Effect of Solution Heat Treatment of Aluminum Alloy 4032 on the Structure and Corrosion Resistance in 3.5% and 10.5% NaCl Solution

Fadli Nur Cahyo and Bambang Soegijono
Department of Physics, Universitas Indonesia, Depok, Indonesia
E-mail: naufal@ui.ac.id

Abstract. Aluminum Alloy 4032 is usually used as a material for making engine pistons, which has a composition of Aluminum (Al), 21%wt Silicon (Si), 0.82%wt Nickel (Ni) and 0.67%wt Copper (Cu). The alloy is known to have mild properties and should have good corrosion resistance. Heat treatment was carried out with the aim of the enhancement of the corrosion resistance. The solution heat treatment process was performed at 510°C for 2 hours and then quenching to room temperature in water media. Some of the material were also performed an aging process at 171°C with varying duration of time and then cooling to room temperature. Corrosion resistance testing was carried out by electrochemical testing using 3.5% wt and 10.5% wt NaCl solution. The structure before and after heat treatment were characterized by using X-Ray Diffraction (XRD) were analyzed. The results of the characterization indicate that the heat treatment on the Alloy is affected by solution heat treatment and the aging process.

1. Introduction
Aluminum Alloy 4032 is a 4000 series aluminum alloy, which has a very good surface, without hot ductility, good for wrought and cast alloys. The aluminum-silicon alloy 4000 series is identical with good durability, lightweight, very small expansion coefficient and as a good conductor of heat. Aluminum Alloy 4032 has the main alloy is silicon, followed by Nickel and Copper. Aluminum Alloy 4032 is very widely used because it has a striking advantage. In the automotive sector and industry, it is used for several engine components such as pistons, transmission valves, master brake cylinders, bushings for rack and pinion steering systems, hydraulic applications, and many more [1].

Aluminum Alloy 4032 has a lower melting point than other compositions made from the same material or what is often referred to as having eutectic properties. Based on the silicon content, this alloy is divided into three, namely Hypoeutectic alloys which have a silicon content of between 5% - 10%, Eutectic alloys that have a silicon content of between 11% -13%, and Hypereutectic alloys which have a silicon content of between 14% -25% [2]. The presence of silicon alloys into aluminum will increase fluidity, heat resistance. And the addition of silicon can also reduce the value of specific gravity and thermal coefficient of aluminum. The addition of Nickel can improve the properties of aluminum alloys at high temperatures and can also reduce the coefficient of thermal expansion of the alloy. As for copper which is very influential in increasing the strength and stiffness of aluminum both as-cast and also after the heat treatment process, as well as the addition of copper can reduce heat cracking resistance. The presence of Cu and Ni elements, causing this alloy is resistant to rust [3].
Based on the purity of the base material, Al-Si alloys consist of various impurities such as iron, manganese, silver, and copper. The presence of copper and magnesium often added as an alloy of elements to increase the strength and ability of the material to be cast. Impurities and alloying elements will dissolve into solid solutions in the matrix and some form intermetallic particles during the freezing process.

Solution Heat Treatment in Aluminum alloy 4032 aims to produce solid solutions with the number of main alloying elements such as Al, Si, and Cu in aluminum alloys so that their mechanical properties will increase. Solution heat treatment consists of three steps, namely solution, quenching, and aging. Microstructural changes occur because the solution treatment stages include the process of quenching and aging [4]. In the process of heat treatment solution that needs to be considered is the use of temperature does not exceed the eutectic temperature because it will cause overheating, the tensile strength will be ductile and fracture toughness will be reduced, because when overheating the grain boundaries melt.

2. Experimental Procedure

Aluminum-Alloy 4032 samples with a size of approximately 2.6 cm x 2.1 cm x 0.5 cm were used for this experiment. Each of the samples were heat treated differently. For all samples treated were polished with sandpaper. In the first sample only treated normally or not treated (hereinafter referred to as AA 4032 NH). In the second sample (hereinafter referred to as AA 4032 HT) through the Solution Heat Treatment. In the third sample (hereinafter referred to as AA 4032 A5) through the Solution Heat Treatment and the Artificial Aging Treatment. In the fourth sample (hereinafter referred to as AA 4032 A10) through the Solution Heat Treatment and the Artificial Aging Treatment. In the fifth sample (hereinafter referred to as AA 4032 A15) through the Solution Heat Treatment and the Artificial Aging Treatment.

All samples were analyzed at the UPP IPD Research Laboratory, Faculty of Mathematics and Natural Sciences, University of Indonesia. The composition of Aluminum-Alloy 4032 used in this experiment can be seen in TABLE 1. List of compositions of Aluminum Alloy 4032 in weight%.

| Elements | Weight % |
|----------|----------|
| Al       | 76.73    |
| Si       | 21.42    |
| Ni       | 0.82     |
| Cu       | 0.67     |
| Fe       | 0.22     |
| Ag       | 0.10     |
| Mn       | 0.04     |

2.1. Solution Heat Treatment

Solution Heat Treatment was carried out by samples of AA 4032 HT, AA 4032 A5, AA 4032 A10, and AA 4032 A15. Solution Heat treatment is carried out at a temperature of 510 °C with a duration of 2 hours and then quenching using water at room temperature. The process is intended to stabilize physical or mechanical properties or corrosion resistance and is intended to quench the structure of the atoms in solution.
2.2. Artificial Aging Treatment
Artificial Aging Treatment is a heat treatment process carried out on a material to improve its hardness by combining heating above room temperature with heating time [5]. The Artificial Aging Treatment process was carried out at 171 °C at 5 hours, 10 hours and 15 hours in three samples, namely AA 4032 A5, AA 4032 A10, and AA 4032 A15. This treatment is carried out to obtain deposition hardening, which is hardening due to deposition of the second phase which is evenly distributed. Precipitate hardening aims to enhance the metal's resistance to deformation by inhibiting the movement of dislocations by the precipitate.

2.3. Corrosion Test
Corrosion test was carried out using the Digi-Ivy © DY2300 series potentiometer with two different concentration solutions, 3.5% wt and 10.5% wt NaCl solution. Also for the sample, we have prepared by connecting the sample with the wire together, so that the sample can be entered into the solution before the wire collects data. It aims to investigate the change in mass of each sample by heat treatment. The surface area of each sample of Aluminum Alloy 4032 is used to test corrosion with a size of 1 cm x 1 cm. To collect data in the corrosion test process using a Potentiostat, the formula used to calculate the value of the corrosion rate is obtained from Faraday’s Law in Determining the Corrosion Rate of Metals and Alloys [6].

\[
\text{Corrosion rate of alloy, } r = \frac{C \cdot M_i}{n \cdot \rho}
\]  

where C is the constant corrosion rate (3.27 × 10⁻³ mm³ / year used in this study), M is the atomic weight of each element in the alloy (gr/mol), i is the current density in Amperes / cm², where cm² defines the cross-sectional area of the sample tested for corrosion resistance, n is the number of electrons involved in the corrosion process, ρ is the mass of each element in the alloy (gr / cm³).

3. Results and Discussion

3.1. XRD Analysis
In Figure 1, there are results from the XRD Plot sample of Aluminum Alloy 4032 and there are also data from the characterization of the Aluminum Alloy 4032 sample in TABLE 2. Seen from FIGURE 2, each of them identified seven peaks in the graph of each sample. For AA 4032 NH samples, there are seven peaks identified with angle positions of 28,616 °, 38,626 °, 44,867 °, 47,458 °, 56,269 °, 65,214 ° and 78,325 °. For AA 4032 HT samples, there are seven peaks identified with angle positions of 28,616 °, 38,617 °, 44,859 °, 47,473 °, 56,290 °, 65,213 °, and 78,328 °. For AA 4032 A5 samples, there are seven peaks identified with angle positions of 28,481 °, 38,470 °, 44,713 °, 47,352 °, 56,177 °, 65,071 °, and 78,189 °. For the AA 4032 A10 sample, there are seven peaks identified with sample positions of 28,463 °, 38,469 °, 44,713 °, 47,323 °, 56,142 °, 65,073 °, and 78,193 °. For AA 4032 A15 samples, there are seven peaks identified with sample positions of 28,471 °, 38,47 °, 44,715 °, 47,34 °, 56,165 °, 65,079 °, and 78,202 °. In FIGURE 1, there is an X-Ray diffraction pattern that there are seven peaks of the high intensity, namely, (111), (111), (002), (022), (113), (022), and (113) seen clear in the aluminum phase. which value is 3,132 Å, then followed by the AA 4032 A5 which value is 3,131 Å, and 3,116 Å for the AA 4032 NH & AA 4032 HT.
Figure 1. XRD plot of Aluminum Alloy 4032 Non Heat Treatment, Heat Treatment, 5 hours of aging, 10 hours of aging, and 15 hours of aging.

Table 2. Crystallographic parameters of AA 4032 NH, AA 4032 HT, AA 4032 A5, AA 4032 A10, and the AA 4032 A15

| Sample          | AA 4032 NH | AA 4032 HT | AA 4032 A5 | AA 4032 A10 | AA 4032 A15 |
|-----------------|------------|------------|------------|-------------|-------------|
| Highest peak    | Alumunium  | 247.64     | 247.06     | 236.97      | 215.73      | 211.3       |
| height (cps)    | Silicon    | 107.72     | 147.70     | 103.70      | 94.12       | 81.6        |
| Highest peak d (Å) | Alumunium   | 2.329      | 2.329      | 2.338       | 2.338       | 2.338       |
|                 | Silicon    | 3.116      | 3.116      | 3.131       | 3.133       | 3.132       |
| Lattice Parameter (Å) | Alumunium | a = 4.054  | a = 4.053  | a = 4.052   | a = 4.052   | a = 4.051   |
|                 | Silicon    | b = 4.054  | b = 4.053  | b = 4.052   | b = 4.052   | b = 4.051   |
|                 |            | c = 4.054  | c = 4.053  | c = 4.052   | c = 4.052   | c = 4.051   |
| Volume (Å³)     | Alumunium  | 66.630     | 66.581     | 66.55       | 66.535      | 66.501      |
|                 | Silicon    | 160.592    | 160.267    | 159.958     | 160.202     | 159.973     |
| Density (g/cm³) | Alumunium  | 2.69       | 2.69       | 2.69        | 2.69        | 2.69        |
|                 | Silicon    | 2.32       | 2.33       | 2.33        | 2.33        | 2.33        |
| Concentration (%) | Alumunium | 74.8       | 74.5       | 76          | 82.5        | 76.5        |
|                 | Silicon    | 25.2       | 25.5       | 24          | 17.5        | 23.5        |
| Microstrain (%) | Alumunium  | 0.073      | 0.088      | 0.306       | 0           | 0           |
|                 | Silicon    | 0          | 0.116      | 0           | 0           | 0           |
| Crystallite Size (Å) | Alumunium | 1527       | 748.2      | 173.3       | 27913.4     | 27913.4     |
|                | Silicon    | 27913.4    | 27913.4    | 27913.4     | 27913.4     | 27913.4     |
Referring to Table 2, the lattice parameter value has the same value in a, b, and c which means that the aluminum and silicon content has a cubic crystal structure. The highest aluminum peak (111) is at AA 4032 A10, then followed by AA 4032 A15, AA 4032 A5, AA 4032 NH, and AA 4032 HT. This explains that the artificial aging heat treatment and coolant temperature increase the aluminum phase. Based on X-Ray diffraction analysis (XRD) which can explain that Aluminum has more concentration and is resistant to corrosion.

Table 3. Data from the corrosion test of AA 4032 NH, AA 4032 HT, AA 4032 A5, AA 4032 A10, and the AA 4032 A15 in the 3.5 wt% and 10.5 wt% NaCl solution

| Wt % NaCl | Sample      | R (ohm)   | $E_{\text{corrosion}}$ (V) | $I_{\text{corrosion}}$ (A) | Corrosion Rate (mm/year) |
|-----------|-------------|-----------|----------------------------|-----------------------------|--------------------------|
| 3.5 wt%   | AA 4032 NH  | $3,568 \times 10^4$ | -1,403                     | $7,201 \times 10^{-4}$      | 0.170637                 |
|           | AA 4032 HT  | $3,462 \times 10^4$ | -1,426                     | $7,421 \times 10^{-4}$      | 0.17585                  |
|           | AA 4032 A5  | $6,523 \times 10^4$ | -1,450                     | $3,939 \times 10^{-4}$      | 0.09334                  |
|           | AA 4032 A10 | $8,180 \times 10^4$ | -1,430                     | $3,141 \times 10^{-4}$      | 0.07443                  |
|           | AA 4032 A15 | $4,783 \times 10^4$ | -1,405                     | $5,372 \times 10^{-4}$      | 0.127297                 |
| 10.5 wt%  | AA 4032 NH  | $3,474 \times 10^4$ | -1,330                     | $7,396 \times 10^{-4}$      | 0.175258                 |
|           | AA 4032 HT  | $2,380 \times 10^4$ | -1,374                     | $1,080 \times 10^{-3}$      | 0.25592                  |
|           | AA 4032 A5  | $3,939 \times 10^4$ | -1,365                     | $6,522 \times 10^{-4}$      | 0.154547                 |
|           | AA 4032 A10 | $2,960 \times 10^4$ | -1,380                     | $8,679 \times 10^{-4}$      | 0.20566                  |
|           | AA 4032 A15 | $3,416 \times 10^4$ | -1,354                     | $7,523 \times 10^{-4}$      | 0.178267                 |

3.2. Corrosion Testing Analysis: Electrochemical Test

Electrochemical behavior of the samples were carried out by using Potentiodynamic. The data collected were listed TABLE 3 and potentiodynamic curve are shown FIGURE 2. The corrosion mechanism of aluminum alloy 4032 can be explained by anodic and cathodic reactions that occur when the sample is dipped in a solution of NaCl. It is generally stated that a 10.5 wt% NaCl solution gives a higher corrosion rate in these five samples, compared to a 3.5 wt% NaCl solution. It states that there is a trend of decreasing the value of the corrosion rate along with the decreasing concentration of NaCl solution and also it appears that the higher the concentration of NaCl solution which causes the corrosion rate to increase. In a 3.5% NaCl solution, it was seen that AA 4032 A10 which underwent an aging process for 10 hours had the lowest corrosion rate with a value of 0.07443 mm / year. In the 10.5% NaCl solution, it was seen that AA 4032 A5 which underwent an aging process for 5 hours had the lowest corrosion rate with a value of 0.154547 mm / year. The highest corrosion rate among these samples is the corrosion rate of AA 4032 HT, this happens because this sample does not go through an artificial aging process, because it will occur in the form of a second phase precipitation which begins with the nucleation process and the onset of the atomic cluster that becomes the beginning from precipitate and precipitate can increase the strength and hardness of the material. With increasing strength and hardness, it is also due to the dominant aluminum concentration [8]. The corrosion rate in each sample has a very significant difference which is the reason for using the concentration of NaCl solution which has a considerable distance between 3.5 wt% to 10.5 wt%.
Table 3 show the results of potentiodynamic characterization. The corrosion potential (E (V)) that has a negative value, due to the electron content that enters the metal due to anodic reaction (oxidation) which thus shifts the potential to negative, which slows the anodic reaction and speeds up the reaction cathodic. It can be concluded that aluminum alloy 4032 tends to be more or less anodic, depending on the duration and type of heat treatment that has been carried out and the phenomenon on aluminum alloy 4032 treated. With the difference in corrosion potential in each sample, it will also cause a change in the corrosion rate in each sample. The anodic reaction is:

\[ Al \rightarrow Al^{3+} + 3e^- \]  
\[ Al^{3+} + 6(H_2O) \rightarrow (Al(H_2O)_6)^{3+} \]  
\[ 6NaCl + 6H_2O \rightarrow 6NaOH + 6Cl^- + 3H_2 \]  

\[ \text{(2)} \]  
\[ \text{(3)} \]  
\[ \text{(4)} \]
The cathodic reaction is:

\[ O_2 + 2(H_2O) + 4e^- \rightarrow 4OH^- \]  

(5)

Main reaction is:

\[ 2Al^{3+} + 6Cl^- \rightarrow Al_2Cl_6 \]  

(6)

\[ Al_2Cl_6 \text{ works in } 6H_2O, \text{ the result is:} \]  

\[ Al_2Cl_6 + H_2O \rightarrow Al_2(OH)_6 + 6HCl \]  

(7)

Based on Table 3 that has the highest current density is \textit{AA 4032 HT}, so when the current density is lower, the corrosion rate is also lower, because there are not fewer electrons flowing in the material or the smaller electron exchange occurs, so the smaller the rate of formation the corrosion and also the presence of aluminum alloys with silicon make the current density relatively low. Also, the effect of corrosion is from the corrosion test with NaCl which has been concluded that the water content, due to acidic carrier water which makes accelerating the rate of corrosion, so that the rapid occurrence of corrosion on the alloy \[10\].

4. Conclusion

The dependence of the corrosion rate on the concentration of the electrolyte solution with the greater the concentration of the electrolyte solution, the greater the corrosion rate. Based on experimental results that the value of the corrosion rate of aluminum alloy 4032 which has been affected by the heat treatment process, cooling process, and aging. The samples that most resistance to corrosion is AA 4032 A10, with artificial aging and quenching. From XRD data, the unit cell of aluminium and silicon have cubic structure because the lattice parameter have equal value in \(a, b,\) and \(c\).

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