EXPERIMENTAL INVESTIGATIONS AND STUDY CORROSION MODEL OF WELDED 6061 ALUMINIUM EXPOSED IN MARINE ENVIRONMENT

Y. P. Asmara¹*, J. P. Siregar¹, L. H. Shah¹, C. Tezara².

¹Faculty of Mechanical Engineering, Universiti Malaysia Pahang
26600 Pekan, Pahang, Malaysia
Email: ¹YPanca@hotmail.com
Phone: +6094246239; Fax: +609424622
²Department of Mechanical Engineering, Faculty of Science, Technology, Engineering and Mathematics, INTI International University
71800 Nilai, Negeri Sembilan, Malaysia

ABSTRACT

Existing methods to investigate preferential weld corrosion are dominated by empirical data. Such empirical models are limited in representing realistic corrosion mechanism which has segmented regions and individual of localised corrosion. Thus, it needs a concept that can interprete both each segmented regions and multi-reactions for self corrosion reaction and combinations of galvanic corrosion process. This research studied weld corrosion model occured on 6061 aluminium that could be considered fundamental theories of electro-chemical process. The objective of this work is to construct corrosion model on weld aluminium using mechanistic theories to be fit with electrical circuit theories. The research studied corrosion process on two types of filler which are 4043 and 4047 weld filler. Studying electrochemical process involving corrosion mechanism have shown a realistic correlations. Model electro-chemical mechansim revealed that the HAZ region behaved as anode and shows higher corrosion rate on both filler. Electrical circuit model can also predicted galvanic effects on each part of weld regions to simulate both individual corrosion process and combination of galvanic corrosion. Sample with filler 4043 had higher corrosion rate compared to 4047 filler due to its inhomogeneous of microstructures.

Keywords: Preferential weld corrosion; corrosion simulation; mixed potential theories.

INTRODUCTION

Weld aluminium corrosion has grown to be a main concern for automotive industries. Many researchers have investigated the weld corrosion to especially predict the corrosion rate. They also have explored the corrosion process in order to control corrosion. As reported in open literature (Hemmingsen et al., 2002), galvanic corrosion have attacked on welded metal and become a destructive sources for automotive bodies.
The most common problem of welded aluminum is galvanic corrosion where those materials are exposed in marine environments. This types of corrosion occur due to dissimilar microstructure among the weld material (WM), heat affected zone (HAZ) and base metal (BM). Because of thermal cyclic during welding, it creates dissimilar of micro structural heterogeneities which causes galvanic effects and has been considered to be the main sources of weld corrosion. Galvanic corrosions have been found at locations where with different regions of the materials which was due to differences microstructure. One of the region on the welded metal can act as anode or cathode which depend on electronegativity of the metal. If the WM and HAZ are anodic to the BM, galvanic current will start from those anodic areas (Kermani et al., 1997; Lee, S Bond and Woollin, 2005). Furthermore, corrosion also can occur on the metal due to its electro-chemical process between metal and electrolyte (self corrosion) (Alawadhi and Robinson, 2011).

Aluminium is contamplated as corrosion resistance which to attributed thin surface layer of aluminium oxide that was formed due to metal exposures to the air. This oxide layer can protect aluminum from further oxidation. Aluminium is starting to corrode when the metal galvanically in contact with other metal (Kimura, 2007). Corrosion resistance of aluminium can be also reduced by aqueous salts, particularly in the presence of dissimilar metals. Aluminium is oxidized by water to produce hydrogen following this reaction.

\[
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2
\]  

(1)

Corrosion Prediction Models

Models to calculate corrosion consist of many different approach. Each model predicts corrosion rate in different manner. All of these were developed from different systems and assumptions. During the last decade, the models were developed by using only limited variables. Whereas, new variables are indicated to have contributions in corrosion models (Marchebois, 2008).

Mixed Potential Theory

Mixed potential theory is a theory used in electrochemistry that relates the potentials and currents from different corrosion reactions. It is an electrode potential resulting from a simultaneous reaction of single redox couple (Hemingsen (2002). According to the mixed-potential, any electrochemical reaction couple can be divided into oxidation and reduction reactions. Under these theory the total current is zero and the corroding metal is charged neutral.
tions and diffusion process. These corrosion mechanisms are based on physicochemical laws. Elements whose composition were cut into 100 mm × 50 mm by using the MVS-C 6/31 shearing machine. The adapted filler metals were 4043 AlSi and 4047 AlSi. The chemical composition of base material and filler metals are displayed in Table 1 and Table 2.

Table 1. Material composition.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu</th>
<th>Si</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 6061</td>
<td>0.205</td>
<td>0.680</td>
<td>0.0829</td>
<td>0.884</td>
<td>0.167</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.404</td>
</tr>
<tr>
<td>Steel</td>
<td>0.0083</td>
<td>&lt;0.0050</td>
<td>0.286</td>
<td>-</td>
<td>0.0843</td>
<td>0.0683</td>
<td>0.0281</td>
<td>0.0290</td>
<td>98.6</td>
</tr>
</tbody>
</table>

Table 2. Fillers composition (Song, 2009).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>Mg</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>4043</td>
<td>4.5-6.0</td>
<td>&lt;0.80</td>
<td>&lt;0.30</td>
<td>&lt;0.10</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.20</td>
<td>Bal</td>
</tr>
<tr>
<td>4047</td>
<td>11.0-13.0</td>
<td>&lt;0.80</td>
<td>&lt;0.30</td>
<td>&lt;0.20</td>
<td>&lt;0.05</td>
<td>&lt;0.10</td>
<td>-</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Figure 1. Mixed potential theory to calculate couple materials corrosion rate.

Kinetics Model of Uniform Corrosion

A mechanistic model of uniform corrosion can be modeled using fundamental physicochemical laws. Which covers electrochemical reactions and diffusion process (Aberle, 2008). In the case of corrosion occurring on the metal surface, it can be expressed mathematically by using mechanistics data. These corrosion mechanisms are based on several assumptions which can be described as follows: convective diffusion, molecular diffusion and diffusion via solid film (Kopliku, 2008).

EXPERIMENTAL SET UP

Samples

Materials used were aluminium 6061 with the thickness of 2 mm. The materials plates were cut into 100 mm x 50 mm by using the MVS-C 6/31 shearing machine. The adapted filler metals were 4043 AlSi and 4047 AlSi. The chemical composition of base material and filler metals are displayed in Table 1 and Table 2.
Sample Preparation

The materials were cut based on different microstructure regions (Figure 2.a) which includes weld material (WM), heat affected zone (HAZ) and base metal (BM). Each weld regions was machined into a surface area of 1 cm$^2$, 0.4 cm$^2$ of area. All of weld regions were soldered with insulated cooper wire for electrical connection and cold mounted as shown in Figure 2.b.

**Figure 2.** (a) Segmented of weld regions and (b) Samples hold on the block of epoxy.

Electrochemical Corrosion Test

Self corrosion rate and galvanic corrosion rate of samples were measured by using linear polarisation resistance (LPR) technique. The experiments were conducted using solutions containing 3% NaCl. The LPR corrosion rate for all weld regions was calculated by using Stern-Geary coefficient, B of 25 mV. All of experiments to test the corrosion rate were set at temperature 25˚C. Schematic of corrosio test is illustrated in Figure 3.

Further interpretation can be generated using an assumption of equivalent electrical circuit consists of arrangement of resistors. Through this circuit, properties of the surface can be identified as a circuit analogue. The simple equivalent circuit is presented in the Figure 3 below.

**Figure 3.** (a) Schematic potentiostatic/dynamics test to measure corrosion rate, (b) Equivalent circuit for cell experiment circuit used to represent the cell solution.
RESULTS AND DISCUSSIONS

Table 3, Table 4 and Table 5 present a summary of comparison data analysis taken from experiment, equivalent circuit and mixed potential theories model for two types of weld filler. The sole potentials on the BM, the WZ and the HAZ are shown in Table 3. Table 3 shows that at potentiostatic test, the most anodic region was located at HAZ region both for 4043 and 4047 weld filler with current density of $10^{-6}$ A/cm$^2$. The HAZ showed higher corrosion rate followed by BM and WM, respectively.

Table 3. Data used to calculate corrosion rate for self corrosion calculations

<table>
<thead>
<tr>
<th>Model</th>
<th>Potentiostatic 4043</th>
<th>Potentiostatic 4047</th>
<th>Potentiodynamic 4043</th>
<th>Potentiodynamic 4047</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr (BM) (mV)</td>
<td>-0.76</td>
<td>-0.68</td>
<td>-1100</td>
<td>-900</td>
</tr>
<tr>
<td>Ecorr (HAZ) (mV)</td>
<td>-0.80</td>
<td>-0.79</td>
<td>-900</td>
<td>-947</td>
</tr>
<tr>
<td>Ecorr (WM) (mV)</td>
<td>-0.75</td>
<td>-0.67</td>
<td>-700</td>
<td>-671</td>
</tr>
<tr>
<td>R1(BM) (KΩcm$^{-2}$)</td>
<td>-</td>
<td>-</td>
<td>157.73</td>
<td>250</td>
</tr>
<tr>
<td>R2(HAZ) (KΩcm$^{-2}$)</td>
<td>-</td>
<td>-</td>
<td>31.47</td>
<td>49.88</td>
</tr>
<tr>
<td>R3(WM) (KΩcm$^{-2}$)</td>
<td>-</td>
<td>-</td>
<td>1252.96</td>
<td>627.97</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-</td>
<td>-</td>
<td>-6.8</td>
<td>-7.0</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-</td>
<td>-</td>
<td>-6.1</td>
<td>-6.3</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-</td>
<td>-</td>
<td>-7.7</td>
<td>-7.4</td>
</tr>
<tr>
<td>Total corr. current (A/cm$^2$)</td>
<td>-6.0</td>
<td>-6.2</td>
<td>-6.0</td>
<td>-6.2</td>
</tr>
</tbody>
</table>

Table 4 shows data galvanic corrosion that considers couple effects between two segmented regions. From the Table 4, it shows that galvanic corrosion was initiated from the region between BM and HAZ with current density of $10^{-5}$ A/cm$^2$ for both types of filler. The data shows that the highest corrosion rate is found at region between HAZ-WM. As seen in Table 4, HAZ-WM has higher corrosion rate (4043 filler) compare to BM-HAZ or the BM-WM samples.

Table 4. Data used to calculate corrosion rate for galvanic corrosion calculations

<table>
<thead>
<tr>
<th>Model</th>
<th>Galv. Exp. 4043</th>
<th>Galv. Exp. 4047</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr (BM-HAZ) (mV)</td>
<td>-1000</td>
<td>-900</td>
</tr>
<tr>
<td>Ecorr (HAZ-WM) (mV)</td>
<td>-900</td>
<td>-810</td>
</tr>
<tr>
<td>Ecorr (WM-BM) (mV)</td>
<td>-790</td>
<td>-790</td>
</tr>
<tr>
<td>R1(BM-HAZ) (KΩcm$^{-2}$)</td>
<td>125.29</td>
<td>157.73</td>
</tr>
<tr>
<td>R2(HAZ-WM) (KΩcm$^{-2}$)</td>
<td>498.81</td>
<td>62.79</td>
</tr>
<tr>
<td>R3(WM-BM) (KΩcm$^{-2}$)</td>
<td>62.79</td>
<td>99.52</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-5.0</td>
<td>-4.9</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-4.7</td>
<td>-4.6</td>
</tr>
<tr>
<td>Log $I_{corr}$ (A/cm$^2$)</td>
<td>-5.5</td>
<td>-7.2</td>
</tr>
<tr>
<td>Total corr. current (A/cm$^2$)</td>
<td>-6.2</td>
<td>-4.5</td>
</tr>
</tbody>
</table>
Table 5 presents galvanic corrosion on real conditions where all of regions (WM-HAZ-BM) were coupled in the electrolyte. Data recorded from Table 5 was used to verify analog circuit to construct corrosion kinetics that represent real preferential weld corrosion as presented in Figure 4. From the recorded data in Table 5, it is revealed that filler 4043 gave higher corrosion rate.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Mixed theory potential (mV)</th>
<th>Log Icorr</th>
<th>Rp</th>
<th>Rp</th>
</tr>
</thead>
<tbody>
<tr>
<td>4043</td>
<td>-710</td>
<td>-4.8</td>
<td>1.57</td>
<td>-4.5</td>
</tr>
<tr>
<td>4047</td>
<td>-690</td>
<td>-5.1</td>
<td>3.14</td>
<td>-4.8</td>
</tr>
</tbody>
</table>

In order to obtain more realistic model to determine the corrosion current, the galvanic regions were simulated in an analog circuit by varying the weld resistivity parameters in the electric circuit as seen in Figure 4. The simulation will be fitted as accurately as possible with the real corrosion obtained from the experiments data in Table 5.

Figure 4. Several analog corrosion circuit to represent preferential weld corrosion.

The data from Table 5 shows several values of polarisation resistance, current density and corrosion potential that suitable with analog circuit from the Figure 4. Applying analog circuit calculation, the mechanisms preferential of weld corrosion was observed as shown circuit at Figure 4 (c) for 4043 weld filler and Figure 4 (a) for 4047 weld filler.
**Corrosion Mechanism Proposed**

From the analog circuit as presented in Figure 4, it is decided to obtain the best agreement with the data from Table 5 which measure corrosion rate on real conditions. As seen in Figure 5, samples welded with filler 4043 had one anode (HAZ) and two cathodes (BM and WM). While samples welded with filler 4047 had two anodes that corroded at the same time.

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3 \text{H}_2 & \quad \text{Al}_2\text{O}_3 + 3 \text{H}_2 \\
\text{e}^- & \quad \text{e}^- \\
\text{BM} & \quad \text{HAZ} & \quad \text{WM}
\end{align*}
\]

Figure 5. Model corrosion process on filler 4043

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3 \text{H}_2 & \\
\text{e}^- & \quad \text{e}^- \\
\text{BM} & \quad \text{HAZ} & \quad \text{WM}
\end{align*}
\]

Figure 6. Model corrosion process on filler 4047.

**Microstructure**

\[
\begin{align*}
\text{BM} & \quad \text{HAZ} & \quad \text{WM}
\end{align*}
\]

Heterogeneous nuclei (BM) \quad Dendrite (HAZ-WM) \quad Cellular dendrite (HAZ-WM)

Figure 7. Cross section and microstructure of the specimen.
Figure 7 exhibits the cross section and microstructure of the specimen which manifested type of microstructure formation. When welding with a filler metal (or joining two different materials), the fusion zone composition was different from the base metal composition and the weld metal crystal is dissimilar from the base metal crystal structures.

CONCLUSION

Polarization and galvanic electrochemical studies can be used to predict corrosion mechanism on welded samples. During this work a new and more objective method for model corrosion process is demonstrated by modifying the corrosion parameters. The HAZ region behaves as anode and shows higher corrosion rate. Sample with filler 4043 had higher corr rate compared to 4047 filler. Electrical circuit model can also predicted galvanic effects on each part of weld regions to simulate both individual corrosion process and combination of galvanic corrosion. Sample with filler 4043 had higher corrosion rate compared to 4047 filler due to its inhomogeneous of microstructures.

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REFERENCES


