Effect of Nickel on Corrosion Resistance Of Al-Zn-Mg-Cu PM Alloy Produced by Mechanical Alloying

Kahtan S. Mohammed¹, Haider T. Naeem²,³, Raid T. Hadi⁴

¹²School of Materials Engineering, University Malaysia Perils, Muhibba, 02600 Jejawi, Perlis, Malaysia
³⁴College of Engineering, Al-Muthana University, Almuthana, Samawa, Iraq

Abstract: In this research, comparative study of corrosion resistance of PM Al-Zn-Mg-Cu alloy (A) and PM Al-Zn-Mg-Cu-1%Ni alloy (B) produced using mechanical alloying process has been investigated. PM milled alloy (A) and alloy (B) specimens were sintered after compaction then homogenized, aged then retrogressed and reaged. PM Al-alloys were subjected to corrosive media (acidic: 1.0M HCl) and using weight loss method to evaluate their corrosion resistance. The findings of this study indicated that the precipitation hardening is obtained for PM milled Al- alloy A samples after heat treatment led to enhance their resistance of corrosion. Furthermore, the gain of corrosion resistance for PM Al-Zn-Mg-Cu-Ni alloy B specimens more than what PM Al-Zn-Mg-Cu alloy A caused by having in compounds of Al-Ni as well as precipitates of alloying elements, under the same operation conditions. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to show the corroded surfaces.

Keywords: Al-Zn-Mg-Cu-Ni PM alloy; Mechanical alloying; Corrosion resistance

1. Introduction

In aeronautical industries due to their attractive comprehensive properties, such as low density, high strength, ductility, toughness and resistance to fatigue, Al–Zn–Mg–Cu alloys have been widely used as structural materials [1, 2]. However, Al–Zn–Mg–Cu alloys are susceptible to local corrosion, such pitting, inter-granular corrosion (IGC), exfoliation corrosion (EXCO) and stress corrosion cracking (SCC) [3-5]. A major corrosion issue with Aluminum and its alloys is the localized breakdown of the passive film, which lead to the induction and growing of corrosion cavities in chloride containing environments. New heat treatments for Al–Zn–Mg–Cu systems can be improved resistance of corrosion with the optimum of mechanical properties [6, 7]. Recently, the interest of researchers for reducing the susceptibility of corrosion by controlling of grain sizes using manufacturing by means of severe plastic deformation such surface mechanical attrition and equal channel angular processing [8, 9] or by modification of chemical composition of Al-alloys using adding rare earth elements, Bobby et al [10] and Fang et al [11] found that the resistance to SCC or EXCO of the Al-Zn-Mg-Cu alloy can be substantially improved by conquering recrystallization through Sc or Cr, Yb and Zr additions, respectively.

Naeem et al [12] investigated that addition of nickel into Al-Zn-Mg-Cu produced by casting technique led to improve the corrosion resistance in Al-alloys containing 0.5% nickel after series of heat treatments. However, up to now, there is not research which had paid attention to investigate of additions of nickel affecting on corrosion behavior of Al-Zn-Mg-Cu alloys producing using powder metallurgy method. Therefore, research aims to study synergistic effects of nickel, the aging at T6 and the retrogression and reaging on resistance of Al-Zn-Mg-Cu PM produced by mechanical milling alloying.

2. Experimental Procedures

Elemental powder precursors of Al, Zn, Mg, Cu, Cr, Fe, and Ni were used as starting materials to produce two Al based Alloys; A (Al–5.5%Zn–2.5%Mg–1.5%Cu–0.4%Fe–0.2%Cr) and B (Al–5.5%Zn–2.5%Mg–1.5%Cu–0.4%Fe–0.2%Cr–1%Ni) compositions. All compositions are expressed in weight percentages (wt. %).

Table 1: Specification of materials

<table>
<thead>
<tr>
<th>Powder</th>
<th>Description</th>
<th>Particle sizes (µm)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Flake</td>
<td>51</td>
<td>98.00</td>
</tr>
<tr>
<td>Zn</td>
<td>Rounded</td>
<td>18</td>
<td>96.00</td>
</tr>
<tr>
<td>Mg</td>
<td>Rounded</td>
<td>115</td>
<td>98.00</td>
</tr>
<tr>
<td>Cu</td>
<td>Irregular</td>
<td>39</td>
<td>99.50</td>
</tr>
<tr>
<td>Fe</td>
<td>Rounded</td>
<td>200</td>
<td>99.50</td>
</tr>
<tr>
<td>Cr</td>
<td>Irregular</td>
<td>160</td>
<td>99.50</td>
</tr>
<tr>
<td>Ni</td>
<td>Rounded</td>
<td>11</td>
<td>99.50</td>
</tr>
</tbody>
</table>

All Al-Zn-Mg-Cu-Cr-Fe PM and Al-Zn-Mg-Cu-Cr-Fe-1% Ni PM Alloys were produced using the ball milling alloying process then compacted and sintered under a certain conditions as reported in our research [13].

After producing of the sintered A and B alloys; two kinds of Al-Zn-Mg-Cu and Al-Zn-Mg-Cu-Ni PM alloy specimens are homogenized then followed by quenching in cold water immediately after each step. Thereafter the aging at T6 temper then the retrogression and re-aging (RRA) process were conducted on A, B PM alloys according to [14-15].

To preparation of specimens for the corrosion tests, the specimen surfaces were ground with 1200 grit silicon carbide paper and then polished using 3µm diamond paste to obtain a
good surface finish. The coupons were then washed in distilled water, followed by acetone, and then allowed to dry thoroughly.

The corrosion tests were static immersion tests conducted at room temperature using the conventional weight loss method to an accuracy of 0.1 mg. Each specimen was first weighed before being immersed in 250 ml open beakers containing 200 ml of 1 M HCl solution and later taken out after 24, 48 and 72 hours, respectively.

HCl acid solution was chosen as the corroden for accelerated consequences. After each corrosion test, the specimen was immersed in Nitric acid for 1 min and gently cleaned with a soft brush to remove adhered scales. After drying thoroughly, the specimens were weighed again. The weight loss was measured and converted into corrosion rate expressed in millimeters per year (mm/y) as according to Eq. 1., [12].

\[
\text{Corrosion rate (C.R.)} = \frac{K \times W}{A \times T \times D} 
\]

Where,

\[
W = \text{weight loss in mg} = W_0 - W_f \\
W_0 = \text{original weight of the sample,} \\
W_f = \text{final weight of the sample after immersion} \\
D = \text{Density of the sample in g cm}^{-3} \\
A = \text{Total surface area of sample in cm}^2 \\
T = \text{exposure time in hours} 
\]

The corroded surfaces were analyzed using scanning electron microscopy (SEM) coupled with the energy dispersive X-ray spectroscopy (EDS) was used.

3. Results and Discussions

Generally, Aluminum has reacted with Oxygen within the protective layer of Al as assumed:

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

From the solution, the oxide formed and acted as a static barrier that isolated the metal. However, acid solutions may bear upon its properties. On the characteristics of the medium, disintegration of the protective layer or re-passivation of the metal may be come according to [16].

\[
\frac{1}{2}\text{Al}_2\text{O}_3 + 3\text{H}^+ \leftrightarrow \text{Al}^{3+} + \frac{3}{2}\text{H}_2\text{O} \\
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + e^- 
\]

The reformation of oxide layer under the conditions used in this study, which did not appear to come due to an increased dissolution of Aluminum, is observed in all cases.

Aluminum dissolution in chloride solutions has been largely investigated and its chemical mechanism almost clearly understood. It is agreed that several staircase are involved in the chemical mechanism of Al dissolution including of the adsorption of chloride ions at the oxide surface, penetration of the oxide film by chloride ions, dissolution which come about beneath the oxide film at the metallic element oxide at the metal/oxide interface and Cl⁻ aided. This can be represented as following [17]:

\[
\text{Cl}^- \text{(bulk solution)} \rightarrow \text{Cl}^- \text{(adsorbed on Al}_2\text{O}_3 \cdot \text{nH}_2\text{O)} \\
\text{Al}^{3+} \text{(in Al}_2\text{O}_3 \cdot \text{nH}_2\text{O)} + 4\text{Cl}^- \rightarrow \text{AlCl}_6^- 
\]

This process lead to the oxide film thinning [18] thus the corroded of metal was started.

Table 2 shows the results of corrosion rates for PM Al-alloys included; as sintered A-milled, as well the aged in T6#A-milled and RRA#A-milled samples in 1 M HCl solution for interval time included 24 h, 48 h and 72 h.

![Graph of corrosion rates of an Al-Zn-Mg-Cu PM alloy A for several of heat treatments and extrusion process vs. exposure time in 1 M HCl solution](image)

**Figure 1:** Graphs of corrosion rates of an Al-Zn-Mg-Cu PM alloy A for several of heat treatments and extrusion process vs. exposure time in 1 M HCl solution

Table 3 presents the findings of corrosion rates for alloy A and B, corrosion rates of alloy A under different treatments for various durations in HCl solution as shown in Figure1.

It can be observed that the rates of corrosion for the aging temper at T6#A-milled and RRA#A-milled during 24 hours which are decreased than as sintered A-milled about of 26% and 38.4% respectively.

These enhancements of corrosion resistance of samples of alloy A attributed to the distribution precipitations particles under impacts of the aging at T6 and RRA as reported [7, 12, 19].
RRA#B-milled samples in 1 M HCl solution for interval time included 24 h, 48 h and 72 h.

Table 3: Corrosion rate of A PM alloy samples for different procedures in HCL solution.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Types of procedures</th>
<th>Corrosion rate* 10E-01 (mm/y)</th>
<th>After 24h exposure</th>
<th>After 48h exposure</th>
<th>After 72h exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM Milled B</td>
<td>As sintered B-milled</td>
<td>35.094</td>
<td>25.918</td>
<td>23.473</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T6#B-milled</td>
<td>24.346</td>
<td>20.975</td>
<td>18.496</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRA#B-milled</td>
<td>21.165</td>
<td>17.678</td>
<td>16.502</td>
<td></td>
</tr>
</tbody>
</table>

After corrosion test conducted on PM Al-alloys A and B, corrosion rates were calculated of alloy B under different treatments for various durations in HCl solution as shown in Figure 2. It can be explained that the rates of corrosion for the aging temper at T6#B-milled and RRA#B-milled during 24 hours which are decreased than as sintered A-milled about of 31% and 35% respectively.

On the other hand, corrosion resistance of as sintered B-Milled, T6#B-milled and RRA#B-milled more than as sintered A-Milled, T6#A-milled and RRA#A-milled under the same operation conditions. Increasing in corrosion resistance of PM Al-alloy B owing distribution of the Al-Ni intermetallic compounds created during Al-matrix due to the role of mechanical alloying in the increasing solubility of Ni with aluminum [13].

Visible inspection showed that there were no hydrogen bubbles clinging onto the surface of the test specimens. The phenomenon of monotonically decreasing corrosion rate with respect to time indicates some passivation of the matrix alloy. Garcia et al [21] observed in the suit of localized corrosion in HCl solution, the surfaces of aluminum alloys are passive and back up a relatively thick alumina film that does not allow hydrogen to evolve.

Ma et al [22] believe that the black film formed on the surface consists of an Al hydrated oxide compound which protects the bulk stuff from further corrosion in the acid medium. The SEM micrograph of PM Al-alloy A sample after T6 as shown in Figure 3a reveals corroded surface of aluminum matrix. The \( \alpha \)-Al with existent major alloying elements of Zn, Mg and Cu which are evident as presented in Figure 3b. Further, the presence high percentage of chloride ions due to reactions taken place in the base alloy during the immersed in acidic medium as mentioned former (Eq. 5 and 6). The SEM image for PM Al-alloy B after RRA in Figure 4a show that dark area as \( \alpha \)-Al matrix as well as dispersion particles as light which consist of the intercompounds and precipitations. Figure 4b reveals the EDS spectrum the having of nickel element as evidence about create compounds.

4. Conclusions

The results for this study reveals that corrosion rate is decreased of PM milled Al-alloy A samples after applying the aging; retrogression and reaging. On the other hand, regard to PM milled alloys underwent to the aging at T6 and RRA possesses corrosion resistance higher than as sintered samples, due to the precipitation phases of alloying elements are occurred. Furthermore, Corrosion resistance of PM milled Al-alloy B is enhanced more than alloy A due to the additions of nickel led to create dispersion intermetallics as well the precipitations particles.

5. Acknowledgements

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Figure 3: (a) SEM micrograph of corroded surface of PM milled Al-alloy A in 1 M HCl solution after 72 hours; and (b) Corresponding EDS analysis showing the attacked surface and chemical composition of corroded surface.

Figure 4: (a) SEM micrograph of corroded surface of PM milled Al-alloy B, in 1 M HCl solution after 72 hours; and (b) Corresponding EDS analysis showing the attacked surface and chemical composition of corroded surface.

References


