Corrosion characteristics of some aluminium alloys in oxalic acid

M M Singh & Archana Gupta
Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

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The corrosion behaviour of 1060 and 1100 aluminium alloys in different concentrations (0.1, 0.25, 0.5, 0.75, 1.0, 2.0 and 5.0%) of oxalic acid solutions has been investigated by weight loss and potentiostatic polarisation techniques, at 25°C. The data indicate that 1100 aluminium is less corrosion resistant than 1060 aluminium. The corrosion rates of these alloys are a function of the concentration of electrolyte in a narrow range of concentration, only. The anodic polarisation curves of both the alloys exhibit active behaviour at each concentration of oxalic acid and in the whole range of the applied potential. The cathodic polarisation curves are almost linear in both the cases, resembling that for hydrogen evolution reaction. The corrosion behaviour of aluminium alloys in oxalic acid has been explained in terms of the acidity of the solution and self inhibition due to the adsorption of oxalate ions.

Aluminium is highly resistant to most of the acidic and neutral solutions due to the formation of a protective oxide film on its surface. Aluminium equipments, commonly used in textile industries, frequently come in contact with oxalic acid solutions which are used as a neutralizer during the processing of fibres\cite{1,2}. Failure of such apparatus due to corrosion in oxalic acid is widely reported in textile and metallurgical industries. Hence, the understanding of corrosion behaviour of aluminium alloys in oxalic acid solutions is very much desirable.

In the present investigation, an attempt has been made to elucidate the corrosion behaviour of 1060 and 1100 aluminium alloys in different concentrations of oxalic acid, at 25°C.

Experimental Procedure

For the present investigation, 1060 and 1100 aluminium alloys were used. The composition of aluminium alloys are as follows:

Aluminium (1060): Si = 0.12%, Fe = 0.02%, Mn = 0.04% and rest Al.

Aluminium (1100): Si = 0.13%, Fe = 0.32%, Mn = 0.07%, Mg = 0.02%, Cu = 0.01% and rest Al.

Oxalic acid and sodium oxalate (BDH, Analar grade) were used for the preparation of the solutions. These were recrystallized from their aqueous solutions.

Specimens used for weight loss experiments were of 5 x 5 cm in size. These were polished successively with 1/0 to 4/0 grades of emery paper, followed by cleaning with soap and finally with acetone. The weight loss experiments were performed in 500 mL corning glass beakers, containing 300 mL of the electrolyte. Triplicate experiments were performed in an air thermostat maintained at 25 ± 0.2°C, to ascertain the reproducibility of the data.

Potentiostatic polarisation experiments were carried out using a potentiostat (Wenking model POS73). A three-necked glass assembly containing a working electrode of size 1 x 1 cm, platinum foil of size 2 x 2 cm as counter electrode and a Luggin type saturated calomel electrode were used for polarisation measurements. Experiments were performed in unstirred solution, without deaeration. Starting from the open circuit potential, different values of potential were applied on the electrode surface in steps and the resulting steady state currents were measured.

Results and Discussion

In the present investigation, corrosion rate of 1060 and 1100 aluminium alloys has been determined by weight loss and electrochemical techniques, at 25°C. Corrosion rates of 1060 and 1100 aluminium alloys in different concentrations of oxalic acid (0.10, 0.25, 0.50, 0.75, 1.0, 2.0 and 5.0%) have been determined for 24 h immersion period from weight loss, using the formula;
Corrosion rate (mpy) = \frac{534 \ W}{\ DAT}

where \ W = weight loss (mg), \ D = density of specimen (g/cm³), \ A = area of specimen (square inches) and \ T = exposure time (h).

The evaluation of corrosion rate by electrochemical technique has been done with the help of the equation

Corrosion rate (mpy) = \frac{12.4 \times E \times i_{\text{corr}}}{D}

where \ E, i_{\text{corr}}, \text{ and } D \text{ are electrochemical equivalent, corrosion current density and density of specimen, respectively. The corrosion current in the above equation has been determined by extrapolation method}^3.

Fig. 1 illustrates the variation in corrosion rate with acid concentration evaluated by weight loss and electrochemical techniques. There exists a good agreement between the corrosion rates measured by the two techniques. It is noted from the nature of the curves that initially with increase in the acid concentration, corrosion rate increases rapidly up to 1% of oxalic acid. On further increase in its concentration, corrosion rate becomes almost constant for 1060 aluminium, however, rapid increase in corrosion rate of 1100 aluminium continues up to 2% of oxalic acid. Corrosion rate exhibited by 1100 aluminium at each concentration of the electrolyte is higher than that for 1060 aluminium.

As the concentration of oxalic acid is successively increased from 0.1 to 5.0%, the \ pH \ of \ the \ solution decreases gradually. With increase in the acidity of the electrolytic solution the corrosion rate of aluminium alloys is expected to increase as reported earlier \text{ for most of the acidic solutions including those of oxidizing acids. Thus, the initial increase in corrosion rate of different aluminium alloys with concentration up to 2% or less may be very well explained in terms of the decrease in \ pH \ of \ the \ electrolyte. However, at higher concentration, the increase in the corrosion rate is relatively sluggish although the decrease in \ pH \ continues up to 5% oxalic acid. This shows that there are some factors other than the decrease in \ pH \ of \ the \ electrolyte which affect the corrosion rate of aluminium alloys. It is known that oxalate ions act as a good inhibitor for the corrosion of aluminium in acidic solution}^5, \text{ the inhibition of corrosion in the present case, as well, cannot be over ruled.}

To confirm the inhibitive action of oxalate ions, additional experiments were performed by adding sodium oxalate to a solution of oxalic acid of known concentration. The inhibitive action of oxalate ions is quite evident from the nature of the curves in Fig. 2. It was observed that on increasing the oxalate ion concentration in the electrolyte the corrosion rate of aluminium alloys decreases appreciably. An inhibition efficiency of nearly 77-79% was observed at the concentration of 1.00 \text{ M sodium oxalate} (88 \times 10^3 \text{ ppm of oxalate ion}). Thus, it is apparent that even such a large concentration of oxalate ions is not sufficient to ar-
rest the corrosion rate completely. Perhaps this is the reason why no decrease in corrosion rate has been observed at any concentration of oxalic acid used during the present investigation. Once, the corrosion rate becomes constant.

Thus, the variation in corrosion rate of aluminium alloys with increasing concentration of oxalic acid may be explained in terms of both, the increase in acidity of the solution with concentration as well as the self-inhibition of corrosion process due to adsorption of oxalate ions. It appears from the data of the present investigation that in lower acid concentration range the rate of corrosion is probably higher than the inhibition achieved due to adsorption. Hence, the corrosion rate steadily increases with the increasing acid concentration. At higher concentrations, the increase in corrosion rate may be almost completely compensated by the inhibition of corrosion due to adsorption of oxalic acid and the corrosion rate becomes almost constant.

The variation of open circuit potential (OCP) of 1060 and 1100 aluminium alloys with acid concentration has been shown in Fig. 3. It is to be noted from the figure that on increasing the acid concentration from 0.1 to 1%, the OCP of the alloys rapidly shifts towards more active direction. On further increase in acid concentration from 1 to 5% it becomes almost constant for 1060 aluminium and shifts very slightly towards more active direction for 1100 aluminium.

The continuous shift in OCP in active direction in both the cases, with the increase in the concentration of oxalic acid indicates that the corrosivity of oxalic acid increases with its concentration up to 1%. Almost constant values of OCP from 1 to 5% of the solution further indicates that the corrosion rate should be more or less independent of concentration. It may also be noted that the values of OCP at each concentration of oxalic acid are more negative for 1100 aluminium as compared to that for 1060 aluminium. Thus, 1060 aluminium appears to be more resistant to corrosion in oxalic acid at each concentration. Similar results were obtained by other investigators with respect to the relative corrosion resistance of aluminium alloys in nitric acid.

Figs 4 and 5 illustrate the anodic polarisation behaviour of 1060 and 1100 aluminium alloys respectively, in different concentration of oxalic acid, at 25°C. An analysis of the plots reveals that active corrosion behaviour is exhibited by both the alloys in the whole range of potential and at each concentration of oxalic acid. Well defined tafel regions followed by distinct limiting current densities were observed at all concentrations of the acid. It is to be noted from the figures that on increasing the acid concentration, the anodic polarisation curves shift towards higher current density region without any change in their nature. The shift of curves towards higher current density is gradual till 1% of oxalic acid for 1060 aluminium (Fig. 4) and afterwards the curves for 1 to 5% solution almost overlap each other. However, the anodic polarisation curves for 1100 aluminium gradually and continuously shift towards higher...
The shift of $E_{corr}$ values towards more active direction give the indication for the increased probability of corrosion process in lower concentration range. At higher concentrations, almost constant $E_{corr}$ is attained due to the adsorption of oxalate ions. A critical analysis of $i_{corr}$ and $i_L$ values mentioned in the Table 1, reveals that initially the increase in $i_{corr}$ value with concentration is quite appreciable, indicating the dependence of corrosion rate on oxalic acid concentration. Small increment in $i_{corr}$ and $i_L$ from 1 to 5% solution for 1100 aluminium alloy again confirms the slowing down the corrosion process at higher concentrations. The conclusions arrived at from the polarisation experiments are in good agreement with those obtained from weight loss data.

The cathodic polarisation curves for 1060 and 1100 aluminium alloys in solutions containing different concentrations of oxalic acid are depicted in Figs 6 and 7 respectively, at 25°C. It is to be noted from the figures that the cathodic polarisation curves are almost linear and parallel to each other at each concentration of oxalic acid. The shift in cathodic polarisation curves towards higher current density region with increase in the concentration of oxalic acid has been observed for both the alloys. However, the magnitudes of the shift are different for different alloys. A large shift in cathodic polarisation curves occurs as concentration of the acid is raised from 0.1 to 1.0% and

Table 1—Corrosion parameters from polarisation curves of 1060 and 1100 aluminium alloys in different concentrations of oxalic acid, at 25°C

<table>
<thead>
<tr>
<th>Concentration of oxalic acid, %</th>
<th>$i_{corr}$ $\mu$A/cm²</th>
<th>$E_{corr}$ mV</th>
<th>$i_L$ mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>4.58</td>
<td>-840</td>
<td>0.03</td>
</tr>
<tr>
<td>0.25</td>
<td>10.50</td>
<td>-860</td>
<td>0.55</td>
</tr>
<tr>
<td>0.50</td>
<td>13.21</td>
<td>-865</td>
<td>0.79</td>
</tr>
<tr>
<td>0.75</td>
<td>17.83</td>
<td>-875</td>
<td>0.91</td>
</tr>
<tr>
<td>1.0</td>
<td>21.93</td>
<td>-870</td>
<td>1.21</td>
</tr>
<tr>
<td>2.0</td>
<td>22.44</td>
<td>-875</td>
<td>1.26</td>
</tr>
<tr>
<td>5.0</td>
<td>23.50</td>
<td>-890</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Fig. 6—Cathodic polarisation curves of 1060 aluminium in oxalic acid solutions
Fig. 7—Cathodic polarisation curves of 1100 aluminium in oxalic acid solutions
closely spaced curves are obtained in the range 1-5% oxalic acid, in the case of 1060 aluminium. For 1100 aluminium, the curves are almost equidistant in the whole range of experimental concentrations.

The discharge of hydrogen being the only possible cathodic reaction in the acidic solutions and the cathodic polarisation curves being more or less linear it may be assumed that activation controlled hydrogen evolution reaction occurs in the present case, also. The continuous shift in the polarisation curves towards higher current density region may, therefore, be attributed to the increase in the rate of hydrogen ion discharge due to the availability of H⁺ in large extent at higher concentrations of oxalic acid.

However, the relative magnitude of the shift in cathodic polarisation curves from 0.1 to 1% of oxalic acid is much more significant in the case of 1060 aluminium. This seems probably due to the competition between oxalate and H⁺ ions for adsorption at the same sight, oxalate ions seem to be more easily adsorbed on 1100 aluminium at their lower concentrations, and thus the shift in cathodic polarisation curve is not that marked. On the other hand, at higher concentrations of oxalic acid, the inhibition resulted from the adsorption being almost the same for both the alloys, the shift in cathodic polarisation curves at higher concentrations of oxalic acid is almost identical. Although, this interpretation could very well explain the results of the present investigation, it is difficult to correlate the relative adsorbability of oxalate ions with the composition of the alloys chosen.

**Conclusion**

From the present investigation, following conclusions can be drawn:

1. 1060 Aluminium is more resistant towards corrosion in oxalic acid solutions than 1100 aluminium.

2. The rate of corrosion of the aluminium alloys is function of the concentration of oxalic acid in a narrow range of concentration (up to or below 2%) and at higher concentration the corrosion rate becomes almost independent of concentration.

3. Oxalate ions present in the electrolyte solutions seems to act as a self inhibitor.

4. The corrosion of both the alloys follow the same mechanism.

**References**