicted to be about 2.5 times the rate of the uncoupled alloy. These results were in agreement with reported corrosion behavior of G/Al and SiC/Al MMCs; namely, G/Al MMCs corrode extensively, and SiC/Al MMCs are relatively corrosion resistant. Refer to Subchapter 5.1.

Control:

7) Experimental data and modeling showed that reducing galvanic corrosion in P100 G(50%)/6061-T6 Al MMCs to negligible levels in aerated NaCl solutions by the electrical insulation of graphite fibers with continuous coatings required coating materials of great resistivities, >10¹⁷ Ω·cm. This requirement precludes most coatings. Refer to Subchapter 5.2.

8) Al-matrix composites were susceptible to overprotection; thus, cathodic protection is a dangerous technique for galvanic control. Refer to Subchapter 5.2.

9) Cathodic inhibitors reduced galvanic corrosion by 10 to 100 times in galvanic couples containing about 50% P100 G fibers and 6061-T6 Al in aerated 3.15 wt% NaCl, making this a promising technique. Refer to Subchapter 5.2.

II Recommendations to Increase Corrosion Resistance of G/Al and SiC/Al MMCs

G/Al MMCs

1) Prevent Al₄C₃ formation by controlling processing temperatures or by coating the fibers with a diffusion barrier to prevent the interaction of C and Al. It might be advantageous to coat the fibers with diffusion barriers if these composites are to be ultimately welded during the assembly of larger components.

2) Eliminate residual chlorides (in general, all halides) from the microstructure of composites by modifying the fabrication process.

3) Modify the graphite fibers to stifle O₂ reduction so that galvanic corrosion can be reduced to negligible levels. The cathodic inhibition studies demonstrated that galvanic corrosion could
be significantly reduced by inhibiting O₂ reduction. At least one method in which graphite can be modified is by intercalation of anions or cations between graphite planes.

SiC/Al MMCs

1) Prevent Al₄C₃ formation by controlling Si activity in the Al matrix or by coating the SiC with a diffusion barrier.

2) Keep the SiC area fraction under about 0.3 to maintain the galvanic-corrosion rate of SiC/Al MMCs to levels less than the corrosion rate of uncoupled 6061-T6 Al.

III Important Notes

1) Simulated fresh water (0.5 M Na₂SO₄) and simulated seawater (3.15 wt% NaCl) were used in this study; thus, the results may not be fully representative of natural waters.

2) Galvanic corrosion was controlled by diffusion-limited O₂ reduction; thus, the predicted galvanic-corrosion rates were not conservative and may increase dramatically in turbulent environments and splash-spray zones.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Dimensions</th>
<th>Section References</th>
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</thead>
<tbody>
<tr>
<td>$A$</td>
<td>($P^3$) surface area of one side of a cube</td>
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<tr>
<td>$A_1$</td>
<td>area of electrode in couple #1</td>
<td></td>
<td>5.2</td>
</tr>
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<td>area of electrode in couple #2</td>
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</tr>
<tr>
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<td>area of active electrode</td>
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<td>current density</td>
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<td>IR drop through electrode</td>
<td>V</td>
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<tr>
<td>(IR)_{sol}</td>
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<td>Universal gas constant</td>
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<td>r</td>
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<td>surface area of oxide film on graphite</td>
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<td>T</td>
<td>temperature</td>
<td>( ^\circ \text{C} )</td>
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<td>t</td>
<td>thickness of fiber coating</td>
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<tr>
<td>$\beta$</td>
<td>Tafel slope</td>
<td>(V/dec)</td>
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BIOGRAPHICAL NOTE

Birth: 1961, Honolulu, Hawaii

Education:

Graduate School:


1983 - 1985: Massachusetts Institute of Technology, Department of Mechanical Engineering, S.M., Thesis title: "Elevated Temperature Constitutive Relations for Titanium Alloy Ti-10V-2Fe-3Al."

Undergraduate School:

1979 - 1983: University of Hawaii at Manoa, Department of Mechanical Engineering, B.S. with distinction, Marshal in graduating ceremony.

1978 - 1979: Leeward Community College, University of Hawaii (early admit student from high school), Pearl City, Hawaii

High School:

1975 - 1979: Pearl City High School, Pearl City, Hawaii

Fellowships, Scholarships and Awards:

Fall 1988: H.H. Uhlig Award in Corrosion, Presented by the Greater Boston Section of the National Association of Corrosion Engineers.

Fall 1985: Materials Processing Center Industry Collegium Fellowship, Materials Processing Center, MIT, Department of Materials Science and Engineering.

1983-1984: Materials Processing Center Industry Collegium Fellowship, Materials Processing Center, MIT, Department of Mechanical Engineering.


Honor Societies:

1) Sigma Xi (MIT)
2) Phi Kappa Phi (U. of H.)
3) Pi Tau Sigma (U. of H.)
4) Alpha Lambda Delta (U. of H.)
5) Phi Eta Sigma (U. of H.)

Professional Affiliations:

1) The Electrochemical Society
2) The National Association of Corrosion Engineers
3) The Metallurgical Society of AIME ASM International
Publications:


Public Presentations:


Personal Interests:

Golfing, surfing, fishing, and the martial arts (karate: black belt; aikido).
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1 INTRODUCTION

1.1 Purpose of Research

Metal-matrix composites (MMCs) are interesting structural materials because they possess properties such as high strength, high stiffness, lightness, and low coefficients of thermal expansion [Delmonte, 1981]. Metal-matrix composites can also be used above 300°C, which is the limit of organic-matrix composites (OMCs) [Delmonte, 1981], and MMCs do not outgas moisture as do some OMCs which can be critical in space applications [Weeton, Peters, & Thomas, 1987]. The projected applications of MMCs include aerospace, automotive, medical, and sports equipment [Weeton, Peters, & Thomas, 1987], and, in general, wherever weight savings are important. Research on MMCs has been largely focussed on fabrication processing and mechanical properties. Corrosion research has been sparse, and at the onset of this corrosion research program in 1985, there were only about 40 to 50 published articles (in the English language) on the subject covering all types of MMCs. Spectacular corrosion failures of graphite/aluminum (G/Al) MMCs after a few months exposure to marine atmosphere were shown by Pfeifer in 1977 and reports of more corrosion resistant silicon carbide/Al (SiC/Al) MMCs have surfaced more recently. In 1985, little was known about the corrosion mechanisms of G/Al and SiC/Al MMCs. Very few of the published articles were comprehensive in identifying corrosion mechanisms and, in fact, most were speculative and lacked quantitative corrosion data. The goals of this project are 1) to understand the corrosion mechanisms of G/Al and SiC/Al MMCs such that their limits of chemical stability are well defined before they are put into service, and 2) to develop methods to improve corrosion resistance where needed, such as in the G/Al MMCs shown by Pfeifer [1977].

1.2 Research Objectives

This study focussed primarily on G/Al MMCs in which corrosion is severe and secondarily on SiC/Al MMCs in which corrosion is less severe. Aqueous corrosion studies were systematically preformed in neutral deaerated and aerated 0.5 M Na$_2$SO$_4$ (simulated fresh water) and 3.15 wt% NaCl (simulated seawater) at 30°C to establish the effects of H$_2$ evolution, O$_2$ reduction, and chloride on composite corrosion behavior. The electrochemical, corrosion, and degradation behavior of the composite constituents were also characterized systematically in order to understand the interactions occurring between the constituents while the composites corrode. This enabled prediction of composite corrosion behavior and identification of imminent corrosion problems. In addition to studying constituents, a commercial G/Al MMC was also examined which resulted in the identification
of unexpected corrosion problems. This approach ensured that corrosion mechanisms were well characterized so that only the pertinent corrosion problems would be addressed during the development of corrosion control strategies. The following possibilities for corrosion control were investigated: modification of the matrix, insulation of the reinforcement constituents from the matrix, cathodic protection, cathodic inhibition, and modification of the reinforcement constituents.

Constituents that were studied in this program are ultra pure aluminum of 99.999% metallic purity (m5N Al), 6061-T6 Al, high-modulus pitch-based graphite (P100 G) fibers, SiC, TiB₂, and Al₄C₃. Ultra pure Al was investigated for matrix use since it has excellent corrosion resistance. The 6061-T6 Al was studied because it is commonly used for matrices. The P100 G fibers and SiC were studied as they are important reinforcement constituents. Titanium diboride was studied because it is used to enhance graphite-fiber wettability in molten aluminum. Aluminum carbide is a reaction product of Al and graphite or SiC and, accordingly, was studied. The commercial G/Al MMC studied in this program consisted of about 50 vol% of P100 G fibers and 6061-T6 Al.

Electrochemical techniques in concert with microscopy and surface analysis were utilized in this research program. Below is a listing of these techniques.

**Electrochemical:**
1) Potentiodynamic and potentiostatic polarization
2) Zero-resistance ammeter galvanic current measurement
3) In situ corrosion observation under an optical microscope

**Chemical:**
4) Gas analysis by gas-detector tubes

**Surface Analytical:**
5) Optical microscopy
6) Scanning electron microscopy
7) Energy dispersive spectrometer X-ray analysis
8) Auger electron spectroscopy
9) X-ray photoelectron spectroscopy
10) X-ray powder diffraction
1.3 Thesis Format

Each chapter or subchapter can be read independently. A general literature review on the corrosion of Al-matrix composites appears in Chapter 2. Chapter 3 describes the electrochemical, corrosion, and degradation characteristics of the constituents. Chapter 4 identifies the processing-related corrosion problems of the commercial G/6061-T6 Al MMC. The origin of galvanic corrosion in Al-matrix composites and methods for its control are discussed in Chapter 5. Finally, in Chapter 6, general conclusions are drawn.

1.4 References


2 LITERATURE REVIEW OF ALUMINUM-MATRIX COMPOSITES

The first published study in the USA on the corrosion of metal-matrix composites (MMCs) was probably that of Porter and Wolff [1967] in 1967. Today, more than 20 years later, there are only about 60 more unclassified papers in the English speaking literature on this topic. This review will converge on Al-matrix composites which comprise the bulk of corrosion studies on MMCs. The literature on graphite/Al (G/Al), silicon carbide/Al (SiC/Al), boron/Al (B/Al), and alumina/Al (Al₂O₃/Al) MMCs is evaluated in order to provide a broad perspective which will be useful in reaching the goals of this program.

2.1 G/Al MMCs

Though reports in the literature on the corrosion mechanisms of G/Al MMCs are not clear, these composites consistently show poor corrosion resistance in chloride-containing environments. There are apparently three distinct forms of corrosion in G/Al MMCs: 1) The preferential corrosion of diffusion-bonded regions (formed during the consolidation of plates) between adjacent precursor G/Al composite wires, 2) the hydrolysis of Al₄C₃, where Al₄C₃ is a reaction product that can form by the interaction of graphite and molten Al during processing, and 3) the galvanic corrosion between graphite fibers and Al.

Pfeifer [1977] reported that corrosion in G/Al MMC plates during exposure to marine environments primarily occurs at the diffusion-bonded regions between precursor G/Al wires when the diffusion bonds are of low integrity. Vassilatos, Davis, Steckel, and Gudas [1983] also observed preferential corrosion of the diffusion-bonded regions in marine environments. Aylor and Kain [1983] observed severe exfoliation and the expulsion of precursor wires from the sides of G/Al MMC plates in marine environments. In all cases, however, the cause for diffusion-bond corrosion was not determined.

Portnoi, et al. [1981] showed that Al₄C₃ in G/Al MMCs readily decomposes in water producing CH₄ and an undetermined form of aluminum hydroxide.

The following studies which are oriented toward the corrosion performance of G/Al MMCs show that G/Al MMCs have poor corrosion resistance in chloride-containing environments. Corrosion mechanisms were not determined, but many investigators speculated that high matrix corrosion rates result from galvanic corrosion between the graphite fibers and the matrix. Evans and Braddock [1971] reported that G/Al MMCs that were exposed to a O₂-saturated NaCl solution swelled as a result of corrosion that penetrated into the

Electrochemical techniques were employed in the following studies which resulted in the identification of several corrosion mechanisms. Dull, Harrigan, and Amateau [1977] conducted polarization experiments on various G/Al MMCs in NaCl solutions, and determined that O₂ greatly increases the corrosion rate. This indicates that the main driving force for galvanic corrosion is O₂ reduction rather than H₂ evolution. Aylor and Moran [1985] conducted polarization experiments on G/Al MMCs in seawater, but speculated that carbon diffuses into the Al matrix which lowers the integrity of the passive film, making the matrix more susceptible to breakdown. Czyrklis [1985] concluded that the more noble open circuit potential of a G/Al MMC compared to the matrix alloy in a deaerated NaCl solution is evidence for galvanic corrosion. His conclusion is accurate, but as Dull, et. al. [1977] demonstrated, galvanic corrosion should be negligible in deaerated solutions. Saxena, Modi, Yegneswaran, and Rohatgi [1987] attributed the high corrosion rates of G/Al MMCs in marine environments to galvanic corrosion by H₂ evolution; however, since their polarization diagrams appear to have been generated in aerated solutions (they did not make this clear), one should assume that O₂ reduction is the main driving force for galvanic corrosion, as shown by Dull, Harrigan, and Amateau [1977].

2.2 SiC/Al MMCs

In most cases, SiC has no effect on pitting potentials in SiC/Al MMCs, but degradation of SiC/Al MMCs in chloride-containing environments is generally greater than that of the matrix alloys. It is possible that the higher degradation rate results from galvanic corrosion between SiC and Al or the hydrolysis of Al₄C₃, since Al₄C₃ formation can occur during processing by the reaction between SiC and molten Al [Iseki, Kameda, and Maruyama, 1984]. Silicon carbide/Al MMCs, however, are significantly more corrosion resistant than G/Al MMCs [Aylor and Kain, 1983]. These points are elaborated upon in the survey that follows.

When compared to their matrix alloys, the pitting potentials of SiC/6061 Al MMCs containing 25 vol% SiC [Aylor and Moran, 1985] and 20 vol% SiC [Trzaskoma, McCafferty, and
Crowe, 1983), and SiC/5456 Al MMCs containing 20 vol% SiC [Trzaskoma, McCafferty, and Crowe, 1983] are unaltered in chloride-containing solutions. The pitting potential of SiC/2024 Al containing 20 vol% of SiC, however, is depressed by 0.1 V [Trzaskoma, McCafferty, and Crowe, 1983]. The lack of effect on the pitting potential indicates that the passive film integrity is unaffected by the inclusion of SiC. In deaerated NaCl solutions, SiC/Al MMCs and their matrix alloys are spontaneously passive [Aylor and Moran, 1985; Trzaskoma, McCafferty, and Crowe, 1983], but in aerated solutions, the corrosion potentials are about equal to the pitting potentials [Trzaskoma, McCafferty, and Crowe, 1983] showing that SiC/Al MMCs as well as their matrix alloys pit spontaneously.

Since SiC is noble to Al [Lore and Wolf, 1981], galvanic corrosion is possible. Lore and Wolf [1981] found that the degree of corrosion in SiC/6061 Al MMCs in chloride-containing solutions is proportional to the SiC content. In SiC/2024 Al MMCs containing 20 vol% SiC, DeJarnette and Crowe [1981] found that the composites corrode about 40% faster during 1 month exposures to aerated NaCl solutions. Aylor and Moran [1985] also observed that SiC/6061 Al MMCs (25 vol% SiC) are less corrosion resistant than 6061 Al in marine environments.

Corrosion morphology studies have shown that pits form around SiC particles and whiskers [Aylor and Kain, 1983; Aylor and Moran, 1985]. This may result from electrochemical pit formation and Al₄C₃ hydrolysis.

2.3 B/Al MMCs

Boron fibers are noble to Al in aerated NaCl solutions [Sedriks, Green, and Novak, 1971; Bakulin, Ivanov, and Kuchkin, 1978] indicating that galvanic corrosion is possible. Sedriks, et al., [1971] however, could not measure cathodic or anodic currents on pure B electrodes in the aerated NaCl solutions, and, accordingly, found that the cathodic current densities (with respect to matrix area) of B/Al MMCs are unaltered by changing the volume fraction of B fibers. In contrast, they found that anodic current densities (w.r.t. matrix area) increase, and open circuit potentials decrease when the volume fraction of B fibers is increased. They attributed this behavior to the accelerated dissolution of diffusion-bonded fiber-matrix and foil-foil interfaces. In addition, the open circuit potentials of B/Al MMCs are active to the matrix alloys, as observed by Sedriks, et al. [1971] and Bakulin, et al. [1978] in aerated NaCl solutions.
Pohlman [1978] also could not measure galvanic currents between B and Al in NaCl solutions, but did not specify whether solutions were aerated or deaerated. He found, however, an aluminum boride (AlB$_2$ or AlB$_{12}$) at the fiber-matrix interface, and measured galvanic currents between Al and extracted B fibers (from the matrix), and between Al and aluminum boride (boride specie not specified). Unlike the results of Sedriks, et al. [1971] and Bakulin, et al. [1978], Pohlman found that the open circuit potentials of B/Al MMCs are noble to the matrix alloy, but active to B and aluminum boride.

### 2.4 Al$_2$O$_3$/Al MMCs

The corrosion resistance of Al$_2$O$_3$/Al MMCs is sensitive to the matrix alloy, and there is no evidence of galvanic corrosion between Al$_2$O$_3$ and Al.

The corrosion resistance of Al$_2$O$_3$/Al (2% Li) MMCs was compared to conventional Al alloys in chloride-containing environments [Champion, Krueger, Hartmann, and Dhingra, 1978]. Weight loss data show that the corrosion rate of Al$_2$O$_3$/Al (2% Li) MMCs is slightly higher than that of 6061-T6 Al, but significantly lower than that of 2219-T87 Al. There is also no evidence of galvanic corrosion or severe interfacial corrosion at the fiber-matrix interface which contains a Li$_2$O*5Al$_2$O$_3$ reaction layer. Agarwala [1981], however, observed interfacial corrosion in Al$_2$O$_3$/6061 Al MMCs. Interfacial corrosion is also observed in Al$_2$O$_3$/Al (2% Mg) MMCs [Yang and Metzger, 1981], which is caused by the selective attack of Mg$_5$Al$_8$ that precipitates locally near the fibers.

### 2.5 References


DeJarnette, H.M.; Crowe, C.R., Naval Surface Weapons Center, White Oak, MD; unpublished research, 1982.


3 ELECTROCHEMISTRY, CORROSION, AND DEGRADATION OF THE CONSTITUENTS

This chapter is comprised of four independent subchapters, and provides information on the electrochemistry, corrosion, and degradation characteristics of the constituents comprising the graphite/aluminum and silicon carbide/aluminum metal-matrix composites. The findings from this chapter will be subsequently used in Chapter 4 and Chapter 5 to identify corrosion mechanisms and to develop corrosion control methods.

The contents of this chapter are listed below.

3.1 Electrochemistry and Corrosion of Ultra Pure Aluminum and 6061-T6 Aluminum Alloy in Neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl

3.2 Electrochemistry and Corrosion of High-Modulus Pitch-Based Graphite Fibers in Neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl

3.3 The Cathodic Electrochemistry of SiC and TiB₂ in Neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl

3.4 Aluminum Carbide Hydrolysis
3.1 ELECTROCHEMISTRY AND CORROSION OF ULTRA PURE ALUMINUM AND 6061-T6 ALUMINUM ALLOY IN NEUTRAL 0.5 M Na₂SO₄ AND 3.15 wt% NaCl

3.1.1 Introduction

Electrochemical and corrosion data were needed on ultra pure Al of 99.999 % metallic purity (m5N Al) and 6061-T6 Al for this research program concerning the corrosion behavior of Al-matrix composites in simulated fresh water (0.5 M Na₂SO₄) and seawater (3.15 wt% NaCl). Pitting potentials, passive current densities, H₂-evolution and O₂-reduction kinetics, and corrosion behavior were determined. During anodic polarization, m5N Al and 6061-T6 Al were found to have similar pitting potentials and passive current densities. During cathodic polarization, however, the H₂-evolution and O₂-reduction overpotentials were found to be higher on m5N Al than on 6061-T6 Al. Specimens of m5N Al spontaneously passivated in deaerated and aerated Na₂SO₄ and NaCl solutions, in contrast to 6061-T6 Al which pitted spontaneously in aerated NaCl solutions (although it spontaneously passivated in the other solutions).

Potentiodynamic polarization was used to acquire electrochemical data in the form of polarization diagrams which can be used in mixed-electrode models for predicting corrosion behavior of composite materials. A slow scan rate (0.1 mV/s) was used to obtain near steady-state properties.

3.1.1.1 Background

Aluminum is an extremely reactive metal with a high driving force to revert back to its oxide, but it generally has good resistance to aqueous corrosion in near neutral solutions, to atmospheric corrosion, and to gaseous oxidation. The resistance of Al to degradation is provided by a thin film of aluminum oxide which forms on the metal surface providing an effective barrier shielding the metal substrate from the environment. The films formed on Al are generally duplex and consist of a thin inner amorphous barrier layer upon which a thicker porous layer forms. In environments that are not aggressive to the oxide, only the barrier layer forms.

The barrier layer formed in air and oxygen at room temperature appears to reach a steady-state thickness of about 10 Å. Gravimetric measurements indicated that oxide films grown on evaporated Al in dry oxygen attain a steady-state thickness on the order of 10 Å within 10 to 40 minutes at room temperature [Keller and Edwards, 1948a]. It is believed that films formed in dry O₂ represent barrier films of maximum thickness at that temperature [Hunter and
Hunter and Fowle [1956], utilizing an electrochemical technique to measure film thickness, found that barrier films formed in dry atmospheres reach steady-state thicknesses within 1 hour, and that Al exposed to air for one week to several years has barrier layers about 10 Å thick regardless of the porous layer. Hass [1949] determined through using Drude's optical polarization method and resistance measurements that films formed in air after 2 hours exposure are about 10 Å thick and then grow very slowly to about 45 Å within 1 month. More recently, Moshier, Davis, and Ahearn [1987] determined by XPS studies that the films formed on Al (while exposing a clean surface to air, rinsing, and exposing to ultra high vacuum within 6 minutes) are also about 10 Å thick. The barrier films are amorphous at room temperature as determined by electron diffraction [Hass, 1949; Hunter and Fowle, 1956; Keller and Edwards, 1948b] and X-ray diffraction [Keller and Edwards, 1948b]. Moshier, et al. [1987] determined from there XPS studies that the composition of the air-formed-and-rinsed films is slightly hydrated Al₂O₃.

In electrolytes where the Al₂O₃ is scarcely soluble, such as boric acid and acidified organic ammonium salt solutions, the amorphous, barrier-type, anodic films can be grown where the thickness is proportional to the voltage applied between the Al anode and an Al cathode in the same solution by a relationship of about 13 Å/V [Hass, 1949; Walkenhorst, 1947; Taylor and Edwards, 1939]. In dry air and O₂, and in moist air, the amorphous barrier layer is a function of temperature starting at a thickness of 10 Å at room temperature and growing by 0.1 Å/°C to temperatures less than about 450°C [Hunter and Fowle, 1956]. Thus, the barrier film thickness is a function of applied voltage and temperature.

In solutions where Al₂O₃ is soluble such as dilute sulfuric, chromic, oxalic, and phosphoric acids, duplex films grow under anodic polarization [Keller, Hunter, and Robinson, 1953], and the barrier-film thickness is proportional to the applied voltage, but less than the value of 13 Å/V [Hunter and Fowle, 1954]. Keller, et al. [1953] found that the porous layer consists of cells each containing one pore. Troutner [1959] also found duplex films on Al which was exposed to water at 300 °C. He also found by X-ray diffraction that the barrier layer consists of randomly oriented böhmite in an amorphous matrix, and that the outer layer consists of highly oriented böhmite. The chemical composition of anodic films on Al in pH 7 and pH 10 0.05 M Na₂SO₄ corresponds to that of böhmite, and those on Al in pH 2 solutions corresponds primarily to that of Al₂O₃ as determined by XPS [Moshier, et al., 1987].

The Pourbaix diagrams of Al at 25 °C [Deltombe, Vanleugenhaghe, and Pourbaix, 1974] are shown in Figures 3.1.1 and 3.1.2 for böhmite and hydargillite as the stable oxide phases, respectively. Böhmite is an intermediate hydrated alumina which ages into hydargillite, the
most thermodynamically stable form of hydrated alumina [Deltombe, Vanleugenhaghe, and Pourbaix, 1974]. In acidic solutions, the Al dissolution reaction is
\[ \text{Al}^{3+} + 3e^- = \text{Al}, \quad E^* = -1.904 \text{ V}_{\text{SCE}} \] (3.1.1)
and in basic solutions, the overall dissolution reaction is
\[ \text{AlO}_2^- + 4\text{H}^+ + 3e^- = \text{Al} + 2\text{H}_2\text{O}, \quad E^* = -1.503 \text{ V}_{\text{SCE}} \] (3.1.2),
where \( V_{\text{SCE}} \) is the potential with respect to a saturated calomel reference electrode.

Films form on Al in acidic and basic solutions Moshier, et al., [1987], but their formation is an intermediate step in the overall dissolution process. In near neutral solutions, Al is passive and the reaction is
\[ \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6e^- = 2\text{Al} + 3\text{H}_2\text{O}, \quad E^*_{\text{hydrargillite}} = -1.791 \text{ V}_{\text{SCE}} \] (3.1.3).
\[ E^*_{\text{böhmit}} = -1.746 \text{ V}_{\text{SCE}} \]

In halide containing solutions, if the pitting potential is exceeded, the passive film breaks down and Al and its alloys pit. The pitting potential is linearly dependent on the logarithm of the halogen anion concentration [Galvele, 1978]. In order for Al to pit in the open circuit condition, a cathodic reaction must polarize Al to potentials noble to its pitting potential. Oxygen reduction
\[ \text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}, \quad E^* = 0.987 \text{ V}_{\text{SCE}} \] (3.1.4)
and hydrogen evolution
\[ 2\text{H}^+ + 2e^- = \text{H}_2, \quad E^* = -0.241 \text{ V}_{\text{SCE}} \] (3.1.5)
are two possible cathodic reactions. In near-neutral, chloride-containing solutions, ultra pure Al (99.99 %) is a poor catalyst for \( \text{O}_2 \) reduction [Hübner and Wranglén, 1964; Pryor and Keir, 1955], and thus does not pit spontaneously. The reason for poor \( \text{O}_2 \)-reduction kinetics is probably due to high resistivity of aluminum oxide which restricts electron migration through the passive film except at thin spots [Pryor and Keir, 1955; Evans, 1937]. Pryor and Keir [1955] have shown that Cu will deposit on ultra pure Al in localized regions indicating preferred cathodic sites; whereas, Cu uniformly plates on Cu, Fe, Sn, Pb, and Zn under similar conditions. Hübner and Wranglén [1964] found that pits could not be nucleated on Al if hydrogen evolution was the only operating cathodic reaction.
In Al alloys, however, precipitates on the surface that are noble to the matrix can polarize the alloy to the pitting potential in aerated solutions. For example, Hübner and Wranglén [1964] proposed that Al₃Fe acts as local O₂-reduction sites and causes Al alloys to pit in chloride-containing solutions. Akimow and Oleschko [1934], reported open circuit potentials of Al₃Fe (-0.39 to -0.59 V<sub>SCE</sub>), Al₃Mn (-0.44 to -0.90), Al₃Ni (-0.72), Al₂Cu (-0.61), Mg₂Si (-1.52 to -0.67), and of Al (-0.79) in 3% NaCl over a 25 hour period. Specifically, for wrought 6061-T6 Al (the alloy investigated in this study), which pits spontaneously in aerated chloride solutions, the possible precipitates are Mg₂Si and (Fe,Cr)₃SiAl₁₂ [Metals Handbook, 1985]. Although, Mg₂Si is initially active (-1.52 V<sub>SCE</sub>) to Al (-0.79 V<sub>SCE</sub>), it becomes noble (-0.67 V<sub>SCE</sub>) to Al after about 25 hours [Akimow and Oleschko, 1934], and thus can act as a cathodic site. Also, it is possible that (Fe,Cr)₃SiAl₁₂ is noble to Al or that the presence of surface precipitates causes weak spots in the oxide film where O₂ reduction can take place.

Finally, it is also well known that pitting of Al in chloride-containing waters is aggravated by the presence of Cu²⁺ ions [Rowe and Walker, 1961; Porter and Hadden, 1953; Davies, 1959]. The presence of Cu²⁺ has two effects. First, the deposition of Cu is a cathodic process which consumes electrons from the dissolution of Al: Murray, Lamb, and Godard [1967] found that Cu plates onto Fe-rich precipitates adjacent to pits in Al. And second, O₂ reduction has been shown to be about 15 times greater on ultra pure copper (99.99%) than on ultra pure Al (99.99%) [Pryor and Keir, 1955].

3.1.2 Materials

Planar electrodes were fabricated from m5N Al and 6061-T6 Al. The sides of the specimens were coated with either epoxy paint (AMERCOAT 90 Resin, Ameron) or an epoxy adhesive (EPOXY-PATCH, The Dexter Corporation) and inspected with an optical microscope to insure that the Al-epoxy interface was well bonded. The planar surface of the electrodes was polished to a 0.5 μm finish with gamma alumina powder, kept wet, and rinsed with 18 MΩ-cm water about 5 minutes prior to immersion in the aqueous solutions. The surface area of the m5N Al electrodes was 0.713 cm², and that of the 6061-T6 Al electrodes was 0.811 cm² with the exception of small 6061-T6 Al electrodes where the surface area was 0.0233 cm². Only when the small-area 6061-T6 Al electrodes were used is reference to the electrode surface area made on the polarization diagrams; when no reference to surface area is made, the polarization diagrams correspond to the large-area electrodes. However, all results are normalized with respect to surface area.
Solutions of 0.5 M $\text{Na}_2\text{SO}_4$ and 3.15 wt% $\text{NaCl}$ of about pH 7 were prepared from 18 MΩ·cm water and analytical grade reagents. The solutions were deaerated by sparging with pre-purified hydrogen gas, aerated by sparging with 19.5 to 23.5% oxygen balanced with nitrogen, and thermostated to $30 \pm 0.1^\circ\text{C}$. The gas pressure was 1 atmosphere.

3.1.3 Instrumentation and Procedures

Polarization of the Al electrodes was conducted with either a Model 273 EG&G Princeton Applied Research (PAR) potentiostat/galvanostat or a Model 173 EG&G PAR potentiostat/galvanostat equipped with a Model 376 EG&G PAR logarithmic current converter. When measuring currents as low as 1 nA, both instruments were within about 10% of the true current as determined by the following procedure. The accuracy of the current measurement was assessed by inserting a 1 GΩ (2% tolerance) resistor between the working electrode terminal and the auxiliary terminal (to which the reference terminal was connected) of the potentiostat. A potential difference of 1.000 V was set between the working and reference terminals which should theoretically produce a current flow from the auxiliary electrode equal to 1.000 nA assuming 0% tolerance of the 1 GΩ resistor. The measured current was then compared to the theoretical 1.000 nA value.

In generating potentiodynamic polarization diagrams, the Al electrodes were allowed to stabilize at their corrosion potentials ($E_{\text{corr}}$) and were subsequently polarized at a rate of 0.1 mV/s, unless stated otherwise. Polarization diagrams with standard deviation bars were generated from at least three individual polarization diagrams; the average logarithm of the current density ($\log i \, [\text{A/cm}^2]$) was plotted as a function of potential, and the peak-to-peak width between standard deviation bars is equal to two times the standard deviation of $\log i$. The average values of $E_{\text{corr}}$, the average time that the electrodes were in the open circuit condition prior to polarization, and the standard deviation (SD) of these parameters are also tabulated in the caption of the polarization diagrams.

Tafel slopes ($\beta$) were calculated between specific current ranges by taking the average Tafel slope from a set of individual polarization diagrams; this produces a result different from that obtained by measuring the Tafel slope on the polarization diagrams where the average $\log i$ is plotted as a function of potential (as described in the preceding paragraph). The least-squares method was used to calculate the Tafel slopes by fitting linear regions of individual polarization diagrams to straight lines having the form

$$E = \beta \log i + B$$

(3.1.6)
where $E$ is in $V_{\text{SCE}}$, $\beta$ in $V$ per decade of $i$, $i$ in $A/cm^2$, and $B$ in $V$. Exchange current densities were determined by Tafel extrapolation.

### 3.1.4 Results

The results section is divided into cathodic polarization, anodic polarization, and open circuit potential characteristics.

#### 3.1.4.1 Cathodic Polarization

Individual cathodic polarization diagrams of m5N Al are shown in Figures 3.1.3 through 3.1.6; those of 6061-T6 Al are shown in Figures 3.1.7 through 3.1.11. All of the cathodic polarization diagrams are compared in Figure 3.1.12. Tafel slopes and extrapolated exchange current densities for the hydrogen evolution reaction are tabulated in Table 3.1.1.

The polarization diagrams of m5N Al were under activation control in deaerated and aerated 0.5 M Na$_2$SO$_4$ and 3.15 wt% NaCl (Figures 3.1.3 through 3.1.6). Aeration increased cathodic currents at the lower current densities, but concentration polarization due to O$_2$ reduction was not observed (Figure 3.1.12). The open circuit potentials were more noble and the cathodic currents were generally larger in the 3.15 wt% NaCl solutions, as shown in Figure 3.1.12.

The polarization diagrams of 6061-T6 Al that were generated in deaerated solutions were under activation control, and the open circuit potential and cathodic current densities were larger in 3.15 wt% NaCl than in 0.5 M Na$_2$SO$_4$ (Figure 3.1.12). In aerated 3.15 wt% NaCl, concentration polarization due to O$_2$ reduction was observed (Figure 3.1.11) and the diffusion-limited current density was about $4 \times 10^{-6}$ A/cm$^2$. Concentration polarization due to O$_2$ reduction was also observed in aerated 0.5 M Na$_2$SO$_4$ having a slightly higher diffusion-limited current density, but this was observed only when the electrodes were in the open circuit condition for a few minutes before scanning at 2 mV/s (Figure 3.1.8). The region of concentration polarization due to O$_2$ reduction vanished when the 6061-T6 Al electrodes were in the open circuit condition for 1 hour before scanning at 0.1 mV/s (in aerated 0.5 M Na$_2$SO$_4$), as shown in Figure 3.1.9.

#### 3.1.4.2 Anodic Polarization

The individual anodic polarization diagrams of m5N Al are shown in Figures 3.1.13 through 3.1.16; those of 6061-T6 Al are shown in Figures 3.1.18 through 3.1.22. The
anodic polarization diagrams of m5N Al are compared in Figure 3.1.17; those of 6061-T6 Al are compared in Figure 3.1.23.

In deaerated and aerated 0.5 M Na₂SO₄, m5N Al was spontaneously passive at E_{corr} and remained passive throughout the scan to 1 V_{sce} (Figure 3.1.17). The passive current density was approximately 10⁻⁶ A/cm², but increased slightly at potentials noble to -0.60 V_{sce} (in deaerated 0.5 M Na₂SO₄) and noble to 0.1 V_{sce} (in aerated 0.5 M Na₂SO₄), as shown in 3.1.17. There was virtually no difference in the anodic polarization diagrams of m5N Al in deaerated and aerated 3.15 wt% NaCl (Figure 3.1.17). The m5N Al was spontaneously passive and the pitting potentials were -0.750 V_{sce} and -0.725 V_{sce} in the deaerated and aerated 3.15 wt% NaCl solutions, respectively. The passive currents in the 3.15 wt% NaCl were lower than those in the 0.5 M Na₂SO₄ solutions by a factor of about three (Figure 3.1.17).

In the deaerated and aerated 0.5 M Na₂SO₄ solutions, 6061-T6 Al was also spontaneously passive at E_{corr} and remained passive throughout the scan (Figure 3.1.23). There was, however, some discrepancy in the anodic currents between the deaerated and aerated cases near E_{CORR} (Figure 3.1.23). Passive current densities were about 10⁻⁶ A/cm², and increased slightly at potentials noble to about 0.1 V_{sce}. In the aerated 0.5 M Na₂SO₄ solution, the electrodes with the small surface areas had passive current densities about five times greater than the electrodes with the large surface areas, and the passive currents of the small electrodes began to increase significantly at potentials noble to 0.0 V_{sce} (Figure 3.1.23). The pitting potential of 6061-T6 Al was about -0.725 V_{sce} in deaerated 3.15 wt% NaCl; it pitted spontaneously in the aerated solution, as shown in Figure 3.1.23.

3.1.4.3 Open Circuit Potential

The open circuit potentials of m5N Al and 6061-T6 Al were monitored for 1 hour in 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions (Figure 3.1.24). The m5N Al in deaerated and aerated 0.5 M Na₂SO₄ and 3.15 wt% NaCl was active to -1.0 V_{sce} within 5 minutes and stabilized at potentials active to about -1.4 V_{sce} within 1 hour. Examination of m5N Al in the aerated 3.15 wt% NaCl showed that the potential remained in the regime of -1.4 V_{sce} for the duration of the longest examination, which lasted for 27 hours. The 6061-T6 Al electrodes in the deaerated 0.5 M Na₂SO₄ and 3.15% NaCl were active to -1.0 V_{sce} within 5 minutes and stabilized at potentials active to -1.1 V_{sce} within 1 hour. In aerated 0.5 M Na₂SO₄, the potential of 6061-T6 Al was about -0.6 V_{sce} after 5 minutes and gradually decreased to potentials active to -1.0 V_{sce} during the 1 hour examination; however,
if the samples were quickly transferred to aerated 3.15 wt% NaCl, the potential immediately stabilized at -0.73 V_{sce} rather than at -1.0 V_{sce} as in the aerated 0.5 M Na_2SO_4. In aerated 3.15 wt% NaCl, the potential of 6061-T6 Al was steady at about -0.73 V_{sce}.

3.1.5 Discussion

The m5N Al exhibited better corrosion resistance than 6061-T6 Al. Since 6061-T6 Al and m5N Al had almost identical pitting potentials, the better corrosion resistance of m5N Al was due to the large O_2-reduction overpotential on m5N Al which prevented m5N Al from being polarized to its pitting potential while in the open circuit condition. In this discussion, the anodic and cathodic behaviors will be discussed to elaborate upon the corrosion behavior of m5N Al and 6061-T6 Al.

There was little difference in the anodic behavior of m5N Al and 6061-T6 Al in 0.5 M Na_2SO_4 (compare Figure 3.1.17 to 3.1.23). The passive currents were about 10^{-6} A/cm^2 which gradually increased at noble potentials. Moshier, et al.[1987] also measured passive currents in the 10^{-6} A/cm^2 regime in neutral 0.05 M Na_2SO_4, and found by XPS that the oxide film thickened and has a composition corresponding to böhmite at potentials noble to 0 V_{sce}, where the anodic currents increase. The similarity in the anodic behavior of m5N Al and 6061-T6 Al suggested that the alloying elements of 6061-T6 Al have no significant effect on the dissolution characteristics of the passive film. The larger passive current densities that were measured on the small 6061-T6 Al electrodes in contrast to the large 6061-T6 Al electrodes (Figure 3.1.23) were probably due to an edge effect, as thick oxide films were observed to grow inward from the perimeter of the electrodes. In the case of the small electrodes, the thick film covered most of the surface due to the large perimeter-to-area ratio.

There were also no substantial shifts in the pitting potential of m5N Al with respect to 6061-T6 Al in the 3.15 wt% NaCl solutions (compare Figures 3.1.15, 3.1.16, and 3.1.21). In deaerated solutions, 6061-T6 Al and m5N Al were spontaneously passive (Figures 3.1.21 and 3.1.15) since the hydrogen evolution reaction was not able to polarize the electrodes to the pitting potential. An important difference in aerated 3.15 wt% NaCl, however, is that 6061-T6 Al pitted spontaneously (Figure 3.1.22) in contrast to m5N Al which was spontaneously passive (Figure 3.1.16).

Spontaneous pitting of 6061-T6 Al can be attributed to O_2-reduction sites on 6061-T6 Al. Figure 3.1.8 shows that 6061-T6 Al supported substantial O_2 reduction immediately upon
immersion in aerated 0.5 M Na₂SO₄, and also shows that the open circuit potential was equal to -0.650 V_{SCE} which is noble to the pitting potential, -0.725 V_{SCE}, of 6061-T6 Al in deaerated 3.15 wt% NaCl (Figure 3.1.21). Accordingly, 6061-T6 Al pitted spontaneously in aerated 3.15 wt% NaCl (Figure 3.1.22). The overall stability (excluding small perturbations) of the open circuit potential of 6061-T6 Al in aerated 3.15 wt% NaCl (Figure 3.1.24) can be attributed to extremely facile kinetics of Al dissolution once passive film breakdown occurs and to cathodic sites which remain catalytic or become more catalytic and increase in number as pitting progresses. For example, O₂ reduction may occur on unfilmed Al, and H₂ evolution may occur within pits, as observed by Hübner and Wranglén [1964]. Wood, et al. [1974] also suggested that cathodic sites on Al alloys are initially surface precipitates and then later are primarily spots of unfilmed Al.

In contrast, m5N Al was spontaneously passive in aerated 3.15 wt% NaCl (Figure 3.1.16) because of large O₂-reduction overpotentials. The E_{corr}-time diagrams of m5N Al (Figure 3.1.24) also show little oxygen dependency in 0.5 M Na₂SO₄ and 3.15 wt% NaCl.

The cathodic polarization diagrams (Figure 3.1.12) also indicated, quite dramatically, that m5N Al was less catalytic to H₂ evolution when compared to 6061-T6 Al (which had significantly lower hydrogen overpotentials during cathodic polarization). The lower Tafel slopes of 6061-T6 Al compared to m5N Al (Table 3.1.1) could signify either differences in the H₂ evolution mechanism or lower resistance through the oxide film on the 6061-T6 Al electrode (unfortunately, an IR compensation technique was not used which would have corrected for resistance losses through the oxide film). In either case, the lower cathodic overpotentials on 6061-T6 Al are probably due to surface precipitates which act as cathodic sites or cause weak spots in the passive film where cathodic reactions occur more readily.

3.1.6 Conclusions

The inferior corrosion resistance of 6061-T6 Al compared to m5N Al was caused by smaller O₂-reduction overpotentials on 6061-T6 Al since 6061-T6 Al and m5N Al had similar pitting potentials. Consequently, m5N Al was spontaneously passive in aerated 3.15 wt% NaCl, in contrast to 6061-T6 Al which pitted spontaneously in the open circuit condition. The H₂-evolution overpotentials were also smaller on 6061-T6 Al compared to m5N Al, but H₂ evolution was unable to polarize either 6061-T6 Al or m5N Al to the pitting potential in the open circuit condition. In the context of metal-matrix composites, these results suggest that there should be no advantage of utilizing pure Al matrices for enhanced corrosion resistance in
composites reinforced with compounds catalytic to $O_2$ reduction; such as, graphite, SiC, or TiB$_2$.

3.1.7 References


Keller, F. and Edwards, J.D., "Formation of the Natural Oxide Film on Aluminum," *Metal Progress, Vol.54, No.1*, July 1948a, p.35.


Table 3.1.1: Hydrogen Evolution Parameters for m5N Al and 6061-T6 Al at 30°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Tafel Slope $B$; SD (V)</th>
<th>Intercept $B$; SD (V)</th>
<th>$i_o$ (A/sqcm)</th>
<th>Current Range (log $i$ [A/sqcm])</th>
</tr>
</thead>
<tbody>
<tr>
<td>m5N Al</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.101; 0.005</td>
<td>-2.183; 0.023</td>
<td>7.79 E-16</td>
<td>-5 &lt; log $i$ &lt; -3</td>
</tr>
<tr>
<td>m5N Al</td>
<td>3.15 wt% NaCl</td>
<td>-0.120; 0.006</td>
<td>-2.197; 0.028</td>
<td>1.77 E-13</td>
<td>-6 &lt; log $i$ &lt; -4</td>
</tr>
<tr>
<td>6061-T6 Al</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.0609; 0.0030</td>
<td>-1.700; 0.009</td>
<td>9.19 E-18</td>
<td>-5 &lt; log $i$ &lt; -3</td>
</tr>
<tr>
<td>6061-T6 Al</td>
<td>3.15 wt% NaCl</td>
<td>-0.0988; 0.0121</td>
<td>-1.806; 0.047</td>
<td>2.59 E-12</td>
<td>-5 &lt; log $i$ &lt; -3</td>
</tr>
</tbody>
</table>

* $i_o$ was obtained by Tafel extrapolation that was based on $E$ (hydrogen evolution) = -0.662 V/sce, which was calculated using pH = 7, hydrogen gas pressure = 1 atm, and $T$ = 30°C.
(b) Passivation by a film of böhmite Al₂O₃·H₂O.

Figure 3.1.1: Pourbaix diagram of Al at 25°C for unit activities with böhmite as the stable oxide. Reference: Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Corrosion Engineers, 1974, p.172.
Figure 3.1.3: Cathodic polarization diagram of ultra pure Al (99.999 %) in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.509 Vsce, SD = 0.015 V; Avg time at open circuit = 1.45 h, SD = 0.24 h.
Figure 3.1.4: Cathodic polarization diagram of ultra pure Al (99.999 %) in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.475 Vsce, SD = 0.025 V; Avg time at open circuit = 1.20 h, SD = 0.33 h.
Figure 3.1.5: Cathodic polarization diagram of ultra pure Al (99.999 %) in deaerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.403 Vsce, SD = 0.091 V; Avg time at open circuit = 1.08 h, SD = 0.11 h.
Figure 3.1.6: Cathodic polarization diagram of ultra pure Al (99.999%) in aerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg. Ecorr = -1.255 V SCE; SD = 0.122 V; Avg. time at open circuit = 0.99 h; SD = 0.17 h.
Figure 3.1.7: Cathodic polarization diagram of 6061-T6 Al in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.299 Vsce, SD = 0.008 V; Avg time at open circuit = 1.20 h, SD = 0.14 h.
Figure 3.1.8: Cathodic polarization diagram of 6061-T6 Al in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 2 mV/s; Avg Ecorr = -0.650 V SCE, SD = 0.000 V; Avg time at open circuit = 2.37 min, SD = 1.21 min.
Figure 3.19: Cathodic polarization diagram of 6061-T6 Al in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.025 V, SD = 0.043 V; Avg time at open circuit = 1.04 h, SD = 0.08 h.
Figure 3.1.10: Cathodic polarization diagram of 6061-T6 Al in deaerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.161 V; Avg 0.078 V; Avg time at open circuit = 1.81 h; SD = 0.65 h.
Figure 3.1.11: Cathodic polarization diagram of 6061-T6 Al in aerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.733 Vscce, SD = 0.003 V; Avg time at open circuit = 2.72 h, SD = 0.49 h.
Figure 3.1.12: Cathodic polarization diagrams in 0.5 M sodium sulfate and 3.15 wt% sodium chloride solutions of pH 7 at 30°C. The scan rate was 0.1 mV/s except for the diagram at 2 mV/s, as shown in the legend.
Figure 3.1.13: Anodic polarization diagram of ultra pure Al (99.999 %) in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.431 Vsc, SD = 0.012 V; Avg time at open circuit = 1.35 h, SD = 0.37 h.
Figure 3.1.14: Anodic polarization diagram of ultra pure Al (99.999 %) in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.476 Vsce, SD = 0.012 V; Avg time at open circuit = 1.56 h, SD = 0.42 h.
Figure 3.1.15: Anodic polarization diagram of ultra pure Al (99.999%) in deaerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s. Avg Ecorr = -1.391 V vsce, SD = 0.030 V; Avg time at open circuit = 1.27 h, SD = 0.22 h.
Figure 3.1.16: Anodic polarization diagram of ultra pure Al (99.999 %) in aerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.409 V sce, SD = 0.015 V; Avg time at open circuit = 1.23 h, SD = 0.21 h.
Figure 3.1.17: Anodic polarization diagrams of ultra pure Al (99.999 %) in 0.5 M sodium sulfate and 3.15 wt% sodium chloride solutions of pH 7 at 30°C. Scan rate = 0.1 mV/s.
Figure 3.1.18: Anodic polarization diagram of 6061-T6 Al in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.256 Vsce, SD = 0.010 V; Avg time at open circuit = 0.59 h, SD = 0.09 h.
Figure 3.1.19: Anodic polarization diagram of 6061-T6 Al in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.122 V; SD = 0.011 V; Avg time at open circuit = 1.13 h, SD = 0.22 h.
Figure 3.1.20: Anodic polarization diagram of 6061-T6 Al (small electrode: 0.0233 sq cm) in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.978 Vsce, SD = 0.030 V; Avg time at open circuit = 1.07 h, SD = 0.23 h.
Figure 3.1.21: Anodic polarization diagram of 6061-T6 Al in deaerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -1.228 V SCE, SD = 0.029 V; Avg time at open circuit = 0.67 h, SD = 0.18 h.
Figure 3.1.22: Anodic polarization diagram of 6061-T6 Al in aerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.737 V SCE, SD = 0.002 V; Avg time at open circuit = 1.61 h, SD = 0.89 h.
Figure 3.1.23: Anodic polarization diagrams of 6061-T6 Al in 0.5 M sodium sulfate and 3.15 wt% sodium chloride solutions of pH 7 at 30°C. Scan rate = 0.1 mV/s. Sm.A. denotes small-area electrode (Section 3.1.2).
Figure 3.1.24: Avg open circuit potential (from at least three experiments) vs. time diagrams of ultra pure Al (99.999 %) and 6061-T6 Al in deaerated and aerated 0.5 M sodium sulfate and 3.15 wt% sodium chloride solutions of pH 7 at 30°C.
3.2 ELECTROCHEMISTRY AND CORROSION OF HIGH-MODULUS PITCH-BASED GRAPHITE FIBERS IN NEAR NEUTRAL 0.5 M Na₂SO₄ AND 3.15 wt% NaCl

3.2.1 Introduction

In addition to the electrochemistry of matrix materials, it is necessary in this program to understand the electrochemical behavior of the high-modulus, pitch-based graphite fibers. Answers were sought for two questions: 1) Do graphite fibers promote galvanic corrosion of metals with which they are in contact; and 2) What are the corrosion characteristics of the graphite fibers? In pursuit of these questions, electrochemical data on H₂ evolution, O₂ reduction, and carbon oxidation of high-modulus pitch-based graphite fibers were obtained at 30°C. In addition to the electrochemical data, the cathodic and anodic gases were analyzed for thermodynamically stable carbon compounds. Methane, which is thermodynamically stable at cathodic potentials, was not detected during cathodic polarization of graphite fiber electrodes; however, CO₂ and CO were detected during anodic polarization. There was also evidence for the formation of a nonconducting surface oxide on graphite fibers during extensive anodic polarization. Also, the electrochemical properties of graphite fiber electrodes were found to be sensitive to prior electrochemical treatment.

Neutral 0.5 M Na₂SO₄ was chosen to simulate fresh water, and neutral 3.15 wt% NaCl was chosen to simulate seawater. Potentiodynamic polarization was used to acquire electrochemical data in the form of polarization diagrams which can be used in mixed-electrode models to predict corrosion behavior of composite materials. A slow scan rate (0.1 mV/s) was used to obtain near steady-state properties. Cathodic and anodic gases which were evolved during galvanostatic polarization were analyzed for specie identification by chemical reactions in gas detector tubes.

Comprehensive overviews on electrochemical properties of carbon and graphite are available from Kinoshita [1988a] and Randin [1976]. Information regarding mechanical properties [Weeton, Peters, & Thomas, 1987; Delmonte, 1981], physical properties [Kinoshita, 1988a; Weeton, et al., 1987; Delmonte, 1981] and applications [Weeton, et al., 1987; Delmonte, 1981] of graphite fibers are also available. Background information for this research project is presented in the following paragraphs. A brief discussion on pitch-based graphite fiber microstructure will be followed by a discussion on electrochemical reactions that pertain to graphite electrochemistry in the test environments of this study. The electrochemical reactions and standard potentials (E°) were cited from the Atlas of Electrochemical Equilibria in
Aqueous Solutions [Pourbaix, 1974], but in the present document, the standard potentials are reported with respect to a saturated calomel reference electrode ($V_{SCE}$).

The microstructure of pitch-based graphite fibers is described by Dieendorf [1984] as having a core of radially oriented basal graphite planes which is surrounded circumferentially by an outer layer of basal planes; thus, the microstructure in the plane perpendicular to the fiber axis has a spoke-like structure surrounded by an onion skin structure (Figure 3.2.1). The cross section exposing the spoke and onion skin structures was electrochemically examined in this study.

There are three types of electrochemical processes in which graphite can be involved. Graphite can act as an inert electrode, can be consumed in the electrochemical reaction to form carbon compounds, or can be intercalated with ions to form graphite compounds. All three processes can occur simultaneously. The relevant electrochemical reactions are discussed below, beginning with cathodic and ending with anodic reactions.

During cathodic polarization, graphite can act as an inert electrode for $H_2$ evolution and $O_2$ reduction where the equilibrium reactions are

$$2H^+ + 2e^- = H_2, \quad E^* = -0.241 \text{ V}_{SCE} \quad (3.2.1)$$

and

$$O_2 + 4H^+ + 4e^- = 2H_2O, \quad E^* = 0.987 \text{ V}_{SCE} \quad (3.2.2).$$

Also during cathodic polarization, graphite can be reduced to $CH_4$,

$$C + 4H^+ + 4e^- = CH_4, \quad E^* = -0.373 \text{ V}_{SCE} \quad (3.2.3),$$

or be reduced to graphite compounds by the intercalation of cations. Information on the intercalation of cations during cathodic polarization can be obtained from Kinoshita [1988a].

During anodic polarization, graphite can act as an inert electrode for $H_2$ oxidation (3.2.1), and $O_2$ (3.2.2) and $Cl_2$ evolution. The equilibrium reaction for $Cl_2$ evolution is

$$Cl_2 + 2e^- = 2Cl^-, \quad E^* = 1.154 \text{ V}_{SCE} \quad (3.2.4).$$

Also, various carbon compounds may form during graphite oxidation [Van Muylder and Pourbaix, 1974], but $CO_2$ and $CO$ are believed to be the dominant reactions [Kinoshita, 1988b]. The equilibrium reactions for $CO_2$ and $CO$ are
\[
\text{CO}_2 + 4\text{H}^+ + 4e^- = \text{C} + 2\text{H}_2\text{O}, \quad E^* = -0.034 \text{V}_{\text{SCE}} \quad (3.2.5)
\]

and

\[
\text{CO} + 2\text{H}^+ + 2e^- = \text{C} + \text{H}_2\text{O}, \quad E^* = 0.277 \text{V}_{\text{SCE}} \quad (3.2.6),
\]

but CO is thermodynamically unstable with respect to CO\(_2\) by the following reaction:

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- = \text{CO} + \text{H}_2\text{O}, \quad E^* = -0.344 \text{V}_{\text{SCE}} \quad (3.2.7)
\]

Intercalation of anions is also possible, and the reader can consult Kinoshita [1988a] for further details. The intercalation compound known as graphite oxide, however, is of particular interest to us. Graphite oxide is nonconducting [Kinoshita, 1988c] and forms during anodic oxidation of graphite in acid or neutral electrolytes with an oxygen-containing anion such as in H\(_2\)SO\(_4\), HNO\(_3\), or NaClO\(_3\) [Brown and Storey, 1928]. Graphite oxide is of particular interest because the 0.5 M Na\(_2\)SO\(_4\) solution contains SO\(_4^{2-}\) anions and becomes acidic near the graphite electrode during extensive anodic polarization; thus, the formation of graphite oxide in 0.5 M Na\(_2\)SO\(_4\) is anticipated.

3.2.2 Materials

Electrodes were fabricated from high-modulus graphite fibers (Thornel P100: pitch-based with elastic modulus equal to 690 GPa). Fifteen tows (2000 fibers/tow) of about 10 \(\mu\)m diameter fibers were aligned unidirectionally and infiltrated with an epoxy resin (EPON 828 RESIN, Miller-Stephenson Chemical Co., Inc.), and cured at room temperature for at least 12 hours and then subsequently cured at 70°C for 2 more hours. The resulting product, a graphite/epoxy composite rod, was made into electrodes by dissecting the rod perpendicularly to the axis of the fibers. The electrodes were polished to a 0.5 \(\mu\)m finish with gamma alumina powder and rinsed with 18 MΩ•cm water about 5 minutes prior to immersion in the aqueous solutions.

Experiments were conducted in 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl solutions of about pH 7. The solutions were prepared from 18 MΩ•cm water and analytical grade reagents. The solutions were thermostated to 30 ± 0.1°C.

Solutions were deaerated by sparging with pre-purified hydrogen or pre-purified nitrogen gas. The type of gas used in deaeration is specified on all diagrams. Solutions were aerated by sparging with 19.5 to 23.5% oxygen balanced with nitrogen.
3.2.3 Instrumentation and Procedures

3.2.3.1 Polarization

Polarization of the graphite electrodes was conducted with either a Model 273 EG&G Princeton Applied Research (PAR) potentiostat/galvanostat or a Model 173 EG&G PAR potentiostat/galvanostat equipped with a Model 376 EG&G PAR logarithmic current converter. When measuring currents as low as 1 nA, both instruments were within about 10% of the true current as determined by the following procedure. The accuracy of the current measurement was assessed by inserting a 1 GΩ (2 % tolerance) resistor between the working electrode terminal and the auxiliary terminal (to which the reference terminal was connected) of the potentiostat. A potential difference of 1.000 V was set between the working and reference terminals which should theoretically produce a current flow from the auxiliary electrode equal to 1.000 nA assuming 0 % tolerance of the 1 GΩ resistor. The measured current was then compared to the theoretical 1.000 nA value.

The current densities from the graphite electrodes were calculated by assuming an average fiber diameter of 10 μm. Since the graphite electrodes were found to be sensitive to prior electrochemical histories, new electrodes were used when properties of virgin fibers were sought. The use of new electrodes also prevented the possibility of solution contamination by the deintercalation of ions.

In generating potentiodynamic polarization diagrams, the graphite electrodes were allowed to stabilize at their corrosion potentials (E_{corr}) and were subsequently polarized at a rate of 0.1 mV/s. Polarization diagrams with standard deviation bars were generated from at least three individual polarization diagrams; the average logarithm of the current density (log i [A/cm²]) was plotted as a function of potential, and the peak-to-peak width between standard deviation bars is equal to two times the standard deviation of log i. The average values of E_{corr}, the average time that the electrodes were in the open circuit condition prior to polarization, and the standard deviation (SD) of these parameters are also tabulated in the caption of the polarization diagrams. Polarization diagrams without standard deviation bars represent single experiments, excluding the graphs that contain many diagrams where standard deviation bars were omitted to avoid confusion.

Tafel slopes (β) were calculated between specific current ranges by taking the average Tafel slope from a set of individual polarization diagrams; this produces a result different from that obtained by measuring the Tafel slope on the polarization diagrams where the average log i is
plotted as a function of potential (as described in the preceding paragraph). The least-squares method was used to calculate the Tafel slopes by fitting linear regions of individual polarization diagrams to straight lines having the form

\[ E = \beta \log i + B \]  

(3.2.8)

where \( E \) is in \( V_{\text{SCE}} \), \( \beta \) in \( V \) per decade of \( i \), \( i \) in \( A/cm^2 \), and \( B \) in \( V \). Exchange current densities were determined by Tafel extrapolation.

3.2.3.2 Gas Detection

The gases liberated from the graphite electrodes during cathodic and anodic galvanostatic polarization were analyzed for \( \text{CH}_4 \), \( \text{CO}_2 \), and \( \text{CO} \) content. The liberated gases were collected in a nitrogen atmosphere of known volume above the solution of a gas-tight cell. When gas generation was completed, the nitrogen atmosphere was examined for the presence of \( \text{CH}_4 \) (after cathodic polarization) and \( \text{CO}_2 \) and \( \text{CO} \) (after anodic polarization). The electrodes were under galvanostatic control either cathodically or anodically at 0.255 \( A/cm^2 \) for 4 hours. The graphite electrodes were positioned approximately 2 mm below the surface of the solution so that the liberated gases were transferred rapidly from the electrode surface to the nitrogen atmosphere. Separate experiments were conducted for the analysis of each gas, and each experiment was duplicated. The measured potential (without IR correction), \( E_m \), of the electrodes was monitored as a function of time during the gas detection experiments, as well as the real potential (with IR correction), \( E_r \), by using the current interrupter technique [Kuhn, 1987].

Chemical analysis of the gases was performed by chemical reactions of the gases with compounds in gas detector tubes (Dräger gas detector tubes).

To detect \( \text{CH}_4 \), a natural-gas detector tube sensitive to \( \text{CH}_4 \), \( \text{C}_2\text{H}_6 \), and \( \text{C}_3\text{H}_8 \) was used. In natural-gas detection, natural gas present is oxidized to \( \text{CO} \) with fuming sulfuric acid and potassium permanganate. The generated \( \text{CO} \) then reacts with iodine pentoxide and sulfuric acid which results in a color change of the white detector tube to a brownish-green to grayish-violet color. Only semi-quantitative analysis is possible. Carbon monoxide is also detected with these tubes. Other hydrocarbons such as gasoline, benzene, and alcohol are trapped in a pre-tube; thus, these gases do not interfere with \( \text{CH}_4 \) detection [Dräger Instructions, 1986].

In \( \text{CO}_2 \) detection, any \( \text{CO}_2 \) present reacts with a hydrazine compound; this reaction is indicated by a color change of the white detector tube to a blue-violet color by a redox indicator (crystal
violet). Quantitative analysis is possible. Other gases and vapors are said not to interfere with \( \text{CO}_2 \) detection [Dräger Instructions, 1987].

In CO detection, any CO present reacts with iodine pentoxide, selenium dioxide, and fuming sulfuric acid which results in a color change of the white detector tube to a brownish-green color. Quantitative analysis is possible. Although other gases and vapors such as petroleum, benzene, and hydrogen sulfide can in principle interfere with the CO detection, a pre-cleansing layer is designed into the tubes to eliminate these interfering gases. Acetylene will give a false indication of CO presence [Dräger Instructions, 1985]. Contamination or generation of these interfering gases was not anticipated during anodic polarization.

3.2.4 Results

3.2.4.1 Cathodic Polarization

The graphite electrodes were cathodically polarized in deaerated (H\(_2\)-sparged) and aerated solutions of 0.5 M Na\(_2\)SO\(_4\) and 3.15\% NaCl at 30°C. The individual cathodic polarization diagrams are shown in Figures 3.2.2 through 3.2.5, and compared in Figure 3.2.6. The results from the cathodic gas detection experiment are also presented here.

The polarization diagrams from experiments in deaerated 0.5 M Na\(_2\)SO\(_4\) (Figure 3.2.2) had three distinct regions: Region A (log \( i \) [A/cm\(^2\)] < -6) had characteristics of concentration polarization while regions B (-6 < log \( i \) < -5) and C (-5 < log \( i \) < -3) had Tafel characteristics. Similarly, in Figure 3.2.4, the polarization diagram from experiments in deaerated 3.15 wt\% NaCl had the A-type (log \( i \) < -6) and C-type (-6 < log \( i \) < -3) regions of Figure 3.2.2, but lacked the intermediate B-type region. Straight lines were fit to the Tafel regions and values for \( \beta \) and \( B \) were determined (Table 3.2.1). The exchange current density for the reversible hydrogen reaction (3.2.1) was also determined by Tafel extrapolation (Table 3.2.1).

Polarization diagrams of the graphite electrodes in aerated 0.5 M Na\(_2\)SO\(_4\) (Figure 3.2.3) and 3.15 wt\% NaCl (Figure 3.2.5) were similar. Tafel behavior (-7 < log \( i \) < -5) was followed by concentration polarization (log \( i \) > -5). The values for \( \beta \) and \( B \) were determined (Table 3.2.2), and accordingly, the exchange current density for the reversible oxygen reaction (3.2.2) was extrapolated.

During cathodic, galvanostatic polarization, substantial gas evolution was observed, but CH\(_4\) was not detected. A minimum of about 0.2 cm\(^3\) of CH\(_4\) (corresponding to 3.6\% of the
cathodic charge) or 0.02 cm³ of C₂H₆ or C₃H₈ was required for detection of natural gas. During the galvanostatic polarization, the real potential of the graphite electrode was about 2.03 V with an associated IR drop of about 0.29 V. The real potential and the IR drop were relatively constant during the 4 hours of polarization. The electrodes appeared to be physically intact after polarization, but appeared to become encrusted during observation in an optical microscope (Figure 3.2.7). The electrochemical properties of these cathodically polarized electrodes were altered, and Figure 3.2.8 shows that there is little similarity in the anodic polarization diagram of a previously cathodically polarized electrode compared to those of new electrodes.

3.2.4.2 Anodic Polarization

The graphite electrodes were anodically polarized at 30°C in 0.5 M Na₂SO₄ that was deaerated (with H₂ or N₂) or aerated, and in 3.15 wt% NaCl deaerated with H₂. The individual anodic polarization diagrams are shown in Figures 3.2.9 through 3.2.12, and compared in Figure 3.2.13. The results from the anodic gas detection experiments are also presented here.

The anodic polarization diagrams of all experiments over the entire range from 10⁻⁸ to 10⁻³ A/cm² were under activation control and very similar (Figure 3.2.13); however, the Tafel slope varied over the entire regime, and accordingly was not tabulated.

Carbon dioxide and carbon monoxide were detected in the anodic gas that was generated under galvanostatic control at 0.255 A/cm² for 4 hours. Based on reactions (3.2.5) and (3.2.6), at least 25.2% of the charge was utilized for CO₂ formation, and 1.3% of the charge for CO formation. The 25.2% and 1.3% are minimum values since the 0.5 M Na₂SO₄ solutions were not analyzed for dissolved CO₂ or CO. The graphite electrodes were partially consumed (Figure 3.2.14) during anodic polarization.

During the galvanostatic examinations, the measured potential fluctuated substantially with time, but had a characteristic shape with four regions labeled as A, B, C, and D in Figure 3.2.15. Subtraction of the IR drop from the tortuous Eₘ₋ₜ curves showed that the real potential was relatively constant (Figure 3.2.16).

The electrochemical characteristics of the graphite electrodes were altered by the galvanostatic polarization treatment during the anodic-gas detection experiments. Even after grinding and repolishing the surface of the electrodes such that no physical damage was apparent, under an optical microscope at a magnification of 500x, the open circuit potentials were significantly
more positive than those of typical new electrodes in 0.5 M \( \text{Na}_2\text{SO}_4 \) deaerated with \( \text{H}_2 \). Figure 3.2.17 shows that it required removing a depth of 3.0 mm from the surface of a used electrode to regain the characteristic \( E_{\text{corr}} \)-time behavior of new electrodes. However, after only 0.5 mm was removed from the surface, there was no visual trace of fiber degradation at 500x.

3.2.5 Discussion

3.2.5.1 Cathodic polarization

No attempt was made to identify hydrogen evolution mechanisms, but comments were made regarding obvious characteristics. Methane was not detected, but other data generated as a result of the gas-detection experiments revealed that changes occurred in the electrodes. Examination of anodic polarization diagrams was required to reveal these changes.

In the cathodic polarization diagrams generated in the deaerated solutions (Figures 3.2.2 and 3.2.4), region A had characteristics of concentration polarization which was apparently the result of \( \text{O}_2 \) contamination. An estimated 3.0 ppb (by wt) of dissolved \( \text{O}_2 \) would cause the diffusion-limited current density of \( 2.3 \times 10^{-7} \text{ A/cm}^2 \), measured at \(-1 \text{ V}_{\text{sce}} \) from the polarization diagram produced in the deaerated 3.15 wt\% NaCl solution (Figure 3.2.4). The approximation was made utilizing Fick's first law of diffusion and the relationship derived from it:

\[ \frac{i_1}{i_2} = \frac{C_1}{C_2} \quad (3.2.9) \]

In (3.2.9), \( i \) is the diffusion-limited current density, \( C \) the concentration of dissolved \( \text{O}_2 \), and the subscripts refer to separate experiments. The following assumptions were required: linear \( \text{O}_2 \) concentration gradient, constant \( D_{\text{O}_2} \), zero surface concentration of \( \text{O}_2 \), and constant diffusion layer thickness. The values for \( i_1 (4.1 \times 10^{-4}) \) and \( i_2 (2.3 \times 10^{-7}) \) were read from Figures 3.2.5 and 3.2.4, respectively, at \(-1 \text{ V}_{\text{sce}} \). \( C_1 \) was estimated to be 5.37 ppm (by wt) from data on seawater of chlorinity 20 g/kg at 30°C in equilibrium with air saturated with water vapor [Redfield, 1948]; accordingly, \( C_2 \) was calculated to be 3.0 ppb.

The Tafel slopes of region C and the extrapolated values of \( i_o \) (Table 3.2.1) are within the range of compiled values (8: 0.11 - 0.22 V/dec; \( i_o: 2.0 \times 10^{-13} - 8.8 \times 10^{-7} \text{ A/cm}^2 \)) of various authors taken from the reviews of Kinoshita [1988d] and Randin [1976b] for the case of acidic electrolytes. In alkaline electrolytes ranging in NaOH concentration from about 20 to 40 wt\%, Rousar, et al. [1974] measured Tafel slopes ranging from 0.117 to 0.162 V/dec.
and extrapolated values for $i_o$ ranging from $1.5 \times 10^{-3}$ to $2.1 \times 10^{-6}$ A/cm$^2$ on four types of graphite. In region B corresponding to the deaerated 0.5 M Na$_2$SO$_4$ solution, $\beta$ and $i_o$ were much lower than the values published above; however, $\beta$ is still within the range of theoretical values based on hydrogen evolution mechanisms. For example, $\beta$ as low as 0.03 and 0.04 V/dec could be the result of 1) discharge followed by rate-determining chemical desorption, and 2) discharge followed by rate-determining electrode desorption, respectively [Bockris and Reddy, 1970]. Since a B-type region was not observed in the 3.15% NaCl solution, it is unlikely that region B was caused by the intercalation of cations since both solutions contained identical cations; namely, Na$^+$ and H$^+$.  

The open circuit potentials of the graphite fibers in the aerated solutions were about 0.6 V active to the reversible O$_2$ potential (of these aerated solution). Others [Thiele, 1932a; Thiele, 1932b; Thiele, 1934; Kordesch, 1968] have also reported that open circuit potentials were about 0.1 to 0.3 V active to the reversible potential in oxygen saturated solutions. The Tafel slopes (Table 3.2.2) were also in the range of published values (-0.03 to -0.16 V/dec) [Tarasevich, et al., 1968; Tarasevich, Sabirov, and Burshtein, 1971; Yeager and Krouse, 1964; Morcos and Yeager, 1970; Appleby and Marie, 1979] for carbon and graphite electrodes in acid and basic solutions.

The absence of detectable levels of CH$_4$ and physical degradation of the graphite fibers during galvanostatic cathodic polarization at 0.255 A/cm$^2$ for 4 hours was evidence of substantial inertness of the fibers. Note that under these conditions of cathodic polarization, the pH of the solution near the electrode surface was much higher than that of the bulk solution. The readiness of the real potential and IR drop throughout the entire experiment also suggested that the mechanism of the cathodic reaction did not change and that the resistivity of the graphite fibers did not increase significantly over the 4 hour period. However, subsequent anodic potentiodynamic polarization of the previously cathodically polarized electrode (in new solution) showed significantly larger anodic current densities than those of new electrodes (Figure 3.2.8) until all curves merged at about 1.5 V$_{SCE}$. The larger anodic current densities are indicative of electrochemical oxidation of a substance formed during cathodic polarization. The changes in the fibers which occurred in real time under the optical microscope (section 3.2.4.1) also indicated some form of graphite transformation, probably due to intercalation of cations.
3.2.5.2 Anodic Polarization

Several electrochemical oxidation reactions are possible in the various solutions examined, but similarity between the anodic polarization diagrams, despite experimentation in various solutions, led to the conclusion that CO$_2$ formation was the dominant reaction over the potential range studied. Carbon dioxide and carbon monoxide were detected in the anodic gas during galvanostatic polarization, and additional results indicated that a nonconducting surface oxide formed. Also, property changes occurred in the bulk of the fibers.

The anodic polarization diagrams (Figure 3.2.13) of the graphite electrodes in all solutions were identical within the limits of experimental scatter. Hydrogen oxidation was determined to be insignificant since sparging with H$_2$ did not increase anodic currents. Oxygen evolution was also found to be insignificant for the following reasons. At potentials active to 0.556 V$_{sce}$, O$_2$ evolution is thermodynamically impossible in the aerated sulfate solution, yet anodic currents were measured and were identical to those of the deaerated solutions; thus, anodic currents at potentials active to 0.556 V$_{sce}$ cannot be attributed to O$_2$ evolution. Furthermore, based on the assumption that only one mechanism for O$_2$ evolution operates at potentials noble to 0.556 V$_{sce}$ (in Figure 3.2.13), the slopes above 0.556 V$_{sce}$ are much too large for O$_2$ evolution in view of the extremely small O$_2$ exchange current densities (section 3.2.4.1). These findings are supported by those of anodic gas studies by Kokhanov and Milova [1969]. At a current density of 3.7 mA/cm$^2$ (which is slightly higher than the maximum of the polarization diagrams in Figure 3.2.13), Kokhanov and Milova found that O$_2$ accounted for only 3% of the current yield while CO$_2$ and CO accounted for 91% and 6%, respectively, in buffered phosphate solutions ranging from pH 1 to pH 6.7 at 50°C. The results of Kokhanov and Milova also show that CO$_2$ formation is dominant, and in agreement with the results in section 3.2.4.2 which showed that at 0.255 A/cm$^2$, CO formation was low (1.3% of the charge) and that of CO$_2$ was significantly higher (25.2% of the charge). Binder et al. [1964] also reported that during the oxidation of graphite below the reversible oxygen potential, 80% of the charge is utilized in CO$_2$ evolution while the remainder is used in the formation of oxygen-containing compounds. Binder et al. found those results to be independent of H$_2$SO$_4$ concentration (from 20 to 70%) or of phosphoric acid concentration (10 to 85%) from temperatures between 55 and 100°C. Finally, the similarity between the polarization curves from the 0.5 M Na$_2$SO$_4$ and 3.15 wt% NaCl solutions showed that the dominating anodic reaction could not have been the intercalation of anions. If anion intercalation was dominant, one would have expected SO$_4^{2-}$ intercalation to produce different
results than Cl⁻ intercalation. The evidence presented suggests that the dominating anodic reaction was CO₂ formation.

In the 3.15 wt% NaCl solution, at potentials noble to 0.965 V_{SCE}, Cl₂ evolution is thermodynamically possible assuming a P_{Cl₂} of 10⁻⁶ atm. However, since the anodic polarization diagram from the 3.15 wt% NaCl solution (Figure 3.2.13) was identical to those from the 0.5 M Na₂SO₄ solution, the oxidation of Cl⁻ was insignificant compared to CO₂ formation at current densities less than 10⁻³ A/cm².

During the anodic gas detection experiment at 0.255 A/cm², only about 26.5% of the charge was accounted for in the evolution of CO₂ and CO; thus, it was possible that the balance of charge was used in O₂ evolution and the formation of intercalation compounds. Also, as mentioned in the introduction, the SO₄²⁻ anions in the acidified solution adjacent to the anode make it conducive for the formation of nonconducting graphite oxide. Interestingly, large IR drops from the graphite electrodes (section 3.2.4.2) were observed, suggesting the formation of a nonconducting surface oxide.

The tortuous Eₘ-t behavior can be predicted by the modeling of a single fiber based on the relationship

\[ E_m = E_r + (IR)_{ele} + (IR)_{sol} \]  \hspace{1cm} (3.2.10)

and on the corrosion morphology of the fibers. The terms (IR)_{ele} and (IR)_{sol} are the IR drops in the electrode and solution, respectively. The implicit assumption in (3.2.10) is that the current is equally distributed among all fibers in the electrode. The model requires defining the resistance of the electrode as

\[ R = rI/S \]  \hspace{1cm} (3.2.11)

where \( r \) is the resistivity of the surface oxide, \( I \) is the thickness of the surface oxide film, and \( S \) is the area of the oxide film that is normal to the direction of current flow. Due to the low resistivity of P100 graphite fibers (250 x 10⁻⁶ Ω·cm) [Weeton, et al., 1987b], (3.2.11) implicitly assumes that the resistive contribution of the fiber bulk is negligible. The behavior of \( E_m \) as a function of time is best described by the time derivative of (3.2.10):

\[ \frac{dE_m}{dt} = \frac{dE_r}{dt} + \frac{(dI/S)dr}{dt} + rI/S(dI/dt) - rI/S^2(dS/dt) + rI/S(dI/dt) + d(IR)_{sol}/dt \]  \hspace{1cm} (3.2.12)
Some of the terms on the r.h.s. may be reduced to zero for the following reasons: a) \( \frac{dE_r}{dt} \) - considered negligible (Figure 3.2.16); b) \( \frac{dI}{dt} \) - due to galvanostatic polarization; c) \( \frac{d(IR)_{sol}}{dt} \) - a consequence of high solution conductivity. The resulting equation is simplified to

\[
\frac{dE_m}{dt} = (I/S)dr/dt + rI/S(dl/dt) - rI/S^2(dS/dt)
\] (3.2.13).

From (3.2.13) and the corrosion morphology of the fibers, a hypothesis for the \( E_m \)-t characteristics is described below and shown schematically in Figure 3.2.18. The increase in \( E_m \) in regions A and B (Figure 3.2.15) was attributed to the growth of an insulating surface oxide, rendering \( dr/dt \) and \( dl/dt \) positive (Figure 3.2.18). Also, in regions A and B, the rate of increase in surface area was considered negligible (i.e., \( dS/dt = 0 \)) because the corrosion morphology of the fibers (Figure 3.2.14) indicated that the increase in graphite surface area after extensive oxidation was primarily due to the formation of one large cavern along a sector of the fiber or along the fiber perimeter. Thus, during the initial stages of oxidation, the rate of increase in surface area from one embryonic cavern can be considered negligible (Figure 3.2.18). A maximum in \( E_m \) occurs when the increasing surface area balances the effect of the oxide film. In region C, as the cavern grows deeper and longer and \( r \) and \( l \) reach steady state, \( E_m \) decreases. In region D, assuming that the cavern widens rather than deepens (Figure 3.2.18), a new steady state in \( E_m \) may be achieved since \( dS/dt \) becomes smaller. Also, as the surface area increases, the \( dS/dt \) term is attenuated by its coefficient due to \( S^2 \) in the denominator; whereas, in the other terms, attenuation is less severe since only \( S \) is in the denominator.

Interestingly in 1961, Ksenzhek and Chaikovskaya [1962] recorded potential-time curves that were similar in shape to those in Figure 3.2.15 during anodic galvanostatic polarization of porous graphite in 1 N \( H_2SO_4 \) at 20°C. They did not specify the reference electrode, or mention if IR losses were considered, and reported the current density as 15 \( \mu A \) per cubic centimeter of graphite. The fluctuations in potential which Ksenzhek and Chaikovskaya measured were significantly smaller in magnitude than those in Figure 3.2.15 and their experiment ran for many hours; however, the shape of the initial region of their curve was identical to that in Figure 3.2.15. They attributed the maximum in the E-t curve to an electrical activation energy required for the nucleation of a surface oxide, and concluded that the plateau beyond the maximum was a characteristic of the surface oxide.

Finally, during the galvanostatic anodic polarization, as part of the anodic gas detection experiments, it appears that intercalates penetrated the graphite fiber electrodes to a depth of
about 3 mm. Evidence for this is the significant alteration of $E_{corr}$ characteristics following anodic polarization (Figure 3.2.17). This showed the relative ease at which the electrochemical properties of the fibers can be modified.

3.2.6 Conclusions

Electrochemical examination has given data on $H_2$ evolution, $O_2$ reduction, and carbon oxidation of virgin graphite fibers in 0.5 M $Na_2SO_4$ and 3.15% NaCl solutions at 30°C. In the context of the research project on the corrosion of graphite fiber metal-matrix composites, these results have immediate utility and implications. For example, galvanic corrosion rates between graphite fibers and metals can be predicted by using the polarization diagrams, and since graphite fibers are susceptible to anodic oxidation, graphite fiber/aluminum-matrix composites should not be anodized. Also of importance was the observation that the fiber properties were easily altered by electrochemical treatment, probably a result of the intercalation of ions. This observation infers that conventional material treatments may not be satisfactory for graphite fiber composites. For example, an encounter of a graphite fiber composite with an incompatible chemical might not be remedied by cleansing in the conventional sense since the fibers may act as pipelines for undesirable substances into the bulk of the composite. This seemingly unfortunate behavior of the fibers, however, may also be advantageous. The relative ease in which ions are intercalated into graphite can be used to tailor fiber properties. For example, to prevent galvanic corrosion in graphite fiber/aluminum-matrix composites, one might attempt to suppress $O_2$ reduction on the graphite fibers through an intercalation treatment.

3.2.7 References


Table 3.2.1: Hydrogen Evolution Parameters for P100 Graphite Fibers at 30°C

<table>
<thead>
<tr>
<th>Solution</th>
<th>Tafel Slope β; SD (V/dec)</th>
<th>Intercept B; SD (V)</th>
<th>io (A/sqcm) *</th>
<th>Current Range (log i [A/sqcm])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M Sodium Sulfate</td>
<td>-0.060; 0.023</td>
<td>-1.588; 0.149</td>
<td>3.598 E-16</td>
<td>-6 &lt; log i &lt; -5</td>
</tr>
<tr>
<td>0.5 M Sodium Sulfate</td>
<td>-0.160; 0.011</td>
<td>-2.080; 0.028</td>
<td>1.446 E-9</td>
<td>-5 &lt; log i &lt; -3</td>
</tr>
<tr>
<td>3.15 wt% NaCl</td>
<td>-0.153; 0.011</td>
<td>-2.165; 0.035</td>
<td>1.437 E-10</td>
<td>-6 &lt; log i &lt; -3</td>
</tr>
</tbody>
</table>

* — io was obtained by Tafel extrapolation that was based on E (hydrogen evolution) = -0.662 V, which was calculated using pH = 7, hydrogen gas pressure = 1 atm, and T = 30°C.

Table 3.2.2: Oxygen Reduction Parameters for P100 Graphite Fibers at 30°C

<table>
<thead>
<tr>
<th>Solution</th>
<th>Tafel Slope β; SD (V/dec)</th>
<th>Intercept B; SD (V)</th>
<th>io (A/sqcm) *</th>
<th>Current Range (log i [A/sqcm])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M Sodium Sulfate</td>
<td>-0.0817; 0.0033</td>
<td>-0.6377; 0.0269</td>
<td>2.442 E-15</td>
<td>-7.25 &lt; log i &lt; -5.00</td>
</tr>
<tr>
<td>3.15 wt% NaCl</td>
<td>-0.0810; 0.0043</td>
<td>-0.6700; 0.0433</td>
<td>7.433 E-16</td>
<td>-7.00 &lt; log i &lt; -5.00</td>
</tr>
</tbody>
</table>

* — io was obtained by Tafel extrapolation that was based on E (oxygen reduction) = 0.556 V, which was calculated using pH = 7, oxygen gas pressure = 0.215 atm, and T = 30°C.
Figure 3.2.1: Cross-sectional microstructure of high-modulus pitch-based graphite fiber. The arrows point to graphite basal planes. The fiber axis is perpendicular to the plane of the page.
Figure 3.2.2: Cathodic polarization diagram of P100 graphite fibers in deaerated (with hydrogen) 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.197 Vsce, SD = 0.072; Avg time at open circuit = 2.06 h, SD = 1.14.
Figure 3.2.3: Cathodic polarization diagram of P100 graphite fibers in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.020 Vsce, SD = 0.007 V; Avg time at open circuit = 2.20 h, SD = 0.12 h.
Figure 3.2.4: Cathodic polarization diagram of P100 graphite fibers in deaerated (with hydrogen) 3.15 wt\% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg $E_{corr} = -0.348$ V\text{SCE}, SD = 0.010 V; Avg time at open circuit = 2.80 h, SD = 0.24 h.
Figure 3.2.5: Cathodic polarization diagram of P100 graphite fibers in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.070 Vsce, SD = 0.007 V; Avg time at open circuit = 2.98 h, SD = 0.41 h.
Figure 3.2.6: Comparison of cathodic polarization diagrams of P100 graphite fibers in various neutral solutions at 30°C. Scan rate = 0.1 mV/s.
Figure 3.2.7: Micrographs of a previously cathodically polarized graphite/epoxy composite electrode showing changes occurring under an optical microscope. Subsequent to cathodic polarization, the electrode was lightly polished for less than one minute (with 0.05 μm alumina powder and water) and dried with a burst of dichlorodifluoromethane gas. The time shown below the micrographs corresponds to the elapsed time between polishing and picture taking. The electrode was galvanostatically polarized at 0.255 A/cm$^2$ for 4 h in deaerated (with N$_2$) 0.5 M Na$_2$SO$_4$ of pH 7 at 30°C.
Figure 3.2.8: Comparison of the anodic polarization diagram of a previously cathodically polarized P100 graphite fiber electrode to those of new P100 graphite fiber electrodes. The electrode pretreatment entailed galvanostatic polarization at 0.255 A/sqcm for 4 h in 0.5 M sodium sulfate of pH 7 at 30°C, followed by baking at 75°C for 12 h.
Figure 3.2.9: Anodic polarization diagram of P100 graphite fibers in deaerated (with hydrogen) 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.190 Vsc, SD = 0.064 V; Avg time at open circuit = 2.21 h, SD = 1.11 h.
Figure 3.2.10: Anodic polarization diagram of P100 graphite fibers in deaerated (with nitrogen) 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s. Ecorr = -0.197 Vsce. Time at open circuit potential = 2.56 h.
Figure 3.2.11: Anodic polarization diagram of P100 graphite in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.061 Vsc, SD = 0.006 V; Avg time at open circuit = 2.90 h; SD = 1.27 h. (Averaged from 2 experiments)
Figure 3.2.12: Anodic polarization diagram of P100 graphite fibers in deaerated (with hydrogen) 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.353 Vsce, SD = 0.016 V; Avg time at open circuit = 2.72 h, SD = 1.12 h.
Figure 3.2.13: Comparison of anodic polarization diagrams of P100 graphite fibers in various neutral solutions at 30°C. Scan rate = 0.1 mV/s.
Figure 3.2.14: This SEM micrograph shows the dissolution morphology of high-modulus pitch-based graphite fiber electrodes induced by anodic polarization. Polarization of the electrodes was conducted under galvanostatic control at 0.255 A/cm² for 4 h in deaerated (with N₂) 0.5 M Na₂SO₄ of pH 7 at 30°C.
Figure 3.2.15: This diagram shows the measured potential (Em) of P100 graphite fibers during galvanostatic anodic polarization at 0.255 A/sqcm in deaerated (with nitrogen) 0.5 M sodium sulfate of pH 7 at 30°C. Regions A, B, C, and D are referred to in the text.
Figure 3.2.16: This diagram shows the measured (Em) and real (Er) potentials of P100 graphite fibers during galvanostatic anodic polarization at 0.255 A/sqcm in deaerated (with nitrogen) 0.5 M sodium sulfate of pH 7 at 30°C.
Figure 3.2.17: Permanent change in $E_{\text{corr}}$ characteristics of P100 graphite fibers after galvanostatic anodic polarization at 0.255 A/sqcm for 4 h in neutral 0.5 M sodium sulfate at 30°C deaerated with nitrogen. $E_{\text{corr}}$ characteristics return to those of new electrodes as more graphite is ground away from the surface.
Regime of Increasing $E_m$
(Regions A and B in Figure 3.2.15)

Stage 1: Film Formation
Film of Resistivity $r$
Electrode Surface of Area $S$

\[
\frac{dE_m}{dt} = II S \frac{\partial r}{\partial t} + r l \frac{\partial l}{\partial t} - r l \frac{\partial S}{S^2 \partial t}
\]

\[
\frac{\partial l}{\partial t} > 0, \quad \frac{\partial r}{\partial t} > 0, \quad \frac{\partial S}{\partial t} = 0 \quad \Rightarrow \quad \frac{dE_m}{dt}
\]

Stage 2: Cavern Nucleation
Formation of Cavern (CO2 and CO Evolution)
Depth of Cavern, $d$

\[
S = \frac{\pi D^2}{4} + 2wd - wy
\]

\[
\frac{dS}{dt} = \frac{\pi D}{2} \frac{\partial D}{\partial t} + 2d \frac{\partial w}{\partial t} + 2w \frac{\partial d}{\partial t} - \frac{\partial (wy)}{\partial t}
\]

During initial stages of cavern formation, $d$, $w$, and $y$ are very small; therefore,

\[
\frac{dS}{dt} = \frac{\pi D}{2} \frac{\partial D}{\partial t} + 2d \frac{\partial w}{\partial t} + 2w \frac{\partial d}{\partial t} - \frac{\partial (wy)}{\partial t} = 0.
\]

Hence,

\[
\frac{\partial l}{\partial t} > 0, \quad \frac{\partial r}{\partial t} > 0, \quad \frac{\partial S}{\partial t} = 0 \quad \Rightarrow \quad \frac{dE_m}{dt}
\]

Figure 3.2.18a: Schematic diagram showing the proposed mechanism for fluctuations in $E_m$ during galvanostatic polarization.
Maximum in $E_m$

\[
\frac{dE_m}{dt} = I S \frac{dr}{dt} + \frac{r I \partial l}{S \partial t} - \frac{r I \partial S}{S^2 \partial t}
\]

Effect of Film Thickness and Film Resistance Balanced by the Effect of Surface Area Increase Due to Cavern Growth

\[
I S \frac{dr}{dt} + \frac{r I \partial l}{S \partial t} = \frac{r I \partial S}{S^2 \partial t} \quad \rightarrow \quad \frac{dE_m}{dt} = 0
\]

Cross-Sectional Side View

Regime of Decreasing $E_m$
(Region C in Figure 3.2.15)

Cavern Deepens and Gets Longer, and $r$ and $l$ Reach Steady State

\[
\frac{dr}{dt} = 0, \quad \frac{dI}{dt} = 0, \quad \frac{dS}{dt} \uparrow \quad \rightarrow \quad \frac{dE_m}{dt} \downarrow
\]

Top View of Fiber

Regime of Constant $E_m$
(Region D in Figure 3.2.15)

Cavern Widens Rather than Deepens \quad \rightarrow \quad \frac{\partial S}{\partial t} = 0

Large $S^2$ in the coefficient attenuates the term $\frac{r I l \partial S}{S^2 \partial t}$.

\[
\frac{dr}{dt} = 0, \quad \frac{dI}{dt} = 0, \quad \frac{r I l \partial S}{S^2 \partial t} = 0 \quad \rightarrow \quad \frac{dE_m}{dt} = 0
\]

Figure 3.2.18b: Schematic diagram showing the proposed mechanism for fluctuations in $E_m$ (Figure 3.2.15) of P100 graphite fibers during galvanostatic polarization. Regions C and D.
3.3 THE CATHODIC ELECTROCHEMISTRY OF SiC AND TiB₂ IN NEUTRAL 0.5 M Na₂SO₄ AND 3.15 wt% NaCl

3.3.1 Introduction

The H₂-evolution and O₂-reduction characteristics on SiC and TiB₂ were sought to determine the effect of these constituents on galvanic couples with aluminum. Silicon carbide is of interest because it is used as a reinforcement constituent. Titanium diboride is of interest because it is used to enhance the wettability of graphite fibers in molten aluminum.

Cathodic polarization diagrams were generated in neutral deaerated and aerated 0.5 M Na₂SO₄ and 3.15 wt% NaCl at 30°C to simulate fresh water and seawater, respectively. A slow scan rate (0.1 mV/s) was used to obtain near steady-state properties. Silicon carbide and TiB₂ were found to support H₂ evolution and O₂ reduction.

Titanium diboride is an electronic conductor with very low resistivity, ~ 10⁻⁵ Ω·cm [McLeod, Haggerty, and Sadoway, 1984]. Silicon carbide, on the other hand, has resistivities that vary significantly, 10⁻⁵ to 10¹³ Ω·cm, depending on its purity [Ichinose, 1987]. The resistances of the SiC electrodes in this study made it necessary to correct the polarization diagrams for IR losses at current densities greater than about 10⁻⁶ A/cm².

Both SiC and TiB₂ were assumed to be inert electrodes serving as catalysts for H₂ evolution and O₂ reduction. The equilibrium H₂-evolution and O₂-reduction reactions [Pourbaix, 1974] are shown below, respectively:

\[ 2H^+ + 2e^- = H_2, \quad E^* = -0.241 \text{ V}_{\text{SCE}} \]  \hspace{1cm} (3.3.1)

and

\[ O_2 + 4H^+ + 4e^- = 2H_2O, \quad E^* = 0.987 \text{ V}_{\text{SCE}} \]  \hspace{1cm} (3.3.2)

The reader may consult the review by Randin [1981] for more information on nonmetallic electrodes.

3.3.2 Materials

Planar electrodes were fabricated from large samples of SiC and TiB₂ that were purchased from Ceradyne, Inc. The SiC and TiB₂ were hot-pressed to near theoretical densities (>98%) without sintering aids or binders. The sides of the specimens were coated with an epoxy
adhesive (Epoxy-Patch, The Dexter Corporation) and cured for about 2 hours at 70°C. The planar surface of electrodes was polished to 0.05 μm finish with gamma alumina powder, kept wet, and rinsed with 18 MΩ·cm water about 5 minutes prior to immersion in the aqueous solutions. Prior to the 0.05 μm finishing, the electrodes were grounded with diamond paste.

Special precautions were taken when making electrical contact with the SiC electrodes due to their high resistivity. The SiC specimens were cut into square (~9 x 9 mm) wafers about 1 mm thick, and the entire back side of the SiC electrodes were silver painted so that the IR drop through the electrodes would be uniform over the surface area.

Neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl were prepared from 18 MΩ·cm water and analytical grade reagents. The solutions were deaerated by sparging with pre-purified H₂, aerated by sparging with 19.5% to 23.5% O₂ balanced with N₂, and thermostated at 30 ± 0.1°C. The gas pressure was 1 atm.

3.3.3 Instrumentation and Procedures

Polarization of the electrodes was conducted with a Model 273 EG&G Princeton Applied Research (PAR) potentiostat/galvanostat. When measuring currents as low as 1 nA, the instrument was within about 10% of the true current as determined by the following procedure. The accuracy of the current measurement was assessed by inserting a 1 GΩ (2 % tolerance) resistor between the working electrode terminal and the auxiliary terminal (to which the reference terminal was connected) of the potentiostat. A potential difference of 1.000 V was set between the working and reference terminals which should theoretically produce a current flow from the auxiliary electrode equal to 1.000 nA, assuming 0 % tolerance of the 1 GΩ resistor. The measured current was then compared to the theoretical 1.000 nA value.

In generating potentiodynamic polarization diagrams, the electrodes were allowed to stabilize at their corrosion potentials (E_{corr}) and were subsequently polarized at a rate of 0.1 mV/s. Polarization diagrams with standard deviation bars were generated from at least three individual polarization diagrams; the average logarithm of the current density (log i [A/cm²]) was plotted as a function of potential, and the peak-to-peak width between standard deviation bars is equal to two times the standard deviation of log i. The average values of E_{corr}, the average time that the electrodes were in the open circuit condition prior to polarization, and the standard deviation (SD) of these parameters are also tabulated in the caption of the polarization diagrams.

Tafel slopes (β) were calculated between specific current ranges by taking the average Tafel slope from a set of individual polarization diagrams; this produces a result different from that
obtained by measuring the Tafel slope on the polarization diagrams where the average log i is plotted as a function of potential (as was described in the preceding paragraph). The least-squares method was used to calculate the Tafel slopes by fitting linear regions of individual polarization diagrams to straight lines having the form

\[ E = \beta \log i + B \]  

(3.3.3)

where \( E \) is in \( V_{\text{SCE}} \), \( \beta \) in \( V \) per decade of \( i \), \( i \) in \( A/cm^2 \), and \( B \) in \( V \). Exchange current densities were determined by Tafel extrapolation.

### 3.3.4 Results

The SiC and TiB\(_2\) electrodes were cathodically polarized in deaerated and aerated 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl.

#### 3.3.4.1 SiC Results

Individual cathodic polarization diagrams of SiC are plotted in Figures 3.3.1 through 3.3.4 and compared in Figure 3.3.9. In deaerated 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl, the cathodic polarization diagrams of SiC showed a concentration polarization-like regime at current densities less than about 10\(^{-7}\) A/cm\(^2\), similar to those observed for P100 graphite fibers (Section 3.2.4.1). At current densities greater than 10\(^{-7}\) A/cm\(^2\), \( H_2 \) evolution predominated. Values for \( \beta \), \( B \), and extrapolated \( i_o \) are given in Table 3.3.1. In aerated solutions, a Tafel region due to \( O_2 \) reduction was followed by diffusion-limited \( O_2 \) reduction. At potentials active to -0.7 \( V_{\text{SCE}}\), the diffusion-limited current density was about 3 times greater in the NaCl solution than in the Na\(_2\)SO\(_4\) solution. Values for \( \beta \), \( B \), and extrapolated \( i_o \) are given in Table 3.3.2. The SiC electrodes did not show signs of degradation after the cathodic polarization experiments.

#### 3.3.4.2 TiB\(_2\)

Individual polarization diagrams of TiB\(_2\) are shown in Figures 3.3.5 through 3.3.8 and compared in Figure 3.3.9. In deaerated 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl, the cathodic polarization diagrams were under activation control, but there were two distinct regions with a transition at about 10\(^{-5}\) A/cm\(^2\). Values for \( \beta \), \( B \), and extrapolated \( i_o \) are given in Table 3.3.1. In aerated 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl, activation-controlled \( O_2 \) reduction was followed by diffusion-limited \( O_2 \) reduction that was followed in turn by \( H_2 \) evolution. The diffusion-limited \( O_2 \)-reduction current density was about two times greater in the 3.15 wt%
NaCl solution. In the activation-controlled O₂-reduction regime in 3.15 wt% NaCl, there were two distinct Tafel regions (transition at about 2 x 10⁻⁶ A/cm²); whereas, in 0.5 M Na₂SO₄, there was only one Tafel region. Values for β, B, and extrapolated i₀ are given in Table 3.3.2.

3.3.5 Discussion

3.3.5.1 SiC Discussion

Silicon carbide was inert during cathodic polarization in neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions at 30°C. The low H₂-evolution exchange current densities (Table 3.3.1) indicated that SiC was a poor catalyst for H₂ evolution. Consequently, at very low current densities, trace amounts of dissolved O₂ can show up on the polarization diagram as a region of diffusion-limited O₂ reduction. Such a region was evident at current densities less than 10⁻⁷ A/cm². A similar region was also observed on the polarization diagram of the P100 graphite fibers due to an estimated 3 ppb of dissolved O₂ (Section 3.2.5.1).

In the aerated solutions, the open circuit potentials of SiC were about 0.5 V active to the equilibrium O₂ potential, and the exchange current densities were low (Table 3.3.2).

3.3.5.2 TiB₂ Discussion

Titanium diboride was inert during cathodic polarization in neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions at 30°C. In the deaerated solutions, the open circuit potentials were within 25 mV of the reversible H₂ potential and, accordingly, the exchange current densities were not extremely low (Table 3.3.1). In aerated solutions, the open circuit potentials were about 0.8 V active to the reversible O₂ potential.

3.3.6 Conclusions

Silicon carbide and TiB₂ were inert and supported H₂ evolution and O₂ reduction. The cathodic polarization diagrams can be used to predict galvanic corrosion behavior between other materials and these constituents.

3.3.7 References


### Table 3.3.1: Hydrogen Evolution Parameters for Silicon Carbide and Titanium Diboride at 30°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Tafel Slope B; SD (V/dec)</th>
<th>Intercept B; SD (V)</th>
<th>io (A/sqcm) *</th>
<th>Current Range (log i [A/sqcm])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Carbide</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.136; 0.026</td>
<td>-2.183; 0.149</td>
<td>6.90 E-12</td>
<td>-7.0 &lt; log i &lt; -5.5</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>3.15 wt% NaCl</td>
<td>-0.176; 0.027</td>
<td>-2.416; 0.153</td>
<td>1.02 E-10</td>
<td>-7.0 &lt; log i &lt; -5.5</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.212; 0.007</td>
<td>-2.281; 0.035</td>
<td>2.29 E-8</td>
<td>-7.0 &lt; log i &lt; -5.0</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>3.15 wt% NaCl</td>
<td>-0.123; 0.007</td>
<td>-1.832; 0.032</td>
<td>5.64 E-8</td>
<td>-7.0 &lt; log i &lt; -5.0</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>3.15 wt% NaCl</td>
<td>-0.135; 0.004</td>
<td>-1.869; 0.009</td>
<td>5.64 E-8</td>
<td>-7.0 &lt; log i &lt; -5.0</td>
</tr>
</tbody>
</table>

* — io was obtained by Tafel extrapolation that was based on E (hydrogen evolution) = -0.662 Vsc, which was calculated using pH = 7, hydrogen gas pressure = 1 atm, and T = 30°C.

### Table 3.3.2: Oxygen Reduction Parameters for Silicon Carbide and Titanium Diboride at 30°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Tafel Slope B; SD (V/dec)</th>
<th>Intercept B; SD (V)</th>
<th>io (A/sqcm) *</th>
<th>Current Range (log i [A/sqcm])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Carbide</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.0926; 0.0058</td>
<td>-0.8544; 0.0587</td>
<td>5.66 E-16</td>
<td>-8.0 &lt; log i &lt; -6.5</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>3.15 wt% NaCl</td>
<td>-0.0848; 0.0015</td>
<td>-0.8105; 0.0222</td>
<td>7.57 E-17</td>
<td>-8.0 &lt; log i &lt; -6.5</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>0.5 M Sodium Sulfate</td>
<td>-0.196; 0.020</td>
<td>-1.602; 0.158</td>
<td>9.49 E-12</td>
<td>-6.5 &lt; log i &lt; -5.0</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>3.15 wt% NaCl</td>
<td>-0.370; 0.036</td>
<td>-2.757; 0.258</td>
<td>1.07 E-9</td>
<td>-6.5 &lt; log i &lt; -5.875</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>3.15 wt% NaCl</td>
<td>-0.0892; 0.0095</td>
<td>-1.1804; 0.0494</td>
<td>-6.5 &lt; log i &lt; -4.5</td>
<td></td>
</tr>
</tbody>
</table>

* — io was obtained by Tafel extrapolation that was based on E (oxygen reduction) = 0.556 Vsc, which was calculated using pH = 7, oxygen gas pressure = 0.215 atm, and T = 30°C.
Figure 3.3.1: Cathodic polarization diagram of hot-pressed silicon carbide in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = ~0.1 mV/s; \( E_{corr} = -0.329 \) Vsc, SD = 0.077 V; Time at open circuit = 1.05 h, SD = 0.08 h.
Figure 3.3.2: Cathodic polarization diagram of hot-pressed silicon carbide in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = ~0.1 mV/s; Avg Ecorr = -0.049 Vsce, SD = 0.019 V; Avg time at open circuit = 1.37 h, SD = 0.15 h.
Figure 3.3.3: Cathodic polarization diagram of hot-pressed silicon carbide in deaerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = -0.1 mV/s; Ecorr = -0.339 Vsce, SD = 0.052 V; Time at open circuit potential = 1.09 h, SD = 0.03 h.
Figure 3.3.4: Cathodic polarization diagram of hot-pressed silicon carbide in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = -0.1 mV/s; Ecorr = -0.080 V SCE, SD = 0.024 V; Time at open circuit = 1.35 h, SD = 0.33 h.
Figure 3.3.5: Cathodic polarization diagram of hot-pressed titanium diboride in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Ecorr = -0.638 Vsce, SD = 0.025 V; Time at open circuit = 1.59 h, SD = 0.36 h.
Figure 3.3.6: Cathodic polarization diagram of hot-pressed titanium diboride in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Ecorr = -0.241 V sce, SD = 0.007 V; Time at open circuit = 1.35 h, SD = 0.24 h.
Figure 3.3.7: Cathodic polarization diagram of hot-pressed titanium diboride in deaerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Ecorr = -0.676 Vsc, SD = 0.043 V; Time at open circuit = 1.28 h, SD = 0.14 h.
Figure 3.3.8: Cathodic polarization diagram of hot-pressed titanium diboride in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Ecorr = -0.259 Vsce, SD = 0.013 V; Time at open circuit = 1.33 h, SD = 0.08 h.
Figure 3.3.9: Cathodic polarization diagrams of hot-pressed silicon carbide and hot-pressed titanium diboride in neutral solutions at 30°C. Scan rate = 0.1 mV/s.
3.4 ALUMINUM CARBIDE HYDROLYSIS

3.4.1 Introduction

Aluminum carbide is formed by the reaction of aluminum and carbon [Becher, 1963] and by the reaction of aluminum and SiC [Iseki, Kameda, and Maruyama, 1984], making Al₄C₃ of particular interest to corrosion research on graphite/aluminum (G/Al) and silicon carbide/aluminum (SiC/Al) metal-matrix composites (MMCs). In G/Al MMCs, the formation of Al₄C₃ becomes substantial during processing at temperatures much higher than the liquidus temperature, but the reaction can be controlled at lower temperatures [Kendall, 1974]. The reaction and thermodynamic properties are given below [Elliot, 1985]:

\[ 4\text{Al}(l) + 3\text{C}(s) = \text{Al}_4\text{C}_3(s) \]  
\[ \Delta H^\circ = -41,550 \text{ cal} \]  
\[ -\Delta S^\circ = 5.10 \text{ cal/K} \]  
\[ (1500 - 2000 \text{ K}) \]

Aluminum carbide will also form at SiC-aluminum interfaces if the Si activity in liquid Al is low [Iseki, Kameda, and Maruyama, 1984]. The reaction and thermodynamic properties of the Al-SiC reaction [Elliot, 1985] are

\[ 4\text{Al}(l) + 3\text{SiC}(s) = \text{Al}_4\text{C}_3(s) + 3\text{Si}(s) \]  
\[ \Delta H^\circ = 4,170 \text{ cal} \]  
\[ -\Delta S^\circ = -0.03 \text{ cal/K} \]  
\[ (1500 - 1686 \text{ K}) \]

Aluminum carbide hydrolyzes liberating methane gas by the reaction

\[ \text{Al}_4\text{C}_3(s) + 12\text{H}_2\text{O}(l) = 4\text{Al(OH)}_3(s) + 3\text{CH}_4(g) \]  
\[ (3.4.3). \]

Portnio et al. [1980] detected methane evolution from G/Al MMCs containing Al₄C₃. Thus, the rate of Al₄C₃ hydrolysis is important in assessing the environmental degradation resistance of G/Al and SiC/Al MMCs. Consequently, the hydrolysis rate was sought; however, only semi-qualitative data were obtained because completely dense hot-pressed Al₄C₃ specimens were not available and, therefore, the reaction area was unknown at any given moment. The Al₄C₃ specimens were found to be hydrolyzed at a rate of about 1% per hour. The hydrolysis rate was assessed through the volumetric measurement of CH₄ accumulation in a reaction vessel.

Qualitative degradation characteristics of sintered Al₄C₃ in water, and some quantitative mechanical and physical properties were reported by Iseki, Kameda, and Maruyama [1983].
3.4.2 Materials

Pure hot-pressed Al$_4$C$_3$ (78 % of theoretical density, and porous) was purchased from Materials by Metron, Inc., and cut into dimensions of about 7.16 x 5.19 x 2.10 mm weighing about 0.144 g. With the exception of one exposed 7.16 x 5.19 mm surface, all others were coated with paraffin. The Al$_4$C$_3$ specimens were hydrolyzed in pure 18 MΩ·cm water.

3.4.3 Instrumentation and Procedure

The Al$_4$C$_3$ specimens were inserted into the open end of an upside down burette that was immersed in an 18 MΩ·cm water bath thermostated to 30 ± 0.1°C (Figure 3.4.1). The volume of CH$_4$ (that was liberated from the Al$_4$C$_3$) was determined by the amount of water that was displaced from the burette by the CH$_4$ gas. The moles of hydrolyzed Al$_4$C$_3$ was determined by calculating the moles of CH$_4$ evolved using the ideal gas law,

\[ pV = nRT \]  \hspace{1cm} (3.4.4),

and then multiplying the moles of CH$_4$ by the stoichiometric ratio

\[ \text{moles of Al}_4\text{C}_3 \text{ consumed/mole of CH}_4 \text{ formed} \]  \hspace{1cm} (3.4.5).

Consequently, the percentage of Al$_4$C$_3$ that is hydrolyzed is determined by the relation

\[ \left( \frac{\text{moles of hydrolyzed Al}_4\text{C}_3}{\text{total moles of Al}_4\text{C}_3 \text{ specimen}} \right) \times 100 \]  \hspace{1cm} (3.4.6).

A natural-gas detector tube (Dräger) was used to detect CH$_4$. A description of how this tube works can be found in Section 3.2.3.2. The CH$_4$ gas was extracted from the tip of the burette for chemical analysis using a syringe (Figure 3.4.1).

3.4.4 Results

The gas which evolved from the Al$_4$C$_3$ specimens gave a positive indication from the natural-gas indicator tube. Figure 3.4.2 shows plots of the percentage of Al$_4$C$_3$ reacted (with respect to the whole specimen) as a function of reaction time. About 1% of the specimen was hydrolyzed per hour of immersion, and after about 5 to 6 hours, the specimen began to disintegrate. The experiment was terminated after about 10 hours.
3.4.5 Discussion and Conclusions

The rate of $\text{Al}_4\text{C}_3$ hydrolysis is too high for $\text{Al}_4\text{C}_3$ to be tolerated in G/Al and SiC/Al MMCs. The presence of $\text{Al}_4\text{C}_3$ would result in severe degradation problems even in the purest of moist environments where Al, graphite, and SiC are relatively inert. Thus, the formation of $\text{Al}_4\text{C}_3$ should be prevented during manufacturing by controlling parameters such as processing temperature, Si activity (for SiC/Al MMCs), or by coating the reinforcement constituents with diffusion barriers that prevent the interaction of C and Al.

3.4.6 References


Figure 3.4.1: Apparatus for measuring the volume of CH₄ evolved as a result of Al₄C₃ hydrolysis.
Figure 3.4.2: Hydrolysis of hot-pressed aluminum carbide in 18 MΩ·cm water of pH 7 at 30°C. The hydrolysates are methane gas and aluminum hydroxide. Avg %TD of the aluminum carbide specimens = 78.0, SD = 1.5.
4 PROCESSING RELATED CORROSION PROBLEMS OF A COMMERCIAL GRAPHITE FIBER/6061-T6 ALUMINUM ALLOY METAL-MATRIX COMPOSITE

4.1 Introduction

The relatively poor corrosion resistance of graphite/aluminum (G/Al) metal-matrix composites (MMCs) in comparison to their monolithic matrix alloys is well known [Czyrklis, 1985; Vassilaros, et al., 1983; Dull, Harrigan, and Amateau, 1975; Pfeifer, 1977]. Though reports in the literature on corrosion mechanisms on G/Al MMCs are not clear, corrosion of G/Al MMCs is generally attributed to galvanic corrosion between the graphite fibers and the aluminum matrix [Czyrklis, 1985; Vassilaros, et al., 1983; Dull, et al., 1975], and to inferior corrosion resistance of the precursor wire-wire and wire-foil diffusion bonds [Pfeifer, 1977]. At this moment, however, it appears that detailed studies relating corrosion morphology to microstructure have not been previously published. In this study, compelling evidence has been found which correlates localized corrosion of wire-wire diffusion bonds and general pitting of the matrix to residual chlorides in the microstructure which are left behind by the liquid-metal infiltration process.

A graphite fiber/6061-T6 aluminum alloy (G/6061-T6 Al) MMC was the subject of this study. Examination of the MMC in 0.5 M Na$_2$SO$_4$ was essential in order to observe the effects of the residual microstructural chlorides in the matrix of the composite. Substantial pitting localized in the diffusion-bonded regions and occasional pitting throughout the matrix occurred during anodic polarization of cross-sectional areas of G/6061-T6 Al MMC plates in the Na$_2$SO$_4$ solution. Pitting of the 6061-T6 Al matrix was not expected in the Na$_2$SO$_4$ solution because monolithic 6061-T6 Al passivated under similar conditions, as shown in Subchapter 3.1. All results indicated that matrix pitting was due to residual microstructural chlorides. As shown in Subchapter 3.1, 6061-T6 Al was susceptible to chloride induced pitting. Correlation between the microstructure, dissolution morphology, and electrochemical data provided substantial evidence for the attribution of localized corrosion to residual microstructural chlorides in the aforementioned G/6061-T6 Al MMC.

4.1.1 Source of Residual Chlorides

The source of residual chlorides was traced to the liquid-metal infiltration process. A schematic diagram of this process is shown in Figure 4.1. To enhance the wettability of the fibers in molten 6061 Al, the fibers are coated with a Ti-B compound that is presumably TiB$_2$. The process involves coating the graphite fibers (in tows of 2000 fibers) by chemical vapor
deposition using TiCl$_4$ (g), BCl$_3$ (g), and Zn (v). In addition to TiB$_2$, some thermodynamically favorable chlorides which may form during the deposition process are TiCl$_2$, TiCl$_3$, and ZnCl$_2$ [Amateau, 1977]. The coated fibers are immediately processed into precursor wires by infiltrating the tows with molten 6061 Al [Harrigan & Flowers, 1977]. The residual chlorides are presumably integrated into the skin of the precursors while the precursors are extracted from the 6061 Al melt which is covered with an argon atmosphere containing TiCl$_4$ (g), BCl$_3$ (g), and Zn (v) [Harrigan, 1988]. The extracted precursors are then washed in detergent and rinsed in acetone. To make plates, layers of precursor wires are bound together with an acrylic binder and diffusion bonded between 6061 Al surface foils at 538 ± 11°C and 13.8 MPa for approximately 20 minutes. The acrylic binder is consumed during the diffusion-bonding process [Harrigan, 1988].

4.2 Materials

The G/6061-T6 Al MMC precursor wires were produced by Material Concept, Inc. (666 N. Hague Ave., Columbus, OH 43204), from which six-ply (six layers of precursor wires) plates were consolidated by DWA Composite Specialties, Inc. (21119 Superior St., Chatsworth, CA 91311). The composites contained approximately 50 vol % of high-modulus graphite fibers (Thornel P100: pitch-based with an elastic modulus equal to 690 GPa) which were unidirectional and continuous. The G/6061-T6 Al MMCs were heat treated to the T6 condition.

Planar electrodes were made from G/6061-T6 Al MMC precursor wire and six-ply plate having the graphite fibers oriented perpendicularly to the surface of the electrodes. The aluminum surface foils were ground away from the six-ply plate. The sides of the specimens were coated with an epoxy paint (AMERCOAT 90 RESIN, Ameron) before mounting in an epoxy resin (EPON 828 RESIN, Miller-Stephenson Chemical Co., Inc.). About 5 minutes before immersion in the test solution, the planar surface of specimens was polished to 0.05 μm finish with gamma alumina powder and rinsed with 18 MΩ·cm water.

Rod-shaped precursor-wire electrodes that exposed only the 6061-T6 Al skin (Figure 4.2) were made by sealing the tip of the precursor wire with the epoxy paint to shield the cross section of the precursor from the solution. These electrodes will be referred to as precursor-wire skin electrodes. The electrodes were rinsed in methanol and then in 18 MΩ·cm water about 5 minutes before immersion in the test solution.
Solutions of 0.5 M Na₂SO₄ and 3.15 wt% NaCl of about pH 7 were prepared from 18 MΩ·cm water and analytical grade Na₂SO₄ (< 0.0002% Cl) and NaCl. During the potentiodynamic experiments, the solutions were kept at 30 ± 0.1°C, and deaerated with pre-purified hydrogen or aerated with 19.5 to 23.5 % oxygen balanced with nitrogen. While observing the corrosion process under an optical microscope, the solutions were at room temperature and exposed to laboratory air. Gas pressure was 1 atm.

4.3 Instrumentation and Procedure

Optical microscopy and scanning electron microscopy were used for microstructural, and dissolution morphological characterization. Chemical analysis was performed by X-ray energy-dispersive spectrometer (EDS) analysis, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction. Microscopy specimens were polished to 0.05 μm finish with gamma alumina powder.

In situ corrosion observations were made using an optical microscope equipped with a video camera and recorder. A specially designed cell held the specimen horizontally beneath the objective lens of the microscope. There were several millimeters of solution above the specimen surface.

Potentiodynamic polarization examinations were conducted with a Model 173 Princeton Applied Research (PAR) Potentiostat/Galvanostat and a Model 376 PAR Logarithmic Current Converter. The accuracy of the logarithmic current converter was measured to be better than 5% while measuring currents in the nA range, as determined by the following procedure. The accuracy of the current measurement was assessed by inserting a 1 GΩ (2 % tolerance) resistor between the working electrode terminal and the auxiliary terminal (to which the reference terminal was connected) of the potentiostat. A potential difference of 1.000 V was set between the working and reference terminals which should theoretically produce a current flow from the auxiliary electrode equal to 1.000 nA, assuming 0% tolerance of the 1 GΩ resistor. The measured current was then compared to the theoretical 1.000 nA value.

In generating potentiodynamic polarization diagrams, the electrodes were allowed to stabilize at their corrosion potentials (Ecorr) and were subsequently polarized at a rate of 0.1 mV/s. Polarization diagrams with standard deviation bars were generated from at least three individual polarization diagrams; the average logarithm of the current density (log i [A/cm²]) was plotted as a function of potential, and the peak-to-peak width between standard deviation bars is equal to two times the standard deviation of log i. The average values of Ecorr, the average time that
the electrodes were in the open circuit condition prior to polarization, and the standard deviation (SD) of these parameters are also tabulated in the caption of the polarization diagrams.

4.4 Results

4.4.1 Microstructural Analysis

An optical micrograph of the G/6061-T6 Al plate of the plane perpendicular to the axis of the fibers is shown in Figure 4.3. In the figure, the precursor wires are outlined by the diffusion-bonded regions between adjacent wires. A closer view of the diffusion-bonded regions in the optical (Figure 4.4) and scanning electron microscopes revealed that they were contaminated. Chloride as opposed to chlorine was identified on the precursor wire skin by XPS; the binding energy was approximately 201.5 eV, which corresponds more closely to chloride salts [Muilenberg, 1979] than to chlorine [Aitken, 1980]. Although X-ray EDS analysis cannot determine chemical states, it was used extensively to characterize the microstructure because the technique has spatial resolution on the order of a micron. Chlorine signals on the X-ray EDS spectra will be interpreted as chloride in view of the XPS results. The presence of chlorides on precursor skins was also confirmed with X-ray EDS analysis (Figure 4.5). Chloride was found in the diffusion-bond contaminants (spectrum in Figure 4.6), but chloride was not detected in the matrix (Figure 4.7) although an Ar peak may have hidden a small chloride peak. Random samplings were made and spectra shown in the figures are typical examples.

Fiber-matrix interfaces were also examined. The elemental map (Figure 4.8) produced by scanning AES confirmed that Ti was concentrated in the region of the interface where one fiber was pulled out of the matrix (Figure 4.9). A similar map was produced at an energy of approximately 180 eV, but could not be exclusively attributed to B or Cl since their Auger energies are similar, 179 and 181 eV, respectively. Fiber-matrix interfaces examined by X-ray EDS analysis such as in Figure 4.10 produced spectra typical of Figure 4.11 where titanium but not chloride was detected. Because the spatial resolution of X-ray EDS analysis is on the order of a micron, chemical information originated in the interface as well as in the adjacent matrix and fiber. Chloride was also undetectable in the matrix regions away from the fibers. Occasionally, neighboring fibers were bridged by a compound rich in Ti, Cl, and Mg, as shown in the SEM micrograph in Figure 4.12 and the corresponding X-ray EDS spectrum in Figure 4.13. Titanium and chloride were also found in the fiber-matrix interfaces of these bridged fibers.
A futile attempt was made to find Al₄C₃, TiB, and TiB₂ on the graphite fibers by X-ray powder diffraction. The fibers were extracted from the composite by dissolving the matrix in an etching solution consisting of 3 g NaOH and 100 ml of high purity methanol (0.01 % H₂O). This solution does not attack Al₄C₃ [Lo, et al., 1983]. The extracted fibers were pulverized and examined by X-ray diffraction. Although the fibers were completely free from the matrix, etching was apparently incomplete as small peaks of elemental Al were detected in the X-ray diffraction spectrum, as shown in Figure 4.14 comparing the spectrum of virgin P100 fibers to that of the extracted fibers. The major peaks in Figure 4.14 correspond to graphite peaks. Aluminum carbide, TiB, and TiB₂ were not found, but small peaks associated with the extracted fibers were almost coincident with some of the major peaks of TiB and TiB₂ (Figure 4.15); unfortunately, the small peaks also corresponded to the major Al peaks. In addition, if TiB and TiB₂ were present, then peaks corresponding to the other major peaks of TiB and TiB₂ should have been found. Examination by X-ray EDS analysis showed that Ti was present on the extracted fibers. The lack of evidence for Al₄C₃, TiB, and TiB₂ did not substantiate their absence, but suggests that X-ray diffraction may not have the required sensitivity.

In summary, chloride was detected only in diffusion-bonded regions and in regions of bridged fibers.

4.4.2 Dissolution Morphology

The matrix of the G/6061-T6 Al MMCs was prone to localized dissolution and corrosion in 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions. The graphite fibers were relatively inert, but could be oxidized at noble potentials. The details of dissolution morphology are presented below.

In 0.5 M Na₂SO₄ solutions at room temperature, preferential corrosion of the diffusion-bonded regions of the six-ply plate was seen in situ with an optical microscope and video taped in real time. In the video footage, the graphite fibers (black contrast) can be used for scaling as they are about 10 μm in diameter. At open circuit potential, hydrogen evolution was observed on diffusion-bonded regions of newly polished surfaces in aerated 0.5 M Na₂SO₄ (Sequence 4.1 of the video tape) and in aerated distilled water (Figure 4.16). Vigorous hydrogen evolution was also observed (Sequence 4.2) from corroding diffusion-bonded regions of a specimen at open circuit potential that was previously anodically polarized at 2.1 and 2.5 V SCE for a total of 80 minutes in aerated 0.5 M Na₂SO₄. The SEM micrograph in Figure 4.17 shows the localized dissolution of the diffusion-bonded regions as a result of
anodic polarization in 0.5 M Na₂SO₄. The surface of one such electrode was wafered and mechanically broken. The wafer parted predominantly along the corroded diffusion-bonded regions (Figure 4.18) which contained chloride-containing dissolution products, as determined by X-ray EDS analysis. General pitting of the matrix was also observed, and shown in Figure 4.19.

Localized dissolution of the Al matrix also occurred in the planar G/6061-T6 Al precursor-wire electrodes that were anodically polarized in 0.5 M Na₂SO₄. As shown in Figure 4.20 which represents a typical example, pits were concentrated near the perimeter of the planar precursor-wire electrode. Also, during anodic polarization at 0.0 V_{SCE}, H₂ evolution was seen at the perimeter of planar precursor-wire electrodes (Sequence 4.3), indicating pit formation in those regions. When the precursor-wire skin electrodes were anodically polarized in deaerated 0.5 M Na₂SO₄, pits penetrated the 6061-T6 Al skin (Figure 4.21). Polished cross sections of these precursors revealed a 6061-T6 Al shell which encased a severely degraded interior where Al dissolution had propagated towards the core (Figure 4.22). A detailed micrograph of the 6061-T6 Al shell shows where pits initially penetrated the skin (Figure 4.23). In Figures 4.22 and 4.23, the large cavities (black) were the result of mechanical damage during polishing.

The composites were extremely vulnerable to matrix dissolution in chloride solutions above the pitting potential. The footage in Sequence 4.4 shows a planar precursor-wire electrode that was anodically polarized to 0.0 V_{SCE} in aerated 0.5 M Na₂SO₄ and then contaminated with NaCl. The footage shows that once the pit formed, a dissolution front originating at the pit propagated over the surface consuming all aluminum in its path. The optical micrograph in Figure 4.24 shows the degraded precursor.

During anodic polarization at 2.0 V_{SCE} for 3.2 hours at 30°C in deaerated 0.5 M Na₂SO₄, the graphite fibers were partially consumed in addition to diffusion-bond dissolution. In the SEM micrograph (Figure 4.25), the first impression that one gets is that the fiber-matrix interfacial region was consumed preferentially. In actuality, the caverns in the fiber-matrix interfacial region were caused by fiber oxidation. This is clarified in section 4.5 Discussion.

### 4.4.3 Electrochemical Data

Anodic polarization diagrams of the planar G/6061-T6 Al MMC electrodes in the forms of six-ply plate and precursor wire in deaerated 0.5 M Na₂SO₄ are shown in Figures 4.26 and 4.27, respectively. Both diagrams are similar with pitting potentials at approximately
-0.5 \text{ V}_{\text{SCE}}. The anodic polarization diagram of the planar six-ply plate in aerated 0.5 M \text{Na}_2\text{SO}_4 (Figure 4.28) was similar to that in the deaerated solution, but with the exception that the open circuit potential in the aerated solution was closer to the pitting potential. The precursor-wire skin electrode had a pitting potential of about -0.6 \text{ V}_{\text{SCE}} in deaerated 0.5 M \text{Na}_2\text{SO}_4, as shown in Figure 4.29.

4.5 Discussion

The relationship between microstructure, dissolution morphology, and electrochemical data provides new insight into the corrosion mechanisms of commercial G/6061-T6 Al MMCs. A discrepancy was found between the anodic polarization diagram of the planar six-ply plate electrodes and a theoretical polarization diagram (based on the mixed electrode theory) that was generated from the anodic polarization diagrams of monolithic 6061-T6 Al (Subchapter 3.1) and P100 graphite fibers (Subchapter 3.2). The discrepancy between the actual and theoretical polarization diagrams will be related to the dissolution morphology and microstructure.

The generation of the mixed electrode model for a 50% P100 graphite fiber/50% 6061-T6 Al composite in deaerated 0.5 M \text{Na}_2\text{SO}_4 is shown in Figure 4.30, where the polarization curves of the constituents are added and then shifted horizontally along the log i axis to achieve the correct current density. In Figure 4.31, the theoretical polarization diagram of the MMC is compared to the actual diagram of the planar G/6061-T6 Al MMC six-ply plate. The much larger currents of the planar six-ply plate were attributed to pitting of the 6061-T6 Al matrix in the chloride-containing diffusion-bonded regions and precursor interiors, as shown in the SEM micrographs (Figures 4.17, 4.18 and 4.19) and video footage (Sequence 4.2). Attention should also be focused on the pitting potential in the polarization diagram of the six-ply plate in deaerated 0.5 M \text{Na}_2\text{SO}_4 (Figure 4.26) because it is a characteristic feature of anodic polarization diagrams of aluminum in chloride-containing solutions.

In Figure 4.32, the anodic polarization diagram of the precursor-wire skin electrode in deaerated 0.5 M \text{Na}_2\text{SO}_4 is compared to the anodic polarization diagram of monolithic 6061-T6 Al in deaerated 3.15 wt\% NaCl (Subchapter 3.1, Figure 3.1.21). Both diagrams show typical pitting potentials even though the precursor-wire skin electrode was in 0.5 M \text{Na}_2\text{SO}_4. Examination of the precursor-skin electrode verified that the mode of dissolution was pitting (Figures 4.21, 4.22, and 4.23). Presumably, residual microstructural chlorides caused the skin to pit, having the same effect that the chloride ions in the 3.15 wt\% NaCl solution had on the monolithic 6061-T6 Al. The difference in the pitting potentials
(~ 0.1 V) between the two diagrams (Figure 4.32) was anticipated because pitting potentials are dependent on chloride-ion concentration [Galvele, 1978].

The anodic polarization diagrams of the planar G/6061-T6 Al MMC six-ply plate (Figure 4.26) and precursor-wire electrodes (Figure 4.27) in deaerated 0.5 M Na₂SO₄ were similar. This aforementioned similarity indicates that the diffusion bonds did not have significant effects on the electrochemical characteristics. Also, extensive pitting occurred near the perimeter of the planar precursor-wire electrode (Figure 4.20), which was found to be high in chloride concentration, and corresponds to the diffusion-bonded regions of the six-ply plates. The H₂ evolution observed from the perimeter of the planar precursor-wire electrodes (Sequence 4.3) during anodic polarization at 0.0 V_{sce} also indicated that pits were forming in the perimeter region. Due to the high anodic currents in pits, the potential in the pits can be much more reducing than the bulk potential due to ohmic drop in the solution, thus making it possible for H₂ evolution from pits even during anodic polarization. These results indicate that pitting of diffusion-bonded regions in the six-ply plates was not a symptom of diffusion bonding, but caused by chlorides in the diffusion bonds.

The following evidence shows that the G/6061-T6 Al MMCs were prone to pitting in aerated 0.5 M Na₂SO₄ solutions in the open circuit condition. The polarization diagram of the planar six-ply plate in aerated 0.5 M Na₂SO₄ (Figure 4.28) showed that the open circuit potential was close to the pitting potential. In Figure 4.16 and Sequence 4.1, H₂ evolution from diffusion-bonded regions of newly polished six-ply plate confirmed that pitting took place at open circuit potentials. Methane evolution due Al₄C₃ hydrolysis is also possible (Subchapter 3.4), but should predominate at fiber-matrix interfaces where Al₄C₃ is most likely to form.

Finally, as shown in Figure 4.25, the graphite fibers were partially consumed during anodic oxidation at 2.0 V_{sce}. As mentioned in Section 4.4.2 (Dissolution Morphology), the caverns around the perimeter of the fibers were primarily caused by fiber oxidation rather than by interfacial dissolution. This is supported by two observations: 1) In the absence of chlorides, 6061-T6 Al should passivate, and though chlorides were found in the microstructure of the G/6061-T6 Al MMCs, the chlorides were generally not concentrated at fiber-matrix interfaces (Section 4.4.1). 2) The consumption of P100 graphite fibers of the graphite/epoxy composites (Subchapter 3.2, Figure 3.2.14) during anodic polarization in deaerated 0.5 M Na₂SO₄ resulted in cavern formation along the perimeter or cavern formation along a sector of the fibers. Inspection of Figure 4.25 shows that the 6061-T6 Al matrix was intact and that both modes of fiber consumption occurred in the G/6061-T6 Al MMC. During
anodic oxidation, graphite fibers were found to be oxidized to CO₂, CO, and possibly to graphite oxide (Subchapter 3.2).

4.6 Conclusion

Localized dissolution and corrosion in G/6061-T6 Al MMC plates occurred in the regions where residual chlorides were found, which were primarily the diffusion-bonded regions between precursor wires. Also, the anodic polarization diagrams of the G/6061-T6 Al MMCs in 0.5 M Na₂SO₄ confirmed that the 6061-T6 Al matrix pitted due to the presence of microstructural chlorides. The correlation between microstructure, dissolution morphology, and electrochemical data indicate that corrosion of diffusion-bonded regions are caused by residual microstructural chlorides which are left behind by the liquid-metal infiltration process. These findings imply that the inherent corrosion resistance of G/Al MMCs should be improved by excluding chlorides and more generally halides from fabrication processing.

4.7 References


Amateau, M.F., 1977, p.166 (Referenced in Pfeifer [1977]).


Figure 4.1: Schematic diagram of the liquid-aluminum infiltration process for graphite-fiber tows. Reference: Pfeifer, W.H., in Hybrid and Select Metal-Matrix Composites; Ed. by Renton, W.J.; Chapter 6, American Institute of Aeronautics and Astronautics, 1977.
Figure 4.2: SEM micrograph of a G/6061-T6 Al MMC precursor wire showing the 6061-T6 Al skin and subcutaneous graphite fibers.

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5 GALVANIC CORROSION IN ALUMINUM-MATRIX COMPOSITES

This chapter, which is comprised of two independent subchapters, evaluates galvanic corrosion in Al-matrix composites. Subchapter 5.1 discusses the origin of galvanic corrosion in graphite/aluminum and SiC/aluminum metal-matrix composites. Subchapter 5.2 discusses methods which can be used to control galvanic corrosion in Al-matrix composites.
5.1 GALVANIC CORROSION IN ALUMINUM-MATRIX COMPOSITES: ORIGIN

5.1.1 Introduction

Galvanic corrosion has been a major concern ever since aluminum, a very reactive metal, was put in intimate contact with noble reinforcement constituents such as graphite and SiC. The lack of quantitative data on galvanic corrosion of graphite/aluminum (G/Al) and silicon carbide/aluminum (SiC/Al) metal-matrix composites (MMCs) was incentive for this research program.

The effect of P100 graphite (P100 G) fibers, SiC, and TiB₂ on the galvanic-corrosion behavior in couples with 6061-T6 Al and ultra pure Al of 99.999 % metallic purity (m5N Al) was investigated. Titanium diboride was included in this study because it is presumably used as a coating on graphite fibers in some commercial composites (Chapter 4). Galvanic-corrosion rates were predicted using the polarization diagrams from Chapter 3. Galvanic couples between P100 G fibers and 6061-T6 Al were also investigated. In addition, galvanic-corrosion rates of a commercial G/6061-T6 Al MMC were extrapolated from polarization diagrams of the composite. Experiments were conducted in neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl to simulate fresh water and seawater, respectively.

Galvanic corrosion was found to be negligible in deaerated solutions, but substantial in aerated chloride solutions, where the driving force was O₂ reduction. Graphs which can be used to predict galvanic-corrosion rates as a function of P100 G fiber, SiC, and TiB₂ area fractions were developed for aerated 3.15 wt% NaCl solutions. For example, the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of P100 graphite was predicted to be about 80 times greater than that of uncoupled 6061-T6 Al; whereas, the galvanic-corrosion rate in couples with SiC or TiB₂ was predicted to be about 2.5 times that of the uncoupled alloy. This work also demonstrated that m5N Al should not provide an advantage over 6061-T6 Al in pitting resistance if used as a matrix material.

5.1.1.1 Background

Information on galvanic corrosion is presented below, and more information can be obtained from Wesley and Brown [1948]. Galvanic corrosion can be explained in terms of the mixed electrode theory which states that in a corroding system, the total cathodic and total anodic currents must be equal in magnitude. When an isolated piece of material corrodes, local cathodic and anodic sites are present on its surface with a balance between the cathodic and anodic currents. If a galvanic couple is formed, by putting different materials with different
corrosion potentials ($E_{\text{CORR}}$) into electrical contact and then immersing them in an electrolyte, both materials will be polarized to the galvanic potential, $E_{\text{GALV}}$ (if the electrical resistance of the galvanic circuit is negligible). Thus, the noble material tends to be cathodically polarized (with respect to its $E_{\text{CORR}}$), and the active material tends to be anodically polarized (w.r.t. its $E_{\text{CORR}}$). The cathodic polarization of the noble material disrupts the balance between the cathodic and anodic currents, resulting in the cathodic current ($C_{I_N}$) becoming larger in magnitude relative to the anodic current ($A_{I_A}$). On the active material, anodic polarization causes the anodic current ($A_{I_A}$) to become larger in magnitude relative to the cathodic current ($C_{I_A}$). This results in a galvanic current, $I_{\text{GALV}}$, flowing from the noble material to the active material:

$$I_{\text{GALV}} = -(C_{I_N} + A_{I_N}) = A_{I_A} + C_{I_A},$$  \hspace{1cm} (5.1.1)

The condition that the total cathodic and total anodic currents be equal in magnitude is satisfied, as demonstrated by rearranging (5.1.1):

$$-(C_{I_N} + C_{I_A}) = A_{I_N} + A_{I_A}$$ \hspace{1cm} (5.1.2)

The parameters $E_{\text{GALV}}$ and $I_{\text{GALV}}$ are defined schematically with the aid of polarization diagrams describing galvanic corrosion (Figure 5.1.1).

Various types of galvanic couples may form which depend upon the electrodes and electrolyte of the system. The definitions put forth below include cases of concentration polarization and passivation and are thereby somewhat broader than those stated by Wesley and Brown [1948]. A galvanic couple is defined as being under anodic control if the size of the cathode area has no effect on the dissolution rate of the anode (Figure 5.1.2). If the dissolution rate of the anode is proportional to the cathode area, and scales directly with the cathode area, the couple is under cathodic control (Figure 5.1.3). If the dissolution rate of the anode is proportional to the cathode area, but does not scale directly with the cathode area, the couple is under mixed control (Figure 5.1.4). Note that the mode of control may change in some systems if the cathode-to-anode area ratio is changed significantly (Figure 5.1.5). In this document, the dissolution rate of the anode will be referred to as the galvanic-corrosion rate.

### 5.1.2 Materials

The materials used in generating polarization diagrams were described in detail elsewhere. The reader may refer to the appropriate sections: m5N Al and 6061-T6 Al (Subchapter 3.1), P100 Graphite fibers (Subchapter 3.2), SiC and TiB$_2$ (Subchapter 3.3), G/6061-T6 Al MMC six-ply plate (Chapter 4). Galvanic couples were made from small-area 6061-T6 Al electrodes.
(Subchapter 3.1) and planar P100 graphite fiber electrodes (Subchapter 3.2). All electrodes were polished to 0.5 μm finish with gamma alumina powder about 5 minutes prior to immersion in the test solution.

The experiments were conducted in 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions of about pH 7. The solutions were prepared from 18 MΩ•cm water and analytic grade reagents, and thermostated to 30 ± 0.1°C.

Solutions were deaerated by sparging with pre-purified hydrogen gas, and aerated by sparging with 19.5 to 23.5% oxygen balanced with nitrogen. The gas pressure was 1 atm.

5.1.3 Instrumentation and Procedure

Potentiodynamic polarization diagrams, and i_GALV-time and E_GALV-time diagrams were used to study galvanic corrosion. The polarization diagrams were obtained from the preceding chapters with the exception of some polarization diagrams of the G/6061-T6 Al MMCs which were generated in this chapter. Thus, information on instrumentation and procedure for polarization diagrams should be obtained by referring to the previous chapters, as advised in the materials section (5.1.2).

The i_GALV and E_GALV parameters were measured with a self-built ZRA and a self-built electrometer. Field-effect transistor (FET) operational amplifiers with high input impedance (10¹⁵ Ω) and low offset voltage (< 0.5 mV) (OPA 104 CM, Burr-Brown), and high-precision resistors (1 KΩ to 1 GΩ, < 2% tolerance) were used to build the ZRA. The electrometer was built with the OPA 104 CM operational amplifier. The circuitry is shown in Figure 5.1.6. Saturated Calomel or saturated mercury-mercurous sulfate reference electrodes were used to measure E_GALV. The sulfate electrode eliminated the possibility of chloride contamination of the 0.5 M Na₂SO₄ solutions during long experiments. The i_GALV and E_GALV parameters were measured from galvanic couples containing about 50% P100 graphite fibers and 6061-T6 Al.

5.1.4 Results

The polarization diagrams of 6061-T6 Al (Section 3.1.4), m5N Al (Section 3.1.4), P100 graphite (Section 3.2.4), SiC (Section 3.3.4), TiB₂ (Section 3.3.4), and G/6061-T6 Al MMC (Section 4.4) were discussed previously and reference should be made to appropriate sections for details.
Cathodic polarization diagrams of planar G/6061-T6 Al MMC six-ply plate in deaerated and aerated 0.5 M Na₂SO₄ and 3.15 wt% NaCl are shown in Figures 5.1.7 through 5.1.10. In the aerated solutions, the diffusion-limited O₂-reduction current density was about 2.0 x 10⁻⁵ A/cm² in 0.5 M Na₂SO₄ and about 5.0 x 10⁻⁵ A/cm² in 3.15 wt% NaCl. The cathodic curves of the aerated solutions gradually approached the H₂ evolution curves of the deaerated solutions at i > 10⁻⁴ A/cm².

An anodic polarization diagram of the planar six-ply plate in deaerated 3.15 wt% NaCl is shown in Figure 5.1.11. The pitting potential of the six-ply plate was about -0.82 V_{SCE} in 3.15 wt% NaCl (Figure 5.1.11), whereas it was about -0.50 V_{SCE} in 0.5 M Na₂SO₄ (Figure 4.26).

The log i_{GALV} and E_{GALV} measurements of the galvanic couples containing 50% P100 G fibers and 6061-T6 Al are plotted as a function of time over a 100 hour period, as shown in Figures 5.1.12 and 5.1.13, respectively. The galvanic current density, i_{GALV}, is normalized with respect to the 6061-T6 Al electrode area. In the deaerated 0.5 M Na₂SO₄ and 3.15 wt% NaCl solutions, i_{GALV} stabilized at about 3 x 10⁻⁶ A/cm² and E_{GALV} stabilized between -1.2 and -1.4 V_{SCE}. In the aerated 0.5 M Na₂SO₄ solution, i_{GALV} stabilized between 10⁻⁵ and 10⁻⁴ A/cm², and E_{GALV} stabilized between -0.5 and -0.7 V_{SCE}. In aerated 3.15 wt% NaCl, i_{GALV} and E_{GALV} was very stable at about 2.0 x 10⁻⁴ A/cm² and -0.73 V_{SCE}, respectively.

5.1.5 Discussion

Mixed electrode models based on potentiodynamic polarization diagrams of the individual constituents were useful in identifying galvanic couples and quantitatively assessing the severity of galvanic corrosion. The data from the mixed electrode models were used to derive matrix dissolution rates as a function of the area fraction of the noble constituents (ie. P100 G, SiC, and TiB₂). The validity of using the mixed electrode models in predicting galvanic-corrosion rates was checked against the galvanic-couple ZRA results of the P100 G fibers and 6061-T6 Al, and extrapolated values of i_{CORR} derived from the commercial G/6061-T6 Al MMC six-ply plates.

Before discussing the results, it is appropriate to comment on the high electrical resistivity of SiC and its effect on galvanic corrosion. A valid suggestion would be that SiC does not promote galvanic corrosion because it has high resistivities. This may be true for large pieces of SiC where the IR drop through the piece can become significant, and thus prevent galvanic
corrosion. In the context of SiC/Al MMCs, however, very fine SiC particles are used, and the IR drop through a particle is approximately equal to \( \text{irl} \), as a first approximation (Figure 5.1.14). The parameter \( i \) is the cathodic current density on the particle, \( r \) is the particle resistivity, and \( l \) is roughly the size of the particle. Consequently, for very small particles, although \( r \) is high, the IR drop may not be. For example, a particle with \( r = 10^5 \Omega \cdot \text{cm} \), \( l = 40 \mu\text{m} \), and \( i = 10^{-5} \text{ A/cm}^2 \), can only sustain an IR drop of about 4 mV which would have an insignificant effect on galvanic corrosion.

In order to predict galvanic-corrosion rates, the cathodic polarization diagrams of P100 graphite, SiC, and TiB\(_2\) are plotted with the anodic polarization diagrams of 6061-T6 Al and m5N Al in deaerated and aerated 0.5 M Na\(_2\)SO\(_4\) and 3.15 wt% NaCl, as shown in Figures 5.1.15 through 5.1.18. In the sulfate solutions, deaerated and aerated, the polarization diagrams (Figures 5.1.15 and 5.1.16) indicated that the galvanic current densities cannot be greater than the passive aluminum current density, 10\(^{-6}\) to 10\(^{-5}\) A/cm\(^2\). In deaerated 3.15 wt% NaCl, the polarization diagrams (Figure 5.1.17) also indicated that galvanic corrosion would be negligible. In aerated 3.15 wt% NaCl, the polarization diagrams (Figure 5.1.18) indicated that galvanic corrosion would be significant. The data indicated that the main driving force for galvanic corrosion was O\(_2\) reduction. In aerated chloride-free solutions, it was predicted that galvanic corrosion will be controlled by Al passivation; however, in chloride-containing solutions since Al pits, galvanic corrosion will be controlled by diffusion-limited O\(_2\) reduction occurring at the noble constituents.

Attention will be given to the galvanic couples in the aerated 3.15 wt% NaCl solution, in which galvanic corrosion would be most serious. The data from Figure 5.1.18 can be put into useful form where the dissolution rate of the aluminum matrix can be plotted as a function of noble-constituent area fraction. Since Figure 5.1.18 shows that galvanic corrosion is under cathodic control (for all practical purposes), it is necessary to approximate the cathodic current density of P100 G, SiC, and TiB\(_2\) in the pitting regime of 6061-T6 Al and m5N Al in order to predict galvanic-corrosion rates. These values are about 3.2 x 10\(^{-4}\) A/cm\(^2\) for P100 G and about 1.0 x 10\(^{-5}\) A/cm\(^2\) for SiC and TiB\(_2\) (Figure 5.1.18). The rate of aluminum dissolution as a function of noble-constituent area fraction can now be estimated using these current density values and the following equations:

\[
I_{\text{GALV}} = I_N = I_A \quad (5.1.3)
\]
where

\[ I_N = i_N + \frac{t}{n} = i_N \cdot A_N \]  \hspace{1cm} (5.1.4)

and

\[ I_A = i_A + \frac{c}{a} = i_A \cdot A_A \]  \hspace{1cm} (5.1.5).

In 5.1.4, \( i_N \) is the net current density (cathodic) from the noble constituent, and \( A_N \) is the surface area of the noble constituent. In 5.1.5, \( i_A \) is the net current density (anodic) from 6061-T6 Al or m5N Al, and \( A_A \) is the surface area. Substituting 5.1.4 and 5.1.5 into 5.1.3, gives

\[ i_N \cdot A_N = i_A \cdot A_A \]  \hspace{1cm} (5.1.6).

Equation 5.1.6 can be written in terms of area fractions, \( X_N \) and \( X_A \), by dividing both sides of 5.1.6 by \( A_N + A_A \):

\[ i_N \cdot X_N = i_A \cdot X_A \]  \hspace{1cm} (5.1.7)

However, since \( X_N + X_A = 1 \), Equation 5.1.7 can be simplified to

\[ i_A = i_N \cdot \left(\frac{X_N}{1-X_N}\right) \]  \hspace{1cm} (5.1.8).

The Al dissolution rate, \( i_A \), will be referred to as the galvanic-corrosion rate, \( i_{GALV} \). Graphs of galvanic-corrosion rate, \( \log i_{GALV} \), verses \( X_N \) (Figure 5.1.20) and verses \( X_N \) on a logarithmic scale (Figure 5.1.21) were plotted by substituting the values of \( i_N \) for P100 G, SiC, and TiB\(_2\) into (5.1.8). The corrosion rate of uncoupled 6061-T6 Al and m5N Al is also plotted on the graphs.

In Figure 5.1.20, \( X_N \) was plotted on a regular scale from 0 to 1 which makes it easy to read dissolution rates for area fractions within a practical range (ie., \( 0.2 < X_N < 0.8 \)). In Figure 5.1.21, \( X_N \) is plotted on a logarithmic scale which makes it easier to determine the critical area fraction below which the component of galvanic corrosion does not exceed the corrosion rate of the uncoupled matrix. For example, up to 0.07 area fraction of SiC or TiB\(_2\) or 0.002 area fraction of P100 graphite could be included into a m5N Al matrix without increasing the galvanic component above corrosion rate of the uncoupled matrix. Similarly, in a 6061-T6 Al matrix, up to 0.3 area fraction of SiC or TiB\(_2\) or 0.01 area fraction of P100 G could be included. The only reason 6061-T6 Al could accommodate higher area fractions of
noble constituents in comparison to m5N Al, without increasing the galvanic-corrosion rate above the rate of the uncoupled matrix, was because 6061-T6 Al had a higher uncoupled corrosion rate (Figure 5.1.21). The graphs also predicted that the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of P100 graphite would be about 80 times the corrosion rate of uncoupled 6061-T6 Al; whereas, the galvanic-corrosion rate of 6061-T6 Al coupled to SiC or TiB₂ was predicted to be about 2.5 times the rate of the uncoupled alloy. The results also indicated, for all practical purposes, that there would be no advantage in using m5N Al as a matrix material to gain pitting resistance because volume fractions of noble constituents are generally over 0.1 which would provide enough O₂-reduction sites on m5N Al to initiate pitting.

These results explain the poor corrosion resistance of G/Al MMCs and the relatively good corrosion resistance of SiC/Al MMCs in aerated chloride-containing environments, as discussed in the general literature review (Chapter 2).

It is of interest to compare the results from the mixed-electrode models to the actual galvanic couples containing about 50% P100 G and 6061-T6 Al, and to extrapolated values of icorr (from polarization diagrams) from commercial G(50%)/6061-T6 Al MMC six-ply plates. Note that in Figures 5.1.15 to 5.1.18, the galvanic current densities can be read directly from the diagrams for galvanic couples with equal noble and active constituent surface areas. In deaerated 0.5 M Na₂SO₄ and 3.15 wt% NaCl, the mixed-electrode theory predicted galvanic-corrosion densities of about 5 x 10⁻⁷ A/cm² (Figures 5.1.15 and 5.1.17), which were less than the passive current density of 6061-T6 Al, 10⁻⁶ A/cm². The galvanic current density of the actual galvanic couples was about 3 x 10⁻⁶ A/cm² (Figure 5.1.12), and the extrapolated value from the commercial six-ply plate was about 4 x 10⁻⁶ A/cm² (Figures 5.1.22 and 5.1.24). Given the diversity of techniques, there was good agreement between the predicted, actual, and extrapolated values, as the galvanic currents were within an order of magnitude of the passive-Al current density. The results from the aerated 3.15 wt% NaCl were in excellent agreement: The predicted, actual, and extrapolated galvanic current densities were about 3 x 10⁻⁴ (Figure 5.1.18), 2 x 10⁻⁴ (Figure 5.1.12), and 1 x 10⁻⁴ A/cm² (Figure 5.1.25), respectively. There was one exception in which the predicted galvanic-corrosion rate was significantly less than the actual rate. This occurred in aerated 0.5 M Na₂SO₄, where the mixed electrode theory predicted that the galvanic current density should have been equal the passive current density, ~10⁻⁶ A/cm², as shown in Figure 5.1.16. The actual galvanic current density, however, measured by the ZRA technique, was 10 to 100 times greater than the predicted value (Figure 5.1.12). At least one
reason for this behavior could be an edge effect of the small-area 6061-T6 Al electrodes which were used in the galvanic couples. As shown in Figure 3.1.23 and discussed in Section 3.1.5, the small-area electrodes had passive current densities which were about 5 times greater than those of large-area electrodes (used in the mixed electrode models); consequently, Figure 5.1.19 predicts that galvanic current densities are larger when small-area 6061-T6 Al electrodes are used. In the galvanic couples, the passive current densities increased with time as seen by the rise of $i_{\text{galv}}$ (Figure 5.1.12) and by the decrease of $E_{\text{galv}}$ (Figure 5.1.13). A sulfate reference electrode was used to discount the possibility that this behavior could have been caused by gradual chloride contamination from Calomel reference electrodes. Thick oxide films also covered large proportions of the small-area electrodes. The extrapolated galvanic-corrosion rate from the G/6061-T6 Al six-ply plates (Figure 5.1.23) was about $4 \times 10^{-5}$ A/cm$^2$, but should not be compared to the mixed electrode or galvanic-couple results because the commercial six-ply plates were contaminated with microstructural chlorides (Chapter 4).

5.1.5 Conclusions

Polarization diagrams indicated that galvanic corrosion between the noble constituents (ie. P100 G, SiC, and TiB$_2$) and Al (ie. m5N Al and 6061-T6 Al) would be negligible in deaerated 0.5 M Na$_2$SO$_4$ and 3.15 wt% NaCl solutions. This was in agreement with galvanic-corrosion rates measured from P100 G — 6061-T6 Al couples, and with galvanic-corrosion rates that were extrapolated from G/6061-T6 Al MMC polarization diagrams. In aerated solutions, the driving force for galvanic corrosion was O$_2$ reduction. Polarization diagrams predicted that galvanic corrosion would be controlled by Al passivation in aerated 0.5 M Na$_2$SO$_4$; however, P100 G — 6061-T6 Al galvanic couples corroded at rates higher than predicted, which was probably due to an edge effect of the 6061-T6 Al electrodes that were used in the couples. In aerated 3.15 wt% NaCl solutions, polarization diagrams predicted that galvanic corrosion would be controlled by diffusion-limited O$_2$ reduction occurring at the noble constituents. The predicted behavior was in excellent agreement with measured galvanic-corrosion rates from P100 G — 6061-T6 Al couples, and galvanic-corrosion rates extrapolated from G/6061-T6 Al MMC polarization diagrams.

The type of noble constituent had a major effect on the severity of galvanic corrosion. In aerated 3.15 wt% NaCl, the galvanic-corrosion rate was predicted to be about 30 times greater for P100 graphite — Al couples as compared to SiC — Al or TiB$_2$ — Al couples. Also, the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of P100 G was predicted to be about 80 times that of uncoupled 6061-T6 Al; whereas, for 6061-T6 Al coupled to SiC or
TiB$_2$, the galvanic-corrosion rate was predicted to be about 2.5 times that of the uncoupled alloy.

For all practical purposes, it was found that m5N Al should not enhance pitting resistance of composites.

Since galvanic corrosion in the aerated 3.15 wt% NaCl solutions was controlled by diffusion-limited O$_2$ reduction, the predicted galvanic-corrosion rates were not conservative and may increase dramatically in turbulent environments. Also, galvanic corrosion could be severe in splash-spray zones where thin films of solution permit high O$_2$-diffusion rates.

5.1.6 Reference

Figure 5.1.1: Galvanic corrosion represented with polarization diagrams.

Figure 5.1.2: Polarization diagrams depicting galvanic corrosion under various forms of anodic control.
Figure 5.1.3: Polarization diagrams depicting galvanic corrosion under various forms of cathodic control.

Figure 5.1.4: Polarization diagrams depicting galvanic corrosion under mixed control.
For low cathode-to-anode area ratios, galvanic corrosion is under anodic control due to passivation of the anode; for high cathode-to-anode area ratios, the anode is polarized into the pitting regime and galvanic corrosion is under cathodic control.

For high anode-to-cathode area ratios, galvanic corrosion is under cathodic control due to concentration polarization at the cathode; for low anode-to-cathode area ratios, galvanic corrosion is under mixed control.

Figure 5.1.5: Polarization diagrams showing examples of how the mode of control in galvanic corrosion changes as the electrode area ratios change.
Figure 5.1.6: Circuitry for zero-resistance ammeter (ZRA) and electrometer.
Figure 5.1.7: Cathodic polarization diagram of G6061-T6 Al MMC six-ply plate in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg. Ecorr = -1.015 V, SD = 0.056 V; Avg. time at open circuit = 1.28 h, SD = 0.24 h.
Figure 5.1.8: Cathodic polarization diagram of G/6061-T6 Al MMC six-ply plate in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.645 V SCE, SD = 0.009 V; Avg time at open circuit = 1.04 h, SD = 0.08 h.
Figure 5.1.9: Cathodic polarization diagram of G/6061-T6 Al MMC six-ply plate in deaerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.921 V SCE, SD = 0.023 V; Avg time at open circuit = 3.55 h, SD = 0.83 h.
Figure 5.1.10: Cathodic polarization diagram of G/6061-T6 Al MMC six-ply plate in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.825 Vsce, SD = 0.013 V; Avg time at open circuit = 1.28 h, SD = 0.24 h.
Figure 5.1.11: Anodic polarization diagram of G/6061-T6 Al MMC six-ply plate in deaerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s; Avg Ecorr = -0.941 V vsce, SD = 0.028 V; Avg time at open circuit = 1.55 h, SD = 0.97 h.
Figure 5.1.12: Galvanic current densities (normalized with respect to 6061-T6 Al electrode) of 50% P100 G fiber/50% 6061-T6 Al galvanic couples in neutral solutions at 30°C.
Figure 5.1.13: Potentials of 50% P100 G fiber/50% 6061-T6 Al galvanic couples in neutral solutions at 30°C.
Current Through Particle, \( I = i \ A = il^2 \), where \( A = \text{Surface Area} \)

Resistance Through Particle, \( R = l \ r / A = l \ r / l^2 = r / l \)

IR Drop = \( IR = il^2 \cdot r / l = i \ rl \)

Figure 5.1.14: A first-approximation of the IR drop through a particle assuming that cathodic reactions occur on the upper surface, and that current flows in one dimension through the particle.
Figure 5.1.15: A collection of polarization diagrams that were generated in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Galvanic-corrosion rates can be predicted with these diagrams by using the mixed-electrode theory. Scan rate = 0.1 mV/s.
Figure 5.1.16: Collection of polarization diagrams that were generated in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Galvanic-corrosion rates can be predicted with these diagrams by using the mixed-electrode theory. Scan rate = 0.1 mV/s.
Figure 5.1.17: A collection of polarization diagrams that were generated in deaerated 3.15 wt% sodium chloride of pH 7 at 30°C. Galvanic-corrosion rates can be predicted with these diagrams by using the mixed-electrode theory.

Scan rate = 0.1 mV/s.
Figure 5.1.18: A collection of polarization diagrams that were generated in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Galvanic-corrosion rates can be predicted with these diagrams by using the mixed-electrode theory. Scan rate = 0.1 mV/s.
Figure 5.1.19: These polarization diagrams indicate that larger galvanic-corrosion rates are predicted when using the small-area electrode in contrast to using the large-area electrode in aerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s.
Figure 5.1.20: The effect of noble-constituent area fraction (Xn) on the galvanic-corrosion rate of Al (i.e., 6061-T6 Al and m5N Al) coupled to noble constituents in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. The data were derived from polarization diagrams (Figure 5.1.18) scanned at 0.1 mV/s.
Figure 5.1.21: The effect of noble-constituent area fraction (Xn) on the galvanic-corrosion rate of Al (i.e., 6061-T6 Al and m5N Al) coupled to noble constituents in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. The data were derived from polarization diagrams (Fig 5.1.18) scanned at 0.1 mV/s.
Figure 5.1.22: Polarization diagrams of planar G/6061-T6 Al MMC six-ply plate in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. Scan rate = 0.1 mV/s. The Log i value of -5.7 corresponds to the anodic dissolution rate based on the composite surface area. Twice that Log i value, -5.4, corresponds to the anodic dissolution rate of the Al matrix since the graphite fibers are relatively inert and the composite has a 50% Al content.
Figure 5.1.23: Polarization diagrams of planar G/6061-T6 Al MMC six-ply plate in 0.5 M sodium sulfate solutions of pH 7 at 30°C. Scan rate = 0.1 mV/s. The Log i value of -4.7 corresponds to diffusion limited oxygen reduction. Twice that Log i value, -4.4, corresponds to the anodic dissolution rate of the Al matrix since the graphite fibers are relatively inert and the composite has a 50% Al content.
Figure 5.1.24: Polarization diagrams of planar G/6061-T6 Al MMC six-ply plate in deaerated 3.15 wt% NaCl of pH 7 at 30°C. Scan rate = 0.1 mV/s. The Log i value of -5.7 corresponds to the anodic dissolution rate based on the composite surface area. Twice that Log i value, -5.4, corresponds to the anodic dissolution rate of the Al matrix since the graphite fibers are relatively inert and the composite has a 50% Al content.
Figure 5.1.25: Polarization diagrams of planar G/6061-T6 Al MMC six-ply plate in 3.15 wt% sodium chloride solutions of pH 7 at 30°C. Scan rate = 0.1 mV/s. The Log i value of -4.3 corresponds to diffusion-limited oxygen reduction. Twice that Log i value, -4.0, corresponds to the anodic dissolution rate of the Al matrix since the graphite fibers are relatively inert and the composite has a 50% aluminum content.
5.2 GALVANIC CORROSION IN ALUMINUM-MATRIX COMPOSITES: CONTROL

5.2.1 Introduction

The main findings of Subchapter 5.1 are briefly summarized here to put galvanic corrosion of Al-matrix composites into perspective and to emphasize the need for galvanic control studies. The combination of oxygen and chloride in neutral solutions was found to be the principal cause of galvanic corrosion in aluminum-matrix composites. Galvanic corrosion was controlled by the rate at which oxygen is reduced on noble reinforcement constituents. Graphite was found to be much more deleterious than SiC or TiB₂. For example, the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of P100 graphite was about 80 times greater than that of uncoupled 6061-T6 Al; whereas, in couples with SiC or TiB₂, the galvanic-corrosion rate was predicted to be about 2.5 times that of the uncoupled alloy. These results also agree with reports of poor corrosion resistance of G/Al MMC and good corrosion resistance of SiC/Al MMCs.

Based on these findings, methods to control galvanic corrosion were studied with particular emphasis on graphite fiber composites where galvanic corrosion was serious. The general ideas, however, can be applied to other aluminum-composite systems.

Three methods of galvanic control were investigated: 1) Electrical Insulation of Noble Constituents by Continuous Coatings, 2) Cathodic Protection, and 3) Cathodic Inhibition. The first method proved to be impractical because the required resistivity of coating materials was extremely high, which thus eliminates many prospective materials. Cathodic protection resulted in overprotection where corrosion rates increased rather than decreased. Cathodic inhibition reduced galvanic-corrosion rates by 10 to 100 times.

5.2.1.1 Background

Background information on galvanic corrosion can be found in Section 5.1.1.1.

Electrical Insulation: A conducting electrolyte and electrical contact between unlike materials are requirements for galvanic corrosion. Since the conducting electrolyte cannot be eliminated, breaking electrical contact is an obvious and straightforward solution to prevent galvanic corrosion. Figure 5.2.1 schematically shows a fiber that is electrically insulated from the matrix with a continuous coating, and the equivalent galvanic circuit. The polarization diagrams in Figure 5.2.2 show the decrease in galvanic current, I_{GALV}, as the resistance of the galvanic circuit increases. Figure 5.2.3 shows polarization diagrams where the cathode and
anode have equal areas, but the current is normalized with respect to the electrode area. The parameter \(i_{\text{galv}}\) in Figure 5.2.3 represents the galvanic-corrosion rate. Coating graphite fibers with an insulating material is attractive, for if accomplished, composites with inherent corrosion resistance can be produced.

*Cathodic Protection:* Materials that are inherently susceptible to corrosion can be protected from corrosion by cathodic protection. This technique is used successfully in numerous applications; including, aluminum in slightly acidic to near neutral solutions containing various amounts of chloride [Mears & Fahmey, 1941]. The objective of this technique is to polarize the composite to potentials below its pitting potential by an external power source or sacrificial anode. Caution must be exerted when cathodically protecting amphoteric metals, such as aluminum, because cathodic protection can result in overprotection where corrosion rates increase rather than decrease as a consequence of solution alkalinization near cathode surfaces [Uhlig & Revie, 1985]. Alkalinization results from \(H_2\) evolution:

\[
2H^+ + 2e^- = H_2
\]  \hspace{1cm} (5.2.1)

in addition to \(O_2\) reduction in aerated solutions:

\[
O_2 + 4H^+ + 4e^- = 2H_2O
\]  \hspace{1cm} (5.2.2).

The passive aluminum oxide film on aluminum will dissolve if the alkalinity at the cathode surface exceeds a critical value. The critical value is dependent on temperature, the activity of the aluminate ion, and the degree of hydration of the aluminum oxide. For example, if the activity of the aluminate ion is equal to \(10^{-6}\) and hydrargillite is the hydrated form of the oxide, the corresponding critical \(pH\) is equal to 8.6 at 25°C [Deltombe, Vanleugenhaghe, and Pourbaix, 1974].

*Cathodic Inhibition:* Since \(O_2\) reduction was found to be the primary driving force for galvanic corrosion, suppression of this reaction with cathodic inhibitors was an attractive choice. Cathodic inhibitors inhibit cathodic reactions. The effect of cathodic inhibitors on the diminution of galvanic corrosion is shown with polarization diagrams in Figure 5.2.4. The reader can consult Boffardi [1987] for more information on the uses of cathodic inhibitors.
5.2.2 Materials

This section is partitioned into the following three subsections: Electrical Insulation, Cathodic Protection, and Cathodic Inhibition. Some of the materials used in this study are described in previous chapters, and the reader will be directed to the appropriate sections for details.

**Electrical Insulation:** Planar P100 graphite electrodes (section 3.2.2) and planar large-area and small-area 6061-T6 Al electrodes (section 3.1.2) were used.

**Cathodic Polarization:** Planar large-area 6061-T6 Al electrodes (section 3.1.2), planar G/6061-T6 Al MMC six-ply plate electrodes (section 4.2), and planar particulate SiC/6061-T6 Al MMC electrodes were used. The SiC/6061-T6 Al MMC which contained about 13 vol % SiC was made by Alcan International Ltd., Banbury, England. The SiC/6061-T6 Al electrodes were fabricated with the technique that was used for the G/6061-T6 Al electrodes, as described in Section 4.2.

**Cathodic Inhibition:** Planar P100 graphite electrodes (section 3.2.2) and planar small-area 6061-T6 Al electrodes (section 3.1.2) were used. Analytical grade ZnCl₂ and 98% Na₂CrO₄ were used as the source for the cathodic inhibitors, Zn²⁺ and CrO₄²⁻.

The standard solutions used in these various experiments were neutral 0.5 M Na₂SO₄ and 3.15 wt% NaCl at 30 ± 0.1°C. The solutions were prepared from 18 MΩ·cm water and analytical grade reagents. The solutions were either deaerated by sparging with pre-purified H₂ or aerated by sparging with 19.5 to 23.5% O₂ balanced with N₂. The gas pressure was 1 atm.

5.2.3 Instrumentation and Procedure

This section is also partitioned into three subsections: Electrical Insulation, Cathodic Protection, and Cathodic Inhibition. Reference is made to previous sections when possible.

**Electrical Insulation:** Information on the generation of polarization curves for 6061-T6 Al and P100 graphite can be made to Sections 3.1.3 and 3.2.3, respectively. The zero-resistance ammeter (ZRA) is described in Section 5.1.3. High precision resistors (< 2% tolerance) ranging from 1 KΩ to 100 GΩ by multiples of 10 were inserted between the 6061-T6 Al electrode and P100 graphite electrode to increase the resistance of the galvanic circuit, as shown schematically in Figure 5.2.5. Steady-state I_GALV values were measured as a function of galvanic-circuit resistance. The I_GALV measurements were made from galvanic couples that
were allowed to corrode previously for 1 hour or 100 hours in aerated 3.15 wt% NaCl at 30°C. The P100 graphite electrode and the 6061-T6 Al electrode had about equal areas (~0.023 cm²).

**Cathodic Protection:** Potentiostatic cathodic polarization diagrams were generated in deaerated 0.5 M Na₂SO₄ at 30°C by sequentially stepping the potential to more active values starting from the corrosion potential, Eₜₚ. The reported current was the value after 1 hour of polarization. The specimens were polarized at the indicated potentials for approximately 1 hour with the exception of the last data point on the G/6061-T6 Al MMC curve which corresponds to 2.5 hours of polarization (Figure 5.2.6). A cathodically polarized G/6061-T6 Al electrode was videotaped in real time under an optical microscope at high magnification. The video recording technique is described in Section 4.3.

**Cathodic Inhibition:** The standard ZRA setup was used, as described in Section 5.1.3. Galvanic couples formed from P100 graphite and 6061-T6 Al of about equal areas (~0.023 cm²) were immersed in aerated 3.15 wt% NaCl at 30°C. Cathodic inhibitors were added to the virgin solution 1 hour after the galvanic couples were formed. Zinc ions and CrO₄²⁻ in concentrations of 10 ppm were used as cathodic inhibitors.

5.2.4 Results

The results are partitioned into Electrical Insulation, Cathodic Protection, and Cathodic Inhibition.

**Electrical Insulation:** The cathodic polarization diagram of P100 graphite in aerated 3.15 wt% NaCl was obtained from Section 3.2.4; the anodic polarization diagram of 6061-T6 Al in aerated 3.15 wt% NaCl was obtained from Section 3.2.4. Thus, details can be found in the appropriate sections. The ZRA results from aerated 3.15 wt% NaCl showed that I_GALV decreased as the galvanic-circuit resistance was increased. There was no significant difference in the data obtained from the galvanic couples that were operated for 1 hour or those that were operated for 100 hours prior to taking measurements. The data is presented in Figure 5.2.7 where the logarithm of the galvanic-corrosion rate, log i_GALV, is plotted versus the logarithm of the product of the electrode area and the galvanic-circuit resistance, log AR. The reason for plotting the data in this format will be explained in Section 5.2.5. The galvanic-corrosion rate, i_GALV, is the value of I_GALV normalized with respect to the 6061-T6 Al electrode.

**Cathodic Protection:** The monolithic 6061-T6 Al, SiC/6061-T6 Al MMC, and G/6061-T6 Al MMC were overprotected while generating the potentiostatic polarization
diagrams (Figure 5.2.6) in deaerated 0.5 M Na₂SO₄. The 6061-T6 Al corroded uniformly, and the surface was rough, consisting of shallow ubiquitous dimples with diameters of about 40 μm, as shown in Figure 5.2.8. The SiC/6061-T6 Al MMC also corroded uniformly, where SiC particles were exposed and undercut as the matrix receded (Figure 5.2.9). The G/6061-T6 Al MMC provided a dramatic example of overprotection because the continuous fibers stood in relief due to the loss of matrix. Bare graphite fibers, stripped of the 6061-T6 Al matrix, are shown in Figure 5.2.10. Figure 5.2.11 shows a cross-sectional view of the same sample with fibers in relief. Note the new position of the matrix surface and its relatively uniform recession. The overprotection of the G/6061-T6 Al MMC was also captured in real time under high magnification on video tape (Sequence 5.2.1). In the video footage, the graphite fibers can be used for scaling as they are about 10 μm in diameter.

**Cathodic Inhibition:** In Figures 5.1.12 and 5.1.13, log i_{OALV} and E_{OALV}, respectively, are plotted as functions of time over 100 hours for the P100 graphite—6061-T6 Al galvanic couples in the aerated 3.15 wt% NaCl at 30°C. The galvanic-corrosion rate decreased by about 10 to 100 times following the addition of Zn²⁺ (10 ppm) or a combination of Zn²⁺ (10 ppm) and CrO₄²⁻ (10 ppm) to the NaCl solution. The galvanic potential, E_{OALV}, became active after the inhibitors were added to the solution.

**5.2.5 Discussion**

Each of the galvanic control methods will be discussed separately in the following paragraphs. A brief summary, however, is provided as a preview to the detailed discussions. The first method which reduces galvanic corrosion by electrically insulating noble constituents from the aluminum matrix is likely to be impractical for G/Al MMCs due to the extremely high electrical resistivities that were required from coating substances. Cathodic protection is dangerous because aluminum is susceptible to overprotection. The overprotection phenomenon as well as the effect of graphite fibers on overprotection are discussed. Cathodic inhibition was found to be the most successful technique to control galvanic corrosion. The effects of cathodic inhibitors are discussed in addition to long-term goals of this technique.

**Electrical Insulation:** How much electrical resistance is required between a graphite fiber and the aluminum matrix to prevent galvanic corrosion? That is the fundamental question that will be answered in this section.

The following analysis pertains to galvanic corrosion of G/6061-T6 Al MMCs in aerated 3.15 wt% NaCl at 30°C. The polarization diagrams and the galvanic-couple experiments
generated two independent data sets. These two data bases were used to calculate the required electrical resistance which resulted in identical solutions, giving the method credibility. The calculations were done for a composite with equal areas of P100 graphite and 6061-T6 Al since the commercial G/6061-T6 Al MMCs examined in Chapter 4 had 50 vol % of P100 fibers. For other graphite volume fractions, the calculations and some experiments must be modified appropriately.

In order to decrease the galvanic-corrosion rate, a potential difference, which is usually called the IR drop, must be maintained between the cathode and anode, as shown in Figure 5.2.3 (for a galvanic couple with equal cathode and anode areas). The larger the IR drop, the larger the decrease of galvanic corrosion. The required resistance in a galvanic circuit to produce a given IR drop depends on the size of the electrode areas. This point is shown schematically in Figure 5.2.14 where the electrode areas of couple 2, A₂, are twice as large as those of couple 1, A₁. The parameter I is the galvanic current, and R is the resistance in the galvanic circuit; the subscripts make reference to the couples. In order for both couples to have the same galvanic-corrosion rates, they must have identical IR drops. Thus, I₁R₁ must equal I₂R₂, but because A₂ is twice A₁, I₂ is equal to twice I₁. Hence, couple 1 must have a galvanic resistance, R₁, that is twice as large as the resistance of couple 2, R₂.

Each graphite fiber and the surrounding matrix represents one galvanic cell. The galvanic couples that were examined were made of graphite electrodes containing about 30,000 fibers. Thus, it is evident that the data produced from the galvanic-couple measurements must be presented in a way that allow it to be used to calculate the required resistance between an individual fiber and the matrix. For the galvanic-couple data, this is readily done. Since a given i\textsubscript{galv} corresponds to a unique IR drop (Figure 5.2.3) and since IR is equal to i\textsubscript{galv}AR, a given value of i\textsubscript{galv} is associated with a unique value of AR. Consequently, AR can be plotted as a function of i\textsubscript{galv}, as shown in Figure 5.2.7 on a log scale. Note in Figure 5.2.7 that the data from the galvanic couples exposed for 1 hour were similar to those exposed for 100 hours which indicates that the system was relatively stable.

The data presented in this way becomes useful since one can select a particular galvanic-corrosion rate and read the corresponding AR product. The required resistance between the cathode and anode to achieve the required galvanic-corrosion rate can be calculated if the electrode area is known. An example for the G/6061-T6 Al MMC will be given following an explanation of how the polarization diagrams were processed.
Using the polarization diagrams, the goal is to achieve the same plot of log i_{GALV} vs log AR as derived from the galvanic-couple data. This was done by reading the values of i_{GALV} and the corresponding IR drop from Figure 5.2.15, which shows the cathodic P100 graphite and anodic 6061-T6 Al polarization diagrams. In Figure 5.2.16, log i_{GALV} was plotted as a function of log IR. Superposed on Figure 5.2.16 are constant AR lines, and the intersection of these lines with the log i_{GALV}-log AR curve gives the unique values of AR that correspond to i_{GALV}. The values obtained for log i_{GALV} and log AR are plotted with the galvanic-couple data in Figure 5.2.7, showing extremely high correlation between the two methods. If couples of different graphite volume fraction are of interest, the original polarization diagrams can still be used, but new galvanic couples must be examined having the correct anode-to-cathode area ratio.

Finally, the required resistance between a single fiber and the surrounding matrix can be calculated. Suppose that a galvanic-corrosion rate equal to 1/10th of the uncoupled corrosion rate can be tolerated. Thus, i_{GALV} should equal to about 3 x 10^{-7} A/cm^2 which corresponds to an AR value of about 3.16 x 10^{16} \Omega \cdot cm^2 (Figure 5.2.7). The diameter of a graphite fiber is about 10 \mu m which gives a cross-sectional area of about 7.85 x 10^{-7} cm^2. The required resistance is then about 4.0 x 10^{12} \Omega, but this value in its present form is still not very useful. Of greater use from a practical point of view is what types of coating substances and coating thicknesses could be used to achieve the 4.0 x 10^{12} \Omega resistance. To put this problem into perspective, consider the schematic diagram in Figure 5.2.17 showing a fiber of length L, diameter D, with a coating of thickness t and resistivity r. The resistance between the fiber and matrix is approximately equal to the following expression:

\[
R = rt/\pi DL
\]  (5.2.3)

The calculated coating resistivity, r, is about 1.26 x 10^{17} \Omega \cdot cm, if the following assumptions are made; L = 1 m, D = 10 \mu m, t = 0.1 \mu m, and R = 4.0 x 10^{12} \Omega. Materials with resistivities in this range are difficult to find. Increasing the coating thickness by 10 times will only reduce r by 10 times, and even 10^{16} \Omega \cdot cm is high. This calculation indicates that finding suitable coating substances and successfully coating fibers with them may not be a practical solution to galvanic corrosion in MMCs.

_Cathodic Protection:_ The overprotection phenomenon will be explained with the aid of an aluminum potential-pH diagram. During cathodic polarization in a neutral solution, the coordinate of the cathode in potential-pH space on the Pourbaix diagram (Figure 5.2.18) shifts from the vicinity of point 1 (where hydrargillite is stable) to the vicinity of point 2 (where the
aluminate ion is stable) because the cathodic reactions alkalinize the solutions. Consequently, if the critical pH is exceeded during cathodic polarization, aluminum dissolution becomes significant even though a net cathodic current is measured. Thus, cathodic currents that are too large induce overprotection. The polarization diagrams in Figure 5.2.6 and Figure 5.2.19 show that if monolithic 6061-T6 Al and G/6061-T6 Al MMCs are cathodically polarized to the same potential, the cathodic current densities on the G/6061-T6 Al MMC are larger. The result is that G/6061-T6 Al MMCs are more susceptible to overprotection because alkalinization increases as cathodic current densities increase.

**Cathodic Inhibition:** The goal in this phase of the research program was to demonstrate the feasibility of achieving galvanic protection with cathodic inhibitors. Zinc ions (10 ppm) or a combination of \( \text{Zn}^{2+} \) (10 ppm) and \( \text{CrO}_4^{2-} \) (10 ppm) were used as cathodic inhibitors. Although chromates are usually considered as anodic inhibitors, low levels (~10 ppm) inhibit cathodic reactions [Hatch, 1964]. Zinc ions inhibit \( \text{O}_2 \) reduction by precipitation as \( \text{Zn(OH)}_2 \) on cathodic sites due to local alkalinization [Boffardi, 1987]. These inhibitors reduced galvanic corrosion of couples containing about 50% P100 graphite and 6061-T6 Al in aerated 3.15 wt% NaCl by about 10 to 100 times.

The way in which these inhibitors were used required a closed system where the concentration of the inhibitors could be controlled. It would be impossible to use these inhibitors in open systems, such as the ocean. Thus, the eventual goal is to incorporate inhibitors directly into the fibers or to modify the electrochemical properties of the fibers such that \( \text{O}_2 \) reduction is stifled. One possible method is by the intercalation of ions into the graphite structure. Recall from Subchapter 3.2 that the electrochemical properties of graphite were relatively easy to modify by polarization treatments.

**5.2.6 Conclusions**

Three methods were investigated to control galvanic corrosion in Al-matrix composites: 1) Electrical Insulation of Noble Constituents by Continuous Coatings, 2) Cathodic Protection, and 3) Cathodic Inhibition. Particular emphasis was given to G/Al MMCs, where galvanic corrosion is severe. The most promising method was the use of cathodic inhibitors where galvanic-corrosion rates were reduced by about 10 to 100 times. More work is needed as the eventual goal is to develop graphite fibers that do not catalyze \( \text{O}_2 \) reduction so that composites with inherent corrosion resistance can be produced. The electrical insulation of graphite fibers to reduce galvanic corrosion to negligible levels required coating materials of extremely high resistivities (~10\(^{17}\) \( \Omega \cdot \text{cm} \)). This requirement eliminates many candidate
substances, making it difficult to put the method into practice. Cathodic protection is
dangerous because aluminum is susceptible to overprotection. The problem was accentuated in
G/6061-T6 Al MMCs which required higher cathodic current densities for cathodic protection,
resulting in a greater degree of alkalinization during cathodic polarization when compared to
monolithic 6061-T6 Al.

5.2.7 References

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Figure 5.2.1: Shown on the left, is a schematic diagram of a graphite fiber that is electrically insulated from the Al matrix. The equivalent galvanic circuit is shown on the right.
Figure 5.2.2: Galvanic corrosion represented by polarization diagrams. As the resistance of the galvanic circuit increases, the IR drop between the electrodes increases which results in a decrease in the galvanic current.

Figure 5.2.3: In this figure, the polarization diagrams are normalized with respect to electrode area, and represent galvanic corrosion of a couple having equal cathode and anode areas. The figure also shows that as the IR drop increases, the galvanic corrosion rate decreases.
Figure 5.2.4: Polarization diagrams showing the effect of cathodic inhibitors on galvanic-corrosion rates.
Figure 5.2.5: A resistor is placed between a graphite fiber electrode and an aluminum electrode to increase the resistance of the galvanic circuit.
Figure 5.2.6: Potentiostatic cathodic polarization diagrams of monolithic 6061-T6 Al, G/6061-T6 Al MMC, and SiC/6061-T6 Al MMC in deaerated 0.5 M sodium sulfate of pH 7 at 30°C. The time at each point was 1 h except for the point indicated at 2.5 h.
Figure 5.2.7: Diagram of log AR vs log igalv for a galvanic couple containing 50% P100 graphite fiber and 6061-T6 Al in aerated 3.15 wt% sodium chloride of pH 7 at 30°C.
Figure 5.2.8: The SEM micrograph shows an overprotected monolithic 6061-T6 Al cathode. A and B are 6061-T6 Al. The electrode was polarized in deaerated 0.5 M Na₂SO₄ of pH 7 at 30°C.

Figure 5.2.9: The SEM micrograph shows an overprotected SiC/6061-T6 Al MMC cathode. A — SiC. B — 6061-T6 Al matrix. The electrode was polarized in deaerated 0.5 M Na₂SO₄ of pH 7 at 30°C.
Figure 5.2.10: SEM micrograph of an overprotected G/6061-T6 Al MMC cathode. Graphite fibers are shown in relief. The electrode was polarized in deaerated 0.5 M Na₂SO₄ of pH 7 at 30°C.

Figure 5.2.11: Cross-sectional view of the sample in Figure 5.2.10 showing the extent of overprotection. The arrow indicates the new position of the matrix.
Figure 5.2.12: These graphs show the effect of cathodic inhibitors on the galvanic-corrosion rate of couples containing 50% P100 graphite fiber and 6061-T6 Al in aerated 3.15 wt% sodium chloride of pH 7 at 30°C.
Figure 5.2.13: These graphs show the effect of cathodic inhibitors on the galvanic-corrosion potential of couples containing 50% P100 graphite fiber and 6061-T6 Al in aerated 3.15 wt% sodium chloride of pH 7 at 30°C.
The electrode current densities of couples #1 and #2 are identical (that is, $i = i_1 = i_2$); thus, couples #1 and #2 necessarily have identical IR drops.

\[
A_1 = A, \quad A_2 = 2A, \quad i = i_1 = i_2 \quad \rightarrow \quad I_j = i \cdot A_j; \text{ therefore, } I_2 = 2I_1
\]

\[
I_1 \cdot R_1 = I_2 \cdot R_2 \quad \rightarrow \quad R_1 = \frac{I_2 \cdot R_2}{I_1} = 2R_2
\]

**Figure 5.2.14:** This figure shows that in order for the two galvanic couples to have identical IR drops, the ratio of the resistances ($R_1/R_2$) must be inversely proportional to the ratio of the electrode areas ($A_1/A_2$).
Figure 5.2.15: This diagram demonstrates how the IR drop and corresponding $\text{igalv}$ were obtained from the cathodic P100 graphite fiber and anodic 6061-T6 Al polarization diagrams that were generated in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Scan rate = 0.1 mV/s.
Figure 5.2.16: Diagram of log igalv vs log IR for a galvanic couple containing 50% P100 graphite fiber and 6061-T6 Al in aerated 3.15 wt% sodium chloride of pH 7 at 30°C.
Figure 5.2.17: Schematic of an electrically insulating coating on a graphite fiber.
Figure 5.2.18: During cathodic polarization in a neutral solution, the coordinate of the cathode in potential-pH space shifts from point 1 to point 2 because the hydrogen evolution and oxygen reduction (in aerated solutions) reactions alkalize the solution.
Figure 5.2.19: These cathodic polarization diagrams demonstrate that the G/6061-T6 Al MMC requires higher cathodic current densities to achieve the same degree of polarization in comparison to monolithic 6061-T6 Al in aerated 3.15 wt% sodium chloride of pH 7 at 30°C. Therefore, the MMC is more susceptible to overprotection than the monolith because alkalinization increases as cathodic current densities increase.
6 CONCLUSIONS

Presently, the most serious corrosion problem found in graphite/aluminum (G/Al) metal-matrix composites (MMCs) originates from residual microstructural chlorides (left behind by the fabrication process) that lead to the accelerated dissolution and corrosion of diffusion-bonded regions between adjacent precursor wires. Alternative methods of fabrication must be developed that do not leave behind residual halides in composite microstructures. It is equally important to develop fabrication methods that prevent the formation of Al₄C₃ at graphite-Al and SiC-Al interfaces. Because Al₄C₃ hydrolyzes, its presence in G/Al and silicon carbide/aluminum (SiC/Al) MMCs would severely compromise degradation resistance.

G/Al and SiC/Al MMCs were also susceptible to galvanic corrosion. The main driving force for galvanic corrosion was found to be O₂ reduction. In aerated simulated seawater (3.15 wt% NaCl), where Al pits, galvanic corrosion was controlled by diffusion-limited O₂ reduction occurring at noble constituents. The galvanic-corrosion rate (in aerated simulated seawater) of 6061-T6 Al coupled to an equal area of graphite was about 80 times greater than the corrosion rate of uncoupled 6061-T6 Al; whereas, the galvanic-corrosion rate of 6061-T6 Al coupled to an equal area of SiC was predicted to be about 2.5 times that of the uncoupled alloy.

Polarization diagrams indicate that the galvanic-corrosion rate of SiC/Al MMCs can be maintained below the corrosion rate of uncoupled 6061-T6 Al by keeping the area fraction of SiC ≤ 0.3. In G/Al MMCs, where galvanic corrosion was serious, modified graphite fibers that do not catalyze O₂ reduction need to be developed. The cathodic inhibition studies demonstrate that galvanic corrosion of graphite-Al couples can be significantly reduced by inhibiting O₂ reduction.