Corrosion inhibition of 6061 aluminium alloy/SiCp composite in hydrochloric acid medium using 3-chloro-1-benzothiophene-2-carbohydrazide

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The inhibitive action of 3-chloro-1-benzothiophene-2-carbohydrazide (CBTC) on the corrosion behavior of 6061 Al alloy/SiCp composite has been studied at four different temperatures (30°, 40°, 50° and 60°C) in hydrochloric acid medium (0.5 and 1 M) using Tafel extrapolation technique and weight loss method. Polarization curves indicate that CBTC acts as cathodic inhibitor. Inhibition efficiency is found to increase with increasing inhibitor concentration upto a critical value and with decreasing temperature. The inhibition efficiencies obtained by Tafel extrapolation technique and weight loss method are in good agreement. The adsorption of the inhibitor on the composite surface is found to obey Temkins' and Langmuir adsorption isotherms. The inhibition is governed by physisorption mechanism.

Aluminium metal matrix composites (AMCs) have received considerable attention for military, automobile and aerospace applications because of their low density, high strength and stiffness, reduced coefficient of thermal expansion, ease of fabrication and low cost[1]. Further, the addition of ceramic reinforcements (SiC) has raised the performance limits of AMCs[2]. One of the main disadvantages of AMCs is the influence of reinforcement on the corrosion rate. The addition of reinforcing phase could lead to discontinuities in the surface film, thereby increasing the number of active sites available for corrosion to take place[3-5]. The use of these materials in light weight applications is widespread and these usages expose them to environments that could be acidic or alkaline[6]. Pitting attack was reported to be the major form of corrosion in Al alloy/SiCp metal matrix composites[7]. The corrosion studies on aluminium alloy matrix composites have shown that more pits are formed on composites than on un-reinforced alloys[8]. The attack is more aggressive in highly acidic medium. 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. Suma Rao *et al.*[9] studied the inhibition effect of 3-methyl-4-amino-5-mercapto-1,2,4-triazole on the corrosion behaviour of 6061 Al alloy/SiCp composite in HCl medium. 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 30°–50°C[10]. In our earlier communication, we have reported the inhibitive action of ethyl-2-phenyl hydrozono-3-oxobutyrate on the corrosion of 6061 Al alloy/SiCp composite in HCl medium[11].

Most of the efficient inhibitors used in the industry are organic compounds having multiple bonds in their molecules which mainly contain nitrogen and sulphur atoms through which they are adsorbed on the metal surface[12]. The presence of π electron cloud on aromatic ring and electronegative N and S atoms in the inhibitor compound may likely to induce greater adsorption on the composite surface promoting effective inhibition. In the present work, inhibitive action of CBTC on the corrosion behavior of 6061 Al alloy/SiCp composite in 0.5 and 1 M hydrochloric

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acid at four different temperatures has been investigated using Tafel extrapolation technique and weight loss method.

Experimental Procedure

Specimen

6061 Aluminium alloy/SiCp composite specimens having aluminum alloy 6061 as the matrix and 15 vol. % of silicon carbide particles of mean diameter 25 µm in the form of cylindrical bars of length 120 mm and diameter 40 mm were manufactured at Vikram Sarabhai Space Centre, Trivandrum by Stir casting process[13]. The specimen used 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 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.

Inhibitor

3-chloro-1-benzothiophene-2-carbohydrazide (CBTC) was synthesized by following the procedure described elsewhere[14]. 3-chlorobenzo [b] thiophene-2-methyl carboxylate (4.6 g, 0.02 mol) was dissolved in 25 mL methanol and hydrazine hydrate (1.5 g, 0.03 mol) was added to it. The solution was refluxed for nearly 4 h till the solid started separating. Excess solvent was removed under pressure and the contents were poured into ice cold water. The separated solid was filtered and recrystallized using ethanol. The purity of the compound was confirmed by its elemental analysis and melting point (182 ± 1°C). Elemental analysis of the compound is: C 51.9 % (calcd., 51.55 %); S 15.3 % (14.79 %); Cl 8.1 % (8.16 %); O 7.69 % (7.9 %); N 13.46 % (13.57 %); and H 3.36 % (4.03 %). The structural formula of the compound is shown in Fig. 1.
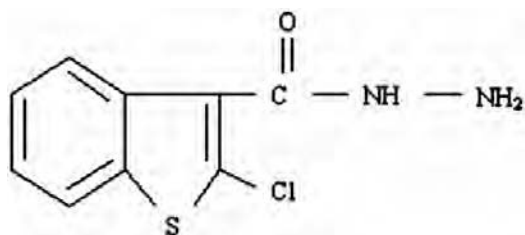

Fig. 1—Structural formula of 3-chloro-1-benzothiophene-2-carbohydrazide (CBTC)

Medium

Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solutions of 0.5 and 1 M HCl.

Tafel extrapolation studies

The potentio-static polarization studies were performed using a Wenking Potentiostat (LB 95 L) and a three electrodes cell system with the saturated calomel electrode as the reference electrode, platinum electrode as counter electrode and the specimen acting as the working electrode. The steady state open circuit potential (OCP) with respect to saturated calomel electrode was noted at the end of 25 – 30 min. 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 performed at 30º, 40º, 50º and 60°C. The results obtained by Tafel extrapolation technique were cross checked by weight loss method.

Weight loss method

Specimen coupon of 1 cm^2 was exposed to 100 mL of 0.5 and 1 M HCl solutions for 6 h at 30ºC. Before exposure the surface was polished with different grades of emery paper and rinsed with distilled water and acetone. The dried specimen was accurately weighed. After exposure, again the specimen was gently polished, rinsed with distilled water and acetone. Finally, it was dried and weighed accurately. The difference in weights of the specimen before and after exposure gives the weight loss. The experiments were repeated in the presence of the inhibitor at 30°C.

Scanning electron microscopy

Scanning electron microscopy (JEOL Model 8340 LA) was used to study the morphology of corroded surface in the presence and absence of inhibitor. The specimens were thoroughly polished with different grades of emery paper, rinsed in acetone followed by distilled water and finally dried before putting on the slide. The specimens were immersed in 100 mL of 1 M HCl with and without inhibitor for 6 h and then removed, rinsed with distilled water and again the photographs are taken. To understand the morphology of the specimen surface in the absence and presence of the inhibitor, the following cases have been

examined: (i) polished surface, (ii) corroded surface in 1 M HCl at 30°C and 60°C, and (iii) inhibited surface in 1 M HCl containing 4.4×10^{-4} mol L^{-1} of the inhibitor at 30°C and 60°C.

Results and Discussion

The electrochemical parameters for the inhibition behaviour of CBTC on the corrosion of 6061 Al alloy/SiCp composite in 0.5 and 1 M HCl solutions at different temperatures, studied by Tafel extrapolation technique and weight loss method are presented in Tables 1 and 2.

It can be seen from the experimental results and the polarization curves (Fig. 2) that there is a large negative shift in the corrosion potential (E_{corr}) with reference to the blank and a drastic reduction in the corrosion current density (I_{corr}) and corrosion rate (CR) values. The large negative shift in the corrosion potential indicates that CBTC is an efficient cathodic inhibitor. The corrosion rate (CR), the degree of surface coverage (θ) and the inhibition efficiency (% IE) are calculated[15] using the following equations:

$$CR \ (\text{mpy}) = \frac{0.1288 \times Eq.wt \times I_{corr}}{D} \qquad \ldots (1)$$

where I_{corr} is the corrosion current density in µA/cm^2; *Eq. wt*, the equivalent weight of the specimen in g; *D*, the density of the specimen in g/cc; and 0.1288, the metric and time conversion factor.

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

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.

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

The inhibition efficiency (% IE) obtained as per the weight loss method was calculated[16] using the following equation:

$$\% IE = \left(\frac{W - W_{inh}}{W}\right) \times 100 \qquad \ldots (4)$$

Table 1—Electrochemical parameters for the corrosion inhibition of Al alloy/SiCp composite in 0.5 M HCl at different temperatures

Temperature °C	$c \times 10^{-4}$ mol L^{-1}	E_{corr} mV	β_a mV/Dec	β_c mV/Dec	CR mpy	Inhibitor efficiency, % Tafel method	Weight loss method
	0	-690	86	105	2054	-	-
	1.1	-752	83	83	382	81.4	75.4
30	2.2	-750	80	90	343	83.3	80.3
	4.4	-750	75	95	246	88.1	85.2
	5.5	-745	78	92	258	87.5	82.8
	6.6	-750	83	93	288	86.0	78.7
	0	-690	88	106	3698	-	-
	1.1	-760	69	94	822	77.8	-
40	2.2	-775	59	93	658	82.2	-
	4.4	-790	65	92	493	86.7	-
	5.5	-782	74	94	504	86.3	-
	6.6	-775	72	91	534	85.6	-
	0	-690	83	83	4930	-	-
	1.1	-760	50	67	1438	70.8	-
50	2.2	-793	48	59	986	80.0	-
	4.4	-775	55	65	698	85.8	-
	5.5	-760	54	68	712	85.5	-
	6.6	-750	61	78	759	84.6	-
	0	-710	106	79	5546	-	-
	1.1	-750	50	56	2160	61.0	-
60	2.2	-760	56	71	1233	77.8	-
	4.4	-770	64	53	822	85.2	-
	5.5	-756	60	57	832	85.0	-
	6.6	-750	70	56	910	83.6	-

Table 2—Electrochemical parameters for the corrosion inhibition of Al alloy/SiCp composite in 1 M HCl at different temperatures

| Temperature °C	$c \times 10^{-4}$ mol L^{-1}	E_{corr} mV	β_a mV/Dec	β_c mV/Dec	CR mpy	Inhibitor efficiency, %	
						Tafel method	Weight loss method
30	0	-700	80	100	4520	-	-
	1.1	-770	44	86	822	81.8	77.8
	2.2	-770	60	80	699	84.6	82.7
	4.4	-770	56	79	534	88.2	87.6
	5.5	-770	58	80	542	88.0	86.3
	6.6	-770	58	88	616	86.4	85.1
40	0	-700	90	100	6573	-	-
	1.1	-760	64	92	1849	71.9	-
	2.2	-770	71	79	1233	81.2	-
	4.4	-770	81	88	905	86.2	-
	5.5	-760	74	94	927	85.9	-
	6.6	-756	71	91	1027	84.4	-
50	0	-720	111	102	7806	-	-
	1.1	-780	56	90	2465	68.4	-
	2.2	-780	74	93	2093	73.2	-
	4.4	-790	56	95	1438	81.6	-
	5.5	-780	58	90	1468	81.2	-
	6.6	-776	59	95	1767	77.4	-
60	0	-700	125	100	11608	-	-
	1.1	-770	74	90	3889	66.5	-
	2.2	-780	58	88	3459	70.2	-
	4.4	-780	64	90	2716	76.6	-
	5.5	-768	75	95	2774	76.1	-
	6.6	-760	70	92	3308	71.5	-
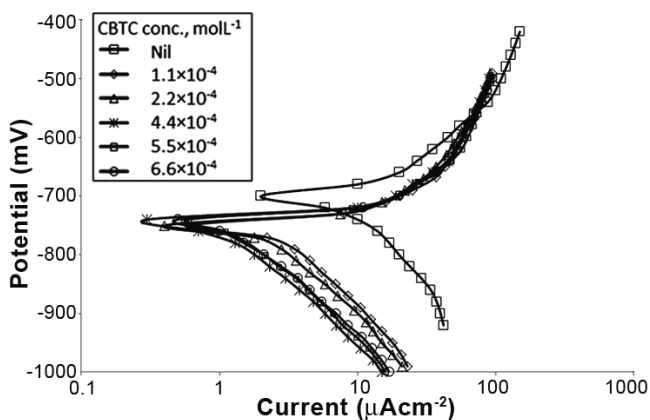
Fig. 2—Potentiostatic polarization curves for Al alloy/SiCp composite in 1 M HCl with and without CBTC at 30°C

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

The *% IE* obtained from Tafel extrapolation technique is in good agreement with that obtained by weight loss method (Tables 1 and 2). It is evident from the results that corrosion rate of 6061 aluminium alloy/SiCp composite increases with the increase in

temperature in the absence of CBTC. This can be attributed to the fact that the rate of chemical reaction increases with increase in temperature. The rise in temperature results in the increase in conductance of the aqueous medium and thereby increases the diffusion rate of hydrogen ions to the composite surface and hence the corrosion progresses faster at higher temperatures. Inhibition efficiency for the compound studied decreases with the increase in temperature from 30°C to 60°C. This may be attributed to the higher dissolution rates of aluminium at elevated temperatures and a possible desorption of the adsorbed inhibitor molecules due to increased solution agitation resulting from higher rates of hydrogen gas evolution[17]. Such a behavior suggests physical adsorption of the inhibitor on the corroding composite surface. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency. A good performance exhibited by the inhibitor compound at lower temperatures may be attributed to the presence of N and S atoms of CBTC which makes it adsorbed quickly on the composite surface[18].

The *% IE* increases upto an optimal concentration of CBTC (4.4×10^{-4} molL^{-1}) at all temperatures both in 0.5 and 1 M HCl medium. 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. Thereafter it is found to decrease marginally, which might be due to desorption of adsorbed molecules at the surface sites.

The surface morphology of 6061 Al alloy SiCp composite was carried out using scanning electron microscope (JEOL Model 8340LA). The SEM images of a fresh specimen and the specimens immersed in 1 M HCl solution with and without inhibitor at 30ºC and 60ºC are shown in Fig 3. The corrosion of 6061 Al alloy/SiCp composite in HCl medium is presumably due to the anodic dissolution either at the grain boundaries or at the metal-media interface. It is observed that the specimen exposed to inhibited solution (Figs 3c and e) is smoother than that exposed to uninhibited acid solution (Figs 3b and d). These observations suggest that the inhibitor forms a protective layer on the composite surface, which, in turn, prevents the attack of acid medium. It is clear from the micrographs that the extent of corrosion of the composite in HCl medium is severe at 60ºC (Fig. 3d) than at 30ºC (Fig. 3b) in the absence of the inhibitor. Addition of inhibitor brings down the corrosion which is evident from the Figs 3d and 3e, wherein the sample surface is covered with the inhibitor showing lesser corroded regions.

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the compound on the composite surface must be known. The surface coverage (θ) values for different concentrations of
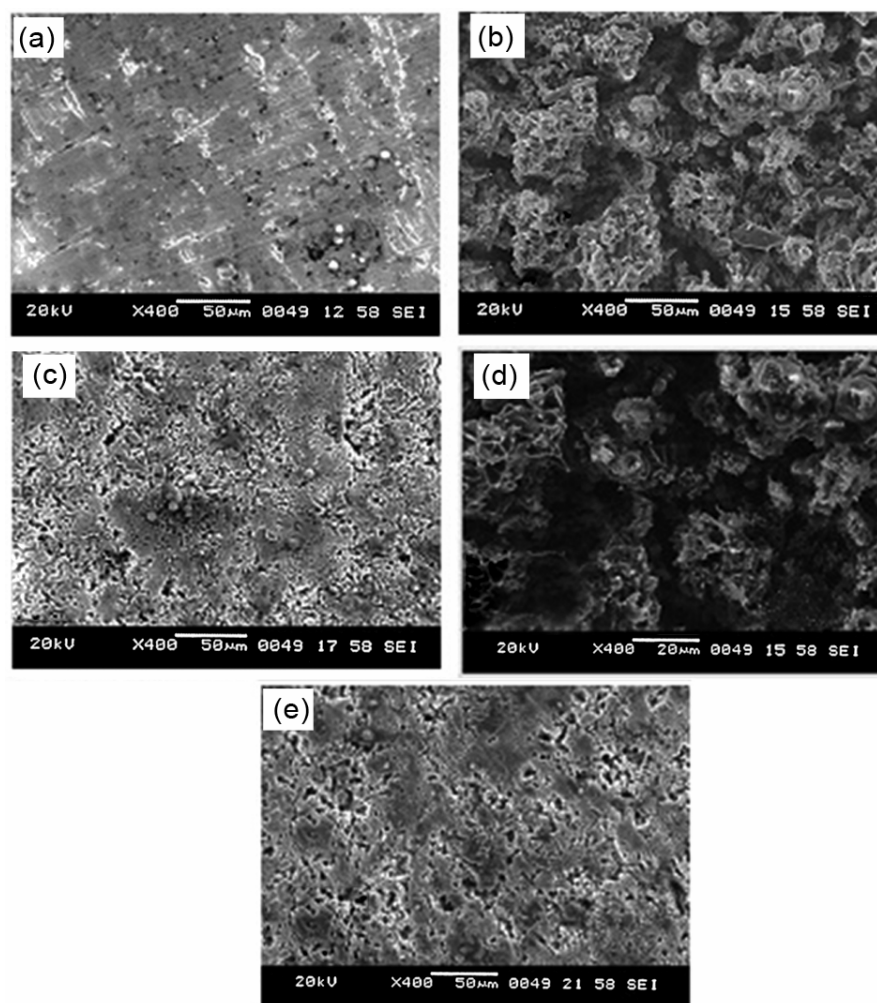

Fig. 3—SEM images of 6061 Al alloy/SiC$_p$ composite (a) fresh polished surface, (b) corroded surface in 1 M HCl at 30ºC, (c) inhibited surface in 1 M HCl containing 4.4×10^{-4} mol L^{-1} CBTC at 30ºC, (d) corroded surface in 1 M HCl at 60ºC, (e) inhibited surface in 1 M HCl containing 4.4×10^{-4} mol L^{-1} CBTC at 60ºC

CBTC from the acid solution are calculated and plotted against log c. The plot of θ versus log c (Fig. 4) yields a straight line proving that the adsorption of the compound on the composite surface follows Temkins' adsorption isotherm.

The equation governing Temkins' adsorption isotherm[19] is represented as

$$\theta = -\left(\frac{1}{f}\right)\ln(Bc) \qquad \ldots (5)$$

where f is the heterogeneity factor; B, the adsorption equilibrium constant; and c, the inhibitor concentration in mol L^{-1}.

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[20]. To further confirm the adsorption behavior of the inhibitor, Langmuir adsorption isotherm was constructed. The Langmuir adsorption isotherm is given by the following equation:
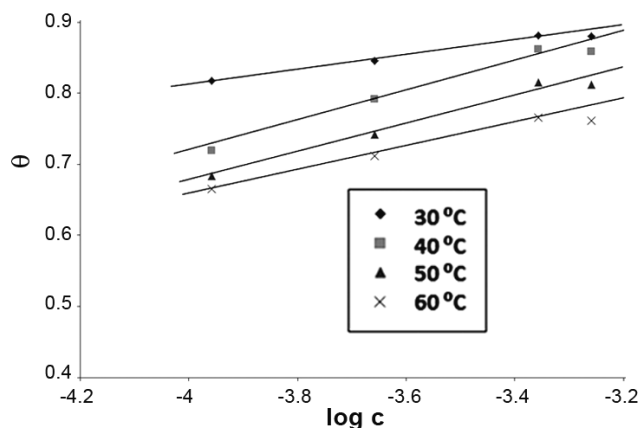
$$\log\frac{\theta}{1-\theta} = \log A + \log c - \left(\frac{Q_{ads}}{2.3RT}\right) \qquad \ldots (6)$$

where θ is the degree of surface coverage; A, the Arrhenius constant; c, the inhibitor concentration in mol L^{-1}; R, the gas constant; T, the temperature in K; and Q_{ads}, the heat of adsorption[21].

The plots of log $[\theta/(1-\theta)]$ versus log c are found to be linear (Fig. 5) suggesting that CBTC followed Langmuir adsorption isotherm in HCl medium[22]. The thermodynamic parameters for the corrosion of 6061 Al alloy/SiCp in the presence of 4.4×10^{-4} mol L^{-1} of CBTC are shown in Table 3. The values of activation energy (E_a) are calculated using Arrhenius equation, as shown below:

$$\ln(r_2/r_1) = -\frac{E_a\Delta T}{(RT_1T_2)} \qquad \ldots (7)$$

where r_1 and r_2 are the corrosion rates at temperatures T_1 and T_2 respectively; ΔT, the difference in

Fig. 4—Temkins' adsorption isotherm curves for the corrosion of 6061 Al alloy/SiCp composite in 1 M HCl in the presence of CBTC
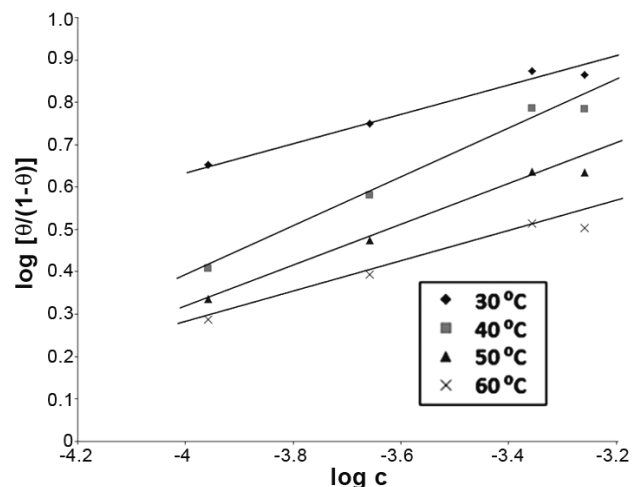
Fig. 5—Langmuir adsorption isotherm curves for the corrosion of 6061 Al alloy/SiCp composite in 1 M HCl in the presence of CBTC

Table 3—Thermodynamic parameters for 6061 Al alloy/SiCp composite in HCl medium at 4.4×10^{-4} mol L^{-1} inhibitor concentration

Acid conc. (c), M	Concentration of inhibitor×10^{-4} molL^{-1}	E_a kJ mol^{-1}	$-\Delta G_{ads}$, kJ mol^{-1}				$-\Delta H_{ads}$ kJmol^{-1}	ΔS_{ads} Jmol^{-1}K^{-1}
			30°C	40°C	50°C	60°C		
0.5	Nil	27.02	-	-	-	-	30.95	214.3
	4.4	32.58	34.89	37.15	38.83	37.93		
		K ⟶	15318.00	23379.00	28030.00	13089.00		
1.0	Nil	26.49	-	-	-	-	20.79	46.2
	4.4	45.80	35.20	35.90	36.10	34.70		
		K ⟶	20808.00	17389.00	12346.00	9113.00		

temperatures; and R, the universal gas constant in joules.

The free energy of adsorption (ΔG_{ads}) and equilibrium constant (K) at different temperatures are calculated from the following Eqs (8) and (9)[23]:

$$\Delta G_{ads} = -RT \ln(55.5K) \qquad \dots (8)$$

where 55.5 is the concentration of water in solution in mol L^{-1}; and T, the temperature in Kelvin.

$$K = \frac{\theta}{c(1-\theta)} \qquad \dots (9)$$

where θ is the degree of surface coverage on the metal surface; and c, the concentration of the inhibitor in mol L^{-1}. Entropy of adsorption (ΔS_{ads}) is obtained by determining the slopes of the plots of -ΔG_{ads} versus temperature and is given in Table 3. Heat of adsorption (ΔH_{ads}) is calculated using the following equation[24]:

$$-\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad \dots (10)$$

Generally, K denotes the strength between adsorbate and adsorbent. The value of K decreases with increasing temperature for CBTC, suggesting that the inhibitor is physically adsorbed on the composite surface[25]. The higher value of E_a in the inhibited solution indicates that CBTC molecules are physically adsorbed on the composite surface[26]. The ΔG_{ads} values obtained for the adsorption of CBTC on the composite surface are less than the threshold value of - 40 kJ mol^{-1}. This indicates that the adsorption process is favoured by physisorption mechanism[27].

The negative values of ΔG_{ads} indicate spontaneous adsorption and strong interaction of inhibitor molecules on to the surface of the composite. ΔH_{ads} values for the adsorption of CBTC in 0.5 and 1 M HCl are not excessively negative, indicating that CBTC is physically adsorbed on the 6061 Al alloy composite surface. Adsorption of the inhibitor molecules at the surface takes place without any reduction of degrees of freedom (i.e. $\Delta S_{ads} > 0$) (Table 3).

Conclusion

The inhibition efficiency of 3-chloro-1-benzothiophene-2-carbohydrazide (CBTC) decreases with an increase in temperature of the medium. From the Tafel plot, it is clear that CBTC acts as a cathodic inhibitor for 6061 Al alloy/SiCp composite in HCl medium. The inhibition efficiencies (*% IE*) obtained from Tafel extrapolation technique and weight loss method are in good agreement. Addition of CBTC to HCl medium increases the activation energy of the

corrosion process for 6061 Al alloy/SiCp composite. The inhibition takes place through adsorption of the compound on to the composite surface and is found to be governed by physical adsorption mechanism. The adsorption of the inhibitor compound on 6061 Al alloy/SiCp composite is found to obey Temkins' and Langmuir adsorption isotherms.

References

1 Sahin Y & Acilar M, *Composite Part A,* 24 (2005) 709.
2 Onat A, Akbulut H & Yilmaz F, *J Alloy Comp,* 436 (2007) 375.
3 Pinto G M, Nayak J & Shetty A N, *J Chem Chem Engg*, 3 (2009) 1.
4 Griffiths A J & Turnbull A, *Corros Sci,* 36 (1994) 23.
5 Trowsdale A J, Voble B, Harris S J, Gibbins I S R, Thomson G E & Wood G C, *Corros Sci,* 38 (1996) 177.
6 Avwiri G O & Igho F O, *Mater Letts,* 57 (2003) 3705.
7 Yadav N S, Choudhary R S & Agarwal C V, *J Electrochem Soc India*, 32 (1983) 235.
8 Pardo A, Marino M C, Marino S, Viejo F, Carboneras M & Arrabbal R, *Corros Sci.* 47(2005) 1750.
9 Suma Rao A, Padmalatha, Jagannath Nayak & Nithyananda Shetty A, *J Met Mater Sci,* 47 (2005) 51.
10 Suma Rao A, Padmalatha, Jagannath Nayak, Nithyananda Shetty A & Hebbar K R, *Corrosion inhibition of Al alloy 15 vol. pct. SiCp composite in HCl using Allyl thiourea*, paper presented at the National Conference on Corrosion and Corrosion Control, METCORR–2005, Surathkal, 2005.
11 Achutha Kini U, Prakash Shetty, Divakara Shetty S, Arun Isloor & Ramadev Herle, *J Chil Chem Soc,* 55 (2010) 56.
12 Muralidharan S M & Iyer S V, *Anticorros Methods Matter* 44 (1997) 100.
13 Zaki Ahmad & Abdul Aleem B J, *J Mater Engg Perform,* 18 (2009) 129.
14 Arun Isloor M, *Studies on the synthesis and Biological activity of some pharmaceutically important Heterocyclic compounds*, PhD Thesis, Mangalore University, India, 2001.
15 Divakara Shetty S & Prakash Shetty, *Indian J Chem Technol,* 15 (2008) 216.
16 Abdallah M, *Corros Sci,* 44 (2002) 717.
17 Rafiquee M Z A, Nidhi saxena, Sadaf Khan & Quaraishi M A, *Indian J Chem Technol,* 14 (2007) 576.
18 Divakara Shetty S, Prakash Shetty & Sudhakar Nayak H V, *Mater Letts,* 61 (2007) 2347.
19 Tebbji K, Oudda H, Hammouti B, Benkaddour M & El Kodada M, *Appl Surf Sci,* 241 (2005) 326.
20 Stayomova A E, Sokolova E I & Roichra S N, *Corros Sci,* 39 (1997) 1595.
21 Shafiq M, Ranjha A M, Yaseen M, Mehdi S M & Hannan A, *J Agric Res,* 46 (2008) 141.
22 Thomas J G N, in *Corrosion,* Vol 2, edited by Shreir L L, Jarman R A & Burstein G T (Butter Worth-Heinemamn), 2000, 17.
23 Quaroishi M A & Sardar R, *Indian J Chem Technol*, 11 (2004) 103.
24 Ramesh Salian V & Airody Vasudeva Adhikhari, *Bull Mater Sci,* 31 (2008) 699.
25 Obot I B & Obi-Egbedi N O, *Corros Sci,* 52 (2010) 198.
26 Bayol E, Gurten A A, Dursun M & Kayakirilmaz K, *Acta Physico-Chimica Sinica*, 24 (2008) 2236.
27 Sathiyanarayanan S, Marikannu C & Palaniswamy N, *Appl Surf Sci,* 241 (2005) 477.