Influence of Heat Treatment on Structure and Corrosion Resistance of 8090 Aluminium Alloy for Ethanol Fuel Tank Application

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Abstract Investigation was carried out to understand the influence of heat treatment on structure and corrosion resistance of 8090 aluminium alloy in ethanol solution for ethanol fuel tank application. Heat treatments were subjected to solutionizing at temperature 525ºC for 4 hours to infiltrate the aluminium crystal by copper atoms and aging at temperature 190ºC with different time to bring copper and lithium atoms out of aluminium crystal during aging process. X-ray diffraction was performed to investigate the phase of each sample with different aging time. Electrochemical experiments were conducted to investigate the corrosion resistance in 3.5% and 7% NaCl solution and 70% and 96% of ethanol solution. The results show different corrosion behaviour of this material. Heat treatment on this material shows significant different results.

1. Introduction
The demand of petroleum-based fuel for vehicles use keeps on rising each year and that makes the supply of petroleum-based fuel is decreasing time after time. The alternative energy is needed to replace petroleum-based fuel and also it is needed to reduce carbon emission caused by petroleum-based fuel in the future [1-3]. One of the alternative energies had been developed for vehicle use is ethanol-based fuel.

The problem of using ethanol as fuel for commercial vehicles lies on corrosion of each vehicle component. Ethanol-based fuel tends to attract water from air because of hygroscopic effect of ethanol, causing water contamination in ethanol-based fuel and the contamination can causes corrosion on each vehicle component, such as fuel tank [4,5]. 8090 aluminium alloy (Al–94.61wt%, Si–2.42wt%, Cu–1.14wt%, Mg–0.83wt%, Mn–0.70wt%, Zr–0.01wt%, Ti–0.20wt%, Zn–0.02%, Fe–0.05wt%, and Si–0.02wt%) is used in this research to investigate the corrosion resistance in ethanol-based fuel and take advantage from its lightweight property with small value of mass density and also this type of alloy has high Young’s modulus [6]. The output of this research is being able to develop fuel tank that is able to resist corrosion caused by ethanol-based fuel and also being able to develop a lightweight ethanol fuel tank for commercial vehicles.

In general, almost all type of aluminium alloys excel in mechanical properties, such as high strength and good corrosion resistance [7,8]. 8090 aluminium alloy has several mechanical disadvantages. Main cause of 8090 aluminium alloy’s mechanical properties disadvantages in corrosion resistance is different applied thermomechanical treatment to reach another mechanical property advantage besides corrosion.
Due to low content of magnesium and zirconium, which both have good corrosion resistance if the alloy has sufficient weight percent inside, 8090 aluminium alloy has poor corrosion resistance. Also, 8090 aluminium alloy has several disadvantages in mechanical properties such as poor toughness and high anisotropy [10].

In this research, each 8090 aluminium alloys with 1.7 cm × 1.5 cm surface area is heat treated differently. 5 different heat treatments conducted in this research, solutionizing and aging process. Solutionizing was done for copper and lithium to infiltrate the aluminium crystal in 8090 aluminium alloy. Only one sample is treated in this way. Solutionizing and aging process also conducted to bring out copper and lithium slowly from the aluminium crystal during aging process occurred. Variations of aging time for each sample that are conducted in this research are 24 hours, 48 hours, 72 hours, and 96 hours. Different heat treatment process will determine the corrosion behaviour for each 8090 aluminium alloy sample. Corrosion behaviour difference for each sample can be seen on the corrosion rate and shift of phase in XRD diffraction graph. Content of water in NaCl and ethanol solution determines corrosion rate value (observed in mm/year). Corrosion rate determines how much thickness loss on a material in a certain environment. Metals tend to have faster corrosion in an environment with high water content because metal alloys are easily reactive to oxygen.

2. Experiment Methods and Material

2.1. Sample Preparation

8090 aluminium alloy was selected in this research. This type of aluminium alloy was selected due to lightweight property with mass density of 2.54 gr/cm³ and barely good corrosion resistance, which is good for application of lightweight fuel tank for commercial vehicles. In Table 1, composition of 8090 aluminium alloy can be seen. 8090 aluminium alloy was cut into 5 square-shaped pieces with 1.7cm x 1.5cm dimension and each piece of sample was heat treated differently. Each aluminium alloy surface was ground with 500 and 2000 grit SiC paper to clean the surface before heat treatment began. First aluminium alloy sample is only solutionized, the second one was gone through solutionizing and aging process for 24 hours, the third one was gone through solutionizing process and aging process for 48 hours, the fourth one was gone through solutionizing process and aging process for 72 hours, and the final one was gone through solutionizing process and aging process for 96 hours. Solutionizing process took 4 hours in furnace with temperature of 525°C and then all 8090 aluminium alloy samples were quenched in water for 5 hours.

2.2. Corrosion Testing

There were two corrosion tests conducted in this research, dipping test in 96% ethanol solution for two weeks and electrochemical test using Digi-Ivy® DY2300 series potentiostat. Electrolytes used in corrosion test were 3.5% NaCl solution, 7% NaCl solution, 70% ethanol solution, and 96% ethanol solution. Two weeks of dipping test using 96% ethanol solution was conducted to investigate changes in mass of each sample with different heat treatment. For electrochemical test, 1cm × 1cm surface area for each 8090 aluminium alloy sample was used.

Electrochemical test was also conducted to investigate different heat treatment effect on corrosion rate of 8090 aluminium alloy samples. To determine the corrosion rate of each sample, first Faraday’s law could be applied in this case [11]. Mathematically, first Faraday’s law defined as [11]:

\[
Corrosion \text{ rate of alloy, } r = \Sigma C \frac{M_i}{n_p \rho} = \Sigma C \frac{M_i}{n_p A}
\]  

(1)

where \( C \) is corrosion rate constant \((3.27 \times 10^{-3} \text{ mm}\text{/year was used in this research})\), \( M \) is atomic weight of each element in the alloy \((\text{g/mol})\), \( i \) is current density in Ampere/cm², \( I \) is current passed the samples (Ampere), \( A \) is area exposed to NaCl solutions and ethanol solutions \((\text{cm}^2)\), \( n \) is number of electrons involved in corrosion process, \( \rho \) is mass density of each element in the alloy \((\text{g/cm}^3)\). Faraday’s law
The corrosion rate equation is in sums form because 8090 aluminium alloy consists of 10 elements (aluminium, lithium, copper, magnesium, manganese, zirconium, titanium, zinc, iron, and silicon).

**Table 1. Compositions of 8090 aluminium alloy**

| Elements | Composition (% wt) |
|----------|--------------------|
| Al       | 94.61              |
| Li       | 2.42               |
| Cu       | 1.14               |
| Mg       | 0.83               |
| Mn       | 0.70               |
| Zr       | 0.01               |
| Ti       | 0.20               |
| Zn       | 0.02               |
| Fe       | 0.05               |
| Si       | 0.02               |

**Table 2. Electrochemical test results of 8090 aluminium alloys in different solutions**

| Solution  | Treatment           | \( E_{\text{corr}} \) (V) | \( I_{\text{corr}} \) (A) | \( r \) (mm/year) |
|-----------|---------------------|-----------------------------|-----------------------------|-------------------|
| 3.5% NaCl | 24 hours of aging   | -0.488                      | \( 4.044 \times 10^{-6} \) | \( 4.735 \times 10^{-2} \) |
|           | 48 hours of aging   | -0.401                      | \( 1.154 \times 10^{-5} \) | \( 1.351 \times 10^{-1} \) |
|           | 72 hours of aging   | -0.722                      | \( 8.888 \times 10^{-5} \) | \( 1.041 \)         |
|           | 96 hours of aging   | -0.507                      | \( 5.285 \times 10^{-5} \) | \( 6.188 \times 10^{-1} \) |
|           | Without aging       | -0.673                      | \( 1.078 \times 10^{-4} \) | \( 1.262 \)         |
| 7% NaCl   | 24 hours of aging   | -1.231                      | \( 1.796 \times 10^{-5} \) | \( 2.103 \times 10^{-1} \) |
|           | 48 hours of aging   | -1.477                      | \( 1.295 \times 10^{-4} \) | \( 1.516 \)         |
|           | 72 hours of aging   | -1.433                      | \( 4.465 \times 10^{-5} \) | \( 5.227 \times 10^{-1} \) |
|           | 96 hours of aging   | -1.49                       | \( 6.629 \times 10^{-5} \) | \( 7.761 \times 10^{-1} \) |
|           | Without aging       | -0.786                      | \( 1.980 \times 10^{-5} \) | \( 2.318 \times 10^{-1} \) |
| 70% Ethanol| 24 hours of aging  | -0.341                      | \( 1.604 \times 10^{-6} \) | \( 1.878 \times 10^{-2} \) |
|           | 48 hours of aging   | -0.471                      | \( 3.514 \times 10^{-6} \) | \( 4.114 \times 10^{-2} \) |
|           | 72 hours of aging   | -0.681                      | \( 2.261 \times 10^{-6} \) | \( 2.647 \times 10^{-2} \) |
|           | 96 hours of aging   | -0.893                      | \( 1.62 \times 10^{-6} \)  | \( 1.90 \times 10^{-2} \) |
|           | Without aging       | -0.295                      | \( 1.41 \times 10^{-6} \)  | \( 1.66 \times 10^{-2} \) |
| 96% Ethanol| 24 hours of aging  | -0.25                       | \( 1.206 \times 10^{-6} \) | \( 1.475 \times 10^{-2} \) |
|           | 48 hours of aging   | -0.411                      | \( 2.072 \times 10^{-6} \) | \( 2.426 \times 10^{-2} \) |
|           | 72 hours of aging   | -0.58                       | \( 2.460 \times 10^{-6} \) | \( 2.880 \times 10^{-2} \) |
|           | 96 hours of aging   | -0.645                      | \( 1.548 \times 10^{-6} \) | \( 1.812 \times 10^{-2} \) |
|           | Without aging       | -0.204                      | \( 1.203 \times 10^{-6} \) | \( 1.408 \times 10^{-2} \) |
3. Results and Discussion

3.1. Corrosion Testing: Dipping Test
The results of dipping test in 96% ethanol solution can be seen on Table 2. 14 days dipping test for each sample resulted in mass reduction. For 24 hours of aging time, there is 0.002 grams mass loss between before and after dipping test. For 48 hours of aging time, there is 0.0038 grams mass loss. For 72 hours of aging time, there is 0.0029 grams mass loss. For 96 hours of aging time, there is 0.0038 grams mass loss. And for 8090 aluminium alloy sample without aging treatment, there 0.0037 grams mass loss. 8090 aluminium alloy with 24 hours of aging time has least mass loss compared to the rest of samples of 8090 aluminium alloy. It was assumed that dipping test in 96% of ethanol solution resulted in mass loss because of oxidation. Oxidation that occurred during this test attacked almost all surface of 8090 aluminium alloy caused some elements in the alloy to dissolve, resulted in mass loss of the alloy. The mass loss is not significant, but the corrosion attacked the structure of 8090 aluminium alloy and it will decrease another mechanical property advantage that the alloy used to have [9].

Figure 1. Tafel plot of electric potential $E$ vs current $I$ in logarithm form in (a) 3.5% NaCl solution, (b) in 7% NaCl solution, (c) in 70% ethanol solution, and (d) in 96% ethanol solution
3.2. Corrosion Testing: Electrochemical Test

The electrochemical behaviour of 8090 aluminium alloy in ethanol solution can be observed from the chemical reaction formula. When ethanol reacts with oxygen, the reaction will produce acetic acid and water. The water and acetic acid content in oxidized ethanol solution are the oxidation agent and also the main cause of the aluminium alloy oxidation. The reaction of ethanol oxidation can be written as:

\[ C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O \]  
\[ \text{(2)} \]

The aluminium alloy will react to acetic acid and water. When the aluminium alloy reacts to acetic acid, product of the reaction is aluminium acetate and hydrogen in form of gas. The reaction will cause corrosion of aluminium alloy [12].

\[ Al + 3CH_3COOH \rightarrow Al(CH_3COO)_3 + \frac{3}{2}H_2 \]  
\[ \text{(3)} \]

Water content also contributes to aqueous corrosion of 8090 aluminium alloy. This type of corrosion will there is enough water content in the ethanol to cause phase separation [1]. The corrosion will create bayerite from reaction of aluminium ion with water or boehmite from the same reaction, which those two products are protective hydrous oxide surface film [12].

\[ Al^{3+} + 3H_2O + 3e^- \rightarrow Al(OH)_3 + \frac{3}{2}H_2 \]  
\[ \text{(4)} \]

\[ Al^{3+} + 2H_2O + 3e^- \rightarrow AlOOH + \frac{3}{2}H_2 \]  
\[ \text{(5)} \]

The results of electrochemical test in 3.5% NaCl solution, 7% NaCl solution, 70% ethanol solution, and 96% ethanol solution can be seen on Figure 1 and the detail of electrochemical test is in Table 2. Electrochemical potential or corrosion potential of 8090 aluminium alloy samples are obviously different in different corrosive environment. Electrochemical test in 3.5% NaCl solution makes the 8090 aluminium alloy sample with 48 hours aging time treatment has least negative electrochemical potential with value of -0.401V. The alloy without aging treatment in 7% NaCl solution has least negative potential with value of -0.786V. The samples without aging process also has least negative potential in 70% ethanol solution and 96% ethanol solution, with value of -0.295V and -0.204V. It can be concluded that corrosion resistance of 8090 aluminium alloy is decreasing due to increment of aging time and the sample with most negative potential value defines the sample is prone to corrode than the others with bigger potential value, which is less prone to corrode in ethanol fuel.

Difference in electrochemical potential for each sample will leads to different corrosion rate. With using mathematical formula from Faraday’s law, corrosion rate for each sample can be calculated. In 3.5% NaCl solution, the sample with 24 hours of aging time has the slowest corrosion rate with value of 4.735 × 10^{-2} mm/year. In 7% NaCl solution, the sample with 24 hours of aging time has the lowest corrosion rate with value of 2.103 × 10^{-1} mm/year. In 70% and 96% ethanol solution, the sample without aging process is the slowest with value of 1.66 × 10^{-2} mm/year and 1.408 × 10^{-2} mm/year. From all electrochemical test that has been done, it can be concluded that water content makes corrosion rate of the alloy faster. Not just water that has big contribution for corrosion of the alloy, acidic substances and solubility of oxygen in the solutions also enhance corrosion rate of the alloys. Acidic substances and solubility of oxygen increase when the concentration of ethanol has small value [13]. It is proven in the experiment that corrosion rate of the alloy in 70% ethanol solution is faster than the alloy in 96% ethanol solution.
3.3. XRD Analysis

The XRD data plot of treated and untreated samples is showed in Figure 2 and the detail of the XRD data can be seen in Table 3. Each sample, treated and untreated 8090 aluminium alloy sample, had 5 peaks identified at (111), (002), (022), (113), and (222). The peaks of 24 hours aging time sample are detected at 38.03º, 44.29º, 64.68º, 77.83º, and at 82.04º angle position. The peaks of 48 hours aging time sample are detected at 38.06º, 44.31º, 64.70º, 77.84º, and at 82.06º angle position. The peaks of 72 hours aging time are detected at 38.04º, 44.29º, 64.68º, 77.83º, and 82.04º angle position. The peaks of 96 hours aging time sample are detected at 38.06º, 44.31º, 64.70º, 77.84º, and at 82.05º angle position. The peaks of sample without aging treatment are detected at 38.08º, 44.33º, 64.72º, 77.86º, and at 82.08º angle position. The peaks of untreated sample are detected at 38.46º, 44.71º, 65.09º, 78.22º, and at 82.43º.

Table 3. Crystallographic parameters of treated and untreated 8090 aluminium alloy samples

| Sample | 24 hours aging time | 48 hours aging time | 72 hours aging time | 96 hours aging time | Without aging | Untreated AA 8090 |
|--------|---------------------|---------------------|---------------------|---------------------|----------------|-------------------|
| Highest peak height (cts) | 18765 | 23846 | 27884.06 | 15428.39 | 15659.75 | 33346 |
| d-spacing (Å) | 2.04345 | 2.04248 | 2.04312 | 2.04239 | 2.04158 | 2.02510 |
| Density (g/cm³) | | | | | 2.7 | |
| Volume (Å³) | 66.26342 | 66.28945 | 66.29299 | 66.30686 | 66.29393 | 66.38882 |
| Lattice Parameter | a = b = c = 4.0466 | a = b = c = 4.0471 | a = b = c = 4.0472 | a = b = c = 4.0474 | a = b = c = -4.0472 | a = b = c = -4.0491 |
| FWHM (º) | 0.1434 | 0.09327 | 0.11925 | 0.16022 | 0.14195 | 0.12065 |
| Crystallite size (Å) | 1086.158 | 1202.718 | 1585.86 | 1633.425 | 974.8201 | 2185.19 |
From the XRD data, the phase that is detected in all samples are only aluminium phase. The aluminium content in the samples have cubic crystal structure because lattice parameter of the unit cell has same value in a, b, and c. Even each sample has cubic crystal structure, the value of a, b, and c is different to each other. The longer aging duration makes the volume of the unit cell is increasing and unit cell volume will shrink if the alloy sample is going through solutionizing treatment only.

Solutionizing and aging treatment reduces height of the highest peak, which means that aluminium content on a certain grain orientation is reducing compared to the untreated 8090 aluminium alloy. The highest aluminium content when solutionizing and aging treatment conducted is the alloy with 72 hours aging time. From the highest peak height data, it can be concluded that the longer aging time does not increase the aluminium content and the alloy will have maximum aluminium content when aging time is reaching 72 hours.

Solutionizing and aging treatment also affect the grain size of 8090 aluminium alloy. When the alloy is only solutionized, the grain size is shrinking from 2185.19 Å to 974.8201 Å. If the sample is aged in 190°C for 24 to 96 hours, the grain size will increase due to duration of aging time from 1086.158 Å to 1633.425 Å. The XRD data of 8090 aluminium alloy defines that solutionizing and aging process will decrease and increase 8090 aluminium alloy’s grain size, all grain size of the samples will shrink when solutionizing process is done and the grain size will increase slowly when the sample is going through aging process for a certain period of time.

4. Conclusion
Corrosion rate varies with solutionizing and aging treatment of 8090 aluminium alloy. In ethanol solutions, 8090 aluminium alloy sample without aging process has the slowest corrosion rate and also the alloy without aging process also has good corrosion resistance with the highest corrosion potential. From XRD data, aluminium phase in the alloy has cubic crystal structure because value of lattice parameter is equal between a, b, and c. solutionizing and aging treatment will affect aluminium content in certain grain orientation and maximum aluminium content in alloy will reach its maximum at 72 hours aging time. Grain size will be affected as well, long aging time will increase the grain size of 8090 aluminium alloy after grain size shrinkage in solutionizing process.

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