The Impact of Aging Time on Structure and Corrosion Resistance of Aluminum 2091 Lithium Alloy for Aerospace Application

Arya Octavian and Bambang Soegijono*
Department of Physics, University of Indonesia, Depok, Indonesia
*E-mail: naufal@ui.ac.id

Abstract. In need of aerospace and automotive industries, the aluminum lithium alloy becomes a worldwide topic because of its corrosion resistance, hardness, and categorized as a lightweight material. This alloy has high resistance to corrosion due to doped alloying element, such as copper. Addition of lithium to aluminum alloys lowers its density. This paper was meant to study the impact of aging time at 190°C for 24 hours, 42 hours, and 72 hours on aluminum alloy crystal. The materials had solutionized at 525°C for 5 hours and had quenched at water before it was artificially aged. Besides corrosion resistance, the structure of this alloy are change as the aging times rise that caused by Al$_2$Cu precipitation. To examine the electrochemical response of this material, potentiodynamic curves were obtained for aluminium lithium alloy 2091 during standard test in natural deaerated 3.5% wt and 7.0% wt NaCl solution after heat treatment. The structure after heat treatment were characterized by using X-ray diffraction. The results showed that aging time modified the structure and lead to change the electrochemical behaviour.

1. Introduction
Aluminum alloys are divided into two different major categories which are wrought composition and cast composition. A further distinction for each category is whether heat-treatable or non-heat-treatable [1]. Al-Li 2091 heat-treatable alloy is start to developed in 1924 by several researcher to determine the properties for aerospace application. This type of aluminum alloy has advantageous properties such as easy to fabricated, available in a wide range of strength value, lightweight, high tensile strength, and resistance to corrosion in various condition [2,3]. Its prominent properties can be applied to many part of aerospace craft. For example, fuselage, wing, empenage, and supporting structure [4]. Because of its higher modulus and lower density, Al-Li become attractive for more investigation.

The additional of lithium atom which is lighter than aluminum makes a displacement towards one of aluminum atom from crystal lattice which can helps block dislocation. Considering at high temperature, solubility of lithium in aluminum is also high. Each wt% of lithium increases the modulus of aluminum about 6% and decreases the density of aluminum about 3% [2]. The Al-Li 2091 alloy provide an increases the specific modulus of approximately 15% and offers a density reduction of approximately about 8% compared to 2xxx series [5].

The heat treatments that have been done into Al-Li 2091 may lead the corrosion to modify based on the quantity and the distribution of microstructure. As a 2xxx series, alloying element copper dissolves in α-Al matrix at 550°C which increase corrosion potential. After aging treatment, nucleation of Al$_2$Cu forms (i.e. α and θ phase) at grain boundaries which more cathodic than α-Al [6]. Furthermore, it can
cause a galvanic action. Although, aluminum may create a thin invisible oxide layer, which protects it from corrosion, when the surfaces are exposed to any environment [3].

The Objective of this work is to study the electrochemical behavior of the Al-Li alloy 2091 after different condition of heat treatment, aging time (AT), using electrochemical corrosion test and trying to make some correlation within its structure.

2. Experimental Procedure

2.1. Material
The material used in this experiment is Al-Li alloy 2091, which have been formed into approximately a rectangle shaped 3 cm in length, 0.7 cm in width, 0.2 cm in thickness. There were 4 samples used in this experiment with various treatment for each sample. Before the experiments, samples were polished using silicon carbide paper grit-180. Its chemical composition is listed in the Table 1.

| Elements | % Weight |
|----------|----------|
| Al       | 94.72    |
| Li       | 1.9      |
| Cu       | 1.85     |
| Mg       | 1.2      |
| Zr       | 0.07     |
| Fe       | 0.07     |
| Si       | 0.02     |
| Ti       | 0.02     |

2.2. Solution Heat Treatment
Solution heat treatment was done to all of the samples at temperature 525°C on furnace for 5 hours and then quenched in the water medium in room temperature. This treatment intended to make the constituents or alloying elements enter into the homogenous solid solution. Followed by rapid cooling or quenching in the water to hold the microstructure.

2.3. Artificially Aging Treatment
Afterwards, only 3 samples were artificially aged below the solvus line at temperature 190°C for 24 hours, 48 hours, and 72 hours. These treatment were done to see assorted effect of one another and also compared to solutionized only sample. XRD analysis for all samples were done at UPP IPD Research Laboratory, Faculty of Mathematics and Natural Sciences, Universitas Indonesia. This test was meant to see the characterization of each treatment of Al-Li alloy 2091.

2.4. Corrosion Test
Corrosion tests data were collected out using Potentiostat. The Working Electrode and the Reference Electrode are used to quantify the current and the voltage, where Ag/AgCl was used as the reference electrode in this experiment [7]. All of the samples were connected with the wire so the samples can be dipped into the solution to collect the data. These electrodes were soaked into 3.5 wt% of NaCl solution. The corrosion rate of each samples had been calculated after all data were collected from Potentiostat. The formula that used to calculated the value of corrosion rate was obtained from Law in Determination Corrosion Rates of Metals and Alloys [8].


\[ r = C \frac{M_i}{n \rho} \]  

(1)

Where \( C \) stands for the constant of corrosion rate (0.129 in mpy; 3.27 in mm/year; \( 3.27 \times 10^{-3} \) in \( \text{mm}^3/\text{year} \)), \( M \) stands for atomic weight of every constituent in alloy (g mol\(^{-1}\)), \( i \) stands for current density (A/cm\(^2\)), \( n \) stands for number of electron involved, \( \rho \) stands for density of every constituent in alloy (g/cm\(^3\)). Corrosion rate constant was used in this experiment is \( 3.27 \times 10^{-3} \) in mm\(^3\)/year. The value of \( i \) has SI unit A/cm\(^2\), where the cm\(^2\) defines the cross-sectional area of the samples that was tested for the corrosion resistance. In this experiment, all of 4 samples have the same cross-sectional area which is rectangle-shaped of 1.05 cm\(^2\) with length for 1.5 cm and width for 0.7 cm.

3. Result and Discussion

3.1. XRD Analysis

The XRD plots of all Al-Li alloy 2091 sample can be seen in Figure 1 and the data of the characterization is served in Table 2. There were five demonstrated peaks, namely, (111), (002), (022), (113), and (222) which are clearly visible for aluminum phase. This happens because the intensity of XRD patterns are equal to the composition of constituent that produce it. For the Solutionized Only sample, five peaks were identified with angle positions of 37.98\(^\circ\), 44.24\(^\circ\), 64.5999\(^\circ\), 77.72\(^\circ\), and 81.96\(^\circ\). For 24 Hours of Aging sample, five peaks were identified with angle positions of 38.00\(^\circ\), 44.24\(^\circ\), 64.63\(^\circ\), 77.74\(^\circ\), and 81.95\(^\circ\). For 48 Hours of Aging sample, five peaks were identified with angle positions of 38.039\(^\circ\), 44.26\(^\circ\), 64.62\(^\circ\), 77.76\(^\circ\), and 81.99\(^\circ\). For 72 Hours of Aging sample, five peaks were identified with angle positions of 37.98\(^\circ\), 44.24\(^\circ\), 64.61\(^\circ\), 77.78\(^\circ\), and 81.99\(^\circ\).

The highest peak value is on Solutionized Only sample which the value is 2.3675 Å. This is believed to be due to the heat treatment lower the intensity of the light that diffracted by atoms in the crystal structure which proportional to the square of the amplitude of the structural factor [9]. All samples have a little difference at each peak which states that there was a slight peak shift caused by heat treatment. This will not change the phase that is already owned by the alloy, but it can affect the differences in the microstructure of the crystal system as evidenced by differences in microstrain.

![Figure 1. XRD plot of aluminum lithium alloy 2091](image-url)
The crystallite system of these samples are cubic, so the lattice parameters have the same value for a, b, and c. For aluminum reference, Solutionized Only sample has the biggest lattice parameter, then followed by 24 Hours of Aging sample, 48 Hours of Aging sample, and 72 Hours of Aging sample. The lattice parameter changes in each sample as the time of artificially aging are raised. This is considered as the impact of Al$_2$Cu precipitations existence in the alloy lattice. The volume are also transformed follow changes in lattice parameter.

Aging heat treatment slightly reduce the height of the peaks. It can be proven by analyzing the diffraction angle which is related to the peak’s width. By considering the crystallite size, the various treatments change the grain of the Al-Li 2091. In certain period of time, the grain size will decrease and increase the grain size. It has commonly assumed that there are deformation and grain growth that depend on the strain.

| Sample | A | B | C | D |
|--------|---|---|---|---|
| Crystallite Size (Å) | 27913.4 | 1839.5 | 27913.4 | 1134.6 |
| Aluminum Magnesium (3.7/0.3) | a = 4.0494 | a = 4.0486 | a = 4.0483 | a = 4.0472 |
| Lattice Parameter (Å) | b = 4.0494 | b = 4.0486 | b = 4.0483 | b = 4.0472 |
| | c = 4.0494 | c = 4.0486 | c = 4.0483 | c = 4.0472 |
| Volume (Å$^3$) | 66.40 | 66.36 | 66.34 | 66.29 |
| Microstrain (%) | 0.044 | 0.071 | 0.050 | 0.094 |

A = Solutionized Only  B = 24 h, aging  C = 48 h, aging  D = 72 h, aging

3.2. Potentiodynamic Curves Analysis

By analysing the corrosion mechanism and understanding the change in corrosion rate, electrochemical behaviour of the Al-Li alloy 2091 samples in this experiment are observed. The outcome potentiodynamic curves test in 3.5 wt% NaCl solution and 7.0 wt% NaCl solution for samples with various heat treatment are shown on Figure 2. For all samples, similar trend are displayed in potentiodynamic polarization curves. $I_{corr}$ and $V_{corr}$ are obtained by applying Tafel plotting exploration. The reactions that represent for corrosion in Al-Li 2091 in NaCl electrolytes are shown below.

Anodic reaction : $\text{Al} \rightarrow \text{Al}^{3+} + 3e$  
(2)

Cathodic reaction : $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$  
(3)

In cathodic reactions, electrons from anodic reaction are absorbed to do some reduction of oxygen in solution. The ion Cl$^-$ plays the role in corrosion by breaking and preventing the aluminum thin oxide layer [10].

Main reaction : $2\text{Al}^{3+} + 6\text{Cl}^- \rightarrow \text{Al}_2\text{Cl}_6$  
(4)

$\text{Al}_2\text{Cl}_6 + 6\text{H}_2\text{O} \rightarrow \text{Al}_2(\text{OH})_6 + 6\text{HCl}$  
(5)
A = Solutionized Only  B = 24 h, aging  C = 48 h, aging  D = 72 h, aging

Figure 2. (a) Potentiodynamic polarization curves of the aluminum lithium alloy 2091 in 3.5 wt% NaCl solution. (b) Potentiodynamic polarization curves of the aluminum lithium alloy 2091 in 7.0 wt% NaCl solution.

Potential corrosion $E_{\text{corr}}$ (V) and corrosion current $I_{\text{corr}}$ (A) affect changes in the corrosion rate. Table 3 shows solutionized only samples and 72 hours of aging samples have significant values of corrosion rate. It is expected that in solutionized sample, the alloying elements are solutionized into the solution of aluminum which increasing the current transition to anodic dissolution of these metals exceeds the ability of oxygen. Aging time not only increase the current density in Al-Li 2091 alloy, but also increase the corrosion rate due to the precipitate size [6]. The release of electrons in an anodic reaction can make the metal potential more negative which can accelerate the cathodic reaction and decelerate anodic reaction and this can slow down the rate of corrosion [11].
Table 3. Data from the corrosion test of the aluminum lithium alloy 2091 in the 3.5 wt% and 7.0 wt% NaCl solution.

| NaCl Solution | Sample                | R (ohm)  | $E_{\text{corrosion}}$ (V) | $I_{\text{corrosion}}$ (A) | Corrosion Rate (mm/year) |
|---------------|-----------------------|----------|----------------------------|-----------------------------|--------------------------|
| 3.5%          | Solutionized Only     | $3.734 \times 10^2$ | -0.921                     | $6.880 \times 10^{-5}$       | $7.623 \times 10^{-1}$ |
|               | 24 Hours of Aging     | $4.659 \times 10^2$ | -0.876                     | $5.515 \times 10^{-5}$       | $6.111 \times 10^{-1}$ |
|               | 48 Hours of Aging     | $3.578 \times 10^2$ | -0.868                     | $7.182 \times 10^{-5}$       | $7.958 \times 10^{-1}$ |
|               | 72 Hours of Aging     | $3.322 \times 10^2$ | -0.861                     | $7.735 \times 10^{-5}$       | $8.571 \times 10^{-1}$ |
| 7.0%          | Solutionized Only     | $4.627 \times 10^1$ | -1.495                     | $5.535 \times 10^{-4}$       | 6.153                    |
|               | 24 Hours of Aging     | $1.432 \times 10^3$ | -0.890                     | $1.795 \times 10^{-5}$       | $1.989 \times 10^{-1}$ |
|               | 48 Hours of Aging     | $1.754 \times 10^2$ | -1.457                     | $1.465 \times 10^{-4}$       | 1.623                    |
|               | 72 Hours of Aging     | $5.070 \times 10^2$ | -1.597                     | $5.068 \times 10^{-5}$       | $5.615 \times 10^{-1}$ |

4. Conclusion
Variation of heat treatment in aluminum lithium alloy 2091 cause various impacts in structure and corrosion rate on its structure and corrosion rate. Structural changes in these alloys are caused by artificial aging. Solution heat treatment has great impact at corrosion rate due to the reaction of every constituent in its solution. Lower artificial aging time at 190°C resulted lower the rate of corrosion.

Acknowledgement
The authors thanks for the financial supports from the Universitas Indonesia under grant Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA), No. 2239/UN2.R3.1/HKPO5.00/2018.

References
[1] J. R. Davis, “Corrosion of Aluminum and Aluminum Alloys,” 1999.
[2] E. A. Starke, Historical Development and Present Status of Aluminum-Lithium Alloys. Elsevier Inc., 2013.
[3] M. Engineering, “Effect of Aging on the Corrosion of Aluminum Alloy 6061 Effect of Aging on the Corrosion of Aluminum Alloy 6061,” 2010.
[4] J. Stailey and D. Lege, “Advances in aluminium alloy products for structural applications in transportation To cite this version : HAL Id : jpa-00251921,” 1993.
[5] K. Welpmann et al., “MECHANICAL PROPERTIES AND CORROSION BEHAVIOUR OF 2091 SHEET MATERIAL To cite this version : HAL Id : jpa-00226609,” 1987.
[6] V. Gadpale, P. N. Banjare, and M. K. Manoj, “Effect of ageing time and temperature on corrosion behaviour of aluminum alloy 2014” 2018.
[7] A. Vats, “Corrosion Measurement , Friction testing and XRD Analysis of Single Layer CrN Coatings on AISI 304 Stainless Steel,” no. 5, pp. 435–445, 2017.
[8] Z. Ahmad, “Application of Faraday’s Laws In Determination of Corrosion Rates of Metals and Alloys,” in Principle of Corrosion Engineering and Corrosion Control (Butterworth-Heinemann, United Kingdom, 2006), pp. 58–61.
[9] J. Kepler and N. Year, “X-ray crystallography,” no. 1784.

[10] J. Anggono, S. Tjito, D. F. Teknik, J. Teknik, M. Universitas, and K. Petra, “Studi Perbandingan Kinerja Anoda Korban Paduan Aluminium dengan Paduan Seng dalam Lingkungan Air Laut.”

[11] G. Bellefontaine, “THE CORROSION OF CoCrMo ALLOYS FOR BIOMEDICAL,” no. January, 2010.