THE INHIBITION ACTION OF ETHYL-2-PHENYL HYDROZONO-3-OXOBUTYRATE ON THE CORROSION OF 6061 Al ALLOY/SiCp COMPOSITE IN HYDROCHLORIC ACID MEDIUM

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ABSTRACT

The inhibition behavior of ethyl-2-phenyl hydrozono-3-oxobutyrate on the corrosion of 6061 Al alloy/SiCp composite in 0.1, 0.5 and 1 N hydrochloric acid solution at four different temperatures (30-60 °C) has been investigated using potentiostatic polarization techniques and weight loss method. The results indicated that the corrosion inhibition efficiency and the extent of surface coverage were increased with the increase in inhibitor concentration up to a critical concentration. The adsorption of the inhibitor compound on the composite surface was found to obey Temkins’ and Langmuir adsorption isotherms. The potentiostatic polarization results have revealed that oxobutyrate acts as an efficient cathodic inhibitor for the corrosion of 6061 Al alloy/SiCp composite in HCl medium. The thermodynamic parameters for the corrosion and adsorption processes were determined.

Keywords: Composite materials, Polarization technique, Corrosion, Adsorption.

INTRODUCTION

Aluminium, its alloys and composites represent an important category of materials due to their high technological value and wide range of applications, especially in aerospace industry and military applications. The use of these materials in light weight applications is widespread and these usages expose them to environments that could be acidic or alkaline. Generally aluminium alloys and composites are highly resistant to corrosion owing to the formation of a protective oxide layer on their surface. Corrosion does take place when this protective Al2O3·3H2O layer is either unstable or defective. Corrosion in Al alloys and composites takes one of the two forms – pitting or intergranular corrosion. Pitting takes place in environments where the protective Al2O3·3H2O film is partially stable. In these cases, corrosion usually originates adjacent to the flaws in the microstructure of the film. Inter-granular corrosion results in selective corrosion at the grain boundaries or any precipitate free zones that might be found adjacent to them, with the remainder of the matrix undergoing very little corrosion. Inter-granular corrosion occurs because of the formation of precipitates on the grain boundaries, which are more anodic with respect to the interior of the grains. As a result preferential dissolution occurs at these sites where these precipitates or precipitate free zones undergo anodic reactions.

Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching and in various chemical process industries wherein aluminium alloy composites are used. In such cases it becomes very important to use corrosion inhibitors so as to protect the material against excessive corrosion. The effect of any particular organic compound on the corrosion behavior of metals in acid system depends on the type of metal and its interaction with the surface of the metal. The inhibiting action of organic compounds has been mainly attributed to adsorption of the compound on the surface of the material. This adsorption affects the electrochemical behavior involved in the corrosion process of metals/alloys/composites.

The inhibition effect of 3 – methyl – 4 – amino – 5 – mercapto – 1,2,4 – triazole on the corrosion behavior of 6061 Al alloy/SiCp composite has been reported. This triazole compound was found to act as an anodic inhibitor with a maximum efficiency of 58% at 30 °C. Allyl thiourea was used as an inhibitor for the corrosion of Al alloy/SiCp composite in HCl medium and showed a maximum efficiency of 70% in the temperature range of 30 – 50 °C.

In the present work, inhibitive action of ethyl-2-phenyl hydrozono-3-oxobutyrate on the corrosion behavior of 6061 Al alloy/SiCp composite in 0.1, 0.5 and 1 N hydrochloric acid medium at four different temperatures (30-60 °C) has been investigated using potentiostatic polarization techniques. The results obtained were cross checked by the weight loss method.

EXPERIMENTAL

Specimen: Aluminium alloy SiC composite specimens having aluminium alloy 6061 as the matrix and containing 15 vol. % of silicon carbide particles of mean diameter 25µm in the form of cylindrical bars of length 120mm and diameter 40 mm are manufactured at Vikram Sarabhai Space Centre (VSSC) Trivandrum by Stir casting process with pouring temperature 700-710°C, stirring rate 195 rpm, extrusion at 457°C, extrusion ratio 30:1, direct extrusion speed 6.1m/min to produce 40mm diameter cylindrical bars. This composite material has the chemical composition (%wt): 0.25 Cu; 1.0 Mg; 0.60 Si; 0.20 Cr and balance Al. The specimen with an exposed bottom surface area of 0.95 cm² was polished with emery papers of different grades degreased with acetone and then rinsed with distilled water and finally dried in air.

Inhibitor: Ethyl-2-phenyl hydrozono-3-oxobutyrate was prepared as per the reported procedure. Aniline (0.01mol) was dissolved in dilute HCl (8 ml) and cooled to zero °C. To this, a cold solution of sodium nitrite (0.02mol) was added with stirring. The diazonium salt solution obtained was filtered into a cooled solution of ethylacetocetate (0.01mol) and sodium acetate (0.15mol) in ethanol (50 ml). The resulting yellow solid was filtered, washed and recrystallized. The purity of the compound was checked by the elemental analysis adjacent to melting point (68 °C). The structural formula of the inhibitor compound is shown in Figure1.

Fig. 1. Structural formula of ethyl-2-phenyl hydrozono-3-oxobutyrate.

Medium: Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solution of 0.1, 0.5 and 1N HCl.

Tafel extrapolation studies: The polarization studies were performed
The electrochemical parameters for the inhibition behavior of ethyl-2-phenoxyhydrozone-3-oxobutyrate on the corrosion of 6061 Al alloy/SiCp composite in 0.1, 0.5 and 1 N HCl solution were studied by potentiostatic polarization technique at four temperature levels. The results are presented in Table 1. It can be seen from the fitted results and the polarization curves (Figure 2) that there is a large negative shift in the corrosion potential ($E_{corr}$) and a drastic reduction in the corrosion current density ($I_{corr}$) and corrosion rate (CR) values. The shift in corrosion potential in the negative direction indicates that oxobutyrate is an efficient cathodic inhibitor. The corrosion rate, the degree of surface coverage ($\theta$) and the percentage inhibitor efficiency ($\%IE$) were calculated by using the following relations.

**RESULTS AND DISCUSSION**

A comparison of the inhibition efficiency obtained from Tafel extrapolation technique, linear polarization technique and weight loss method at 30 °C are given in Table 2. The results obtained by the three methods are in good agreement.

### Table 1. Electrochemical parameters for the corrosion inhibition of 6061 Al alloy/SiCp composite in HCl media.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C ppm</th>
<th>0.1 N HCl</th>
<th>0.5 N HCl</th>
<th>1 N HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{corr}$</td>
<td>$CR$</td>
<td>$%IE$</td>
<td>$E_{corr}$</td>
</tr>
<tr>
<td>30</td>
<td>-690</td>
<td>34</td>
<td>-</td>
<td>-690</td>
</tr>
<tr>
<td>40</td>
<td>-700</td>
<td>7.4</td>
<td>78.2</td>
<td>-750</td>
</tr>
<tr>
<td>50</td>
<td>-700</td>
<td>4.9</td>
<td>85.6</td>
<td>-740</td>
</tr>
<tr>
<td>100</td>
<td>-720</td>
<td>4.0</td>
<td>88.2</td>
<td>-750</td>
</tr>
<tr>
<td>150</td>
<td>-715</td>
<td>4.4</td>
<td>87.4</td>
<td>-745</td>
</tr>
<tr>
<td>60</td>
<td>-700</td>
<td>82</td>
<td>-</td>
<td>-690</td>
</tr>
<tr>
<td>50</td>
<td>-750</td>
<td>20.6</td>
<td>74.9</td>
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</tr>
<tr>
<td>100</td>
<td>-750</td>
<td>18.0</td>
<td>78.1</td>
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<tr>
<td>150</td>
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<td>15.0</td>
<td>81.7</td>
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<tr>
<td>60</td>
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<td>165</td>
<td>-</td>
<td>-690</td>
</tr>
<tr>
<td>50</td>
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<td>42.1</td>
<td>74.5</td>
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<td>37.0</td>
<td>77.6</td>
<td>-760</td>
</tr>
<tr>
<td>150</td>
<td>-765</td>
<td>27.7</td>
<td>83.2</td>
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<tr>
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<td>316</td>
<td>-</td>
<td>-710</td>
</tr>
<tr>
<td>50</td>
<td>-765</td>
<td>123</td>
<td>61.0</td>
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<tr>
<td>100</td>
<td>-790</td>
<td>94.1</td>
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<td>-760</td>
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<tr>
<td>150</td>
<td>-765</td>
<td>53.4</td>
<td>83.1</td>
<td>-770</td>
</tr>
</tbody>
</table>

Corrosion rate (mpy) = \[
\frac{0.1288 \times Eq.wt \times I_{corr}}{D}
\]  \hspace{0.5cm} (1)

where,  
- $I_{corr}$ = Corrosion current density in µA/cm².  
- $Eq.wt$ = specimen equivalent weight in g.  
- $D$ = specimen density in g/cc

0.1288 is the metric and time conversion factor.

\[
\theta = \left(\frac{I_{corr} - I_{corr(inh)}}{I_{corr}}\right)
\]  \hspace{0.5cm} (2)

Where, $I_{corr}$ and $I_{corr(inh)}$ are the corrosion current densities in µA/cm² in the absence and presence of the inhibitor respectively.

\[
\%IE = \frac{\theta}{100}
\]  \hspace{0.5cm} (3)

The inhibition efficiency by weight loss method was calculated by using the following expression 14:

\[
%IE = \left(\frac{W - W_{inh}}{W}\right) \times 100
\]  \hspace{0.5cm} (4)

Where, $W$ and $W_{inh}$ are the values of weight loss of the specimen after immersion in test solution without and with inhibitor, respectively.

A comparison of the inhibition efficiency obtained from Tafel extrapolation technique, linear polarization technique and weight loss method at 30 °C
Table 2. Comparison of % IE values for all the three methods at 30 °C

| Acid concentration (N HCl) | Inhibitor Concentration (ppm) | % IE | | Tafel Extrapolation Technique | Linear Polarisation Technique | Weight Loss Method |
|---------------------------|-------------------------------|------|-----------------|-----------------------------|-----------------|
|                           |                               |      | Tafel Extrapolation Technique | Linear Polarisation Technique | Weight Loss Method |
| 0.1                       | 25                             | 78.2 | 75.1            | 72.7                        |                 |
|                           | 50                             | 85.6 | 82.3            | 81.3                        |                 |
|                           | 100                            | 88.2 | 85.2            | 84.8                        |                 |
|                           | 150                            | 87.4 | 85.8            | 83.2                        |                 |
| 0.5                       | 25                             | 78.6 | 75              | 74.5                        |                 |
|                           | 50                             | 83.4 | 82.6            | 79.4                        |                 |
|                           | 100                            | 85.5 | 85.2            | 84.3                        |                 |
|                           | 150                            | 85.1 | 84.5            | 83.5                        |                 |
| 1                         | 25                             | 75.3 | 72.4            | 72.7                        |                 |
|                           | 50                             | 79.8 | 75.3            | 80.1                        |                 |
|                           | 100                            | 82.5 | 78.6            | 82.7                        |                 |
|                           | 150                            | 81.9 | 77.8            | 81.2                        |                 |

The % IE increases with increase in concentration of oxobutyrate (Table 1). The increase in % IE may be due to the blocking effect of the surface by both adsorption and film formation mechanism which decreases the effective area of attack. The variation of % IE with temperature is shown in Figure 3. The inhibition efficiency decreases with increase in temperature. The rise in temperature results in the increase in conductance of the aqueous acid medium and thereby increases the diffusion rate of hydrogen ions to the composite surface and hence the corrosion progresses faster at higher temperatures. The results indicate that oxobutyrate is an effective inhibitor with maximum IE value of 88 % in 0.1 N HCl containing 100 ppm of inhibitor.

The surface analysis of 6061 Al alloy SiCp composite was carried out using scanning electron microscope (JEOL Model 8340LA). The scanning electron micrographs of a fresh specimen of 6061 Al alloy SiCp composite is shown in Figure 4a. The micrographs for the specimens immersed in 1 N HCl solution at 30° C in the absence and presence of inhibitor are shown in Figures 4b and 4c respectively. The corrosion of Al alloy SiCp in HCl medium is presumably due to the anodic dissolution either at the grain boundaries or at the metal-media interface. It is seen from the Figure 4c that the surface of 6061 Al alloy SiCp exposed to inhibited solution is smoother than that exposed to uninhibited acid solution (Figure 4b). These observations suggest that the inhibitor forms a protective layer on the composite surface, which prevent the attack of acid on the surface.

To understand the mechanism of corrosion inhibition, the adsorption behavior of the inhibitor compound on the composite surface must be known. The surface coverage values for different concentrations of oxobutyrate from the acid solution were calculated. The surface coverage values (θ) were tested graphically by fitting to suitable adsorption isotherm. The plot of θ versus log c (Figure 5) for different concentrations of oxobutyrate shows a straight line indicating that the adsorption of the compound on the composite surface follows Temkins adsorption isotherm. The applicability of Temkins adsorption isotherm verifies the assumption of mono-layer adsorption on a uniform homogeneous composite surface with an interaction in the adsorption layer.
To further confirm the adsorption behavior of the inhibitor, Langmuir adsorption isotherm was constructed. Plots of log \[ \frac{\theta}{(1-\theta)} \] versus log \( c \) are found to be linear (Figure 6) suggesting that the molecules are adsorbed over the metal surface forming a barrier, which prevents the contact of the metal with electrolyte\(^{17,18}\).

The thermodynamic parameters for the corrosion of Al alloy/SiCp composite in the presence of oxobutyrate are studied (Table 3). The equilibrium constant (\( K \)) is determined by the relation:

\[
K = \frac{\theta}{c(1-\theta)} \quad (5)
\]

Where \( \theta \) is the degree of surface coverage on the metal surface and \( c \) is the concentration of the inhibitor in molL\(^{-1}\).

The free energy of adsorption (\( \Delta G_{\text{ads}} \)) is calculated from the following equation\(^{19,20}\):

\[
\Delta G_{\text{ads}} = -RT \ln(55.5K) \quad (6)
\]

Where 55.5 is the concentration of water in solution in molL\(^{-1}\) and \( T \) is the temperature in Kelvin.

The negative values of \( \Delta G_{\text{ads}} \) indicate spontaneous adsorption and strong interaction of inhibitor molecules on to the surface of the composite. The \( \Delta G_{\text{ads}} \) values obtained for 100 ppm of oxobutyrate were less than 40 kJ molL\(^{-1}\) nd this indicates that the inhibition is governed by physical adsorption mechanism.

**CONCLUSIONS**

1. Oxobutyrate acts as an efficient cathodic inhibitor for corrosion of 6061 Al alloy/SiCp composite in 0.1 – 1 N hydrochloric acid medium.
2. The corrosion rate decreases with increase in inhibitor concentration and increases with rise in temperature in the presence of the inhibitor.
3. The adsorption of the compound on the surface of Al alloy/SiCp composite was found to obey both Temkins and Langmuir adsorption isotherms and governed by physical adsorption mechanism.
4. The inhibition efficiency obtained by polarization techniques and weight loss method are in good agreement.

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