Corrosion Behaviour of Al (6063) Alloy (As-Cast and Age Hardened) in H\textsubscript{2}SO\textsubscript{4} Solution

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Abstract
The heat treatment and corrosion of aluminum 6063 alloy was investigated. The aim of this work was to determine the effect of heat treatment on the microstructure and the corrosion of aluminum 6063 alloy using weight loss method. The samples conditions were; as-cast, solution treated, supersaturated and age hardened condition. They were soaked in a 10 molar solution of sulphuric acid and monitored with time. The corrosion rate was calculated for various immersion periods. The result shows that the corrosion rate of the alloy was due to the nature of heat treatment given to the samples. Similarly, it was also found that the corrosion rate of the Al(6063) alloy was higher in the as-cast sample compared to the heat treated alloy. The passivation on the heat treated Al(6063) alloy was a little more stable therefore reducing the corrosion rate after 35 days of immersion for the aged hardened samples.

Keywords: heat treatment, Aluminum (6063), H\textsubscript{2}SO\textsubscript{4} solution, corrosion, age hardening

1. Introduction
The importance of selection and use of engineering materials for design and subsequent manufacture of component parts cannot be over emphasized.

Most applications of engineering some cases meet service requirements hence the need to enhance their properties before putting them to use (Higgins, 2001; Khalifa, 2009).

The case of aluminum and Al(6063) are not exception. Aluminum (Al) is one of the most abundant metals on earth which is silvery-whitish in appearance. Aluminum, as indicated by its position in the electrochemical series, is a thermodynamically reactive metal; among structural metals, only beryllium and magnesium are more reactive. Aluminum owes its excellent corrosion resistance and its use as one of the primary metals of commerce to the barrier oxide film that is bonded strongly to its surface and that, if damaged, re-forms immediately in most environments. On a surface freshly abraded and then exposed to air, the barrier oxide film is only 1 nm thick but is highly effective in protecting the aluminum from corrosion. The oxide film that develops in normal atmospheres grows to thicknesses much greater than 1 nm and is composed of two layers (Hatch, 1984; ASM, 2005). The inner oxide next to the metal is a compact amorphous barrier layer whose thickness is determined solely by the temperature of the environment. At any given temperature, the limiting barrier thickness is the same in oxygen, dry air, or moist air. Covering the barrier layer is a thicker, more permeable outer layer of hydrated oxide. Most of the interpretation of aluminum corrosion processes has been developed in terms of the chemical properties of these oxide layers (Scamans, 1987; Kiourtsidis & Skolianos, 2007). The film growth can be visualized as the result of a dynamic equilibrium between opposing forces-those tending to form the compact barrier layer and those tending to break it down. If the destructive forces are absent, as in dry air, the natural film will consist only of the barrier layer and will form rapidly to the limiting thickness. If the destructive forces are too strong, the oxide will be hydrated faster than it is formed and little barrier will remain. Between these extremes, where the opposing forces reach a reasonable balance, relatively thick (20 to 200 nm) natural films are formed (David, 1987; Alaneme, 2010). As shown by this diagram, aluminum is passive (is protected by its oxide film) in the pH range of approximately 4 to 8.5. The limits of this range, however, vary somewhat with temperature, with the specific form of oxide film present, and with the presence of substances that can form soluble complexes or insoluble salts with aluminum (Alaneme, 2011; Hutchings et al., 2000). Beyond the limits of the passive range, aluminum corrodes in aqueous solutions because its oxides are soluble in many acids and
bases, yielding $\text{Al}^{3+}$ ions in the former and $\text{AlO}_2^-$ (aluminate) ions in the latter. There are, however, instances when corrosion does not occur outside the passive range, for example, when the oxide film is not soluble or when the film is maintained by the oxidizing nature of the solution (Hatch, 1984).

There are several properties that make aluminum one of the most widely used elements, these include: non-toxic, impervious, non-sparking, decorative, easily formed, machined, strong, low density corrosion resistant, electricity conductor, non-magnetic, non-combustible highly reflective heat barrier and conductor, malleable and can be easily worked (Zhu & Hihara, 2010). Depending on its purity, for example 99.996 percent pure aluminum has a tensile strength of about 49 MPa, rising to 700 MPa following alloying and suitable heat treatment (Nnuka, 2000; Singla et al., 2009; ASTM, 1994; Pinto et al., 2009). There are numerous other aluminum properties which are of particular use in a number of chemical and industrial applications. Al(6063) alloy has medium strength property, and is readily suited to welding, high specific strength and stiffness, improved high temperature property controlled thermal expansion resistance, and improved wear and attraction resistance (Nunes & Ramanathan, 1995).

2. Materials and Methods

Al(6063) alloy with base composition 0.56Si, 0.28Fe, 0.08Cu, 0.23Mn, 0.61Mg, 0.05Zi, 0.02Cr, and 0.04Ti was used in this study. Aluminum 6063 alloy was sourced, washed and air dried for about six (6) hours. A total of twenty five (25) pieces of 48x48x2 mm were sized. The samples were kept in cool dry place before further treatment.

From the 25 samples sized there categories of samples were further prepared there were;

- The as cast Al(6063) alloy sample which was used as the controlled experiment.
- The solutionized aluminum 6063 alloy which was subjected to a temperature of 550 °C in the furnace.
- Artificially aged aluminum 6063 alloy at temperature of 180 °C for 30mins, 60 mins and 120 mins.

From the twenty five (25) pieces which were used for the study, the as-cast condition (5 pieces) and others developed by heat treatment of solutionized and water quenched and fifteen (15) pieces were artificially aged hardened at 180 °C and at different times of 30 mins, 60 mins and 120 mins. The solutionized and quenched temper were achieved by the samples at 550 °C then quenched in water.

The materials used for the research included among others; aluminum 6063 alloy sample, electric furnace (induction furnace), crucibles, electrical weighting balance, measuring cylinder, water weighting beaker, tetraxosulphate (vi) acid and nitric acid.

The corrosion tests were carried out in 10 wt% H$_2$SO$_4$ which was prepared using standard procedures. The specimens for the test were cut to 48x48x2mm, after which the sample surface were mechanically polished with emery papers starting from 320 grit down to 600 grit corresponding to particles sizes of the silicon carbide of 33, 23 and 17 micron respectively (1 micron = 10$^{-4}$ cm) as revealed in the literature (10).

The samples were degreased with acetone and then rinsed in distilled water before immersion in still solution of 10wt% H$_2$SO$_4$ in de-ionized water exposed to atmosphere air.

The electro-chemical experiment was monitored for 7, 14, 21, 28 and 35 days. The corrosion test results were evaluated using weight loss and corrosion rate.

The weight loss (mg) for each sample was evaluated by finding the difference in weight (final weight initial weight) considering the total surface area of the specimen in accordance with ASTM G311 standard recommended practice (ASTM, 1994).

Corrosion rate for each specimen was evaluated from the weight loss measurement following standard procedures.

3. Results and Discussion

The result of the findings is presented in Table 1 for weight losses and corrosion rates of the different samples in Tetraxosulphate (vi) acid. Figures 1-3 shows the different plots of the result also obtained.
Table 1. Result of weight loss and corrosion rate of heat treated Al(6063) Alloy

<table>
<thead>
<tr>
<th>Sample Time</th>
<th>Weight Loss As Cast Sample (Gram)</th>
<th>Corrosion Rate As Cast Sample (Mm/Yr)</th>
<th>Weight Loss Solutionized Sample At 550°C Quenched In Water (Gram)</th>
<th>Corrosion Rate Solutionized Sample At 550°C Quenched In Water (Mm/Yr)</th>
<th>Weight Loss Aged Hardened Sample at 180°C 30 Mins (Gram)</th>
<th>Corrosion Rate Aged Hardened Sample at 180°C 30 Mins (Mm/Yr)</th>
<th>Weight Loss Aged Hardened Sample at 180°C One Hour (Gram)</th>
<th>Corrosion Rate Aged Hardened Sample at 180°C One Hour (Mm/Yr)</th>
<th>Weight Loss Aged Hardened Sample at 180°C Two Hours (Gram)</th>
<th>Corrosion Rate Aged Hardened Sample at 180°C Two Hours (Mm/Yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.095</td>
<td>0.000797</td>
<td>0.150</td>
<td>0.001257</td>
<td>0.090</td>
<td>0.000754</td>
<td>0.100</td>
<td>0.000838</td>
<td>0.120</td>
<td>0.001584</td>
</tr>
<tr>
<td>14</td>
<td>0.150</td>
<td>0.000629</td>
<td>0.250</td>
<td>0.001048</td>
<td>0.170</td>
<td>0.000715</td>
<td>0.190</td>
<td>0.000782</td>
<td>0.240</td>
<td>0.001584</td>
</tr>
<tr>
<td>21</td>
<td>0.230</td>
<td>0.000643</td>
<td>0.340</td>
<td>0.000950</td>
<td>0.270</td>
<td>0.000754</td>
<td>0.280</td>
<td>0.000754</td>
<td>0.320</td>
<td>0.000894</td>
</tr>
<tr>
<td>28</td>
<td>0.300</td>
<td>0.000629</td>
<td>0.380</td>
<td>0.000796</td>
<td>0.350</td>
<td>0.000733</td>
<td>0.360</td>
<td>0.000637</td>
<td>0.380</td>
<td>0.000796</td>
</tr>
<tr>
<td>35</td>
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<td>0.000520</td>
<td>0.400</td>
<td>0.000671</td>
<td>0.360</td>
<td>0.000350</td>
<td>0.380</td>
<td>0.000637</td>
<td>0.390</td>
<td>0.000654</td>
</tr>
</tbody>
</table>

Figure 1. The weight loss (a) and corrosion rate (b) plots for the as-cast samples immersed in 10wt% H₂SO₄ solution

Figure 1, presents the weight loss and corrosion rate plots for the as-cast samples immersed in 10wt% H₂SO₄ solution. It was observed that while they was increase in the weight loss as the number of days increased, they was also a drop in the mass loss in the 7th to 14th days of immersion. Figure 1(b) shows that the corrosion rate of the samples dropped rapidly up to the 14th day as a result of the formation of passive films on the surface of the samples which led to temporary seizure of the corrosion attack. Corrosion attack was also restored after the 14th day as observed from Figure 1(b) due to gradual break down of the passive films. However the corrosion rate after the weight gain as seen in Figure 1(a) is considerably lower than what was observed at the earlier stages of immersion suggesting that the passive films formed on the surface of the sample were stable.
Figure 2 shows the weight loss and corrosion plots of the material (Al6063) subjected to solution treatment and quenched in water. It was found that there was an increase in the weight loss as the number of days for immersion also increased. In the early days of immersion the corrosion rate was intense and decreased with time indicating that the passive films formed on the surface of the specimens remained stable to a large extent till the completion of the immersion test. The corrosion behavior the as-cast sample is quite different from the solutionized sample as can be observed from the shape of the plots, there is steady and progressive drop in the corrosion rate of the solutionized sample implying that there was stability of passive film formation which is in agreement with (Alaneme, 2011). The corrosion rate drop could also be attributed to the fact that, the alloy on quenching retains Mg$_2$Si in the solution and produced a supersaturated solution of Mg$_2$Si in aluminum at room temperature in this condition; the alloy is somewhat stronger and harder because there is more Mg$_2$Si actually in solid solution in the aluminum. Therefore there is reduction in the corrosion rate with increase in time.

Figure 3 shows the weight loss and corrosion plots of solutionized samples quenched in water after heating to 550 °C and immersed in 10wt% H$_2$SO$_4$ solution.
Figure 3 shows the result of samples of aluminum (6063) alloy that were of age hardened at the temperature of 180°C for a period 30 min, 60 mins and 120 mins. By carrying out this age hardening process there was an improvement in the properties of the alloy by tempering.

The treatment which is largely called precipitation treatment increased the amount of intermediate coherent precipitate by accelerating the rate of diffusion, and so strength and hardness of the alloy was increased.

The weight loss pattern of aged hardened specimens as shown in Figure 3 is to a large extent similar to the solution treated and quenched specimen. The weight loss tends to increase for specimen aged hardened for longer period. The corrosion behavior of the aged hardened specimen showed that for the specimen aged at 120 mins it corroded more at shorter times and stabilizes after 21st day. For the sample of 30 and 60 mins ageing the corrosion rate was well reduced indicating that Al(6063) alloy heat treated can be satisfactorily applied in an acidic environment.

4. Conclusion

The influence of corrosion on heat treated Al(6063) immersed in 10wt% tetraoxosulphate (vi) acid solution has been successfully studied. The results obtained showed that the corrosion susceptibility of heat treated Al(6063) was found to be lower than the monolithic aluminum alloy as can be observed from the slope of the graph.

It was also noted that the passive films formed on the alloy was sufficiently stable which contributed in the reduction of the corrosion rate on the heat treated alloy after 35 days of immersion, therefore for applications of Al(6063) in acidic environment ageing of 30 min and 60 mins is recommended.

Further methods such as; hydrogen evolution, thermometric and electrochemical methods are recommended for consideration.

References


