Benzimidazole as corrosion inhibitor for heat treated 6061 Al-SiC\textsubscript{p} composite in acetic acid

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Abstract. 6061 Al-SiC\textsubscript{p} composite was solutionized at 350 °C for 30 minutes and water quenched. It was then underaged at 140 °C (T6 treatment). The aging behaviour of the composite was studied using Rockwell B hardness measurement. Corrosion behaviour of the underaged sample was studied in different concentrations of acetic acid and at different temperatures. Benzimidazole at different concentrations was used for the inhibition studies. Inhibition efficiency of benzimidazole was calculated for different experimental conditions. Thermodynamic parameters were found out which suggested benzimidazole is an efficient inhibitor and it adsorbed on to the surface of composite by mixed adsorption where chemisorption is predominant.

1. Introduction
Aluminium alloys, particularly 6061, reinforced with SiC have been the focus of the attention because of their application potential in an extensive range of demanding applications, such as automobiles, aerospace and defense. There are many other applications which involve exposure of the composites to potential corrosive environment [1], [2]. Because of the duplex nature of the composites, they are prone to accelerated corrosion compared to their monolithic counterpart. Corrosion of these composites not only limit their service life but also lead to deterioration of their unique mechanical properties for which they are designed [3]. Studies reveal the role of micro structural changes and processing routes on the corrosion behaviour. Also, aging treatment was found to have influence on the corrosion rate as the heat treated samples showed higher corrosion rates as compared to the non-treated samples [4]-[6].

Corrosion studies in organic acid solutions are rare in comparison with similar studies in mineral acids. Acetic acid is a frequently used organic acid in many industrial processes [7]. At high temperatures, these acids dissociate, generating new aggressive ions which cause faster corrosion and they can provide sufficient protons to act as true acids [8], [9].

Adding inhibitors to the corrosion medium, is a general practice for the corrosion protection. Heterocyclic organic compounds which contain oxygen, sulphur, phosphorous, nitrogen and aromatic rings are considered to be the most active and resourceful inhibitors in acidic corrosive medium for the metals, alloys and composites [10], [11]. Latterly, benzimidazole have established considerable reputation on their corrosion inhibition properties for metals and alloys, owing to the existence of aromatic rings and nitrogen atom [12]. In the present study benzimidazole is used as inhibitor.
2. Experimental work

2.1. Specimen
6061 Al-SiCₚ composite material with 15 vol% SiC particles of size 23 µm and 99.9% purity is studied. The composites were cast in the form of cylinders each of 90 mm diameter and 240 mm length by stir casting technique. These cylinders were extruded at 430 ºC – 480 ºC with extrusion ratio of 30:1. The experiments were performed with composite in extruded rod form. The extruded samples were cut in cylinders of 5 cm length and diameter of 1 cm. The composition of base metal alloy is given in Table 1.

Table 1. Composition of 6061 aluminium alloy (matrix)

| Element | Cu       | Mg        | Si       | Mn       | Cr       | Others | Al     |
|---------|----------|-----------|----------|----------|----------|--------|--------|
| Weight %| 0.15-0.4 | 0.8-1.2   | 0.4-0.8  | 0.15     | 0.04-0.35| 1.25   | Balance |

For corrosion tests, heat treated cylindrical coupons were mounted in epoxy material. The specimens were polished with various grades of emery paper and wet polished with diamond paste. Acetone was used to clean and dry the samples.

2.2. Electrolyte for Corrosion Tests
Test solutions were prepared using distilled water and analytical grade acetic acid for all the experiments. Range of concentrations of acetic acid for corrosion tests was decided to be 10%, 20% and 30 volume%.

2.3. Methods
The samples for heat treatment were polished and solution treated at a temperature of 350 ºC for 30 minutes. They were then water quenched at room temperature. This was followed by aging the quenched composites at 140 ºC (T6 treatment) for various durations of time. The aging behaviour of the composite was studied using Rockwell hardness measurement. Rockwell B Hardness (HRB) tests were performed immediately after aging. Each hardness value was the average of at least three measurements in two samples. Time taken for under aging the sample was found out as one hour, using aging curve and then corrosion tests were performed on under aged samples.

For corrosion tests, an area of 1 cm² of the polished, under aged 6061 Al- SiCₚ specimens were exposed to 150 ml of acetic acid solution (10, 20 and 30 volume%) at different temperatures like 30 ºC, 35 ºC, 40 ºC, 45 ºC and 50 ºC. Experiments were carried out in the presence (50, 100 and 200 ppm) and absence of inhibitor. Electrochemical measurements were performed with a potentiostat under software control, BIOLOGIC, SP-150. Polarization scans were initiated from -250 mV...
cathodically and scanned to approximately +250 mV anodically, all potentials being relative to the open-circuit corrosion potential. Potentiodynamic scan rates were 10 mV/s. A three electrode cell consisting of a large area platinum as counter electrode, saturated calomel electrode (SCE) as a reference electrode and sample as working electrode was used. All potentials are referenced to the SCE. The corrosion rate is obtained from the expression (1)

\[
\text{Corrosion Rate (mpy) } = \frac{0.129 \times EW \times i_{corr}}{D}
\]

where, \(i_{corr}\) is the corrosion current density in \(\mu A/ cm^2\), \(EW\) is the equivalent weight of the corroding specimen in gm and \(D\) is the density of the corroding species in gm/cm\(^3\).

2.4. Inhibitor
As obvious from literature, benzimidazole has established considerable responsiveness on its inhibition properties. So, for the present study benzimidazole at different concentrations such as 50 ppm, 100 ppm and 200 ppm, is chosen as inhibitor. The details of inhibitor such as molecular structure, abbreviation and molar mass are given in Table 2. Optimized structure of inhibitor is shown in Figure 2.

| Inhibitor    | Structure         | Abbreviation | Molar mass (g/mol) |
|--------------|-------------------|--------------|-------------------|
| Benzimidazole| ![Image](image1)  | BI           | 118.14            |

![Image](image2)

Figure 2. Optimized structure of benzimidazole (BI).

3. Results and discussion
Rockwell B hardness values of 6061 Al-SiCp composite, which are T6 treated at 140 °C are given in Table 3 and aging curve is displayed in Figure 3. The hardness measurements showed a sharp rise in hardness for the first few hours, it reaches a peak value and then decreases.

| Time of Aging (hours) | Rockwell B hardness values |
|-----------------------|---------------------------|
| 0                     | 62                        |
| 1                     | 68                        |
| 2                     | 73                        |
| 3                     | 78                        |
| 4                     | 88                        |
| 5                     | 79                        |

From the hardness profile of Figure 3, the aged specimens can be categorized into three groups namely a) under aged b) peak aged and c) over aged. The variation in hardness is associated with the microstructural evolution. The formation of Mg and Si clusters takes place initially. This occurs in successive stages. The aging sequence for 6061 Al alloy and its composite are as follows: Supersaturated solid solution \(\rightarrow\) clusters of solute atoms and vacancies (Primitive Guinier-Preston [GP] zones) \(\rightarrow\) needle shaped GP zones \(\rightarrow\) rod shaped, metastable, semi-coherent \(\beta'\) phase \(\rightarrow\) stable, incoherent, Mg;Si precipitate (\(\beta\) phase) [13]. Formation of primitive GP zones contribute considerably to the rise in hardness. Peak-aging is related to the dense population of \(\beta\) needle-shaped precipitates. Since these precipitates are coherent precipitates; large amount of lattice strain is developed because of lattice mismatch. This results in high hardness. Only a part of these precipitates remain in the
microstructure during over-aging as the metastable phases like β’ form. These precipitates are incoherent and thereby the lattice strain involved is less, which results in the lowering of hardness values [14]. Corrosion rates (mpy) of under aged sample at 140 ºC, in the presence and absence of inhibitor at different temperatures are shown in Table 4.

Table 4. Corrosion rates of under aged sample with and without inhibitor, at different temperatures.

| Temperature | Concentrations of Acetic acid (vol %) | Corrosion rates (mpy) [Inhibitor: BI] |
|-------------|--------------------------------------|---------------------------------------|
|             | 0 ppm  | 50 ppm  | 100 ppm  | 200 ppm  |
| 30 ºC       | 10 %   | 4.5   | 3.9   | 3.5   | 3.2   |
|             | 20 %   | 5.7   | 4.7   | 3.9   | 3.5   |
|             | 30 %   | 6.2   | 5.5   | 4.8   | 4.0   |
| 35 ºC       | 10 %   | 6.0   | 5.1   | 5.0   | 4.4   |
|             | 20 %   | 7.2   | 5.9   | 5.6   | 5.0   |
|             | 30 %   | 8.4   | 7.0   | 5.9   | 5.2   |
| 40 ºC       | 10 %   | 10.2  | 6.7   | 5.2   | 4.6   |
|             | 20 %   | 15.0  | 7.7   | 5.8   | 5.3   |
|             | 30 %   | 17.8  | 12.9  | 8.8   | 8.0   |
| 45 ºC       | 10 %   | 14.7  | 8.5   | 8.0   | 7.2   |
|             | 20 %   | 17.8  | 9.7   | 8.4   | 7.9   |
|             | 30 %   | 18.9  | 13.3  | 10.6  | 8.9   |
| 50 ºC       | 10 %   | 24.1  | 13.5  | 11.8  | 10.0  |
|             | 20 %   | 25.3  | 19.6  | 15.9  | 11.8  |
|             | 30 %   | 30.6  | 21.3  | 17.8  | 12.6  |

**Figure 3.** Hardness variation with time in T6 treatment at 140 ºC.
The results indicate that under aged 6061 Al-SiC composite is reasonably susceptible to corrosion in lower concentrations of acetic acid. But its corrosion rate is comparatively higher at higher temperatures like 45 °C and 50 °C, in all the three selected concentrations of acetic acid. Corrosion rate of the 6061 Al-SiC increases with increase in temperature for all concentrations of acetic acid. It is possibly because of the increased kinetics of the reaction. As the acid concentration increases from 10 % to 30 %, corrosion rate shows an increase, as more acidic ions are present and so, more number of metal ion dissolution will take place leading to an increase in the corrosion rate. Tafel plots for the sample in 10% acetic acid at 30 °C in the presence and absence of inhibitor is presented in Figure. 4. Similar Tafel plots were obtained for all other experimental environments, from which corrosion rates were calculated.

![Figure 4](image-url)  
**Figure 4.** Tafel plots for underaged 6061 Al-SiCp composite in 10% acetic acid at 30 °C with and without inhibitor.

### Table 5. Inhibition efficiency of BI

| Temperature (°C) | Inhibitor concentration (ppm) | Inhibitor efficiency (IE) (%) | Acetic Acid (%) |
|------------------|-------------------------------|-------------------------------|-----------------|
|                  |                               | 10 %                          | 20 %            | 30 %            |
| 30 °C            | 50                            | 13.29                         | 17.05           | 10.29           |
|                  | 100                           | 21.81                         | 30.42           | 21.79           |
|                  | 200                           | 28.53                         | 37.98           | 34.19           |
| 35 °C            | 50                            | 14.41                         | 17.88           | 16.28           |
|                  | 100                           | 16.02                         | 22.10           | 29.15           |
|                  | 200                           | 25.73                         | 29.90           | 37.05           |
| 40 °C            | 50                            | 33.71                         | 48.15           | 27.61           |
|                  | 100                           | 48.31                         | 60.82           | 50.22           |
|                  | 200                           | 54.08                         | 64.58           | 53.14           |
| 45 °C            | 50                            | 41.91                         | 45.21           | 29.46           |
|                  | 100                           | 45.00                         | 52.33           | 43.64           |
|                  | 200                           | 50.46                         | 55.60           | 52.89           |
| 50 °C            | 50                            | 44.02                         | 22.34           | 30.50           |
|                  | 100                           | 50.75                         | 37.05           | 41.98           |
|                  | 200                           | 58.56                         | 53.25           | 58.90           |
Aluminum is an exceptionally reactive metal, but it has a good corrosion resistance due to the formation of passive oxide film. But, aluminum is susceptible to galvanic corrosion when it is coupled to a nobler material. This is a matter of great concern that, whether the reinforcement constituents will encourage galvanic corrosion of the metal or alloy matrix. The degree of galvanic corrosion depends on the environment to which the MMC is exposed and on the properties and amount of the reinforcement constituent. Corrosion in Al based MMCs is also influenced by microstructural changes during fabrication, caused by the reinforcement/matrix reactions, which may lead to the formation of new phase or intermetallics at the reinforcement/matrix interface [15].

![Figure 5](image1.png)

**Figure 5.** Arrhenius plots for 10 % acetic acid in the presence of BI.

![Figure 6](image2.png)

**Figure 6.** Plot of ln (CR/T) vs. (1/T) for 10% acetic acid in the presence of BI.

**Table 6.** Activation parameters for the corrosion of 6061 al-sic in acetic acid in the presence of BI

| Acetic acid concentration | Inhibitor concentration | Ea (KJ/mol) | ΔH# (KJ/mol) | ΔS# (J/mol K) |
|--------------------------|-------------------------|-------------|--------------|---------------|
|                          | 0 ppm                   | 67.671      | 64.985       | -62.926       |
| 10 vol %                 | 50 ppm                  | 42.585      | 41.597       | -145.658      |
|                          | 100 ppm                 | 46.274      | 43.673       | -137.990      |
|                          | 200 ppm                 | 47.541      | 45.780       | -132.589      |
| 20 vol %                 | 0 ppm                   | 61.622      | 59.099       | -82.962       |
|                          | 50 ppm                  | 45.356      | 42.809       | -140.772      |
|                          | 100 ppm                 | 50.887      | 48.103       | -122.713      |
|                          | 200 ppm                 | 53.128      | 50.585       | -113.355      |
| 30 vol %                 | 0 ppm                   | 64.135      | 61.592       | -73.957       |
|                          | 50 ppm                  | 43.534      | 41.976       | -142.134      |
|                          | 100 ppm                 | 52.536      | 48.378       | -120.174      |
|                          | 200 ppm                 | 54.145      | 50.728       | -110.856      |

From Table 5, it is apparent that, BI is an effective inhibitor. The maximum inhibition efficiency obtained using BI was 64.58%. It was attained at 40 °C in 20 % acetic acid when 200 ppm of BI was added. Activation energy (Ea) for the corrosion processes of Al-SiC samples in varying concentrations...
of acetic acid at different temperatures was calculated from the Arrhenius equation and the enthalpy of activation ($\Delta H^\#$) and entropy of activation ($\Delta S^\#$) values for the corrosion process were calculated from transition state theory equation. Free energy of adsorption was calculated using the relation (2)

$$\Delta G_{ads} = -RT \ln[55.5 \times \frac{\theta}{C(1-\theta)}]$$  \hspace{1cm} (2)

where, $\Delta G_{ads}$ = Free energy of adsorption (KJ/mol), $R$ is real gas constant, $T$ is temperature (K), $C$ is concentration of inhibitor (mol/dm$^3$), $\theta$ is surface coverage of inhibitor molecules. Figure 5 shows Arrhenius plots for 10% acetic acid in the presence of BI, at different temperatures. The plot of ln $(CR/T)$ against $(1/T)$ for 10% acetic acid are shown in Figure 6. Activation energy, enthalpy of activation, entropy of activation and free energy of adsorption for other experimental conditions were also calculated.

**Table 7.** Free energy of adsorption ($\Delta G_{ads}$) of inhibitor BI

| Acetic acid concentration | Temperature | Free energy of adsorption ($\Delta G_{ads}$) (KJ/mol) |
|---------------------------|-------------|------------------------------------------------------|
|                           |             | 50 ppm      | 100 ppm    | 200 ppm    |
| 10 %                      | 30 °C       | -24.960     | -24.723    | -23.881    |
|                           | 35 °C       | -25.613     | -24.158    | -23.912    |
|                           | 40 °C       | -28.905     | -28.685    | -27.484    |
|                           | 45 °C       | -30.292     | -28.792    | -27.540    |
|                           | 50 °C       | -30.999     | -29.864    | -28.852    |
| 20 %                      | 30 °C       | -25.700     | -25.855    | -24.959    |
|                           | 35 °C       | -26.271     | -25.174    | -24.444    |
|                           | 40 °C       | -30.472     | -30.006    | -28.622    |
|                           | 45 °C       | -30.647     | -29.569    | -28.086    |
|                           | 50 °C       | -31.994     | -28.360    | -28.273    |
| 30 %                      | 30 °C       | -24.230     | -24.720    | -24.544    |
|                           | 35 °C       | -25.982     | -26.126    | -25.269    |
|                           | 40 °C       | -28.157     | -28.884    | -27.386    |
|                           | 45 °C       | -28.846     | -28.646    | -27.797    |
|                           | 50 °C       | -29.433     | -29.914    | -28.889    |

It is a common supposition that the adsorption of inhibitors on to the sample surface is the first step in the inhibition mechanism. Organic molecules could be adsorbed on the metal surface by one of the following mechanisms:
- Electrostatic interaction between charged surface of metal and the charge of inhibitor.
- Interaction of unshared electron pairs in the inhibitor molecule with the metal.
- Interaction of $\pi$-electron with metal.
- A combination of all the above types [16].

BI is a 5-membered N-containing heterocycle (imidazole), attached to a benzyl nucleus. It is very stable towards oxidation and reductive agents. It contains two nitrogen hetero-atoms: N1 or ‘pyrrolic’ nitrogen atom at the 1-position in the molecule, whose unshared electron pair take part in imidazole $\pi$-
electron sextet and N3 or ‘pyridyne’ nitrogen atom at the 3-position in the molecule, whose unshared electron pair is free and eases the reaction with acids to give salts. So it is apparent that ‘pyridine’ N3 is a donor of electrons in BI molecule. However BI is an organic base which protonize in an acid medium, predominantly affecting the nitrogen atom (N3) in the imidazole ring. Thus, they become cations. Also the presence of acetate ions in the solution should be considered too. They have a strong adsorbability on the metal surface which brings about a negative charge supporting the adsorption of cation type inhibitors [17]. The inhibitors are classified into three groups according to the temperature effects:

- Inhibitors whose IE decreases with temperature increase. The value of the activation energy Ea found is greater than that in the uninhibited solution.
- Inhibitors whose IE does not change with temperature variation. The activation energy does not change with the presence or absence of inhibitors.
- Inhibitors in whose presence the IE increases with temperature increase, while the value of Ea for the corrosion process is smaller than that obtained in the uninhibited solution.

Studies also indicate that the corrosion process taking place in the presence of powerful inhibitors is characterized by an activation energy whose value is smaller than that of the uninhibited process. The lower value of the activation energy of the process in the presence of an inhibitor when compared to that in its absence is because of chemisorption, while the opposite is the case with physical adsorption. It is considered that the increase of IE with temperature increase, is owing to the change in the nature of adsorptions. To be exact, the inhibitor is adsorbed physically at lower temperatures, while chemisorption is favored as temperature increases. [18].

It has been reported that the ΔGads value up to -20 KJ/mol or less negative specifies a physisorption, while values more negative than -40 KJ/mol involves chemisorption where sharing or transfer of electrons between inhibitor and metal to form a coordinate type bond takes place [11]. Values of ΔGads between this ranges indicates that adsorption may involve mixed interactions, i.e. chemical and physical adsorption. Recently studies has attributed values of ΔGads between -27.10 to -32.41 KJ/mol to chemisorption which involves direct adsorption in the presence of lone pairs of electrons and π-electrons [19].

It is obvious from Table 5, IE increases with temperature. Table 6 displays that, Ea values obtained for inhibited solutions are smaller than that obtained in the uninhibited solution. Values of ΔGads for BI, comes in the range of -23.88 KJ/mol to -31.99 KJ/mol. Taking into consideration the literature and results mentioned above, subsequent inferences could be drawn concerning the inhibitor:

Experimental nature of data confirmed that the inhibition effect attained is good with BI. This effect can be credited to a strong adsorption bond, which can be attributed to chemisorption. The lower value of the activation energy in the presence of BI when compared to that in its absence is attributed to its chemisorption. ΔGads values obtained proposes that the inhibitor is adsorbed physically at lower temperatures, while chemisorption is favored as temperature increases. In view of this, it can be established that the inhibitor get adsorbed on the metal surface by mixed adsorption, where chemisorption is significant.

4. Conclusions
Aging profile of T6 treated Al-SiCp was obtained using Rockwell B hardness. Under aged sample was subjected to corrosion in acetic acid. Highest corrosion rate obtained was 30.69 mpy at 50 °C in 30 volume % acetic acid. Corrosion was inhibited using BI and maximum efficiency of inhibition obtained was 64.58 %. Activation parameters and free energy of adsorption were found out for all experimental conditions. IE increases with temperature and Ea values obtained for inhibited solutions are smaller than that obtained in the uninhibited solution which suggested that BI gets adsorbed on the composite surface by mixed adsorption, where chemisorption is predominant.
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