PITTING CORROSION AND METASTABLE PITTING INITIATION RATE OF 5083 ALUMINUM ALLOY IN SYNTHETIC SEA WATER AS A FUNCTION OF MEDIUM PH

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Abstract

Pitting corrosion Al-5083 has been studied in synthetic sea water at different pH values including 7.5, 8, 8.2 and 8.5. Potentiodynamic polarization has been used in this research. Effect of pH on corrosion potential, corrosion rate, polarization resistance and potential of pitting initiation has been investigated. Rate of initiation of the metastable pits were measured by using the potentiostatic polarization test. Morphology of the samples after the potentiostatic test was investigated using the optical microscopy (OM) and scanning electron microscopy (SEM). Results obtained revealed that, there is a meaningful connection between medium’s pH, pitting potential and metastable pitting rate. Results also revealed that increasing solution’s pH to 8.5 will increase the difference between corrosion potential and pitting potential but variations in metastable pitting rate is not linear.

Keywords: Aluminum Alloy 5083; pitting corrosion; potentiodynamic polarization; metastable pits

1. INTRODUCTION

Aluminum-magnesium alloys are a very important group of medium strength alloys and as un-heat-treatable alloys they owe their strength to solid solutions [1] and cold work strain hardening [2]. These alloys are used in a wide range of applications such as cryogenic tanks, trailers, armored vehicles and especially in submarines [3]. These alloys also have a good flexibility, weldability and corrosion resistance [4].

High strength aluminum alloys have heterogeneous microstructure and hence they are susceptible to pitting [5,6]. In the new Al-alloys, weight percent of magnesium as a strengthening component is higher than 3.5%. These alloys are supersaturated in temperatures less than 200°C and this makes them more prone to localized and intergranular stress cracking corrosion [2]. When the temperature raises a little higher than this limit, Al\textsubscript{3}Mg\textsubscript{2}(\beta) phase content increases and usually leads to the formation of active precipitation of \( \beta \) phase on grain boundaries [7].

Presence of precipitate in salty media causes pitting due to easier transferring of ions and the formation of weak oxidation layer [8,9]. Anodic and cathodic reactions around these compounds cause pitting on their surface [10,11]. Apart from the amount of intermetallic compounds, temperature and concentration of chlorine ion and pH of solution highly effects the initiation of metastable pits [12]. One of the most conventional electrochemical methods for determination of pitting potential (Epit) is potentiodynamic polarization test. But Epit is not enough to investigate corrosion. Therefore, potentiostatic polarization test is used to determine the rate of pitting initiation in metastable pits. Probability of production of stable pits is directly proportional to occurrence of metastable pits. Study of metastable pits is thus more reasonable due to more probable occurrence and being easier to investigate [13]. Applying a potential equal to the pitting potential (Epit) during potentiostatic polarization test changes values of current in metastable pits and produces transient spikes. With calculation of electric current peaks, the number of metastable pits is measured [12]. Time needed for formation of a metastable pit is divided into two parts including time for
growth of pit (tg) and time for repassivation (trp). Gupta et al.[13] found out that the time needed for growth of pits in alloy 5083 is more than trp. In some metastable pitting in alloy 5083 it’s been observed that current rises and this rise in current shows growth of metastable pits and simultaneous repassivation. After reaching a sharp current density peak it’s less probable to see an overlap for metastable pits [13].

Variations of pH in sea water and its effects on corrosion of alloy 5083 are almost neglected. Because of wide range of acidity variations in this environment, variations of pH in sea water was investigated after synthesizing sea water, by using potentiodynamic polarization.

2. EXPERIMENTAL PROCEDURE

Samples used in this study are prepared from alloy 5083 aluminum-magnesium alloy in (10×10×3) mm3 sizes. Chemical composition of the alloy is given in table 1. Surface of samples were ground by sandpapers and finally were polished by diamond pastes of 1μm and 0.25μm size. Samples were degreased in acetone and were washed by ethanol. All the corrosion tests were performed in synthesized sea water at ambient temperature and according to ASTM- D1141 standard. Chemical composition of sea water is given in table 2 [14]. Tests were done in four different pH values ranging at 7.5, 8, 8.2 and 8.5. Potentiodynamic polarization in the range of -1.75V to 0.0 V with scan rate of 0.5 mV/s, were performed in mentioned conditions. Conventional triple electrodes consist of working electrode, platinum counter electrode and a saturated calomel electrode (SCE) as reference were used.

In this study, an applied potential close to Epit is used to compare metastable pitting events in various environment conditions. For production of current transients, potentiostatic polarization was used. Current transient were selected at potential at an average Epit. In this study a transient even should last for at least 1.5 s and experience an increase in current of at least 0.4 μA/cm2, to be counted as a pit. After the transient event if the current gets down to the baseline current value it’s considered to be a metastable pit and if not it’s considered to be a stable pit.

AUTOLAB-AUT8491 was used to perform potentiodynamic polarization and potentiostatic polarization tests. For analyzing the results, NOVA 1.8 software was used.

**Table 1** Chemical composition of alloy 5083.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
<th>V</th>
<th>In</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>4.27</td>
<td>0.19</td>
<td>0.45</td>
<td>0.08</td>
<td>0.29</td>
<td>0.054</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

**Table 2** Chemical composition of synthesized sea water based on ASTM D1141.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>NaCl</th>
<th>MgCl2</th>
<th>Na2SO4</th>
<th>CaCl2</th>
<th>KCL</th>
<th>NaHCO3</th>
<th>KBr</th>
<th>H3BO3</th>
<th>SrCl2</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cons. (g/L)</td>
<td>24.530</td>
<td>5.200</td>
<td>4.090</td>
<td>1.160</td>
<td>0.695</td>
<td>0.201</td>
<td>0.101</td>
<td>0.027</td>
<td>0.025</td>
<td>0.003</td>
</tr>
</tbody>
</table>

For the comparison of the results obtained in corrosion tests, a 3.5 % NaCl standard test solution was used. SEM and OM also were used to examine the corroded surfaces.
3. RESULTS AND DISCUSSIONS

In Fig. 1 shows the microstructure of alloy 5083 before putting it into the solution. Fig. 2 shows the morphology of the pits with the use of optical microscopy. As it is shown, increasing the applied potential of potentiostatic polarization test from 25 mV under pitting potential to 25 mV above pitting potential increases the number of pits.

Distribution and internal morphology of the pits is shown in Figs. 3a and b respectively. As it can be seen, pits are unevenly distributed without any preferred orientation.

Fig. 1 OM image of alloy 5083 before potentiodynamic polarization test.

Fig. 2 OM image of surface of alloy 5083 samples in synthesized sea water of pH=8.2 in potentiostatic polarization test after 2 minutes in: (a) $E_{\text{pit}}-25$ mV, (b) $E_{\text{pit}}$ and (c) $E_{\text{pit}}+25$ mV.
pH of the solution highly effects the initiation of metastable pits [12]. In some studies [17] it's been stated that the initiation of pitting in stainless steels, is independent of pH of solution. Some researchers have shown that, pH inside the pits, is not affected by the pH of solution [18].

Whereas, other researchers showed that pH of 7075 aluminum alloy has a significant effect on initiation of metastable pitting [12]. The main reason for the present differences of nucleation and growth of pits due to pH variations could be related to the amount of intermetallic compounds in Al- matrix.

Investigation of actual and exact behavior of these alloys in corrosion and pitting needs electrochemical tests. Electrochemical test in 3.5% NaCl solution were performed due to the demand for the comparison of behaviors in synthesized sea water. Fig. 4 shows the results of potentiodynamic polarization tests in synthesized sea water and the 3.5% NaCl solution. As it can be seen, synthesized sea water as compared to 3.5% NaCl solution, not only changes the corrosion potential of alloy 5083, but also changes the initiation potential of pitting. The main reason of these variations is due to the extra ions which exist in synthesized water and also their role in spreading the pits in the alloy.

Fig. 3 SEM image taken after the potentiostatic polarization test (a) distribution of pits on the corroded surface, and (b) image inside a pit.

Fig.4 Potentiodynamic polarization curves obtained for alloy 5083 in synthesized sea water and 3.5% NaCl solution.
Fig. 5 shows the polarization behavior of alloy 5083 in synthesized sea water with different pH values. As it can be seen, first of all the change in pH causes a change in corrosion potential. With increasing pH from 7.5 to 8.5, corrosion potential decreases from -592 mV to -1225 mV. These changes show the reduction of thermodynamic activities of surface with increasing of pH. Results also showed that increasing pH from 7.5 to 8.5 causes an increase in corrosion rate and corrosion current density (Figs. 6 and 7).

The important point in these curves is the change in the initiation of pitting and its difference with corrosion potential. Results in Table 3 and Fig. 8 show that the difference in corrosion potential and pitting potential increases with increasing of pH. This means that increasing of pH, causes an increase in the range of resistance to pitting in synthesized water. In areas of the sea water with pH of around 8.5, it can be predicted that the risk of pitting on alloy 5083 has been decreased. On the hand, risk of pitting is increased as pH decreases.

![Potentiodynamic polarization curves for AA5083 in synthesized sea water with different pH values.](image)

![Variations of corrosion rate in terms of pH.](image)
Fig. 7 Variation of corrosion current density in terms of pH

Fig. 8 Variations of pitting with corrosion potential in terms of pH.

Table 3 Results obtained from potentiodynamic polarization test for AA5083 in synthesized sea water.

<table>
<thead>
<tr>
<th>pH</th>
<th>Corrosion rate (mpy)</th>
<th>Corrosion current density (μA/cm²)</th>
<th>Eₚit (V)</th>
<th>E_corr (V)</th>
<th>Eₚit - E_corr (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>0.955</td>
<td>0.731</td>
<td>-0.445</td>
<td>-0.592</td>
<td>0.147</td>
</tr>
<tr>
<td>8</td>
<td>1.115</td>
<td>0.854</td>
<td>-0.454</td>
<td>-0.703</td>
<td>0.249</td>
</tr>
<tr>
<td>8.2</td>
<td>1.327</td>
<td>1.016</td>
<td>-0.556</td>
<td>-1.067</td>
<td>0.510</td>
</tr>
<tr>
<td>8.5</td>
<td>2.973</td>
<td>2.276</td>
<td>-0.422</td>
<td>-1.225</td>
<td>0.803</td>
</tr>
</tbody>
</table>
Metastable pitting was characterized by current fluctuations when the alloy is held potentiostatically at $E_{pl}$ which is measured with help of potentiodynamic polarization diagrams [13].

Diagrams of potentiostatic polarization at pitting potential with various values of pH are given in Fig. 9. In Fig. 10, metastable pitting rate at various values of pH are given. As it can be seen, without consideration of shape and size of the pits, highest pitting rate is at pH value of 8. Pitting rate has been increased by increasing the value of pH from 7.5 to 8 due to the probability of dissolving of protective oxide layer. With considering Table 3 and Fig 7, in pH values of 8.2 to 8.5, due to a more passive layer, the initiation rate of pitting of metastable pits decreases.

![Fig. 9](image1.png)  
Fig. 9 Current transients for: (a) pH=7.5, (b) pH=8, (c) pH=8.2, (d) pH=8.5, obtained at $E_{pl}$.

![Fig.10](image2.png)  
Fig.10 Metastable pitting rate (defined following 35 min) for alloy 5083 and various pH.
Frequency of pitting events of metastable pits can be measured by calculating and investigation of metastable pits in time intervals of 100 s in i-t diagram. In Fig.11, number of metastable pits for time intervals of 100 s is given for all solutions with different values of pH. In Fig.11a it can be observed that the number of pits is very high in first 900 s and thus pitting rate is also high but this value decreases by time. It should be noted that nucleation of pits is occurred during the whole process in less than 35 min. Gupta et al.[13] observed the same procedure.

In Fig.11b number of pits increased and however in times more than 1600 s rate of metastable pits decreased but we still have nucleation of pits. At pH value of 8.2 in times of less than 100 s no pits were observed. After that a uniform distribution of metastable pitting event is observed. Reduction of number of pits can be related to increasing of alloy passive window at this value of pH (Fig.11c). However at first corrosion is very high for pH value of 8.5, but with increasing the thickness of passive layer this value decreases in such a way that in times of more than 1000 s number of created pits gets really low. Contrary to previous cases, there is no nucleation of pits in times more than 1800 s (Fig.11d).

![Fig. 11](image)

**CONCLUSION**

Investigation of corrosion behavior of alloy 5083 in synthesized water with different values of pH shows that:

1. Extra ions in synthesized sea water and their role in production and growth of the pits in compare to 3.5% NaCl solution causes a change in both corrosion and pitting initiation potential of these two environments.
2. General corrosion of alloy 5083 increases with increasing the pH of environment from 7.5 to 8.5
3. Tendency of alloy to pitting decreases as difference between corrosion potential and pitting potential increases and also as pH of environment increases from 7.5 to 8.5.

4. Rate of metastable pits in alloy 5083 with pH of 7.5 to 8 increases at first and then decreases so that at pH value of 8.5 reaches to the lowest value.

5. However general corrosion of alloy 5083 decreases with decreasing of pH, but probability of pitting is higher and as a result the need for supervision and prediction of this behavior increases.

References


