The Effect of Copper on Corrosion Resistance and Structure of Al-8%wt Si Alloys for Engine Block Application

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Abstract. Al-Si Alloys are mostly used in an application for the engine block. An experimental investigation was carried out to understand the corrosion resistance of alloys with various Copper (Cu) content in Al-Si alloys. The corrosion properties of Aluminium alloys (Al-Si-0wt%Cu, Al-Si-2wt%Cu, Al-Si-5wt%Cu, and Al-Si-9wt%Cu) were investigated. X-ray diffraction and Electrochemical test were performed to investigate the structure of each sample, and corrosion resistance in 3.5%wt and 7%wt NaCl solution, and coolant water were used to understand the corrosion rate of Al-Si alloys. X-ray diffraction shows a different diffraction pattern from one sample to another. The effect of Copper addition shows marks different in corrosion resistance and structure of this alloy.

1. Introduction
Pure Aluminium does not have sufficient strength; therefore various materials are added to improve mechanical properties [1]. Recently, Aluminium-Silicon alloys are used in application for the engine block due to their good properties such as low density, good formability, high strength and excellent corrosion resistance with various condition are relative to other mixture [2]. The influence mixture of alloys is very important on microstructure. Corrosion is main factor for the failure aluminium alloys [3]. The additional of Copper content in Aluminium-Silicon could improve their hardness and strength [4]. Generally, addition of Copper may change the corrosion resistance. Copper is needed when combining in Aluminium-Silicon to investigate the appropriate properties of these alloys. The aluminium alloys (Al-Si-0 wt%Cu, Al-Si-2wt%Cu, Al-Si-5wt%Cu, and Al-Si-9wt%Cu) were used in this research to investigate corrosion resistance. These alloys are resistant to attack from water, concentration and viscosity, making Aluminium alloys useful in a various environments and take advantage from its lightweight property. Therefore, this research attempts to investigate the characteristic of ethylene-glycol as coolant water. Ethylene Glycol is mostly used as coolant in engine block, in a pH range between 7 and 8, so it is great heat adsorption capacity [5].

To understand this behavior, various Copper content (0 wt%, 2 wt%, 5 wt%, and 9 wt%) Aluminium-Silicon were tested using electrochemical test in 3.5% wt and 7% wt NaCl solution, and coolant water. Content of water in NaCl and coolant water solution determine corrosion rate value (observed in mm/year). Corrosion rate has a major impact on structural integrity. It determines the rate of corrosion at material thickness will be loss in a specific environment.
2. Experimental Methods and Materials

2.1. Sample Preparation

This type of Aluminium-Silicon alloy with various Copper was selected in this experiment to achieve the appropriate properties of these alloy. The chemical composition of the alloys Al-Si-Cu-Mg-Zn-Fe are given in Table 1. There were four samples used in this experiment, and each of the sample was given different Copper content. These alloys were cut into four pieces with 2 cm of diameter dimensions. The size of the exposed area affects the result of the measured corrosion behaviour when potentiodynamic polarization tests. Small scale of sample area tend to better than big scale measurements on electrochemical experiments [6]. The exposed area to the corrosive solution was 0.949 cm². A Copper wire was provided an electrical connection. Prior each aluminium alloy surface was further ground with 120, 240, 400, and 2000 grit SiC paper to scarp of layer on the surface before the corrosion test began.

2.2. Corrosion Testing

There were two corrosion tests conducted in this experiment. Electrochemical measurements were carried out in 3.5 wt% NaCl and 7 wt% NaCl, and coolant water solution at room conditions. Different concentration of NaCl was taken for corrosion behaviour to investigate the surface degradation in different environmental condition [4]. A computer-controlled Digi-Ivy© DY2300 potentiostatic was used for the electrochemical measurements. It was used to measure the current and voltage between Working Electrodes and the Reference Electrode [1]. The polarization curves were obtained potentiodynamically over the range -2.0- + 2.0 V at a scan rate of 0.05 Vsec⁻¹. The formula to measure the corrosion rate of each sample, applying First Faraday’s law in this case [7].

\[
 Corrosion\ rate\ of\ alloy, \ r = \sum C \frac{M_i}{n_i} = \sum C \frac{M_i}{n_i \rho A} \tag{1}
\]

where \( r \) is corrosion rate, \( C \) is corrosion rate constant (3.27 \times 10^{-3} \text{ mm}^3/\text{year} \) was used in this research), \( M \) is atomic weight of each element in the alloy (g/mol), \( I \) is current density in Ampere/cm², \( n \) is number of electrons involved in corrosion process, \( \rho \) is mass density of each element in the alloy (g/cm³). Faraday’s law corrosion rate equation in sums form because Al-8Si aluminium alloy consist of six elements (Aluminium, Silicon, Magnesium, Iron, Copper, and Zinc).

| Table 1. Chemical Composition of Alloy in weight percent. A11 (Cu=0%), A12 (Cu=2%), A13 (Cu=5%) and A14 (Cu=9%) |
|---|---|---|---|---|---|---|---|
| Alloy | Mg | Si | Fe | Cu | Zn | Al |
| A11 | 4 | 8 | 0.4 | 0 | 2 | Balance |
| A12 | 4 | 8 | 0.4 | 2.1 | 2 | Balance |
| A13 | 4 | 8 | 0.4 | 5.12 | 2 | Balance |
| A14 | 4 | 8 | 0.4 | 9.45 | 2 | Balance |
3. Results and Discussion

3.1 XRD Analysis
To describe a better identification of the phase, the X-Ray Diffraction plots of Aluminium-Silicon alloy with various Copper content samples are shown in Figure 1 and the data of characterization was served in Table 2. Figure 1 shows there were four identified peaks. For A11 with 0wt% Cu, four identified peaks with angle positions 28.942°, 37.953°, 44.219° and 64.659°. For A12 with 2wt% Cu, four identified peaks with angle positions 26.415°, 38.054°, 44.129°, and 64.422°. For A13 with 5wt% Cu, four identified peaks with angle positions 29.025°, 38.063°, 44.323°, and 64.741°. And for A14 with 9wt% Cu, five identified peaks with angle positions 29.020°, 38.063°, 44.378°, and 64.741°. And from Figure 1, X-Ray Diffraction pattern shows that the highest intensity peak value on A11 with 0wt% Cu which the value is 541.97 cps. For A12 with 2wt% Cu the height peak value is 645.53 cps. For A13 with 5wt% Cu the height value is 610.12 cps. And for A14 with 9wt% Cu the height value is 82.29 cps. It seems that the Copper content significantly causes the phases in the alloys [8]. We can be concluded that the intensity value is decreasing due to Aluminium is balance. In fact, as these alloys have a small difference of shift peaks from A11 to A14 caused Copper addition.

The lattice parameters have the same value for a, b and c, so the crystal system on these alloys are cubic. From Table 2, size of volume crystal from Aluminium-Iron phase was changed along with the additional of Copper from sequentially A11, A12, A13 and A14. Meanwhile in Aluminium phase, A14 has the biggest lattice parameter then followed by A13, A12 and A11. Each volume of these alloys are also transformed following alteration in lattice parameter.
Table 2. Crystallographic Parameters of the Aluminium-Silicon with Various Copper Content (A11, A12, A13 and A14)

| Sample                  | Al1  | Al2  | Al3  | Al4  |
|-------------------------|------|------|------|------|
| Highest Peak’s Height (cps) |      |      |      |      |
| Aluminium Iron          | 0.880| 64.490| 5.510| 64.75 |
| Aluminium               | 541.97| 645.53| 610.12| 82.29 |
| d spacing (Å)           |      |      |      |      |
| Aluminium Iron          | 2.165| 2.050| 2.162| 2.435 |
| Aluminium Iron          | 2.368| 2.362| 2.362| 2.365 |
| Lattice Parameter (Å)   |      |      |      |      |
| Aluminium               | a = 6.039| a = 5.745| a = 6.052| a = 5.694 |
| Iron                    | b = 6.039| b = 5.745| b = 6.052| b = 5.694 |
| Aluminium               | c = 6.039| c = 5.745| c = 6.052| c = 5.694 |
| Volume (Å³)             |      |      |      |      |
| Aluminium Iron          | 220.249| 189.65| 221.675| 184.614 |
| Aluminium               | 66.003| 66.300| 66.087| 52    |
| Density (g/cm³)         |      |      |      |      |
| Aluminium Iron          | 5.87 | 6.81 | 5.83 | 7     |
| Aluminium               | 2.71 | 2.7  | 2.71 | 2.73  |
| Concentration (%)       |      |      |      |      |
| Aluminium Iron          | 0    | 2.8  | 0.4  | 19.7  |
| Aluminium               | 100  | 97.2 | 99.6 | 80.3  |

It is shown in Figure 1, the phase that is detected in each samples, there is a single peak which described as an Aluminium and Aluminium-Iron phase at angle points. In this case, it is considered that which peak has the highest intensity. The concentration an Aluminium greater than Aluminium-Iron, hence the height of intensity peak for Aluminium more dominant than Aluminium-Iron. Both of these phases have cubic crystal structure because of the lattice parameter has the same value in a, b, and c.

3.2. Potentiodynamic Polarization Curves Analysis

The polarization curves prove Tafel type behavior of these samples in the active condition. The potentiodynamics curves in NaCl solution is shown in Figure 2, and the data were collected in Table 3. The corrosion mechanism of these Aluminium-Silicon alloys can be depicted by the anodic and cathodic reaction when the sample dipped in NaCl and coolant water solution. It can be caused an electron transfer process which make electrochemical reaction will be occur. From Table 3, the corrosion potential of alloys shifts to more a negative value, and corrosion current density is reduced with increasing Copper content. The electrochemical reaction on electrode can be written as follows [11]:

The anodic reaction is:

$$Al \rightarrow Al^{3+} + 3e^- \quad (2)$$

$$Al^{3+} + 6(H_2O) \rightarrow (Al(H_2O)_6)^{3+} \quad (3)$$
When NaCl reacts with H\(_2\)O:

\[
6\text{NaCl} + 6\text{H}_2\text{O} \rightarrow 6\text{NaOH} + 6\text{Cl}_6 + 3\text{H}_2
\]  
\[(4)\]

The cathodic reaction is:

\[
\text{O}_2 + 2(\text{H}_2\text{O}) + 4e^- \rightarrow 4\text{OH}^-
\]  
\[(5)\]

Main reaction is:

\[
2\text{Al}^{3+} + 6\text{Cl}^- \rightarrow \text{Al}_2\text{Cl}_6
\]  
\[(6)\]

\(\text{Al}_2\text{Cl}_6\) works in \(6\text{H}_2\text{O}\), the result is:

\[
\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O} \rightarrow \text{Al}_2(\text{OH})_6 + 6\text{HCl}
\]  
\[(7)\]

The result of the reaction between NaCl and H\(_2\)O generate Cl\(^-\) ion, it was absorbed into the protective film on these alloys. So, this is one of the triggering factors of the process nucleation of corrosion on the alloy surface [10].

Potentiodynamic polarization curves of Aluminium-Silicon alloys in coolant water is shown in Figure 2. The polarization curves show that the samples tendency to positive corrosion potential because of anodic polarization. The main cathodic reaction is reduction of oxygen under the condition[5][12]. Generally, the film formed during the dipping in the presence of that Silicon enhances the growth of a protective film which prevents corrosion during anodic polarization. Thus, the corrosion rate in coolant water solution is lower than NaCl solution. Mostly, coolant water contains Ethylene-Glycol for cooling applications. Ethylene-Glycol molecule is larger than water, so the adsorption of the surface is better. Thus, the aluminium alloy is more completely protected by Ethylene-Glycol, which more effective prevent aluminium alloy from the corrosion attack.

The anodic reaction is:

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^-
\]  
\[(8)\]

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3
\]  
\[(9)\]

The cathodic reaction is:

\[
\text{O}_2 + 2(\text{H}_2\text{O}) + 4e^- \rightarrow 4\text{OH}^-
\]  
\[(10)\]

When Alumunium alloy in environment with low content of oxygen, the Aluminium oxide film will be formed on Aluminium surface. When the electrochemical test used in Ethylene-Glycol as the solution, it would be reduced and Aluminium-Alcohol will appeared [13]. Main reaction is:

\[
\text{CH}_2\text{CH}_2(\text{OH})_2 + e^- \rightarrow \text{OHCH}_2\text{CH}_2\text{O}^- + \text{H}
\]  
\[(11)\]

\[
\text{Al}^{3+} + 3\text{OHCH}_2\text{CH}_2\text{O}^- \rightarrow \text{Al}(\text{OHCH}_2\text{CH}_2\text{O})_3
\]  
\[(12)\]

Where there is no oxygen in the environment, the cathodic reaction that occur are either reduction of Ethylene-Glycol or reduction of water:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^-
\]  
\[(13)\]
Hence, the protective film is formed on each alloys which are contain combination of Aluminium Oxide and Aluminium Alcohol [14].

3.3. Corrosion Testing: Electrochemical Test

The current-potential curves were obtained from each potentiodynamic polarization test. The result of electrochemical test in 3.5% NaCl solution, 7% NaCl solution, and coolant water solution can be seen on Table 3. Corrosion potential of Aluminium-Silicon with various Copper are evidently different in different medium. Electrochemical test in 3.5% NaCl solution makes the A14 alloy with 9wt% Copper content has the most negative corrosion potential (\(E_{corr}\)) with value of -1.247 V. Meanwhile, the A11 alloy with 0wt% Copper content in 7% NaCl solution has the most negative potential with value of -1.494 V. The A14 alloy with 9wt% Copper content in Coolant water solution has the most negative potential with value of -0.744 V; therefore, it can be concluded that corrosion resistance of Aluminium-Silicon alloy is depend on Copper content and phases. In an environment with high content of NaCl, all alloys are prone to be corroded due to Hydro Chloride Acid concentration.

The differences of electrochemical current (\(I_{corr}\)) for each sample will affect the different corrosion rate. The Faraday’s Law formula was used to calculate corrosion rate for each sample. In 3.5% NaCl solution, the A11 alloy with 0wt% Copper content has the slowest corrosion rate with value is 1.172 x 10^{-2} mm/year. In 7% NaCl solution, the A13 alloy with 5wt% Copper content has the slowest corrosion rate with value is 2.816 x 10^{-2} mm/year. Meanwhile, in coolant water solution, the A12 alloy with 2wt% Copper content has the slowest corrosion rate with value of 3.079 x 10^{-4} mm/year. After electrochemical test has been done, there some factors that affect the corrosion rate are effect of pH and water content. These two factors are important components of a failure analysis because a lot of the failures related to environments are linked to corrosion. Solutions with different percentages varying the NaCl concentration enhance corrosion rate of the alloy. When the concentration of NaCl is increased, corrosion rate of the alloy has great value. Meanwhile, the effect of pH between NaCl and coolant water also affect the corrosion rate. It was shown that the corrosion rate was reduced with increasing the value of pH [9].

| Solution | Sample | R (ohm) | \(E_{corr}\) (V) | \(I_{corr}\) (A) | Corrosion Rate (mm/year) |
|----------|--------|---------|------------------|-----------------|-------------------------|
| 3.5 wt%  | A11    | 3.837 x 10^2 | -1,163           | 6,695 x 10^{-5} | 1.172 x 10^{-2}        |
|          | A12    | 2.751 x 10^2 | -1,181           | 9,339 x 10^{-5} | 1.634 x 10^{-2}        |
|          | A13    | 3.756 x 10^2 | -1,051           | 6,841 x 10^{-5} | 1.197 x 10^{-2}        |
|          | A14    | 1.146 x 10^2 | -1,247           | 2,242 x 10^{-4} | 3.924 x 10^{-2}        |
| 7 wt%    | A11    | 5.555 x 10^1 | -1,494           | 4,625 x 10^{-4} | 8.096 x 10^{-2}        |
|          | A12    | 3.649 x 10^1 | -1,454           | 7,041 x 10^{-4} | 1.232 x 10^{-1}        |
|          | A13    | 1.597 x 10^2 | -0,507           | 1,609 x 10^{-4} | 2.816 x 10^{-2}        |
|          | A14    | 2.624 x 10^1 | -1,448           | 9,790 x 10^{-4} | 1.713 x 10^{-1}        |
|          | A11    | 5.761 x 10^3 | -0,623           | 4,460 x 10^{-6} | 7.807 x 10^{-4}        |
| Coolant Water | A12 | 1.461 x 10^4 | -0,705           | 1,759 x 10^{-6} | 3.079 x 10^{-4}        |
|          | A13    | 1.278 x 10^4 | -0,673           | 2,010 x 10^{-6} | 3.518 x 10^{-4}        |
Figure 2. (a) Potentiodynamic polarization curves of the samples in 3.5 wt% NaCl; (b) Potentiodynamic polarization curves of the samples in 7 wt% NaCl; (c) Potentiodynamic polarization curves of the samples in Coolant Water

4. Conclusion

From this study of the corrosion behaviour of the Aluminium-Silicon alloy engine block in 3.5% NaCl solution, 7% NaCl solution, and coolant water solution to investigate the corrosion resistance. It can be concluded that various of Copper content influence the corrosion rate. The environments have a great effect on corrosion behaviour in alloy. In NaCl solution, when Copper content is increased, the corrosion potential of alloys shifts to more a negative value and corrosion current density is reduced. From the above result it is clear that the passive film became weak in corrosion caused by Cl⁻ ion was the reason of corrosion pit. In coolant water solution, Aluminium-Silicon alloys with various Copper content have the slowest corrosion rate than 3.5% NaCl solution and 7% NaCl because of Ethylene Glycol molecule is larger than water. Thus, it prevents alloys from the corrosion attack because the surface of these alloys more completely protective by Ethylene Glycol. The presence of the intermetallic phases in these alloys has shown that the oxide film is not consistent. However, the
additional of Copper content contributes to improve hardness, strength, and corrosion behaviour. So, it can be applied in an application for engine block.

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