Corrosion Behaviour of 6061 AI-SiC Composites in KOH Medium

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Abstract: The present research work deals with the corrosion behaviour of 6061 Al-15% (vol) SiC_(P) composites. The addition of the reinforcement like SiC to Aluminium has been reported to decrease the corrosion resistance of the matrix due to several reasons, one of them being galvanic action between the reinforcement and the matrix. In the present work, the corrosion behaviour of 6061 Al-15% (vol) SiC_(P) composites in KOH at different concentration (0.5M, 1M, 1.5M) and different temperature (30° C, 35° C, 40° C, 45° C, 50° C) was determined by Tafel extrapolation technique. The inhibition action of 8-Hydroxyquinoline on corrosion behaviour of 6061 Al-15% (vol) SiC_(P) composites in KOH at different concentration of inhibitor (200ppm, 400ppm); different concentration of medium (0.5M, 1M, 1.5M) and different temperature (30° C, 35° C, 40° C, 35° C, 40° C, 50° C) was investigated. The results indicate that corrosion rate of Al-SiC composite in KOH increases as the concentration of medium increases and also as temperature of medium increases. The results indicate that the inhibitor is moderately effective in inhibiting the corrosion of 6061 Al-15% (vol) SiC_(P) composites. As the inhibitor concentration increases, the corrosion rate decreases. The surface morphology of the metal surface was investigated using scanning electron microscope (SEM). Activation energy was evaluated using Arrhenius equation, and enthalpy of activation and entropy of activation values were calculated using transition state equation.

Keywords: Corrosion, 6061 Al-SiC composite, KOH, 8-Hydroxyquinoline, Tafel.

1. INTRODUCTION

The word Corrosion stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which metal transfers electrons to environment and undergoes a valence change. It is a natural process which occurs with all metals except the least active noble metals like Gold and Platinum. Most metals are found in nature in the form of chemical compounds such as oxides, sulphides, carbonates, chlorides etc. In the refining process energy is added to the ore to extract the metal. The same amount of energy needed to extract metals from their ores is liberated during the chemical reactions that produce corrosion. Corrosion returns the metal to its combined state in chemical compounds that are similar to the ores from which metals were extracted. Corrosion is theoretically equivalent to the reverse of extractive metallurgy, if the material getting deteriorated is a metal. It must be noted that the deterioration by physical cause is not corrosion, but it termed as erosion, galling, wear etc. Corrosion of structural elements is a major issue for any industry because of the chemical environment of the chemical processing such as cleaning, pickling, descaling, acidizing acid pickling.

Al-SiC is a metal matrix composite consisting of Silicon carbide particles dispersed in a matrix of Aluminium alloy. The Silicon carbide reduces the density of Al and improves its stiffness and wear resistance. Aluminium matrix composite possess high Young's modulus/ density and yield strength/ density ratios together with tailorable coefficient of thermal expansion and high thermal conductivity and hence look very promising and find applications in aerospace, military and automobile industries. However, one of the main draw backs of Aluminium matrix composite is the decrease in corrosion resistance compared to the base alloy. Base alloys inherently develop a protective oxide surface film which imparts corrosion resistance ; but, addition of reinforcing phase leads to in homogeneities and can cause discontinuities in the surface film, increasing the number of sites where corrosion can be initiated and making the composite more venerable to corrosion attack. The preferential localized attack has been based on factors, such as reactive silicon carbide matrix, presence of crevices and pores, processing routes, presence of secondary phases and the volume percentage of reinforcement. It is therefore important to add corrosion inhibitors to decrease the corrosion rate of Al composites. So a detailed study on the corrosion behaviour of this composite is relevant.

Inhibitors are substances, which can retard the rate and extent of corrosion, when added to a corroding environment in small concentration. Hundreds of organic and inorganic compounds have been studied and recommended as inhibitors of corrosion for various metals in various environments i.e. aqueous, nonaqueous, molten salt and dry atmospheres. Inhibitors properties are reported at various temperatures, ranging from very low to very high values. A wide variety of compounds are reported as inhibitors for metal matrix composites and these are mainly organic compounds usually containing N, S or O atoms and rare earth compounds.

The investigation was mainly focused to study the corrosion behaviour of 6061 Al-SiC composite in Potassium Hydroxide solution at three different concentrations viz. 0.5M, 1M, 1.5M at five different temperatures like 30, 35, 40, 45, 50°C by Tafel extrapolation technique. Meanwhile, to add corrosion inhibitors to decrease the corrosion rate of the composite and 8-Hydroxyquinoline is selected as inhibitor in the present work to understand the effect of temperature on the inhibition action coupled with the study of influence of thermodynamic and kinetic parameters on the corrosion inhibition.

2. EXPERIMENTAL PROCEDURE

2.1 Material Preparation

The 6061 Al-SiC composites were cast in the form of 10 cylinders each of 90 mm diameter and 240 mm length by stir at NIIST (formerly casting technique RRL). Thiruvananthapuram. These cylinders were extruded at 430ºC-480ºC with extrusion ratio of 30:1 (two rods each of 11.5 mm diameter) at Serval Engineers, Mangalore. The experiments were performed with composite in extruded rod form. Reinforced SiC (average particle size is about 25 micron) has 99.8percentpurity. The extruded material is in the form of cylindrical rods of 1.15cm in diameter. The samples were cut from these rods and metallographically mounted up to 20mm height using cold setting resin. This exposed flat surface of the mounted part was polished using 1/0, 2/0, 3/0, 4/0 grit level and finally disc polished using diamond paste.

2.2 Medium

The corrosion studies were conducted in a Potassium Hydroxide solution of different concentrations viz. 0.5M, 1M and 1.5M. KOH pellets and distilled water were used to prepare the KOH solution for all experiments. 0.5M, 1M, 1.5M KOH solutions were prepared by dissolving28, 56, 84g of KOH pellets in 11itre of distilled water respectively.

2.3 Temperature

The corrosion studies were conducted in five different temperatures such as 30, 35, 40, 45 and 50° C. A water thermostat was used to maintain the required constant temperature.

2.4 Inhibitor

8-Hydroxyquinoline was used as the inhibitor for corrosion inhibitor studies at different concentrations viz.200 and 400ppm.

2.5 Method

Tafel polarization studies were carried out by using CH instrument's electrochemical analyzer and a three electrode Pyrex glass cell with Platinum counter electrode and saturated Calomel electrode as reference electrode. An area of 1.038 cm² of the polished Al-15% (vol) SiC composite specimens were exposed to alkaline solution of concentration 0.5M at 30° C with and without inhibitor. The polarization studies were made from -0.250V to 0.250V against open circuit potential (OCP) with a scan rate of 0.01V/sec and the corresponding corrosion currents, i, recorded. From the potential, E Vs log i plots, corrosion potential, E_{corr}, and corrosion current density, i_{corr}, were determined. The corrosion rate (C.R), in mpy, is calculated using the relation:

Corrosion Rate (mpy) =
$$0.129 \times EW \times i_{corr}/D$$
 (1)

Where, I_{corr} = corrosion current density in μ A/cm², D=density of the corroding material, 2.77 g/cm³, E.W=9.15g/mol,equivalent weight of corroding material (atomic weight/oxidation number).

The surface coverage (θ) is calculated as

$$\theta = (i_{\text{corr}} - i_{\text{corr (inh)}}) / i_{\text{corr}}$$
⁽²⁾

Where, i_{corr} is the corrosion current density in the absence of inhibitor and i_{corr} (inh) is the corrosion current density in the presence of inhibitor.

The percentage inhibition efficiency (%IE) = $\theta \times 100$ (3)

The experiments were repeated for the temperatures such as 35, 40, 45 and 50^oC and for the concentrations such as 1M and 1.5M with 8-Hydroxyquinoline as inhibitor. E_{corr}, i_{corr}, C.R, θ and %IE for each experiment were determined.

2.6 Microstructural Studies

6061 Al-SiC composite specimens were polished as per standard metallographic practice, belt grinding followed by polishing on emery papers, finally on polishing wheel using diamond paste to obtain mirror finish. After polishing the specimens were etched with kellar's reagent and observed under Scanning Electron Microscope (SEM).

The microstructure of corroded samples of 6061 Al-SiC composite at three different concentrations of KOH with and without the addition of inhibitor, were examined under SEM to obtain the type of corrosion.

3. RESULT AND DISCUSSIONS

3.1 Corrosion Behaviour in KOH Medium

The corrosion rates were determined using Tafel extrapolation technique. Typical Tafel plots are shown in figures 1 to 12.



Figure 1. Tafel plot for 0.5M KOH solution at different temperatures



Figure 2. Tafel plot for 1M KOH solution at different temperatures



Figure 3. Tafel plot for 1.5M KOH solution at different temperatures



Figure 4. Tafel plot for 0.5M KOH at 30^oC with different concentrations of 8-Hydroxyquinoline



Figure 5. Tafel plot for 0.5M KOH at 40^oC with different concentrations of 8-Hydroxyquinoline



Figure 6. Tafel plot for 0.5M KOH at 50⁰C with different concentrations of 8-Hydroxyquinoline



Figure 7. Tafel plot for 1M KOH at 30^oC with different concentrations of 8-Hydroxyquinoline



Figure 8. Tafel plot for 1M KOH at 40^oC with different concentrations of 8-Hydroxyquinoline



Figure 9. Tafel plot for 1M KOH at 50°C with different concentrations of 8-Hydroxyquinoline



Figure 10. Tafel plot for 1.5M KOH at 30^oC with different concentrations of 8-Hydroxyquinoline



Figure 11. Tafel plot for 1.5M KOH at 40^oC with different concentrations of 8-Hydroxyquinoline



Figure 12. Tafel plot for 1.5M KOH at 50^oC with different concentrations of 8-Hydroxyquinoline

The corrosion rates are calculated for various experiments from these plots and tabulated. Values of corrosion rates in KOH solution obtained for different temperatures are presented in the Table 1.

Table 1. Corrosion rates of 6061Al-SiC Composite in different concentrations of KOH and at temperatures

Medium	Temperature (⁰ C)	Corrosion Rate
		(mpy)
	30	37.982
	35	40.372
0.5M KOH	40	45.714
	45	49.550
	50	54.572
	30	65.718
	35	75.760
1M KOH	40	85.885
	45	93.759
	50	105.629
	30	97.535
	35	112.860
1.5M KOH	40	117.199
	45	134.894
	50	150.822

3.2 Inhibition Behaviour of 8-Hydroxyquinoline

Corrosion rates obtained for different concentrations of 8-Hydroxyquinoline and the inhibition efficiency of 8-Hydroxyquinoline are tabulated in tables 2, 3 and 4.

Table 2. Corrosion rates of 6061Al-SiC Composite in KOH solutions with inhibitor 8-Hydroxyquinoline at 30^{0} C

Medium	Corrosion Rate (mpy)				
	0 ppm	100 ppm	200 ppm	400 ppm	600 ppm
0.5M KOH	37.98	37.01	35.01	31.91	31.79
1M KOH	65.71	62.98	55.79	52.56	51.95
1.5M KOH	97.53	85.80	82.02	61.28	55.39

Table 3. Corrosion rates of 6061Al-SiC Composite in KOH	ł
solutions with inhibitor 8-Hydroxyquinoline	

		Corre	osion rate (i	mpy)
Medium	Temperature	Inhibi	tor concent	ration
	(ºC)	0ppm	200pp m	400pp m
0.5MKOU	30	37.982	35.009	31.915
0.5MKOH	40	45.714	40.582	34.814
	50	54.572	46.514	37.550
	30	65.719	55.798	52.560
IM KOH	40	85.885	75.300	64.535
	50	105.629	81.547	72.107
1 5M KOU	30	97.535	82.029	61.280
1.514 KOH	40	117.199	89.340	74.550
	50	150.822	132.68 5	116.45 3

Table 4. Inhibition Efficiency of 8-Hydroxyquinoline in KOH

		Inhibition ef	ficiency (%)	
Medium	Temperature(⁰ C)	Inhibitor concentration		
		200ppm	400ppm	
	30	7.825	15.971	
0.5M KOH	40	11.226	23.843	
	50	14.760	31.914	
	30	15.095	20.020	
1М КОН	40	12.320	24.850	
	50	17.110	31.730	
	30	15.890	37.159	
1.5M KOH	40	23.770	36.390	
	50	12.025	22.780	

3.3 Thermodynamic Parameters

The effect of temperature on the corrosion rate of 6061 Al-SiC composite was studied by measuring the corrosion rate at different temperature between 30° C to 50° C. Activation energy (Ea) for the corrosion process of 6061 Al-SiC composite in KOH was calculated from the Arrhenius equation.

$$\ln(v_{\rm corr}) = B - (Ea/RT) \tag{4}$$

Where B is a constant which depends on the metal type and R is the universal gas constant. The plot $ofln(v_{corr})versus$ reciprocal of absolute temperature (1/T) gives a straight line whose slope = -Ea/R, from which the activation energy values for the corrosion process were calculated. Arrhenius plots are shown in the figure 13 to 15.

The enthalpy of activation (Δ H#) and entropy of activation (Δ S#) values for the corrosion process were calculated from transition state theory equation.

$$v_{\text{corr}} = (\text{RT/Nh}) \exp(\Delta S \#/\text{R}) \exp(-\Delta H \#/\text{RT})$$
(5)

Where h is Planck's constant, and N is Avagadro's number and R is the ideal gas constant. A plot of $ln(v_{corr}/T)$ versus (1/T) gives a straight line with slope= - Δ H#/R and intercept = $ln(RT/Nh) + (\Delta$ S#/R). The free energy of adsorption of inhibitor is calculated using formula as,

$$\Delta G_{ads} = -RT ln \left[\frac{55.5 \times \theta}{C (1-\theta)} \right]$$
(6)

Where, ΔG_{ads} = Free energy of adsorption (J/mol), R = Real gas constant, T = Temperature (K), C = Concentration of inhibitor (mol/dm³), $\boldsymbol{\theta}$ = Surface coverage.



Figure 13. Arrhenius plots for 0.5M KOH



Figure 14. Arrhenius plots for 1M KOH



Figure 15. Arrhenius plots for 1.5M KOH

The plot of $ln(v_{corr}/T)$ versus (1/T) are shown in Figure 16 to18.



Figure 16. Plot of ln(v_{corr}/T) versus (1/T) in 0.5M KOH



Figure 17. Plot of $ln(v_{corr}/T)$ versus (1/T) in 1M KOH



Figure 18. Plot of $ln(v_{corr}/T)$ versus (1/T) in 1.5M KOH

The value of Ea, Δ H#, Δ S# and Δ G# for 8-Hydroxyquinoline on 6061 Al-SiC composite in different KOH concentrations and temperatures is listed in Table 5 and 6.

Table 5. Activation parameters for the corrosion	of 6061Al-
SiC Composite in KOH solution	

Medium	Inhibitor concentration	Ea (KJ/mol)	∆H# (KJ/mol)	∆S# (J/molK)
1000000	0ppm	9.519	7.607	-135385
0.5M	200ppm	9.768	9.186	-135 202
KOH	400ppm	10.891	11.430	-133.489
	Oppm	13.136	10.018	-118.707
1M	200ppm	13.550	10.641	-118.541
KOH	400ppm	17.290	12.220	-108.098
	0ppm	18.124	15.464	-99.751
1.5M	200ppm	19.995	17.359	-95.353
KOH	400ppm	26.680	28.226	-75.607

Table 6. Standard free energy (ΔG #) values

Medium	Temperature (⁰ C)	Standard free energy (\Delta G#)		
		0 ppm	200 ppm	400 ppm
0.5M	30	48.572	50.181	51.850
KOH	40	49.924	51.534	53.184
	50	51.276	52.887	54.518
	30	45.923	46.607	44.944
1M KOH	40	47.108	47.794	46.024
	50	48.293	48.981	47.104
1.516	30	45.688	46.250	51.134
1.5M KOH	40	46.685	47.203	51.980
	50	47.683	48.157	52.647

The table 7 shows the free energy of adsorption of inhibitor (8-Hydroxyquinoline) for corrosion of 6061 Al-SiC composite in KOH at different concentrations.

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Table 7. Free energy of adsorption (ΔG_{ads}) of inhibitor

Medium	Temperature (⁰ C)	Free energy of adsorption (KJ/mol)	
		200ppm	400ppm
	30	-20.498	-20.754
0.5M KOH	40	-22.221	-22.761
	50	-23.753	-24.577
	30	-22.362	-21.473
1M KOH	40	-22.481	-22.903
	50	-24.236	-24.552
	30	-22.516	-23.636
1.5M KOH	40	-24.551	-24.337
	50	-23.124	-23.333

4. DISCUSSIONS

4.1 Corrosion Behavior in KOH Medium

The results indicate that the 6061 Al-SiC composite is highly susceptible to corrosion in 1.5M KOH while its corrosion rate is comparatively lower in 0.5M KOH even at 50°C. Corrosion rate is high at 50°C and is lower at 30°C for every concentrations of KOH. Corrosion rate of the 6061 Al-SiC increases with increase in temperature. It would be possible because of the increased kinetics of the reaction. As the KOH concentration increases from 0.5M to 1.5M, corrosion rate shows an increase, because the loss of passivity of the specimen due to thinning of primary oxide layer by the chemical dissolution action of hydroxide ions(OH-) on increasing the concentration of the alkali. The hydroxide ions formed increase the pH at the film/solution interface considerably; the increased local pH on the metal surface accelerates the corrosion reaction, and damage the passive film.

4.2 Inhibition using 8-Hydroxyquinoline

8-Hydroxyquinoline is moderately effective in bringing down the corrosion rate as its presence brings down the corrosion rate considerably. Among the 2 concentration studied, the lowest corrosion rate was obtained at 400ppm of 8-Hydroxyquinoline in all alkali concentrations. Since, 8Hydroxyquinoline is adsorption type inhibitor its spread over the surface of the metal like an umbrella and protects the metal from corrosion. However, if sufficient quantity is not added then the surface of the metal is left uncovered which results in severe corrosion attack. It has been observed from the figures 4 to 12 that the inhibitor 8-Hydroxyquinoline acts as a cathodic inhibitor. It displaces the corrosion potential in the negative direction and reduces corrosion current, there by retard cathodic reaction and suppresses the corrosion rate. Inhibition efficiency increases with the increase in inhibitor concentration in all media. A maximum inhibition efficiency of about 37% could be achieved with 400ppm of inhibitor

addition in 1.5M KOH at 30^oC. The inhibition efficiency of 8-Hydroxyquinoline in different KOH concentration is shown in figures 19 to 21.



Figure 19. Inhibition efficiency of 8Hydroxyquinoline in 0.5M KOH



Figure 20. Inhibition efficiency of 8Hydroxyquinoline in 1M KOH



Figure 21. Inhibition efficiency of 8Hydroxyquinoline in 1.5M KOH

Table 8.	Adsor	ption	isotherms
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SI. No	Name	Verification plot
1	Langmuir	c/θvsc
2	Frumkin	θ vs log c
3	Bockris-Swinkels	$\theta/(1-\theta)$ vs log c
4	Temkin	θ vs log c
5	Virial Parson	θ vs log (θ /c)
6	Flory Huggins	$\log (\theta/c) \text{ vs } \log (1-\theta)$
7	El-Awady	$\log \frac{\left[\theta/(1-\theta)\right] \text{ vs } \log \theta}{c}$
8	Freundlich	$\log \theta$ vs $\log c$

Various adsorption isotherms are listed in the above table 8. Verification plots were plotted for each isotherms and it was found that Temkin adsorption isotherm exhibits straight line.



Figure 22. Temkin adsorption isotherm for corrosion of 6061 Al-SiC composite

From the table 7 it is clear that the ΔG_{ads} values for 8-Hydroxyquinoline (C₉H₇NO) ranges between -20KJ/mol to -25KJ/mol and it is observed that the inhibition efficiency decreases with increase in temperature. From these two observations it can be concluded that this inhibitor get adsorbed on the metal surface by mixed adsorption, which is also supported by enthalpy of activation shown in table 5.

4.3 Characterization Using SEM

The SEM images of the surface of the Al-SiC composite are shown in figures 23 to 25. The figure 23 shows the SEM micrograph of corroded sample without inhibitor and the figure 24 and 25 show the SEM micrographs of corroded sample with inhibitor at 30° C.



Figure 23. SEM micrograph of corroded 6061 Al-SiC composite in 0.5M KOH at 30^oC



Figure 24. SEM micrograph of corroded 6061 Al-SiC composite in 1.5M KOH with inhibitor (200ppm) at 30^oC



Figure 25. SEM micrograph of corroded 6061 Al-SiC composite in 1.5M KOH with inhibitor (400ppm) at 30^oC

The SEM images shown that Al-SiC composite have undergone both uniform and galvanic corrosion. The galvanic corrosion is due to presence of SiC particles in Al matrix which act as cathode site. This can be seen in the SEM images

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where the matrix adjacent to the SiC particle has been corroded.

5. CONCLUSIONS

- 1. 6061 Al-SiC composite is highly susceptible to corrosion in KOH.
- 2. Corrosion rate of the sample increase with increase in concentration of the solution. Also, corrosion rate of the sample increases with increase in temperature because of the increased kinetics of reaction.
- 3. 8-Hydroxyquinoline is found to be moderately effective as a corrosion inhibitor and the inhibition efficiency increases with inhibitor concentration for a given set of conditions.
- 4. The highest efficiency of 37% was observed at 400ppm concentration of the inhibitor.
- 5. The standard free energy values confirm that inhibitor molecules get adsorbed on to the surface of the composite by mixed adsorption.

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