Corrosion Inhibition of 6061 Al alloy–15 vol% SiC(p) Composite in 0.1 M Hydrochloric Acid

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Abstract

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, automobile 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. Corrosion inhibitors are chemical compounds (organic or inorganic) added to the corrosive medium to reduce the rate of acidic attack on the composite. The organic compounds adsorb on the metal surface forming a barrier between the metal and the corrosive environment. Some structural features of the organic compounds help them to do so. These include the presence of oxygen, nitrogen or sulphur atoms as well as the presence of double bonds. In the present work, inhibition efficiency of Propanoyl(1E)-N-(2-acetylphenyl)-2-oxopropanehydrazonoate (PAOH) on the corrosion of 6061 Al alloy- 15 vol. % SiC(p) composite in 0.1 M hydrochloric acid medium in the 30-60 ^{0}C temperature range using Potentiostatic Polarization (Tafel extrapolation and Linear Polarization) techniques. The results obtained indicate that PAOH is an efficient cathodic inhibitor with 91.6 % of inhibition efficiency over the range of temperature studied. The adsorption of the compound on the composite surface is found to obey Langmuir adsorption isotherm. Inhibition is governed by mixed adsorption mechanism with predominant physical adsorption type. Thermodynamic parameters for the adsorption processes were determined from the experimental data.

Keywords: Potentiostatic polarization, Langmuir Adsorption Isotherm, Cathodic Inhibitor, Mixed Adsorption Mechanism.

I. Introduction

Aluminium metal matrix composites have lower corrosion resistance in comparison to the Al base alloys, due to the presence of the reinforcing SiC particles in the composite. The presence of SiC can lead to in-homogeneities and cause discontinuities in the surface film, increasing the number of active sites available for corrosion to take place [1]. Aluminium, its alloys and composites represent an important category of materials in the industries, due to their properties. Hence they find applications in aerospace industry, automobile industry and military applications [2, 3]. The use of these materials in light weight applications is widespread and these usages expose them to environments that could be acidic or alkaline [4]. Pitting attack is reported to be the major form of corrosion in Al alloy/SiCp metal matrix composites [5]. 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 corrosion.

Most of the efficient inhibitors used in the industry are organic compounds having multiple bonds in their molecules which contain hetero atoms of nitrogen, oxygen and sulphur through which they are adsorbed on the composite surface [6]. In the present work, inhibitive action of Propanoyl(1E)-N-(2-acetylphenyl)-2-oxopropanehydrazonoate (PAOH) on the corrosion behavior of 6061 Al alloy- 15 vol. % $SiC_{(p)}$ composite in 0.1 M hydrochloric acid at four different temperatures have been investigated using potentiostatic polarization (Tafel extrapolation and Linear polarization) techniques.

II. Methodology

A. *Specimen*: 6061 Al alloy- 15 vol. % $SiC_{(p)}$ composite specimens of chemical composition (%wt): 0.25 Cu; 1.0 Mg; 0.60 Si; 0.20 Cr and balance Al were used for the measurement of corrosion rate. The specimen with an exposed surface area of 0.95 cm^2 was polished with emery papers of different grades degreased with acetone and then rinsed in distilled water and finally dried in air. Propanoyl(1E)-N-(2-acetylphenyl)-2-oxopropanehydrazonoate (PAOH) is prepared by dissolving 2amino-acetophenone (1.0 g, 7.4 mmol) in dilute hydrochloric acid (12.0 ml i.e 5.0 ml of 12 M HCl dissolved in 7.0 ml water) and cooled to 0 °C in an ice bath. To this, a cold solution of sodium nitrite (1.24 g, 17.97 mmol in 10.0 ml water) is added, with the temperature of the reaction mixture kept below 5 °C. The resulting diazonium salt solution is filtered into a cooled solution of ethylacetoacetate (1.5 ml, 11.5 mmol) and sodium acetate (2.7 g, 32.9 mmol) in ethanol (100 ml). The resulting solid is filtered, washed with ice cold water, dried in air, and recrystallized from methanol. (Yield 3.65 g, 68.5 %). Purity of the compound

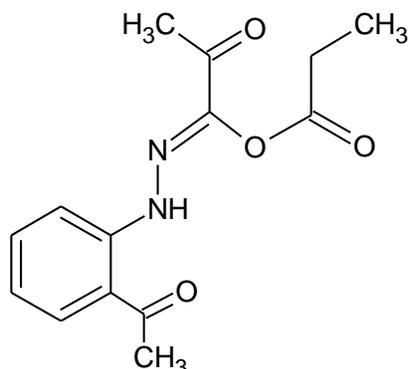was checked by it elemental analysis and melting point (114-115 °C). Structural formula for PAOH is shown in Fig. 1.

Fig. 1. Structural formula of PAOH

B. *Medium*: Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solution of 0.1 M HCl

C. *Eletrochemical studies*: The polarization studies were performed by using a Wenking Potentiostat and a three electrode cell containing 100 ml of electrolyte at 30 °C either with or without inhibitor. The steady state open circuit potential (OCP) with respect to saturated calomel electrode was noted at the end of 25 – 30 minutes. Tafel extrapolation studies were made from ± 250 mV versus OCP in steps of 20 mV from the cathodic side and the corrosion currents were noted. The Tafel plots of potential versus log I were drawn and the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}) were determined. The corrosion rate, the degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated. The experiments were repeated at 40, 50 and 60 °C with an accuracy of ± 1 °C. The results were also cross checked Linear polarization technique. Linear polarization studies are carried out in the potential (*E*) range of -20 mV versus OCP to +20 mV versus OCP with a scanning rate of 5 mV/min from the cathodic side and the steady state corrosion currents (*I*) are noted. The plots of E versus I are drawn. The slope of this curve is used to determine the corrosion current density (I_{corr}) and the corrosion rate (*CR*)

III. RESULTS AND DISCUSSIONS

Inhibition effect of PAOH on the corrosion of 6061 Al alloy- 15 vol. % SiC$_{(p)}$ composite in 0.1 M HCl solution at different temperatures, studied by Tafel extrapolation technique is presented in Table I. It can be seen from the polarization curves (Fig. 2) and their fitted results that there is a negative shift in the

corrosion potential (E_{corr}) and a drastic reduction in corrosion current density (I_{corr}).The shift in corrosion potential in the negative direction less than -80 mV indicates that PAOH is a mixed inhibitor.

Table I
Tafel Extrapolation results for the corrosion inhibition of 6061 Al alloy – 15 vol. % SiC$_{(p)}$ composite in 0.1 M HCl at different temperatures.

T (°C)	c (mmol L^{-1})	E_{corr} (mV)	CR (mpy)	IE (%)	T (°C)	c (mmol L^{-1})	E_{corr} (mV)	CR (mpy)	IE (%)
	0	-690	34	-		0	-690	165	-
	0.09	-750	11.2	68.91		0.09	-747	65.7	60.16
30	0.18	-760	10.3	71.33	50	0.18	-766	53.4	67.64
	0.36	-764	5.7	84.23		0.36	-794	31.2	81.08
	0.45	-769	3.0	91.61		0.45	-800	18.5	88.79
	0.54	-762	4.0	88.92		0.54	-784	22.6	86.30
	0	-700	82	-		0	-700	316	-
	0.09	-752	29.2	64.39		0.09	-760	136.1	56.92
40	0.18	-750	24.7	69.88	60	0.18	-774	110.9	64.89
	0.36	-769	14.4	82.43		0.36	-792	65.7	79.19
	0.45	-775	8.1	90.15		0.45	-810	41.9	86.73
	0.54	-760	10.0	87.83		0.54	-796	51.2	83.80

The corrosion rate, the degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated by using the following relations.

$$CR = \frac{0.129 \times Eq.wt. \times I_{corr}}{D} \qquad (1)$$

where, I_{corr} = Corrosion current density in µA/cm^2, $Eq.wt$ = Equivalent weight of the specimen in g, D = Density of the specimen in g/cc, 0.129 is the metric and time conversion factor.

$$\theta = \frac{\left(I_{corr} - I_{corr(inh)}\right)}{I_{corr}} \qquad (2)$$

where, I_{corr} and $I_{corr(inh)}$ are the corrosion current densities in µA/cm^2 in the absence and presence of the inhibitor respectively.

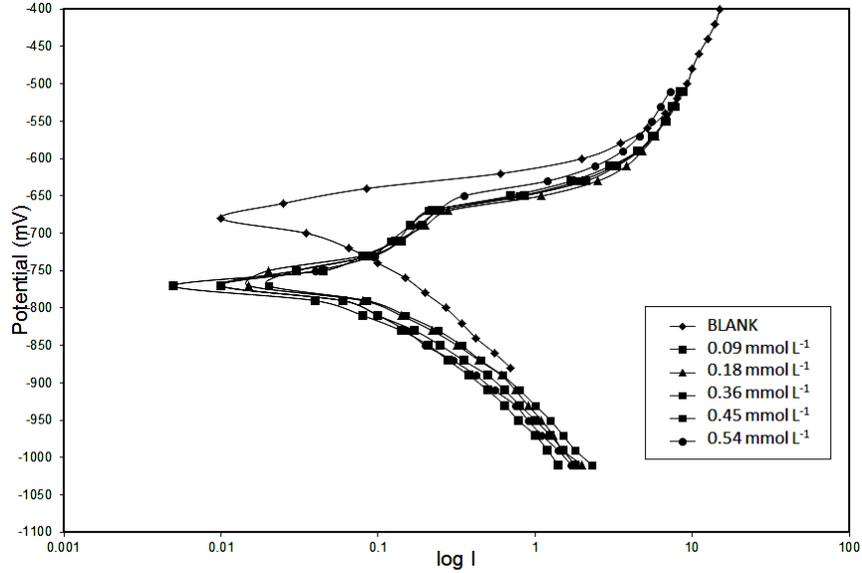$$\% \, IE = \theta \times 100 \qquad (3)$$

Figure 2 Potentiostatic polarization curves for 6061 Al alloy- 15 vol. % SiC(p) composite in 0.1 M HCl with and without inhibitor at 30 ºC.

Table II
Linear Polarization results for the corrosion inhibition of 6061 Al alloy- 15 vol. % SiC(p) composite in 0.1 M HCl at different temperatures.

T (ºC)	*c* (mmol L⁻¹)	*OCP* (mV)	*CR* (mpy)	IE (%)	*T* (ºC)	*c* (mmol L⁻¹)	*OCP* (mV)	*CR* (mpy)	IE (%)
	0	-650	43	-		0	-700	86	-
	0.09	-760	14.9	65.32		0.09	-760	36.2	57.89
30	0.18	-760	13.2	69.33	50	0.18	-760	29.8	65.30
	0.36	-760	7.4	82.71		0.36	-760	17.1	80.13
	0.45	-760	5.0	88.44		0.45	-760	11.2	86.95
	0.54	-760	5.8	86.60		0.54	-760	13.9	83.87
	0	-660	70	-		0	-720	133	-
	0.09	-750	27.4	60.85		0.09	-770	60.8	54.28
40	0.18	-750	22.8	67.37	60	0.18	-780	48.2	63.75
	0.36	-750	13.0	81.42		0.36	-780	26.7	79.92
	0.45	-750	8.5	87.88		0.45	-780	20.9	84.26
	0.54	-750	10.6	84.92		0.54	-780	24.0	81.95

The corrosion current density (I_{corr}) for Linear polarization technique was calculated by using the following expression [8]

$$I_{corr} = 0.026 / slope \qquad (4)$$

The % IE obtained from Tafel extrapolation technique is in good agreement with that obtained by Linear polarization technique (Table I & II). It is observed from the results that corrosion rate of 6061 Al

alloy- 15 vol. % SiC$_{(p)}$ composite increases with increase in temperature in the absence of PAOH. The IE for the compound studied decreases with increase in temperature from 30 to 60°C indicating desorption of the inhibitor molecules taking place at higher temperatures [9]. It is also observed from the results that IE increases up to a critical inhibitor concentration at the temperatures studied. 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 SEM images of the specimens immersed in 1 M HCl solution at 30° C in the absence and presence of inhibitor are shown in Figs. 3a and 3b respectively. It is observed that the specimen exposed to inhibited solution (Fig. 3b) is smoother than that exposed to uninhibited acid solution (Fig. 3a), indicating that the inhibitor forms a protective layer on the composite surface, which in turn prevents the attack of acid.
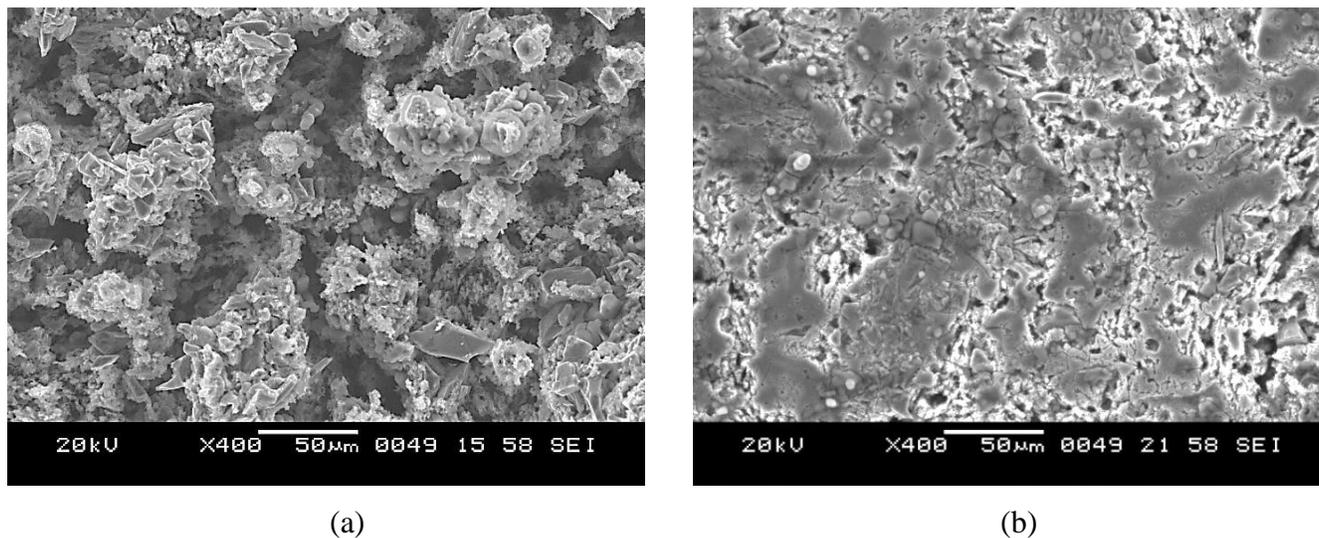

<div align="center">(a)</div>

<div align="center">(b)</div>

Fig. 3 SEM images of 6061 Al alloy- 15 vol. % SiC$_{(p)}$ composite (a) Corroded surface in 1 M HCl and (b) Inhibited surface in 1 M HCl containing 0.45 mmol L^{-1} of PAOH.

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adorbates on the composite surface must be known [10]. The log[θ/(1-θ)] values for different concentrations of the inhibitor, were tested graphically by fitting to various isotherms. The log [θ/(1-θ)] shows a linear relationship with log c (Fig. 4), indicating that the adsorption of the compound on the composite surface obeys Langmuir adsorption isotherm [11].
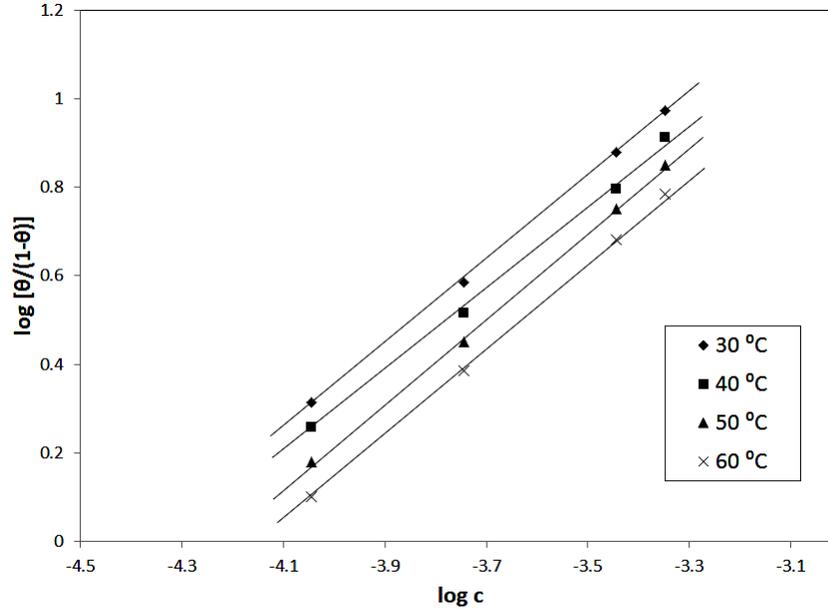
Fig. 4 Langmuir adsorption isotherm for the adsorption of PAOH, on 6061 Al alloy–15 vol. % SiC$_{(p)}$ composite surface in 0.1 M HCl at different temperatures.

The thermodynamic parameters for the corrosion of 6061 Al alloy- 15 vol. % SiC$_{(p)}$ in the presence of 0.45 mmol L^{-1} of PAOH are shown in Table III. The values of activation energy (E_a) were calculated using Arrhenious equation [12].

$$\ln(r_2/r_1) = -\frac{E_a \, \Delta T}{(R \times T_1 \times T_2)} \qquad (5)$$

where, r_1 and r_2 are the corrosion rates at temperatures T_1 and T_2 respectively, ΔT is the difference in temperatures, R is the universal gas constant in joules.

Table III
Activation energy (E_a), Gibb's free energy of adsorption (ΔG_{ads}) for 6061 Al alloy- 15 vol. % SiC$_{(p)}$ composite in 0.1 M HCl in the absence and presence of 0.45 mmol L^{-1} of PAOH.

c (mmol L^{-1})	E_a (kJ mol^{-1})	-ΔG_{ads}(kJ mol^{-1}) Temperature (°C)			
		30	40	50	60
Blank	62.10	-	-	-	-
0.45	73.62	35.56	36.27	37.04	37.65

The higher the value of E_a in the inhibited solution of HCl indicates that the PAOH retards the corrosion process more effectively at lower temperatures. The values of free energy of adsorption (ΔG_{ads}) and equilibrium constant (K) were calculated by using the following equations [13].

$$\Delta G_{ads} = -RT \ln(55.5K) \qquad (6)$$

where 55.5 is the concentration of water in solution in $molL^{-1}$ and T is the temperature in Kelvin.

$$K = \frac{\theta}{c(1-\theta)} \qquad (7)$$

where θ is the degree of surface coverage on the metal surface and c is the concentration of the inhibitor in $molL^{-1}$. The negative values of ΔG_{ads} indicate spontaneous adsorption and strong interaction of inhibitor molecules on to the surface of the composite. The ΔG_{ads} values for the compound studied in 0.1 M HCl at different temperatures were less than 40 $kJmol^{-1}$. However, these values are nearer to -40 $kJmol^{-1}$. This indicates that the inhibition is governed by mixed adsorption mechanism, predominantly physical adsorption type [14].

IV. CONCLUSIONS

- PAOH acts as a mixed inhibitor for corrosion of 6061 Al alloy- 15 vol. % $SiC_{(p)}$ composite in 0.1 M HCl medium.
- The inhibition efficiency of the compound decreases with increase in temperature.
- The adsorption of the compound on the surface of 6061 Al alloy- 15 vol. % $SiC_{(p)}$ composite was found to obey the Langmuir adsorption isotherm and the inhibition was governed by mixed adsorption mechanism.
- The study revealed that the presence of the inhibitor increases the activation energy of the corrosion process.
- The results obtained by Tafel extrapolation technique and Linear polarization technique are in good agreement.

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