Numerical Modelling of Galvanic Structural Joints Subjected to Combined
Environmental and Mechanical Loading

by

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ABSTRACT

Dissimilar metal joints such as aluminum-steel joints are extensively used in automobile, naval and aerospace applications and these are subjected to corrosive environmental and mechanical loading resulting in eventual failure of the structural joints. In the case of aluminum alloys under aggressive environment, the damage accumulation is predominantly due to corrosion and is accelerated in presence of other metals. During recent years several approaches have been employed to develop models to assess the metal removal rate in the case of galvanic corrosion. Some of these models are based on empirical methods such as regression analysis while others are based on quantification of the ongoing electrochemical processes. Here, a numerical model for solving the Nernst-Planck equation, which captures the electrochemical process, is implemented to predict the galvanic current distribution and, hence, the corrosion rate of a galvanic couple. An experimentally validated numerical model for an AE44 (Magnesium alloy) and mild steel galvanic couple, available in the literature, is extended to simulate the mechano-electrochemical process in order to study the effect of mechanical loading on the galvanic current density distribution and corrosion rate in AE44-mild steel galvanic couple through a multiphysics field coupling technique in COMSOL Multiphysics®. The model is capable of tracking moving boundaries of the corroding constituent of the couple by employing Arbitrary Langrangian Eulerian (ALE) method.

Results show that, when an anode is under a purely elastic deformation, there is no apparent effect of mechanical loading on the electrochemical galvanic process. However, when the applied tensile load is sufficient to cause a plastic deformation, the local
galvanic corrosion activity at the vicinity of the interface is increased remarkably. The effect of other factors, such as electrode area ratios, electrical conductivity of the electrolyte and depth of the electrolyte, are studied. It is observed that the conductivity of the electrolyte significantly influences the surface profile of the anode, especially near the junction. Although variations in electrolyte depth for a given galvanic couple noticeably affect the overall corrosion, the change in the localized corrosion rate at the interface is minimal. Finally, we use the model to predict the current density distribution, rate of corrosion and depth profile of aluminum alloy 7075-stainless steel 316 galvanic joints, which are extensively used in maritime structures.
I dedicate this dissertation to my mom, Chandra and dad, Muthegowda. Love you both to the maximum.
I would like to express my sincere gratitude to the many people without whose support this dissertation would not have materialized. First, I would like to thank my advisor prof. K.N. Solanki, for his guidance, encouragement and belief in me throughout this endeavor. Next, I would like to express my gratitude to my committee members prof. Konrad Rykaczewski and prof. Yang Jiao for their support and helpful remarks to improve my dissertation. I would like to extend special thanks to Mr. B. Gholami, Dr. Bhatia, Dr. Adlakha, Mr. S. Turnage and Ms. M. Rajagopalan, for many engaging conversations and discussions during my time.
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CHAPTER 1

1. MOTIVATION

Corrosion is a surface phenomenon known as the attack of metals or alloy by their environment, as air, water or soil in chemical or electrochemical reaction to form more stable compounds and this can result in structural failure and great economic loss. Corrosion is a consideration in virtually all engineering applications. Each year, industries invest time and money into trying to curtail the effects of corrosion. Many different corrosive environments have been studied and monitored to develop corrosion control methods (Revie 2011). The corrosion damage of equipment, production facilities, infrastructure etc has severe consequences, including loss of property, interruption of production, and outage of electricity, water etc. Such disruptions occur at a very high cost to society. The corrosion cost is invariably high and was about 5% of U.S GDP (“Cost of Corrosion Study Overview” 2015). The corrosion process of the metal is accelerated when electrically coupled to a more noble metal and is known as galvanic corrosion.

As, with the increase in use of metals in all fields of technology, it is inevitable to have dissimilar metal joints. The majority of aviation, automobile, electronics industries etc are in the quest to find lighter metals to increase efficiency and performance, dissimilar metal joints. An example of such effort was in the early 1980s when Volvo conducted a “Light Component Project”, which resulted in a concept car (Mellde 1985). Galvanic corrosion is one of the major hurdles to the use of magnesium parts in the automobile industry, and it has acknowledged as a vital issue if magnesium is used in exterior components in a vehicle (Isacsson et al. 1997). In many aircraft and aerospace vehicles the dissimilar
metals are joined in such a way that the electrical resistance is minimum, in such situation galvanic corrosion is the primary concern.

Researchers have studied the various factors that influence the extent of galvanic corrosion. Some of these factors being cathodic to anodic ratio, the type of materials combined, geometric defects, solution conductivity, and temperature (Hihara and Latanision 1992; Mansfeld and Kenkel 1975b; Mansfeld and Kenkel 1975a). However, the effect of applied loads on corrosion is still of great interest as aircraft, aerospace, naval structures etc., regularly experience static/cyclic loads. According to the recent LMI Cost of Corrosion Study (Herzberg et al. 2012), the annual cost of corrosion for U.S. Navy Ships and Aviation in 2010 was a combined ~$5.75 billion, and more than 80% of structural failures were due to combined environmental and mechanical loading. This translates into, on average, 20% down time due to unscheduled maintenance every year (Nickerson 2015). The majority of failure/maintenance issues result from the galvanic incompatibility (mix materials joint) coupled with mechanical loading.

To date, the traditional approach to understanding the degradation behavior of dissimilar joints has provided a somewhat myopic view because the experimental and modeling behavior analyses are restricted to a specific loading scenario instead of structural life prediction methodologies within a combined loading framework. Hence, understanding the combined environmental and mechanical loading in structural elements and how it initiates corrosion, in addition to improving upon predictive capability, would undoubtedly aid in improvement in availability and mission readiness. Numerical simulations are essential in advancing our understanding and establishing predictive methodologies of galvanic corrosion (Verbrugge 2006; Deshpande 2010b; Jimmy X. Jia,
Song, and Atrens 2006). However, there are few systematic numerical studies in the literature on simulations of general galvanic corrosion processes, especially, to study the effect of combined environmental and mechanical loading in galvanic coupled joints.
CHAPTER 2

2. LITERATURE REVIEW

Studies by Astley (Astley 1988), Adey and Niku (Adey and Niku 1988) have indicated that numerical methods are promising for studying galvanic corrosion, and in particular for predicting the galvanic current density distribution. There is an abundant amount of analytical work reported in literature to investigate galvanic corrosion. Waber et al. (Waber and Rosenbluth 1955; Waber 1955; Waber and Fagan 1956) have used linear and equal corrosion kinetics (equal polarization parameter) for semi-infinite and parallel anode and cathode surfaces. This work has been extended by Kennard and Waber (Kennard and Waber 1970), by using unequal and linear polarization parameters for anode and cathode surfaces and McCafferty (McCafferty 1977) has applied these unequal and linear polarization parameters to circular systems. Galvanic corrosion over semi-infinite coplanar surfaces has been investigated by Verbrugge (Verbrugge 2006) using the conformal mapping technique. Lately, Song (Song 2010) has developed an analytical approach to examine the galvanic corrosion in some practical applications such as steel–aluminium joint exposed to bio-fuel, galvanic couple with corrosion inhibitors such as passive spacer and a scratched organic coating. A numerical model solving the Laplace and Nernst-Planck equations for a galvanic couple comprised of Al and Al4%Cu, has been reported by Murer et al (Murer et al. 2010). They have compared model predictions for current density with those obtained using Scanning Vibrating Electrode Technique (SVET). Most of the numerical modelling work reported in the literature employs boundary element method based commercial software called BEASY. Jia et al. (J. X. Jia,
Song, and Atrens 2007) have recently studied the influence of geometrical factors on the galvanic current distribution for the magnesium alloy AZ91D coupled to steel was investigated using a Boundary Element Method (BEM) model and experimental measurements. All the above mentioned work considers stationary anode and cathode surfaces. During galvanic corrosion, however, the corrosion rate is at its peak at the junction of the galvanic couple and it decreases along the distance away from the junction due to IR drop. Hence, the corroding material moves faster near the junction, resulting in pit formation. Simulation of the movement of the corroding material requires explicit tracking of the anodic interface. Bharadwaj et al. reported a methodology where the governing equation for the electric potential was solved iteratively over a computational domain varying due to galvanic corrosion. The new co-ordinates of the domain were manually calculated on the basis of the corrosion rate/interface velocity. Arbitrary Langrangian Eulerian (ALE) application mode in COMSOL Multi-Physics®, which is capable of explicitly tracking the moving interface is used to determine the corrosion rate and corroded surface profile of anode by Kiran B. Deshpande(Deshpande 2010b). The numerical model results has already been compared to experimentally namely SVET (Scanning Vibrating Electrode Technique) and the immersion technique by Deshpande(Deshpande 2010a)(Deshpande 2010b). Galvanic corrosion of zinc and aluminum coatings coupled with mild steel was simulated by Cross et al. using a time-dependent finite element model (Cross, Gollapudi, and Schuh 2014). They obtained good agreements with experimental measurements of open circuit potential without considering any external mechanical load.
Xu and Cheng studied the effect of tensile load on steel pipeline corrosion for geometries with initial defects (Xu and Cheng 2012b), (Xu and Cheng 2013). Moreover, effect of defects with different simple geometries on distribution of local potential and current density have been simulated using FEM and compared with experimental results (Xu and Cheng 2014). They concluded that the mechanical-electrochemical interaction has insignificant effect on corrosion rate under elastic deformation. Nevertheless, plastic deformation at the defect, which can be considered as a local galvanic cell, can increase the local activity of corrosion significantly and cause more stress concentration at the defect. However, there has been no numerical study on effect of plastic deformation on chemical processes involved in galvanic corrosion with explicitly tracking anodic electrode dissolution in electrolyte. For this purpose, in the present work, we extend Deshpande’s work to see the effect of loading and other factors such as area ratio, electrolyte depth and conductivity on the galvanic corrosion rate and surface profile of corroded anode. Initially, we replicate the Deshpande’s validated numerical model (Deshpande 2010b) and then the mechanical-electrochemical interaction is incorporated to the numeric model to see the effect of loading on rate of corrosion.
3. INTRODUCTION

3.1 The Concept of Galvanic Corrosion:

This section gives a brief discussion about the basic concepts of galvanic corrosion and electrochemical process involved in galvanic corrosion.

3.1.1 Definition

Bimetallic corrosion occurs when two metals, with different potentials, are in electrical contact while immersed in an electrically conducting corrosive liquid, because the metals have different natural potentials in the liquid, a current will flow from the anode (more electronegative) metal to the cathode (more electropositive), which will increase the corrosion on the anode. In general the corrosion which occur are similar to those that would occur on single, uncoupled metal, but the rate of attack is increased depending on the potential difference.

Figure 1: Schematic of Galvanic Corrosion
Figure 2: Galvanic series where metals are ranked on the basis of the potential they exhibit in seawater at 2.4–4 m s⁻¹ for 5–15 days at 5–30 °C, as taken from ASTM G82 (“ASTM G82 - 98(2014) Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance” 2015)
Figure 3: Galvanic corrosion after 1000 hours salt spray test in laboratory where stainless steel bolts have been screwed into an anodized aluminum block.

### 3.1.2 Fundamental Requirements

The main conditions required for galvanic corrosion

1. Potential difference between dissimilar materials (or other conductors, such as graphite).
2. Electrical contact between dissimilar materials for electron transport (can be direct contact or a secondary connection such as a common grounding path).
3. Exposure to conductive medium for ionic transport

Figure 4: The galvanic corrosion of stainless steel cable ladder with mild steel bolts used in naval ships when exposed to actual atmospheric conditions for a period of 6 months (a) and the galvanic corrosion of aluminum with stainless steel screws after 6 month exposure at the Atmospheric Test Site, Corrosion Laboratory, and NASA (“KSC Corrosion Technology Laboratory -- Galvanic Corrosion” 2015).
3.1.3 Affecting Factors

Major Factors Affecting the rate of corrosion are

1. Electrode Potential: The value of the potential for any alloy, even in sea water, can be changed by a variety of factors such as temperature, velocity, biocide treatment etc. However, the relative ranking (Shown in the fig) of alloys remains largely unchanged by these factors.

2. Electrode Efficiency: Some metals, such as titanium, are not very efficient at reducing dissolved oxygen compared with copper alloys. e.g. cathode efficiency of Ti and Cu alloys in reducing $O_2$ or $H^{2+}$ despite titanium being much more electropositive.

3. Electrolyte: Electrolyte factors that have a major influence on bimetallic corrosion are composition, pH and, in particular, electrical conductivity, which affects both the intensity and distribution of corrosion, preferred PH for galvanic corrosion is very small or very large (ie PH >> 7 or PH << 7).


5. Area Ratio: The larger the cathode compared to the anode, the more oxygen reduction can occur and, hence, the greater the galvanic current and, therefore, corrosion.

6. Aeration and flow rate: The majority of practical situations involving bimetallic corrosion arise in aqueous solutions under conditions where the cathodic reaction is reduction of dissolved oxygen. As with single metal corrosion, bimetallic
corrosion is therefore partly dependent upon the rate at which oxygen can diffuse to the surface from the bulk of the electrolyte.

7. Metallurgical condition and composition: In some cases differences in corrosion potential can exist between coupled metals or alloys of nominally the same composition. Subjection to cold working often tends to make a metal/alloy more anodic. In some alloys heat treatment can produce galvanic differences.

3.2 Transport in Solution

During corrosion processes, species need to move around or be transported in solution. It can be said that under some conditions the rate of corrosion depends on the speed of the transport process. In galvanic corrosion, two transport processes occur, namely diffusion and migration.

3.2.1 Diffusion:

Diffusion is a process where species move under the action of concentration gradient. This process involves species moving from high to low concentration until even concentration is achieved for all species. Two states of diffusion will be discussed, the steady-state and the non-steady state.

The steady-state diffusion occurs when there is no change in the concentration of reactant with time. The flux or flow of reactants under steady-state conditions can be represented by Fick’s first law of diffusion (Fontana 1986).

\[
J(x) = -D \frac{dC(x)}{dx}
\]  

(1)
where, \( J(x) \) is the flux or rate of movement of molecules across a unit area (mol m\(^{-2}\) s\(^{-1}\)), \( D \) is the diffusion coefficient (m\(^2\) s\(^{-1}\)), \( \frac{dc(x)}{dx} \) is the concentration gradient. In this equation, a negative sign is used because the diffusion occurs from a higher to a lower concentration area.

The second type of diffusion is the non-steady or transient state. This is a process where the concentration of species at any point changes with time. In this case, Fick’s second law of diffusion applies:

\[
\frac{∂C}{∂t} = -D \frac{∂^2 C}{∂t^2}
\]  

(2)

3.2.2 Migration

Migration is the process where charged species are transported due to a local electrical voltage gradient that exists over a distance in the solution, known as the potential gradient:

\[
Potential \ gradient = \frac{V}{x}
\]  

(3)

where, \( V \) is the potential and \( x \) is the distance.

In this process, ions move or migrate due to a static electrical force depending on its charge. The flux of ions due to migration is given by the equation below:

\[
Migration \ flux = \frac{zFdc(x)}{RT}
\]  

(4)
where, \( z \) is the charge on the ion, \( F \) is Faraday’s constant (96485 C mol\(^{-1}\)), \( D \) is the diffusion coefficient, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (298 K), \( v \) is ion velocity, \( C(x) \) is the ion concentration.

Another transport process is convection, but we assume the conductive electrolyte to be stationary hence neglect convection. In considering the concentration distribution of species, the mass balance principle is applied, which states that the total concentration of material in the system under study must be constant by the law of conservation of mass. In the system under study, both mass transport and chemical reactions influence the overall concentration distribution. Combining the effects of diffusion and migration, the Nernst-Planck equation may be constructed (Perez 2004). The Nernst-Planck equation is a conservation of mass equation describing the flux of chemical species in a medium under the influence of an ionic concentration gradient and electrical potential distribution. In the theory of dilute solution, the transport of aqueous ionic species is governed by the mass balance equation which describes diffusion under concentration gradient and chemical reaction. It extends Fick’s First Law of Diffusion for the case where diffusing particles are influenced by electrostatic force. If the diffusing particles are themselves charged, they influence the electric field on moving. The potential distribution therefore acts to ensure that the solution remains close to electroneutrality at all points throughout the domain. Regions of non-electraneutrality may exist in reality at interfaces with other materials where static charges exist, but these regions are not explicitly considered. The behavior of each species in solution is therefore governed by the Nernst-Planck law for the case where electroneutrality is enforced.
### 3.2.3 Nernst-Planck Equation

Transport of species \(i\) can be represented by Nernst-Planck equation as,

\[
N_i = D_i \nabla c_i - z_i F u_i c_i \nabla \phi + c_i V
\]  

(5)

where, \(N_i\) is the flux, \(D\) is the diffusion coefficient, \(c_i\) is the concentration of the species, \(z_i\) is the charge, \(F\) is the Faraday constant and \(u_i\) is the mobility of species \(i\), respectively and \(\phi\) is the electric potential and \(V\) is the velocity of solvent/electrolyte. In the above equation, species flux is equated with the three additive fluxes associated with diffusion, migration and convection.

The conservation of flux of species \(i\) can be written as,

\[
\frac{\partial c_i}{\partial t} = -D_i \nabla^2 c_i - Z_i F u_i \nabla \cdot (c_i \nabla \phi) + \nabla \cdot (c_i V)
\]  

(6)

In the model, electroneutrality of the solution is assumed everywhere. The potential, \(V\), governed by Poisson’s equation, states:

\[
\nabla^2 V = \frac{\sigma}{\varepsilon}
\]  

(7)

where, \(\sigma\) - charge density, \(\varepsilon\) - permittivity of the electrolyte. In this case, the excess charge density is assumed to be zero at all points due to the assumption of electroneutrality. Therefore as found by Sharland (Sharland, Jackson, and Diver 1989), it is permissible to replace the Poisson’s equation by the equation of local charge neutrality,

\[
\sum_i z_i [i]_x = 0
\]  

(8)
where, \([i]_x\) is the concentration of species \(i\) at position \(x\) in the pit.

### 3.2.3 Nernst Equations

The First Law of Thermodynamics states that during a chemical reaction in an isolated system, energy is conserved. The energy may be converted from one form to another. The tendency of a reaction to proceed in a given direction can be explained through the Gibbs free energy, \(G\). The change in free energy \(\Delta G\) is determined solely through the initial and final states of the system. Reactions can proceed spontaneously only if the total Gibbs free energy of the system decreases which means the free energy of the reactants must be greater than the free energy of the products.

\[
\Delta G = \sum \mu_{products} - \sum \mu_{reactants}
\]  \hspace{1cm} (9)

where, \(\mu\) is the chemical potential. Hence, if \(\Delta G = 0\) the reaction tends to proceed spontaneously in the given direction; if \(\Delta G = 0\) the reaction tends to proceed spontaneously in the reverse direction and if \(\Delta G = 0\), the reaction is in equilibrium which means it will not have tendency to proceed in either direction.

Electrochemical cells generate electrical energy as a result of electrochemical reactions and reactions can only proceed if the change in free energy \(\Delta G = 0\),

\[
\Delta G = \Delta G^0 + RT \ln \left( \frac{\text{product of activities of reactants}}{\text{product of activities of products}} \right)
\]  \hspace{1cm} (10)

Considering a simple electrode reaction under equilibrium conditions
\[ O + ne^- \rightleftharpoons R \]  \hspace{1cm} (11)

Where O is the oxidized species, R the reduced species, and n is the number of electrons associated with the reaction. If all the components of the reaction are in the standard state, then the standard electrode potential for the reaction is defined by

\[ \varphi_{eq}^0 = -\Delta G^0 / nF \]  \hspace{1cm} (12)

where, \( \Delta G^0 \) is the Gibbs free energy for the reaction.

\[ \varphi_{eq} = \varphi_{eq}^0 - \frac{RT}{zF} \ln \left( \frac{\text{product of activities of reactants}}{\text{product of activities of products}} \right) \]  \hspace{1cm} (13)

Equation (13) is the Nernst equation, used to describe the potential variation of the electrode reaction at the equilibrium. The potential of the electrode changes according to the concentration of the reduced and oxidized species.

\[ \varphi_{eq} = \varphi_{eq}^0 - \frac{RT}{zF} \ln \left( \frac{\text{product of activities of reactants}}{\text{product of activities of products}} \right) \]  \hspace{1cm} (14)

Substituting into the equation above the gas constant, \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \), the absolute temperature \( T = 298 \text{ K} \) and the Faraday’s constant \( F = 96485 \text{ C mol}^{-1} \), the equation below is obtained

\[ \varphi_{c,eq} = \varphi_{c,eq}^0 + 0.0592 \frac{z}{z} \ln \left( \frac{\text{product of activities of reactants}}{\text{product of activities of products}} \right) \]  \hspace{1cm} (15)
3.3 Kinetics Involved in Corrosion Process

3.3.1 Butler-Volmer Kinetics

Thermodynamics explains the concept of corrosion tendency, but it does not give any idea on rate of corrosion, which is measured by kinetics principles. In practice we are interested in the rate at which the corrosion reaction is taking place. The rate of a chemical reaction can be defined as the number of moles of atoms reacting per unit time and per unit surface of an electrode. In the case of an electrochemical reaction, which involves charge transfer, the rate of reaction (corrosion) is calculated in terms of equivalent current or charge transfer rate, which can presented by equation below

\[ i = nFv \]  

(16)

where, \( i \) is current density of charge-transfer (Am\(^{-2}\)), \( n \) is number of mole of electron, \( F \) is Faraday’s constant (96485 C mol\(^{-1}\)), \( V \) is rate of reaction (mols\(^{-1}\)m\(^{-2}\)). Applying this formula to the oxidation-reduction reaction representative of the corrosion of any metal at equilibrium

\[ \text{Red} \equiv O_X + ne^+ \]  

(17)

When this reaction equilibrium is disturbed by either anodic or cathodic polarization, the reaction rates are given by Arrhenius law.

\[ \text{Anodic reaction rate: } k_{\text{red}}C_{\text{red}}exp\left(\frac{-\Delta G^*}{RT}\right) \]

(18)
Cathodic reaction rate: 
\[ k_{ox} C_{ox} \exp \left( \frac{-\Delta G_c^*}{RT} \right) \]  
(19)

\[ \Delta G a^* = \Delta G_{a,ch} - anF\eta \]  
(20)

\[ \Delta G c^* = \Delta G_{c,ch} + (1 - \alpha)nF\eta \]  
(21)

Where \( k_{red} \) and \( k_{ox} \) are reduction and oxidation reaction rate constants respectively, \( C_{red} \) and \( C_{ox} \) are concentrations of reacting species, \( \Delta G a^* \) and \( \Delta G c^* \) are activation energies of anodic and cathodic reactions respectively, \( R \) is the gas constant and \( T \) is the temperature in Kelvin (K). The electrochemical Gibbs energy of activation can be decomposed into the Gibbs chemical activation energy \( \Delta G_{c,ch} \) (which does not depend on the potential) and electrical energy of charge transfer. The \( \eta \) represents the change in potential at the metal-electrolyte interface \( \Delta E = E - E_{rev} \), and \( \alpha \) is the coefficient of charge transfer \((0 < \alpha < 0)\), which reflects the ratio of charge transfer between the two partial reactions, anodic and cathodic. The reaction rates can be expressed by the anodic and cathodic current densities, given below,

\[ i_a = zF k_{red} C_{red} \exp \left( -\frac{\Delta G_{c,ch}}{RT} \right) \exp \left( \frac{anF\eta}{RT} \right) \]  
(22)

\[ i_c = zF k_{ox} C_{ox} \exp \left( -\frac{\Delta G_{c,ch}}{RT} \right) \exp \left( -\frac{(1 - \alpha)nF\eta}{RT} \right) \]  
(23)

For a reversible electrode at equilibrium, the current density becomes the exchange current density, that is
\[ i_o = zF k_{rea} c_{rea} \exp \left( -\frac{\Delta G_{ch}}{RT} \right) = zF k_{ox} c_{ox} \exp \left( -\frac{\Delta G_{ch}}{RT} \right) \] (24)

\[ i_o = zF k_{rea} c_{rea} \exp \left( -\frac{\Delta G_{ch}}{RT} \right) = zF k_{ox} c_{ox} \exp \left( -\frac{\Delta G_{ch}}{RT} \right) \] (25)

\[ i = i_a - i_c = i_o \left[ \exp \left( \frac{\alpha nF}{RT} (E - E_{rev}) \right) - \exp \left( -\frac{(1 - \alpha)nF}{RT} (E - E_{rev}) \right) \right] \] (26)

The equation (above add number) is called Butler-Volmer equation for an electrode reaction. This relation between current density and overpotential is valid only when reaction is governed only by charge transfer, and concentration polarization has no effect (Revie 2008).

3.3.2 Polarization Curves

The kinetics of the electrochemical reactions at the interface between electrodes and electrolyte can be quantified by current-potential curves, also known as polarisation curves shown in Figure below. These curves are expressed as Butler-Volmer relations between current density and over potential. When at equilibrium, the anodic and cathode currents are equal to each other and no net current flows through the system (electrode), i.e. the over potential is zero.

\[ i_0 = |i_a| = |i_c| \] (27)

3.3.3 Tafel Slope Constants

When there is sufficient overpotential, the anodic or cathode current becomes negligible depending upon whether the over potential is positive or negative respectively (Kear and Walsh 2005). When \( \eta \) is anodic, that is positive, the second term in the Butler-Volmer
equation becomes negligible and the anodic current density \((i_a)\) can be expressed by the equation (below, number it later) and it’s overpotential equation (below), with \(\beta_a\) obtained by plotting \(\log |i|\) versus \(\eta\) (below figure)(Kanno, Suzuki, and Sato 1980).

\[
i = i_a = i_0 \exp \left[ \frac{\alpha nF}{RT} \eta_a \right]
\]

\[
\eta = \eta_a = \beta_a \log \left( \frac{i_a}{i_0} \right)
\]

\[
\beta_a = 2.303 \frac{RT}{anF}
\]

Similarly, when \(\eta\) is cathodic, that is negative, the first term in the Butler-Volmer equation becomes negligible and the cathodic current density \((i_c)\) can be expressed by a simpler equation

\[
i = i_c = i_0 \exp \left[ \frac{(1 - \alpha)nF}{RT} \eta_c \right]
\]

\[
\eta = \eta_c = \beta_c \log \left( \frac{i_c}{i_0} \right)
\]

\(\beta_c\) is the cathodic Tafel slope coefficient described in Eq. 1.32. It can be obtained from the slope of a plot of \(\log |i|\) versus \(\eta\), as shown in Figure 1-4. The intercept between the two straight lines yields the value for \(i_0\)(Kear and Walsh 2005).

\[
\beta_c = -2.303 \frac{RT}{(1 - \alpha)nF}
\]
3.3.4 Corrosion Rate from Current Density

The rate of corrosion can be calculated from current density using Faraday’s law (Tait 1994)

\[ C_R = \frac{M}{zF \rho} i_{couple} \]  

(34)

Where M is the molar mass of the corroding species, z electron number, F is the Faraday’s constant, \( \rho \) is the density of the corroding species and \( i_{couple} \) is the galvanic current density in Am\(^{-2}\).

3.4 Effect of Mechanical Load on Galvanic Corrosion

As mentioned in the previous section, studying interaction of mechanical loading and corrosion process leading to failure of material will be a particular focus in this research. From a thermodynamic aspect, Gibbs function always grows with respect to increase in the excessive pressure absolute value for an initially undeformed solid under compression or tension. Each process of compression or tension can be considered as consisting of two independent processes – one resulting in thermoelastic effects (low energy) and the other responsible for strength properties of crystal (high energy). The first term can be neglected as a higher order term in Gibbs function. It is shown that the hydrostatic part of stress tensor affects the local value of the chemical potential of a certain point independently of the direction of mechanical loading and that with an increase in hydrostatic pressure, the mechanochemical activity is increased as well (Gutman 1994).
It is observed that elastic deformation caused by an external load decreases the equilibrium electrical (electrode) potential of system with positive ions ($\varphi_{a,eq}^0$) by (Gutman 1994),

$$\Delta\varphi_{a,eq}^e = -\frac{\Delta P V_m}{zF}$$

(35)

where $\Delta\varphi_{a,eq}^e$ is equilibrium potential shift of anode due to elastic deformation, $V_m$ is molar volume of the electrode, $z$ is charge number, $F$ is Faraday’s constant and $\Delta P$ is magnitude of hydrostatic stress. Under plastic deformation, however, the change in electrical potential can be governed by effective plastic strain $\varepsilon_p$ (Gutman 1994),

$$\Delta\varphi_{a,eq}^p = -\frac{TR}{zF} \ln \left( \frac{\nu \alpha}{N_0} \varepsilon_p + 1 \right)$$

(36)

where $\Delta\varphi_{a,eq}^p$ is equilibrium potential shift of anode due to plastic deformation, $T$ is absolute temperature, $R$ is ideal gas constant (8.314 J/mol K), $\nu$ is the orientation-dependent factor, $\alpha$ is a constant coefficient of $10^9 - 10^{11}$ cm$^{-2}$ and $N_0$ is the initial dislocation density (Shintani et al. 2010; Klimanek and Pötzsch 2002)(Barlat et al. 2002) before plastic deformation. Therefore, the overall equilibrium potential of anodic reaction under continuous elasto-plastic deformation becomes (Gutman 1994),

$$\varphi_{a,eq} = \varphi_{a,eq}^0 - \frac{\Delta P V_m}{zF} - \frac{TR}{zF} \ln \left( \frac{\nu \alpha}{N_0} \varepsilon_p + 1 \right)$$

(37)

We can assume that in case of metal dissolution, only the anodic current is affected by the mechanical load directly. The above equations can be used in the governing equations to couple the electrochemical and mechanical process.
During plastic deformation, particularly, in the stage of strain hardening, the density of mobile dislocations is increased with the increasing stress by activation of new dislocations. The density of new dislocations, \( \Delta N \), is calculated (Gutman 1998)

\[
\Delta N = N_0 \left[ \exp \left( \frac{n \Delta \tau}{\alpha k N_{\text{max}} T} \right) - 1 \right]
\]

(38)

where \( N_0 \) is the initial density of dislocations prior to plastic deformation, \( \Delta \tau \) is the hardening intensity, \( n \) is the number of dislocations in a dislocation pile-up, \( \alpha \) is a coefficient of \( 10^9 \)–\( 10^{11} \) cm\(^{-2}\), \( k \) is Boltzmann constant, \( N_{\text{max}} \) is the maximum dislocation density, and \( T \) is temperature. The plastic strain at the hardening stage can be expressed by:

\[
\varepsilon_p = \frac{N_0}{\alpha \nu} \left[ \exp \left( \frac{n \Delta \tau}{\alpha k N_{\text{max}} T} \right) - 1 \right]
\]

(39)

Figure 5: Schematic of equilibrium potential variation along the free surface of a microstructure with plastic deformation in corrosive solution.

The theory illustrated by Gutman through Evans diagram, where a mechanical deformation can lead to a redistribution of electrochemical heterogeneities and increasing
area for cathodic reaction. Moreover, an increase of slip steps, micro-cracks and surface defects generated during plastic deformation would reduce the activation energy of hydrogen evolution (Gutman 1994). The mechanoelectrochemical effect on cathodic reaction can be described by:

\[ i_c = i_{0,c} \left( \frac{\sigma_{mises} V_m}{10^6 F (-\beta)} \right) \]  

(40)

3.5 Galvanic Corrosion Rate Measurement

The measurement of corrosion is very essential and there are numerous ways to measure the corrosion rate. Few of the methods employed in the work are mentioned below.

3.5.1 Immersion Experiment

**Weight loss measurements:**

The simplest way of measuring the corrosion rate of a metal is to expose the sample to the test medium (e.g. sea water) and measure the loss of weight of the material as a function of time. Although these tests are simple, there is no simple way to extrapolate the results to predict the lifetime of the system under investigation.

**Depth profiling:**

In this method, the sample is exposed to the test medium (electrolyte) for a certain duration and then the depth of corrosion is measured. There are various techniques to measure the depth of corrosion, Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS) are few of the many techniques.
3.5.2 Electrochemical Tests

Polarization Curves or Mixed Potential Theory:

As, galvanic corrosion works like a battery, the corrosion rates can be calculated by using Faraday’s law as mentioned in Equation (40). Hence, we need to determine the galvanic corrosion current. When reaction mechanisms for the corrosion reaction are known, the corrosion currents can be calculated using Tafel Slope Analysis and a plot of log I versus E is called a Tafel plot. The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation. The Butler-Volmer relationship for current density is based on the identifying the anodic and cathodic reactions that are taking place on each electrode. At the equilibrium potential (zero overpotential) the anodic and cathodic currents are equal; this point is known as the exchange current. However, when the overpotential is not equal to zero, the anodic and cathodic currents are different. The current densities and tafel slope constants are obtained by the Equations (27-33). The point of intersection of anodic branch of an alloy with a lower $E_{corr}$ and cathodic branch of an alloy with a higher $E_{corr}$ represents the corrosion potential and the current density of the galvanic couple. Corrosion rate prediction obtained using this method is fairly accurate when $E_{corr}$ of the constituent alloys are more than approximately 120 mV apart depending on the slopes of the polarization curves, as reported by Hihara et al (Hihara and Latanision 1992) and Hack (Baboian 2005) have previously used the mixed potential theory approach in order to investigate galvanic corrosion of various couples using sectional electrode technique.
Figure 6: A classical Tafel plot analysis. As reproduced from (“Electrochemical Corrosion Measurements” 2015).

**SVET (Scanning Vibrating Electrode Technique):**

The Scanning Vibrating Electrode Technique uses a single wire to measure voltage drop in solution. This voltage drop is a result of local current at the surface of a sample. Measuring this voltage in the solution images the current at the sample surface. Current can be naturally occurring or the current can be externally controlled using a galvanostat. SVET has been used in the past to investigate the galvanic corrosion behavior. Isaacs (Isaacs 1988) investigated the galvanic corrosion behavior of antimony–tin soldered and lead–tin soldered copper using SVET. Simoes et al. studied SVET and scanning electrochemical microscopy (SECM) imaging of cathodic protection of aluminum by a Mg-rich coating.
CHAPTER 2

4. METHODOLOGY

4.1 Governing Equations

Transport of species $i$ can be represented by Nernst-Planck equation as,

$$N_i = D_i \nabla c_i - z_i F u_i c_i \nabla \phi + c_i V$$ (41)

where, $N_i$ is the flux, $D$ is the diffusion coefficient, $c_i$ is the concentration of the species, $z_i$ is the charge, $F$ is the Faraday constant and $u_i$ is the mobility of species $i$, respectively and $\phi$ is the electric potential and $V$ is the velocity of solvent/electrolyte. In the above equation, species flux is equated with the three additive fluxes associated with diffusion, migration and convection.

The conservation of flux of species $i$ can be written as,

$$\frac{\partial c_i}{\partial t} = -D_i \nabla^2 c_i - z_i F u_i \nabla \cdot (c_i \nabla \phi) + \nabla \cdot (c_i V) \quad (42)$$

Now in the simplest case the following assumptions are made to simplify

1. Electrolyte solution is well mixed: no concentration gradient exists in the electrolyte solution.

2. The solvent is incompressible: divergent of velocity leads to zero.

3. The solution is electro-neutral.

4. Dissolution reaction takes place at the anode surface whereas hydrogen evolution reaction takes place at the cathode surface (which can be validated from the polarization
curves and the mixed potential theory). Thus, cathode surface is assumed to be not corroding.

With the above assumptions, Equation (36) becomes:

$$\nabla^2 \phi = 0$$  \hspace{1cm} (43)

The above equation takes the form of the Laplace equation for the electric potential and represents the upper bound for the rate of corrosion, as transport by convection and by diffusion are neglected (Verbrugge 2006).

Eq. above is solved over the electrolyte domain subject to boundary conditions, as shown schematically in Fig. 4. The boundary conditions at the anode and the cathode surfaces are vital in order to predict the correct corrosion rates. The polarization data obtained experimentally for individual alloys (Fig. 2 and Fig. 3) are used as the boundary condition for the anode and the cathode surfaces. The following boundary condition is applied at the anode surface as shown in figure below

The general equations for defining distribution of current field in a solution during electrochemical reactions are:

$$\nabla \phi = -\frac{f(\varphi)}{\sigma}$$  \hspace{1cm} (44)

where $\sigma$ is the electrical conductivity of the electrolyte solution and $f(\phi)$ is the current density of anodic (lower $E_{corr}$) species. $f(\varphi)$ is a piecewise linear interpolation function which is obtained from the polarization curve (potential and current density data) of the anodic species. The potential gradient is obtained by dividing the current density value (corresponding to the potential field at anode and cathode) by the conductivity of the
electrolyte solution. Thus, the model is capable of handling non-linear boundary conditions using a piecewise linear interpolation approach.

\[ i_i = -\sigma \nabla \varphi_i \quad (45) \]

### 4.2 Model and Finite Element Method

A finite element model is employed to solve the Laplace equation, Equation (43) using boundary condition for an electrochemical process. The boundary conditions are given in Figure 7 and 8. We use COMSOL Multiphysics® to solve the both electrochemical and solid mechanics problem. COMSOL has a special module called Corrosion module where a Corrosion Secondary interface can be chosen. It describes the current and potential distributions in a corrosion cell under the assumption that the variations in composition in the electrolyte are negligible. The interface can be combined with interfaces modeling mass transport to describe concentration dependent (tertiary) current distributions. The interfaces also describe how the geometry of the cell is affected due to the deposition/dissolution of species on the electrodes. In COMSOL we couple the solid mechanics module with the Corrosion module using multiphysics coupling field technique. The mesh type used was triangular and an adaptive mesh refinement technique was selected. A plane stain approximation and large plastic strain plasticity model with isotropic hardening is used for solid mechanics problem. A solver of MUMPS (multifrontal massively parallel sparse) was selected for solution. In order to ensure reliability of the FE modelling, all initial conditions were obtained from experimental tests or accredited theoretical calculations (Deshpande 2010a). The boundary condition of solution is that the solution boundary is electrically isolated, except the solution/anode
and solution/cathode interface that is set as a free boundary and is shown in the Figure 7 and 8. The FE simulation contains three aspects, i.e., (i) mechanical elasto-plastic solid stress analysis of the Magnesium AE44 - mild steel couple and Al 7075 T6 – Stainless steel 316 couple (ii) electrochemical potential and current density analyses in solution and at the cathode/solution interface, and (iii) simulation and analysis of mechanoelectrochemical effect of both the galvanic couple, i.e., the interaction of mechanical stress/strain and electrochemical corrosion behavior of the AE44 and Al 7050 in solution. Number of elements convergence study is done for each cases and found that 120 elements in case of AE44-mild steel model and 250 elements in Al 7050-stainless steel 316 model is sufficient to provide converged results with reasonable accuracy.

4.3 Boundary Conditions

![Boundary Conditions](image)

Figure 7: The schematic of a computational domain along with the governing equation and the boundary conditions for galvanic corrosion of AE44 - mild steel couple under mechanical loading

On obtaining the solution for the Laplace equation subjected to the above boundary conditions, we obtain potential and current density distribution in electrolyte, anode and
cathode surfaces. Corrosion rate or interface velocity can then be calculated from current density using Eq. (4). The ALE method is employed to incorporate the moving interface during corrosion.

The general equations for defining distribution of current field in a solution during electrochemical reactions are:

$$\nabla i_i = Q_i$$  \hspace{1cm} (46)

Since galvanic corrosion works like a battery, Faraday’s law applies. Hence it possible to calculate the rate at which the metal is consumed at the anode

$$C_R = \frac{M}{zF\rho}i_{couple}$$  \hspace{1cm} (47)

Where M is the molar mass of the corroding species, \(z\) is the electron number, \(F\) is the faraday’s constant, \(\rho\) is the density of the corroding species and \(i_{couple}\) is the intensity of coupling current.

4.4 Arbitrary Langrangian Eulerian (ALE) Method

ALE method is a moving mesh technique which enjoys the advantages of both Eulerian and Langrangian frames of reference and can capture greater deformation with higher resolution (Donea et al. 2004). ALE method comprises of two frames: a reference frame with X, Y co-ordinates for a 2-D formulation and a spatial frame with x, y co-ordinates. The reference frame has fixed co-ordinates while the spatial frame has co-ordinates moving with time, subject to boundary conditions. We incorporate the ALE method using COMSOL MultiPhysics®. The geometry and boundary conditions considered for this
moving mesh technique are shown below in Figure 8. In COMSOL MultiPhysics®, the mesh displacement is obtained by solving the following equations:

\[
\frac{\partial^2}{\partial x^2} \frac{\partial x}{\partial t} + \frac{\partial^2}{\partial y^2} \frac{\partial x}{\partial t} = 0 \quad \text{and} \quad \frac{\partial^2}{\partial x^2} \frac{\partial y}{\partial t} + \frac{\partial^2}{\partial y^2} \frac{\partial y}{\partial t} = 0
\]  

(48)

The above equations dictate smooth deformation of the mesh considering the constraints placed on the boundaries. The normal component \( n \) of velocity vector \( v \) of the anode surface is calculated using Faraday’s Equation (34) and can be represented as

\[
n \cdot v = \frac{M}{zF \rho} i_{\text{couple}} = \frac{M}{zF \rho}
\]  

(49)

Figure 8: The boundary conditions and governing equations for moving mesh technique (ALE) in COMSOL Multiphysics® whereas, that of cathode is considered to be zero as the cathode surface is assumed to be non-corroding. It can be seen from the mixed potential theory as shown in Figure 10 that at the potential of the galvanic couple dissolution (anodic) reaction takes place at the anode surface and hydrogen evolution (cathodic) reaction takes place at the cathode
surface. There are positive and negative current densities associated with anodic and cathodic reactions, respectively. If the cathode boundary is also moved using the equivalent boundary condition as applied to the anode surface, it depicts deposition where cathode boundary is moved into the electrolyte solution due to negative current density. In order to capture the realistic scenario of hydrogen evolution reaction where no material is lost or accumulated, the cathode surface is assumed to be non-corroding.
CHAPTER 5

5. RESULTS

5.1 Galvanic Corrosion without Loading

Here we replicate the results from Deshpande’s work (Deshpande 2010b) on AE44 (Magnesium alloy) and mild steel galvanic couple exposed to 1.6 wt% NaCl solution, so as to keep it as a base model and extend work on it. In his work, he has compared his numerical model results with that of mixed potential theory and experimental results based on immersion technique and SVET. The electric potential, $E_{couple}$ and the current density, $i_{couple}$ of the galvanic couple are estimated from the intersection of the two polarization curves of the individual constituent alloys. Deshpande (Deshpande 2010b) modeled the electrodes (cathode and corroding anode) just as a moving line element but here we model the electrodes as an entire 2 D block so as to apply load and to see the effect of loading (strain) on galvanic corrosion. The current density of the galvanic couple is a critical parameter since it forms the basis for corrosion rate estimation using Faraday’s law (Tait 1994). The input for the simulations are obtained from the polarization curves shown before in Figure 6, and standard electrochemical properties are used for AE44 and mild steel.

Table 1: The material properties used in the model are given in the table.

<table>
<thead>
<tr>
<th>Material properties</th>
<th>AE44 Mg alloy</th>
<th>Mild steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg m$^{-3}$)</td>
<td>1820</td>
<td>7850</td>
</tr>
<tr>
<td>Electrical conductivity (MSm$^{-1}$)</td>
<td>9.1</td>
<td>4.03</td>
</tr>
</tbody>
</table>
Figure 9: (a) The schematic of a computational domain along with the governing equation and the boundary conditions, (b) Cross section of a corroded galvanic couple (Deshpande 2010a), (c) Surface plot of electrolyte potential gradient for AE44–mild steel galvanic couple when exposed to the electrolyte solution at \( t = 3 \) days, (d) The predicted profile using the numerical model and the data obtained from the immersion experiment conducted by Deshpande, after 3 days of immersion in 1.6 wt% NaCl electrolyte solution (electrical conductivity of 2.5 Sm\(^{-1}\)).

It can be noticed that the electrolyte potential varies from \(-1.28\) V along the cathodic region to \(-1.43\) V along the anodic region at time \( t = 0 \). Now, from the mixed potential theory the potential of the same galvanic couple is estimated to be \(-1.35\) V. This difference in electric potential between anode and cathode energizes the Mg to dissolve in the electrolyte solution. The contour plot of the absolute potential gradient indicates the current density is maximum at the junction of galvanic couple which causes higher corrosion at the junction and the corrosion rate decreases along the distance away from the junction towards anode, eventually forming a pit at the junction. The contour plot of
electric potential of our model matches exactly as that of Deshpande’s (Deshpande 2010b) as seen in Figure 9c.

![Figure 9c: Comparison of electric potentials](image)

Figure 9c: Comparison of electric potentials

Table 2: The peak current density and corrosion rate obtained is compared with the work in literature.

<table>
<thead>
<tr>
<th>Galvanic Couple</th>
<th>Mixed Potential Theory</th>
<th>Deshpande (1D, line electrode)</th>
<th>ALE (2D electrodes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current density (A/m²)</td>
<td>Corrosion rate</td>
<td>Current density (A/m²)</td>
</tr>
<tr>
<td></td>
<td>mm y⁻¹</td>
<td>nm s⁻¹</td>
<td>mm y⁻¹</td>
</tr>
<tr>
<td>AE44–mild steel</td>
<td>96.05</td>
<td>231</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The initial peak current density at the anodic region as predicted by the numerical model is 87.05 A/m² and the current density gradually decreases to around 31 A m⁻² away from the junction towards anode. The galvanic current density predicted by the mixed
potential theory is about 96 A m$^{-2}$. The peak current density predicted at the junction of from ALE is comparable with that of mixed potential theory (current is measured by Scanning Vibrating Electrode Technique). The rate of corrosion values obtained by modelling the entire electrodes is compared with that of Deshpande’s model (Deshpande 2010b) and experiment (Deshpande 2010a) and is tabulated in the Table 2. The profile of the anode surface for AE44–mild steel couple after 3 days of constant exposure to the electrolyte solution is shown in Figure 8a. It can be seen that a 1.6 mm deep pit at the AE44 side of the galvanic couple is predicted by the numerical model which is compared with results obtained from the immersion test, which is around 2 mm.

Table 3: The corrosion rates of the galvanic couple calculated using mixed potential theory, predicted using the ALE method and estimated from the two experimental techniques.

<table>
<thead>
<tr>
<th>Galvanic Couples</th>
<th>Corrosion rate (mm y$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mixed potential theory</td>
</tr>
<tr>
<td></td>
<td>From current density</td>
</tr>
<tr>
<td>AE44–mild steel</td>
<td>231</td>
</tr>
</tbody>
</table>

Finally the corrosion rates predicted by all the numerical and experimental methods are compared in the Table 3. It is found that the rate of galvanic corrosion predicted by numerical modelling is very close enough to all the other methods.
5.2 Effect of Electrolyte Depth

If there is only a limited amount of electrolyte, the composition of the electrolyte may significantly change as a result of electrochemical reactions. One important solution factor is the thickness of thin-layer electrolytes, which is encountered in atmospheric environments. The thickness of an electrolyte affects corrosion processes in several different ways. First, it affects the lateral resistance of the electrolyte and, thus, affects the potential and current distribution across the surface of the coupled metals. Second, it affects the transport rate of oxygen across the electrolyte layer and, thus, the rate of cathodic reaction. Third, it changes the volume and the solvation capacity of the electrolyte and, thus, affects the formation of corrosion products.

One parameter that can easily be varied is the thickness of the electrolyte film. The effect of electrolyte depth on galvanic corrosion is investigated using the numerical model while maintaining equal surface area of both AE44 and mild steel and the conductivity of electrolyte is maintained at 2.5 Sm\(^{-1}\) (1.6% NaCl). The electrolyte thickness is varied from 0.16 mm to 10 mm. The depth profile obtained from numerical model solution for different electrolyte thickness is shown below in the Figure 11.
The predicted surface profile of Mg alloy (AE44) from numerical model for different electrolyte thickness of 3% NaCl concentration at $t=3$ days.

The effect of electrolyte thickness for AE44-mild steel galvanic couple is shown in the Figure 11. It is seen that as the thickness of the electrolyte decreases, galvanic corrosion becomes intense at a narrow region near the junction. Usually, the total galvanic corrosion is less in a thin electrolyte film than in bulk but galvanic corrosion at the junction might be more severe in case of thin electrolyte film as shown in the above Figure 11. We can observe that for the electrolyte thickness of 0.16 mm, the galvanic corrosion is acute at the junction and is almost negligible further away from the junction. As the electrolyte thickness increases the galvanic corrosion is more uniform throughout the anodic surface and the total corroded mass is more in case of bulk electrolyte.
The spatial variation of current density of AE44-mild steel couple for different electrolyte thickness of 3% NaCl concentration.

The spatial variation of the current density is obtained using the numerical model and is plotted in the Figure 12 above. It can be seen in the Figure 12, that the anodic current density at the junction of the couple does not vary significantly. However, it decreases with decrease in the electrolyte depth away from the junction. The anodic current density is found to decrease with decrease in the electrolyte depth away from the junction and even at the junction. It can also be seen that the spread of galvanic interaction over the anode surface is restricted to a region closer to the junction with the decrease in the electrolyte depth. The obtained results are comparable with that of McCafferty (McCafferty 1977), where he showed that the total anodic current density increases with increase in the electrolyte depth, eventually attaining a value closer to the bulk electrolyte. It can also be noticed that the increase in electrolyte thickness, increases the drop in the current density between cathode and anode, from about -40 Am\(^{-2}\) to 40 Am\(^{-2}\).
for 10 mm electrolyte thickness and about -5 Am$^{-2}$ to 5Am-2 for thin film electrolyte (0.16 mm thickness), which results in higher overall corrosion.

The effect of electrolyte depth on galvanic corrosion has been considerably debated in literature hence we try to plot the peak current density at the junction of the galvanic couple, to find the maximum rate of corrosion at junction. We make note of the average anodic current density and peak anodic current density, so as to measure the average and maximum rate of anodic corrosion at the junction. The average anodic current density is calculated by integrating the anodic current density over Mg AE44 surface. The Figure 13 gives us the average and peak current densities for different thickness of electrolyte. It can be seen that the peak current density slightly increase initially up to the thickness of 0.64 mm and then decreases with increase in electrolyte thickness reaching a saturation value after about 2.5 mm thickness. This suggests that the corrosion at the immediate junction increases with increase in electrolyte thickness and reaches a maximum around 0.64 mm thickness and then decreases with increases in thickness reaching a steady value after 1.5 mm thickness. The average anodic current density increase with the increase in electrolyte thickness implying that the overall rate of corrosion increase with increase in thickness. It can be noticed that the electrolyte thickness of about 10 mm is sufficient to create a bulk like electrolyte condition.
Figure 13: The average and peak anodic current densities are plotted against thickness of electrolyte of 3% NaCl concentration.

The effect of electrolyte is an arguable one, the experiments conducted by Jia et al. (Jimmy X. Jia, Song, and Atrens 2006) have shown that the galvanic current density for Mg and steel couple of equal surface area increase with increase in electrolyte thickness. Jia et al. accredited this increase in the galvanic current density to a larger area of electrolyte for the ionic current to flow and a reduced resistance against the current flow with increasing electrolyte depth but in case of thin film electrolyte the availability of oxygen for cathodic reaction should be considered and hence further research is needed to address this point. Zhang and Valeriote (Zhang and Valeriote 1993) conducted an experiment, where they tested the effect of electrolyte thickness on galvanic current for two different spatial variations of zinc - steel galvanic couple and reported that the galvanic current increased for the couple with larger spatial variation (4 cm) and
decreased for smaller variation (3 mm) with increase in electrolyte thickness. They attributed this opposite behavior to the fact that the current over the steel surface of the smaller variation couple was oxygen-diffusion limited and was inversely proportional to the electrolyte depth, while for the larger spatial variation, the current was not diffusion limited and depended only on the potential of the steel surface.

Table 4: The potential range, average and peak current densities and corresponding corrosion rates are tabulated for different electrolyte thickness of 3% NaCl concentration.

<table>
<thead>
<tr>
<th>Electrolyte thickness (mm)</th>
<th>0.16</th>
<th>0.32</th>
<th>0.64</th>
<th>1.50</th>
<th>5.00</th>
<th>10.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Potential (V)</td>
<td>-1.10</td>
<td>-1.16</td>
<td>-1.20</td>
<td>-1.24</td>
<td>-1.30</td>
<td>-1.31</td>
</tr>
<tr>
<td>Maximum Potential (V)</td>
<td>-1.48</td>
<td>-1.47</td>
<td>-1.46</td>
<td>-1.44</td>
<td>-1.42</td>
<td>-1.40</td>
</tr>
<tr>
<td>Potential range (V)</td>
<td>0.38</td>
<td>0.31</td>
<td>0.26</td>
<td>0.20</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Average Current density (Am⁻²)</td>
<td>17.13</td>
<td>23.25</td>
<td>32.15</td>
<td>43.98</td>
<td>58.06</td>
<td>61.45</td>
</tr>
<tr>
<td>Peak Current density (Am⁻²)</td>
<td>84.37</td>
<td>85.96</td>
<td>89.65</td>
<td>87.86</td>
<td>87.14</td>
<td>87.06</td>
</tr>
<tr>
<td>Average Corrosion Rate (mmy⁻¹)</td>
<td>41.25</td>
<td>55.99</td>
<td>77.43</td>
<td>105.92</td>
<td>139.82</td>
<td>147.99</td>
</tr>
<tr>
<td>Maximum Corrosion Rate (mmy⁻¹)</td>
<td>203.18</td>
<td>207.01</td>
<td>215.90</td>
<td>211.59</td>
<td>209.86</td>
<td>209.66</td>
</tr>
</tbody>
</table>

The average rate of corrosion increases with the increase in electrolyte thickness attributing to the increase in galvanic current with increase in area of electrolyte. The maximum corrosion occurs at region of interface, where the current density is maximum. The maximum rate of corrosion does not follow a conventional trend, initially it increases
minimally with increase in electrolyte thickness (from 0.16 mm to 0.64 mm), reaches a maximum value at 0.64 mm thickness and then decreases to reach a saturation bulk value.

Figure 14: Surface plot of electrolyte potential gradient for AE44–mild steel galvanic couple when exposed to the electrolyte solution of 3% NaCl concentration with different depth (a) 0.16 mm, (b) 0.64 mm and (c) 1.5 mm and (d) 10 mm.

The electrolyte potential varies from -1.1 V on cathode region to -1.48 V on the anode region for an electrolyte thickness of 0.16 mm and varies from -1.3 V on cathode to -1.41 V on the anode. We observe that the electrolyte potential variation decreases with the increase in electrolyte depth.
5.3 Effect of Solution Conductivity

Galvanic action of a bimetallic couple depends on the surface condition of the metals, which, in turn, is determined by environmental conditions. A metal surface exhibits different potentials in different electrolytes. A galvanic series provides information on the polarity of a bimetallic couple but is environment-specific because the relative position of each metal changes with solution. For instance, the corrosion rates of Magnesium and mild steel in coupled and uncoupled conditions in several solutions vary. In all the solutions, galvanic action results in protection of mild steel, but the amount of Magnesium corrosion varies with solution composition. The difference in the corrosion rates in magnesium sulfate and sodium sulfate solutions indicates the significant effect of cations on the reaction kinetics. The conductivity of the electrolyte is a very important factor because it determines the distribution of galvanic corrosion across the anode surface. When conductivity is high, as in seawater, the galvanic corrosion of the anodic metal is distributed uniformly across the surface. As the conductivity decreases, galvanic corrosion becomes concentrated in a narrow region near the junction as shown below in Figure 15. Usually, the total galvanic corrosion is less in a poorly conducting electrolyte than in a highly conducting one.
Figure 15: The predicted surface profile of AE44 from numerical model for different conductivity of electrolyte at t=3 days.

Here, different wt% NaCl solutions are considered to study the effect of conductivity on galvanic corrosion rate and current density. As the salt concentration in the electrolyte changes the conductivity of the electrolyte changes, so we vary the salt concentration from 0.1% to 10% which varies the conductive of the electrolyte from 0.2 Sm$^{-1}$ to 14 Sm$^{-1}$. We consider three different concentration of NaCl solutions, 0.5%, 1.6% and 10% which represent conductivity of solution as 0.5 Sm$^{-1}$, 2.5 Sm$^{-1}$ and 13.5 Sm$^{-1}$ respectively (Weast and Ohio) 1975) [S-15 Results™ Test Report™ of Coralife] at 23°C room temperature. The conductivity was measured using a platinic conductivity cell. The conductivity of a solution also depends upon temperature, hence we maintain standard room temperature of 23°C or 296 K. The electrolyte thickness is about 10 mm in order to assume corrosion in bulk electrolyte environment (as discussed in section 5.2.)
an electrolyte thickness of around 10 mm is sufficient to create bulk like atmosphere for the modeled couple).

The general trend observed for all electrolyte conductivity is that the galvanic corrosion is more intense at the junction and then reduces as moved away from the intersection. It can be seen in the Figure 15, that the overall galvanic corrosion more uniform thought the length of anode and maximum when the conductivity of the electrolyte is high as in the case of 10% NaCl solution with a conductivity of 13.5 Sm\(^{-1}\). In the case of low conductive electrolyte (0.5 Sm\(^{-1}\)), the galvanic corrosion is very intense at the proximity of the junction and drastically reduces as we move away from the junction and can hardly notice any corrosion away from the junction. It can be observed from the Figure 15, that the corrosion at the junction is maximum for electrolyte with low conductivity (0.5 Sm\(^{-1}\)). The rate of corrosion at the junction is found to decrease with an increase in electrolyte conductivity. The Figure 16 gives the initial current density distribution along the electrode surface which can be used to calculate the initial rate at which the material is depleted from the surface using Faraday’s equation, Equation (34). It can be seen from the Figure 16, that the galvanic current distribution is more uniform for electrolyte with high conductivity and hence we find more uniform corrosion throughout AE44 without formation of steep pit for high conducting electrolyte (13.5 Sm\(^{-1}\)). A sudden leap in the current density is noticed for the electrolyte with low conductivity (0.5 Sm\(^{-1}\)), hence we can see concentrated corrosion at the junction resulting in a pit.
Figure 16: The initial spatial current density variation of AE44–mild steel galvanic couple predicted using the numerical model for different conductivity of the electrolyte. The peak anodic current density at the juncture is found to decrease with an increase in electrolyte conductivity, whereas the average current density throughout the surface of the anode increase with an increase in electrolyte conductivity. The initial corrosion rate calculated using initial peak current density on the anode surface (at the junction) are compared for different cases of electrolyte conductivity (different concentration) in the T
Table 5: The galvanic corrosion rates are calculated based on initial peak anodic current density for different conductive values of electrolyte.

<table>
<thead>
<tr>
<th>Conductivity of electrolyte (Sm⁻¹)</th>
<th>NaCl concentration (Wt %)</th>
<th>Initial anodic peak current density (Am²)</th>
<th>Corrosion rate (nms⁻¹)</th>
<th>Corrosion rate (mmy⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.25%</td>
<td>91.86</td>
<td>7.02</td>
<td>221.22</td>
</tr>
<tr>
<td>2.5</td>
<td>1.6%</td>
<td>87.05</td>
<td>6.65</td>
<td>209.63</td>
</tr>
<tr>
<td>13.5</td>
<td>10%</td>
<td>81.58</td>
<td>6.23</td>
<td>196.47</td>
</tr>
</tbody>
</table>

Measuring the peak current density informs us about the maximum corrosion rate and the site of maximum corrosion. It can be comprehended from the Table 4 and Figure 16 that the maximum corrosion occurs at the junction of a galvanic couple in a low conductive electrolyte. The corrosion rate at the junction for a low conductive electrolyte (0.5 Sm⁻¹) is about 12.68 % more than that of an electrolyte with high conductivity (13.5 Sm⁻¹). In case of high conducting electrolyte the corrosion is more uniform as seen in Figure 15 and hence corrosion rate at the intersection is less even though the overall corrosion is maximum for high conducting electrolytes.
Figure 17: Surface plot of electrolyte potential gradient for AE44–mild steel galvanic couple when exposed to the electrolyte solution with different NaCl concentration (a) 0.25%, (b) 1.6% and (c) 10% at t = 3 days.

It can be observed from the Figure 17, that the electrolyte potential varies from −1.19 V along the cathodic region to −1.46 V along the anodic region for the case (a) with the electrolyte conductivity of 0.5 Sm$^{-1}$ (vitiation of about 0.27 V). The variation of the electrolyte potential reduces with the increase in electrolyte conductivity as shown in the Figure 14. The potential varies for -1.27 V to -1.43 V for the case (b) with electrolyte conductivity of 2.5 Sm$^{-1}$ and variation further decreases from -1.33 V to -1.39 V for case (c) with electrolyte conductivity of 13.5 Sm$^{-1}$. Hence, higher the conductivity of electrolyte lower the electrolyte potential variation.
5.4 Effect of Area Ratio

When a piece of metal is freely corroding, the electrons generated at anodic areas flow through the metal to react at cathodic areas exposed to the environment where they restore the electrical balance of the system. The fact that there is no net accumulation of charges on a corroding surface is quite important for understanding most corrosion processes and ways to mitigate them. However, the absolute equality between the anodic and cathodic currents expressed in the following equation does not mean that the current densities for these currents are equal (Roberge, n.d.).

\[ I_{\text{anodic}} = I_{\text{cathodic}} \]  \hspace{1cm} (50)

When the Equation (49) is expressed in terms of current densities by considering the relative anodic \(S_a\) and cathodic \(S_c\) surface areas and their associated current densities \(i_a\) and \(i_c\) expressed in units of Am\(^2\), for example, it becomes clear that a difference in the surface areas occupied by each reaction will have to be compensated by inequalities in the current densities.

\[ I_{\text{anodic}} = i_a S_a = I_{\text{cathodic}} = i_c S_c \] \hspace{1cm} (51)

\[ i_a = i_c \frac{S_c}{S_a} \] \hspace{1cm} (52)

The implications of the surface area ratio \(S_c/S_a\) (cathode area to anode area) in the last equation are particularly important in association with various forms of local cell corrosion such as galvanic corrosion for which a large surface area ratio is a serious aggravating factor. It is easy to understand that the effect of a certain amount of anodic
current concentrated on a small area of metal surface will be much greater than when the effect of the same amount of current is dissipated over a much larger area. This factor is an important amplifying factor of the anodic current when $S_a/S_c$ is $>> 1$ and a stifling factor when it is $<< 1$.

Larger the cathode compared with the anode, more oxygen/hydrogen reduction, or other cathodic reaction, can occur and, hence, the greater the galvanic current. From the standpoint of practical corrosion resistance, the least favorable ratio is a very large cathode connected to a very small anode. As the corroding element is anode, its area is maintained constant and area of the cathode is varied so as to obtain different area ratios of cathode to anode. The predicted depth profile is plotted to study the effect of area ratio on galvanic corrosion. A 3% NaCl and 10 mm deep electrolyte solution is used as boundary condition for all the area ratios.
Figure 18: The predicted profile using the numerical model of AE44–mild steel galvanic couple when exposed to 3% NaCl electrolyte solution for 72 hours with different area ratios. The area of the anode is kept constant and cathode area is varied to obtain different area ratios.

The obtain results convey that the rate of corrosion of AE44 increases with the increase in area of the cathode (mild steel) and is very sensitive to change in area. It can be observed from the above Figure 18, that the percentage (%) change in the thickness of corroded metal at the metallic intersection (~19% change between 0.1 and 10 area ratio) is much less when compared to that at the surface further away from the junction (~105 % change between 0.1 and 10 area ratio). We can also observe that the corrosion is maximum at the interface irrespective of area ratios, hence considering area ratio as a major factor in overall galvanic corrosion rather than localized corrosion at the junction.

The rate of corrosion at the junction of the couple does not vary as much as overall rate of corrosion for different area ratios but the overall corrosion is much greater in case of smaller anode can be further bolstered by observing the spatial current density distribution shown in Figure 19. The influence of area ratio has been studied previously by many, Jia et al. (Jimmy X. Jia, Song, and Atrens 2006) have studied the effect of geometrical factors such as area ratio on galvanic current density of AZ91D Magnesium alloy- to steel using experimental measurements and a BEM model which is in agreement with the trend we observe.
Figure 19: The spatial current density distribution for AE44-mild steel galvanic couple when exposed to 3% NaCl electrolyte solution for different cathode to anode ratios. The area of the anode is kept constant and cathode area is varied to obtain different area. The current density variation is maximum for the area ratio of 10 and hence the corrosion is maximum for cathode to anode area ratio of 10 as observed in the previous Figure 18. The cathodic spatial current density for the area ratio of 10 is plotted only up to 10 mm distance from junction towards cathode (on the cathode end) as current density converges to almost to near zero. We can observe from the figure that, as the area of the cathode (mild steel) increases for a fixed area of AE44 the current density variation on the anode (AE44) increases. The peak and the average anodic current densities are estimated from the spatial variation of the current density. The peak anodic current density is the maximum value of current density attained over Mg surface which is observed at Mg–steel juncture. The Figure 20 below illustrates the variation of peak and average anodic current density with change in area ratio.
Figure 20: The average and peak anodic current densities are plotted against different area ratios when exposed to an electrolyte of 3% NaCl concentration.

The Figure 20 above shows that as the area ratio is decreased from 0.1 to 10, the peak and average anodic current density is increased but the increase in peak current density on the surface of AE44 is much less (72.48 Am\(^{-2}\) to 94.31 Am\(^{-2}\)), when compared to change in average current densities (23.52 Am\(^{-2}\) to 69.25 Am\(^{-2}\)), suggesting that the reduction in corrosion at the interface is much less when compared to reduction in overall corrosion.

The table below gives the peak and average anodic current densities and corresponding corrosion rates.

Table 6: The range of electrolyte potential range, peak and average anodic current densities and corresponding corrosion rates are tabulated for different cathode to anode ratios when AE44 – mild steel couple is exposed to 3% NaCl electrolyte solution.
<table>
<thead>
<tr>
<th>Minimum Potential (V)</th>
<th>-1.31</th>
<th>-1.30</th>
<th>-1.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Potential (V)</td>
<td>-1.48</td>
<td>-1.41</td>
<td>-1.41</td>
</tr>
<tr>
<td>Potential range (V)</td>
<td>0.38</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>Average Current density (Am-2)</td>
<td>23.52</td>
<td>60.04</td>
<td>69.25</td>
</tr>
<tr>
<td>Peak Current density (Am-2)</td>
<td>72.48</td>
<td>87.05</td>
<td>94.31</td>
</tr>
<tr>
<td>Average Corrosion Rate (mmy-1)</td>
<td>56.64</td>
<td>144.59</td>
<td>166.77</td>
</tr>
<tr>
<td>Maximum Corrosion Rate (mmy-1)</td>
<td>174.55</td>
<td>209.64</td>
<td>227.12</td>
</tr>
</tbody>
</table>

5.5 Galvanic Corrosion under Mechanical Loading

5.5.1 Magnesium AE44 – Mild Steel Galvanic Couple

The effect of uniaxial elastic stress on galvanic corrosion AE44 – mild steel couple is investigated in the work below. The effects of elastic and plastic deformations on equilibrium potential of anodic reaction have been derived by Gutman (Gutman 1994). Xu and Cheng (Xu and Cheng 2012a) applied the equations derived by Gutman to study the effect of uniaxial elastic stress on single metal corrosion of X100 pipeline steel in a near-neutral pH solution by developing a numerical model and comparing it with experimental results. They found that the elastic stress has no significant effect on electrochemical corrosion potential of the steel hence, further studied the effect of plastic strain on corrosion of an X100 pipeline steel and concluded that the mechano-electrochemical effect developed on the steel is small in elastic region, and becomes very significant under plastic strain(Xu and Cheng 2012b). The equations derived by Gutman were experimentally verified by Xu and Cheng(Xu and Cheng 2012b) for a single metal
corrosion and not galvanic corrosion. In this work, we apply the Gutman (Gutman 1994) equations and develop a finite element model to study mechano-electrochemical effect on galvanic corrosion of bimetallic Magnesium alloy AE44 and mild steel couple through a multiphysics field coupling technique in COMSOL Multiphysics®.

![Figure 21: The boundary conditions for static stress analysis of AE44 and mild steel couple.](image)

Here, the previous 2-D model used to study galvanic corrosion is coupled with mechanical loading. The electrolyte part of the model is omitted and only the electrodes are subjected to loading. The two electrodes are (AE44 and mild steel) are assumed to be bonded together. We perform a stationary mechanical elasto-plastic solid stress analysis on the galvanic couple. A tensile load of about 160 MPa is applied onto the anode end, sufficient to cause plastic deformation in Magnesium AE44. The left end of the mild steel is fixed. The boundary conditions and the dimensions are given in the Figure 21. We use 2-D triangular element with plane stain approximation and large plastic strain plasticity.
model with isotropic hardening. The adaptive mesh refinement technique was utilized as it eliminated mesh elongation and smearing to provide a smoother and better mesh quality and direct (MUMPS) solver was used. The material properties assigned are tabulated in the Table 6. The plastic strain is very important factor to consider while studying the mechanoelectrochemical effect on galvanic corrosion given by Gutman’s equations, Equation (37). Hence, the effective plastic strain and Von-Mises stress are the main results to be analyzed. The solution obtained for the static study is shown in the Figure 22 and 23.

Table 7: The material properties of AE44 and mild steel are tabulated (“For Casting Buyers | AFS - American Foundry Society” 2015).

<table>
<thead>
<tr>
<th>Material properties</th>
<th>AE44 Mg alloy</th>
<th>Mild steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg m^{-3})</td>
<td>1820</td>
<td>7850</td>
</tr>
<tr>
<td>Young's modulus (GPa)</td>
<td>45</td>
<td>205</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>Initial yield stress (MPa)</td>
<td>142</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>Isotropic tangent modulus (GPa)</td>
<td>3.5</td>
<td>205</td>
</tr>
<tr>
<td>Electrical conductivity (MSm⁻¹)</td>
<td>9.1</td>
<td>4.03</td>
</tr>
</tbody>
</table>

It can be observed from the Figure 22 that, only Magnesium alloy AE44 is plastically deformed at the junction, as yield strength of AE44 (142 MPa from Table 6) is much less than that of mild steel’s (470 MPa) and moreover while solving the corrosion problem, we assume that external load on the specimen does not affect the current density in the cathode and ion activity in the electrolyte, hence we choose a load sufficient enough to plastically deform Magnesium alloy AE44. Due to the stress concentration at the electrodes interface, the anode plastically deforms to a greater extent in the vicinity of the junction and material away from junction is under elastic strain. The deformed anode is shown in the Figure 22 and 23.

Figure 22: The effective plastic strain distribution on Magnesium alloy AE44 and mild steel under a tensile load of 160 MPa.
Figure 23: Von Mises stress distribution on AE44 and mild steel under the tensile load.

It is seen that, there is a non-uniform stress and strain distribution on the specimen.

Moreover, there is a stress concentration at a narrow region near the junction of the bimetallic couple. The Von Mises stress on the surface of AE44 – mild steel couple varies from 1.43 MPa to 5.06 MPa, as seen in the Figure 23. Since, the initial rate of corrosion depends on initial current density distribution on the top surface of the electrode, it is vital to know the variation of effective plastic strain and hydrostatic stress on the surface of AE44, hence they are plotted on the surface of the anode, as shown in Figure 24.
Figure 24: The variation of plastic strain and hydrostatic stress on the surface of the anode (AE44) is plotted along the distance from the interface when subjected to a load of 160 MPa.

It can be observed that a narrow region near the junction has the maximum plastic strain of 1.52% and hydrostatic stress of 184.82 MPa as seen from Figure 24. The plastic strain and hydrostatic stress reduces drastically as we move away from the junction. Now, at the pre-strained condition, we solve the galvanic corrosion of AE44 and mild steel.

The electrochemical corrosion potential of the Magnesium AE44 alloy is affected by external load, as proposed by Gutman’s theory of Mechanoelectrochemical Interactions (Gutman 1998; Gutman 1994) given by Equation (37) and detailed explanation is given in the Governing equation section 1.1.6. The dislocation density of AE44 under a pre strain is taken to be around $4 \times 10^{13} \text{m}^{-2}$. Takashi et al. (Shintani et al. 2010) have studied Evaluation of Dislocation Density in a Mg-Al-Mn-Ca Alloy and Klimanek et al. (Klimanek and Pötzsch 2002) have reported the dislocation density of
Magnesium under compressive strain conditions. The galvanic couple, AE44 and mild steel which is subjected to a tensile load of 160 MPa is exposed to an electrolyte with a NaCl concentration of 1.6 wt%. We couple the solution of solid mechanics to the corrosion module through multiphysics field coupling technique in COMSOL Multiphysics®. Initially, only the metal electrodes are chosen to participate in the static solid mechanics analysis, whereas the entire model is (electrodes with the electrolyte) is selected for the time dependent corrosion solution. The ALE method is employed to incorporate the moving interface during corrosion. The boundary conditions and governing equations for computational domain and moving mesh technique (ALE) is given in the Figure 25(a) and (b).

![Figure 25](image)

As explained earlier in section 1.1.6, according to Gutman’s Mechanoelectrochemical Interactions theory, the equilibrium potential of a metal varies under different loading conditions and it found that when the anode (AE44) is under an elastic deformation, there is no apparent effect on the potential of the electrode (Gutman 1994)(Xu and Cheng 2012a). However, when the applied tensile strain is sufficient to cause a plastic
deformation, the change in the electrode potential is very significant (Xu and Cheng 2012b)(Gutman 1994). The plastic strain changes the local equilibrium electrode potential and hence the corresponding the net anodic dissolution current density increases significantly which results in increased rate of corrosion. The increase in rate of galvanic corrosion is dependant on the amount of plastic stain. The more the plastic stain, the greater is the increase in the rate of galvanic corrosion. The depth profile obtained for the galvanic couple AE44 and mild steel under a tensile load of 160 MPa is compared with that of no load condition and immersion experiment result conducted by Deshpande(Deshpande 2010b) as shown in Figure 26.

Figure 26: The depth profile predicted for Mg alloy AE44 using the numerical model for with and without tensile load of 160 MPa conditions and results obtained from the immersion experiment conducted by Deshpande, after 3 days of immersion in of 1.6 wt% NaCl electrolyte solution (electrical conductivity of 2.5 Sm-1).
It can be observed from Figure 26, that the maximum and overall rate of corrosion is more in case of plastically deformed anode (AE44). In the case of plastically deformed anode, the rate of galvanic corrosion was found to be maximum in the vicinity of the junction due to the localization of plastic strain, as shown in Figure 22, 23 and 24. The rate of corrosion is dictated by the current density distribution along the anode surface and hence, we plot the spatial current density variation along the anode and cathode surface. We compare the current density distribution for the cases with load and without load in order study the effect of mechanical loading on spatial current density distribution of AE44.

Figure 27: The spatial current density distribution on the surface of AE44-mild steel galvanic when exposed to 1.6% NaCl electrolyte solution couple under tensile load of 160 MPa and no load condition.

It can be seen that that the current density on the AE44 surface under a tensile load of 160 MPa is 98.91 Am\(^{-2}\) at the vicinity of the junction and gradually decreases to about 34.51
Am\(^2\) as we move away, whereas the initial peak current density under no load condition is about 87.05 Am\(^2\) and gradually decrease to around 31 Am\(^2\). This increase in current density is due to the fact that the equilibrium potential decrease significantly under plastic strain conditions as governed by the Equation (36). The reduced local equilibrium potential increases the current density which in turn increases the rate of corrosion. The change in local potential is significantly more in the plastic region, hence the corrosion rate of AE44 is increased significantly at the proximate of intersection. The norm current density contour plot is shown in the Figure 28 and it is seen that it varies from 900 Am\(^2\) to 4.52 Am\(^2\) on the electrode surface under the tensile load and varies from 740 Am\(^2\) to 2.46 Am\(^2\) under no load condition. The maximum norm current density is at the vicinity of intersection for both the cases but relatively higher under loading.

Figure 28: The contour plot of norm current density distribution on AE44–mild steel galvanic couple with (a) and without (b) tensile load of 160 MPa, when exposed to the electrolyte solution of 1.6 % NaCl concentration at t = 3 days.
Figure 29: The contour plot of electrolyte potential distribution for AE44–mild steel galvanic couple with (a) and without (b) tensile load of 160 MPa, when exposed to the electrolyte solution of 1.6 % NaCl concentration at $t = 3$ days.

The change in electrolyte potential for both the cases is very minimal, as we assume that the external load has no influence on the electrolyte ionic activity. The localized strain only changes the potential of electrodes.

Table 8: The corrosion rates with and without load are calculated and compared below.

<table>
<thead>
<tr>
<th>Galvanic Couples</th>
<th>Corrosion rate (mm y$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ALE method</td>
</tr>
<tr>
<td></td>
<td>No load</td>
</tr>
<tr>
<td>AE44–mild steel</td>
<td>231</td>
</tr>
</tbody>
</table>

The rate of corrosion for the galvanic couple is calculated and is compared for with and without load conditions and the experimental results conducted by Deshpande (Deshpande 2010a). The corrosion rate is calculated from both current density and pit growth captured by moving mesh technique (ALE).
5.5.2 Aluminum Alloy 7075-T6 and Stainless Steel 316 Joint:

The results obtained from galvanic corrosion of Aluminum Alloy 7075-T6 and Stainless Steel 316 galvanic couple with and without tensile loading of 300 MPa are presented in this section. The initial electrochemical parameters for FE simulation derived from the Tafel plots. The Tafel plots are obtained from the experiments and exchange and limiting current densities are obtained from the literature (McIntyre, n.d.),(Gereng 2015). In order to show the capability of the numerical simulation in modeling the effect of mechanical loading on corrosion process, a bolted plate, which acts as a galvanic cell in the presence of saline electrolyte is considered. The anode and cathode are made of aluminum alloy 7075-T6 and stainless steel 316, respectively and the geometric model of the joint is shown below Figure 30. Al 7075 plate is 1mm in thickness and 6mm in length. The joint is exposed to the electrolyte of 3 wt% NaCl solution (5 Sm⁻¹) for a period of 15 days. The symmetry of the joint is used and only half the cross-section of the bolted plate is modeled. The electrochemical properties are obtained from polarization experiment. Standard mechanical properties of electrodes were used here. A triangular mesh with adaptive mesh refinement is used and MUMPS (multi-frontal massively parallel sparse) was selected for solution. The electrodes are perfectly bonded and zero flux is considered at the cell boundary. Simulations with and without coupling external mechanical load were carried out to demonstrate the influence of elasto-plastic deformation on corrosion rate.

Initially a static mechanical elasto-plastic solid stress analysis is performed on the galvanic couple to calculate the plastic strain and hydrostatic stress induced in the couple due to external tensile load of 300 MPa. The load is chosen so as to plastically deform Al
7050 (yield strength is 400 MPa). Due to the stress concentration at the electrodes interface, the anode plastically deforms in the vicinity of the cathode as see Figure 31. The maximum plastic strain is about 3% at the intersection of Al and stainless steel due to stress concentration and majority of the joint away from the joint is only under elastic strain.

Figure 30: The boundary conditions along with the governing equations are provided in the above schematic of galvanic corrosion for Aluminum Alloy 7075-T6 and Stainless Steel 316 joint under a tensile load of 410 MPa.

Figure 31: The plastic strain distribution (a) and Von Mises stress distribution (b) on Aluminum Alloy 7075-T6 and Stainless Steel 316 joint under a tensile load of 100 MPa. The corrosion process is allowed for a period of 15 days to notice significant amount of corrosion. It is evident from Figure 32, that the plastic deformation significantly increases
the corrosion rate (change in thickness). The depth profile shows that the rate of galvanic corrosion is increased significantly at the vicinity of junction due to the accumulation of plastic strain at junction as seen in Figure 30. The rate of corrosion away from the junction is not significantly affected. The elastic deformation, nevertheless, does not distinctively affect the corrosion process, which is in accordance with reported experiments.

Figure 32: The change in total electrode thickness is measured along the length of the corroding electrode Aluminum Alloy 7075-T6 with and without tensile load of 300 MPa when exposed to electrolyte of 3% NaCl for 15 days.

It can be noticed that the galvanic corrosion of the anode is amplified by the applied external loading and higher corrosion of the electrode can be seen at the region with higher plastic strain (higher stress concentration) as seen in Figure 32. It can be concluded that the rate of corrosion is affected by amount of loading (plastic strain and elastic strain) on the corroding electrode and it is found to increase with increase in loading. The equilibrium potential shift of anode due to plastic deformation is governed by Equation (36) and hence the total equilibrium potential of anode under plastic strain
becomes lesser than that of the bulk, which enhances the corrosion. Though the plastic deformation reduces the potential of Stainless steel, it also increases the cathodic current (Hydrogen evolution) hence the effect of plastic strain can be neglected at cathode (Gutman 1994). To further illustrate the effect of plastic deformation, the current density at t=15 days for with and without mechanical loading conditions has been plotted in Figure 33, where a significant increase in the current density for the joint under loading is noticed.

Figure 33: Electrode current density distribution of Aluminium Alloy 7075-T6 T6 and Stainless Steel 316 joint under no load and tensile load of 300 MPa at time t = 15 days. The maximum current density is seen at the junction of the electrodes and hence, the rate of galvanic corrosion is maximum at the vicinity of the intersection. It can be observed form the Figure 33, that the current density is increased for galvanic corrosion under a tensile load. The induced plastic strain near the junction decreases the local potential which explains the increased galvanic current density hence increased rate of galvanic corrosion.
The corrosion current for several Al 7075 plate with different initial strain conditions were calculated experimentally to see the effect of elasto-plastic strain on the electrode potential and corrosion current can be seen in the Figure 34. The corrosion current is found to increase with an increase in strain.

The change in electrolyte potential is minimal as the electrolyte potential varies from -1.33 V on the cathode region to -1.41 V on the anode region and from -1.33 V on the
cathode region to -1.41 on the anode region for with and without tensile loading conditions.
CHAPTER 5

6. CONCLUSION

1. A numerical model for solving the Nernst-Planck equation, which captures the electrochemical process is employed and this model is capable of tracking the moving boundary for a 2-D electrode during galvanic corrosion and can handle nonlinear boundary conditions. The current density and corrosion rates obtained for the galvanic couple AE44 – mild steel were compared with those calculated by Deshpande (Deshpande 2010b) from numerical model, mixed potential theory and experimental techniques employing Scanning Vibrating Electrode Technique (SVET) and immersion technique.

2. The electrolyte depth has a noticeable effect on surface profile and rate of corrosion of AE44 – mild steel couple. The peak current density does not vary with the increase in electrolyte depth but the average current density increased significantly with an increase in depth attributing to a larger area for the current to pass and thus reduced the resistance against the current flow. The overall corrosion of AE44 under deeper electrolytes is found to increase but the corrosion at the proximate of the intersection is not affected by the electrolyte depth.

3. The conductivity of the electrolyte significantly influences the rate of corrosion and surface profile of AE44, especially near the junction. In low conducting electrolyte (0.5 Sm⁻¹) the galvanic current over the Magnesium was concentrated at a narrow edge closest to the mild steel, resulting in a very steep spatial current distribution. The spatial current density variation increased with decrease in conductivity of the
electrolyte and is more uniform in high conducting electrolyte (13.5 Sm⁻¹). The overall rate of corrosion increased with an increase in conductivity. The maximum rate of corrosion at the vicinity of the junction decreased noticeably from 221.22 mmy⁻¹ to 196.47 mmy⁻¹ with an increase in conductivity from 0.5 Sm⁻¹ to 13.5 Sm⁻¹.

4. The cathode to anode area ratio has a significant effect on the corrosion rate. The galvanic corrosion rate of AE44 increased appreciable with the decrease in mild steel surface area but the change in galvanic corrosion rate at the junction was minimal.

5. The validated numerical model is extended to simulate the mechano-electrochemical process through a multiphysics field coupling technique in order to study the effects of mechanical loading on galvanic corrosion of AE44 – mild steel. Results show that, when Magnesium alloy AE44 is under a purely elastic deformation, there is no apparent effect of mechanical loading on the electrochemical galvanic process. However, when the applied tensile load is sufficient to cause a plastic deformation, the local galvanic corrosion activity at the vicinity of the interface is increased remarkably and the rate of galvanic corrosion rate increased significantly with the increase in plastic strain.

6. The mechano-electrochemically coupled numerical model was used to study the effect of mechanical loading on Aluminum Alloy 7075-T6 and Stainless Steel 316 Joint. The plastic deformation significantly increased the galvanic current density on Aluminum Alloy 7075-T6 resulting in enhanced corrosion of Aluminum especially at the juncture where plastic stain is large.
**SCOPE**

The numerical model needs to be developed accounting for ionic species in the thin film electrolyte solution in order to capture oxygen-diffusion limited reaction on cathode surface, and thus the scope exists to carry out further investigations. Other geometrical factors like shape of anode and cathode, insulation distance between anode and cathode can also be studied. Experimental verification of the numerical results for the couple will ascertain the numerical modeling technique and in future we intend to incorporate the effect of concentration gradient into the mechano-electrochemical model. Further we would look into localized forms of corrosion considering the effect of crystallographic orientation and other surface defects of the underlying microstructural corrosion process, leading to pit initiation and evolution.
REFERENCES


