Propargyl as Corrosion Inhibitor for Al-5%Si/15%SiC Composite in 0.5molar Sodium Hydroxide

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Abstract

The corrosion characteristic of Al-5%Si/15%SiC composite in 0.5molar sodium hydroxide solution (caustic soda) using propargyl as corrosion inhibitors was investigated employing gravimetric and potential measurements. The research was carried out at different inhibitor concentrations, time and temperature ranges of 0.5 – 2.5% v/v, 1– 5 hours and 30 – 70 °C respectively. Results obtained revealed that propargyl is a moderate corrosion inhibitor for the composite, with maximum inhibition efficiency of 59.23% at 30 °C and inhibitor concentration of 1.5% v/v. Thermodynamic parameters such as heat of adsorption, free energy and activation energy were obtained from experimental data and the mechanism of inhibition was elucidated. The inhibitor is physically and chemically absorbed unto the surface of the composite.

Introduction

Aluminium Matrix Composites (AMCs) are gaining considerable amount of industrial importance because of their excellent combination of physical, mechanical and electrochemical properties. Due to their interesting combination of properties, these materials are being used in many engineering applications like pistons, track shoes, brake drums, cylinder liners etc in automobile sectors [1], marine [2, 3], mining and mineral processing applications [4, 5].

One of the major limitations of AMCs has been corrosion in aqueous environment and several investigations have been carried out extensively on the corrosion of AMCs with common reinforcements such as SiC and, Al_2O_3. Fang et al. [6] studied the synergistic effect of wear and corrosion on Al_2O_3 particulate reinforced 6061 Aluminium Matrix composite, and reported that under wear-corrosion condition, the corrosion potential shifted to the active side while the current density increased with the decrease of Al_2O_3 volume fraction, and the incorporation of reinforcement was detrimental to the corrosion resistance of the aluminium metal matrix. Ramachandra and Radhakrishna,[3] worked on the sliding wear, slurry erosive wear, and corrosive wear of aluminium/SiC composite and observed that the corrosion resistance of reinforced matrix decreased with increasing SiC content. A comparative study of the corrosion behaviour of Al – Si/ SiC composite and cast iron in three different media, namely synthetic mine water, 3.5%NaCl solution and 3.5% NaOH solution through immersion technique was studied by Saraswathi et al,[2] they reported that the corrosion rate of Al – Si/ SiC composite in 3.5%NaCl solution was minimum followed by synthetic mine water while that of 3.5% NaOH solution was the highest.

One of the methods of combating corrosion in aqueous environment is the application of corrosion inhibitors. Most of the well known inhibitors are organic compounds containing nitrogen, sulphur and/ or oxygen atoms [7]. Zaki and Abdul [8] worked on the degradation of Al 6013/SiC composites in salt water and its control, and reported that the localized attack was concentrated mainly on the Al 6013/SiC interface where addition of cerium chloride drastically suppressed the rate of corrosion. Monticelli et al. [9] studied corrosion and corrosion inhibition of alumina particulate/aluminium alloys metal matrix composites in neutral chloride solutions and reported that among tungsten and molybdenum-containing inorganic salts tested as corrosion inhibitors, only ammonium tetrathiotungstate afforded good inhibiting properties, particularly towards the AA 2014-based MMC. Mishra et al. [10] studied the corrosion

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inhibition of 6061-SiC by rare earth chlorides (lanthanum and cerium chlorides), and reported that the polarization resistance increased after addition of $LaCl_3$ and $CeCl_3$, with maximum increase noticed at 250 ppm $LaCl_3$ and 1,000ppm $CeCl_3$· $CeCl_3$ addition displayed better improvement in polarization resistance. Also rare earth chloride addition resulted in an increase in resistance on both cathodic intermetallic sites and the pitted regions by formation of precipitates of their oxide/hydroxide on those locations, resulting in high pitting nucleation resistance as well as improved corrosion resistance. Hence this research aims at investigating the possibility of using propargyl as corrosion inhibitor for Al-5%Si/15%SiC composite in 0.5molar sodium hydroxide solution

Propargyl Alcohol

Propargyl alcohol has chemical formula $HC{\equiv}C\text{-}CH_2OH$, molecular density 0.949, melting point -53°C and boiling point 114 -115°C. Propargyl alcohol has several major application which include: reactant/chemical intermediate; pharmaceutical intermediate; agricultural chemical intermediate; corrosion inhibitor for steels; solvent stabilizer; and polymer modifier [11].

Materials and Methods

Materials

High purity aluminium electrical wires were obtained from Northern Cable Company (NOCACO) Kaduna, silicon, silicon carbide with average particle size of 10μm, silica sand, bentonite, distilled water, ethanol, sodium hydroxide, and Propargyl.

Methods

The synthesis of the metal matrix composite used in this study was carried out using the stir-casting method at the foundry shop of the National Metallurgical Development Center, (NMDC) Jos, Nigeria, by adding 15% SiC to the Al – 5%Si alloy. The composite produced is of composition Al-5% Si/15%-SiC, after casting, the samples were machined into standard corrosion coupons.

Corrosion testing

The coupons were polished, degreased in absolute ethanol, dried, weighed and stored in a dessicator. The coupons were immersed in 0.5M NaOH with varying time and temperature. The first set of tests were carried out without inhibitor to serve as control. Then in solutions containing propargyl of concentrations 0.5, 1.0, 1.5, 2.0 and 2.5% v/v. The weight loss and potential methods were used. The weight loss and potential of each sample were measured after 1 hour over a period of 5 hours. From the date obtained, corrosion rate, inhibitor efficiency, degree of surface coverage, free energy, activation energy and heat of absorption were determined.

Corrosion rate and Inhibitor Efficiency (%)

The weight loss was determined by finding the difference between the initial weight of the coupons and the new weight after 1hour using the relationship [12 and 13]

$$W = W_o - W_F \qquad \text{(Eq.1)}$$

Where W =Weight loss, W_o = Initial Weight, W_F = Final weight.

The corrosion rate was determined from standard expression for measurement of corrosion rate in mills per year (mpy) [12 and 13]

$$mpy = \frac{534W}{DAT} \qquad \text{(Eq. 2)}$$

Where W = Weight loss (mg), D = Density of material (g/cm^3), T = Time of exposure (hours), A = Total surface area (in^2).

Measurement of Potential

After the test coupons were immersed in the solution a reference electrode (platinum) was also immersed in the solution, the electrode and coupons were then connected to a potentiostat, which was used to measure the corrosion potential with respect to the reference electrode.

Inhibitor Efficiency

The inhibitor efficiency (IE) was computed using the relationship [13 and 14]

$$\text{Inhibitor Efficiency (IE)} = \frac{CR_o - CR}{CR_o} \times 100\% \qquad \text{(Eq. 3)}$$

Where CR and CR_o are the corrosion rates with and without the inhibitors respectively.

Degree of Surface coverage

The degree of surface coverage(θ) was calculated from the equation

Degree of surface coverage (θ)= $\frac{CR_o - CR}{CR_o}$ (Eq. 4)

Where CR and CR_o are the corrosion rates with and without the inhibitors.

Reaction kinetics

The activation energy Ea of the corrosion reaction was calculated using the Arrhenius equation given by [13]

$$Log\frac{R1}{R2} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \quad \text{(Eq. 5)}$$

Where $R1$ and $R2$ are the corrosion rates at any given two different temperatures $T1$ and $T2$ while the free energy of adsorption was determined using the given relationships

$$\Delta G(ads) = -RT \ln(55.5\,K) \quad \text{(Eq. 6)}$$

Where $K = \frac{\theta}{C(I-\theta)}$

Where K = Equilibrium constant, θ = is the degree of surface coverage, C= is the concentration of inhibitor (% v/v)

Also the heat of adsorption $\Delta Hads$ of the inhibitors was calculated using the equation [13]

$$\Delta Hads = 2.303R\left\{\left(Log\frac{\theta_2}{1-\theta_2}\right) - \left(Log\frac{\theta_1}{1-\theta_1}\right)\right\} \times \frac{T_2T_1}{T_{2-}T_1}\,(KJ/mol) \quad \text{(Eq. 7)}$$

Where $\theta 1$ and $\theta 2$ are degree of surface coverage at any two temperatures $T1$ and $T2$.

Results and Discussion

Results

Microstructure of the produced composite

The microstructure of the produced composite is given in figure 1

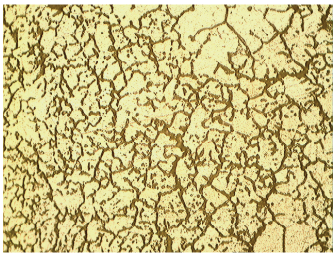

Fig. 1. Micrograph of as cast Al-5%Si/15%SiC (Mag x 200).

The Microstructure shows the presence of matrix phase (white) and the SiC reinforcement (dark patches)

The variation of the corrosion rate with time of exposure is given by Figures 2-4, while Figures 5-7 show the variation of potential difference with time and Figures 8-10 the variation of inhibitor efficiency with time at the three different temperatures.

Discussion

Figure 1 shows the produced composite in the as cast condition, it shows the reinforcement (SiC) uniformly distributed in the matrix (Al-Si alloy).

Visual observation of coupons (without and with inhibitor) after 5 hours of exposure reveals changes in colour of the coupons from bright shiny surfaces to dull ones showing uniform corrosion. Pits were also observed on the samples which are indications of corrosion attack by the alkaline media. However the changes in colour were more intense with the solutions without inhibitor so was the presence of pits.

Effect of inhibitor concentration and time on corrosion rate

Figures 2 - 4 show the variation of corrosion rate with time in the presence of propargyl as corrosion inhibitor at temperatures of 300C, 500C and 700C. In these graphs the trend showed a decrease in corrosion rate with variation in concentration from 0.5-1.5%v/v, while from 2.0-2.5%v/v there was an increase in corrosion rate.

Figures 5 - 7 showed the variation of potential difference with time. These graphs showed that the highest potentials were associated with 1.5% v/v which is in line with the observation from the gravimetric measurement. It was evident from Figures 2 – 7 that the corrosion rates of the composite increases with increase in temperature. This is attributed to the increase in electrochemical activity as was established by Mishra et. al.[10]

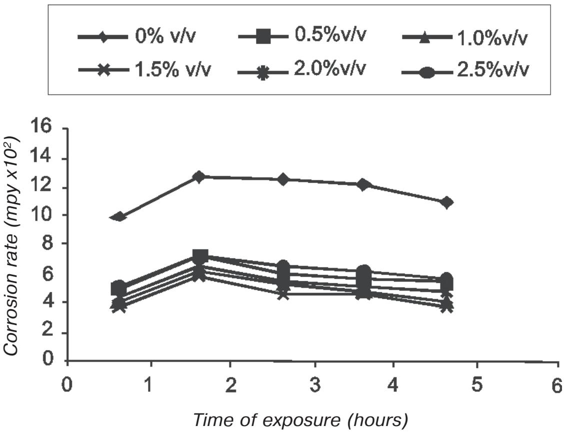

Fig. 2. Variation of corrosion rate with time of exposure at 30 °C.

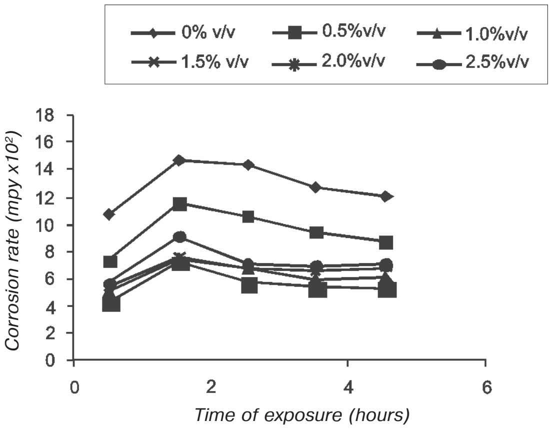

Fig. 3. Variation of corrosion rate with time of exposure at 50 °C.

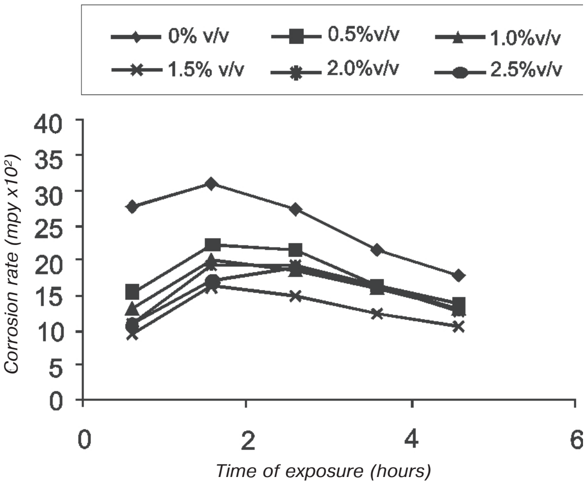

Fig. 4. Variation of corrosion rate with time of exposure at 70°C.

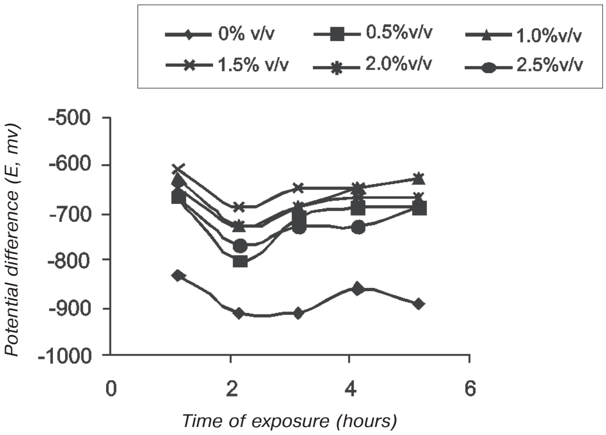

Fig. 5. Variation of potential with time of exposure at 30 °C.

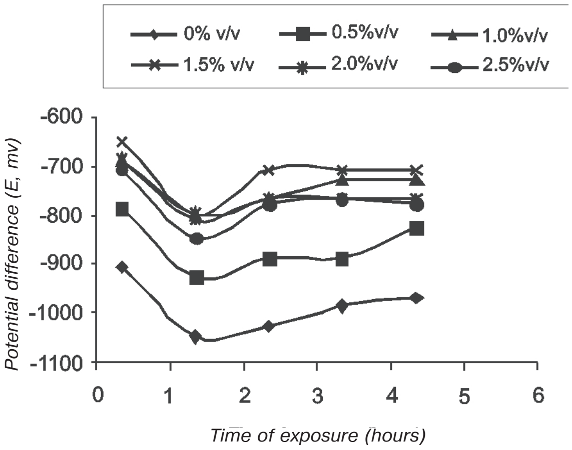

Fig. 6. Variation of potential with time of exposure at 50 °C.

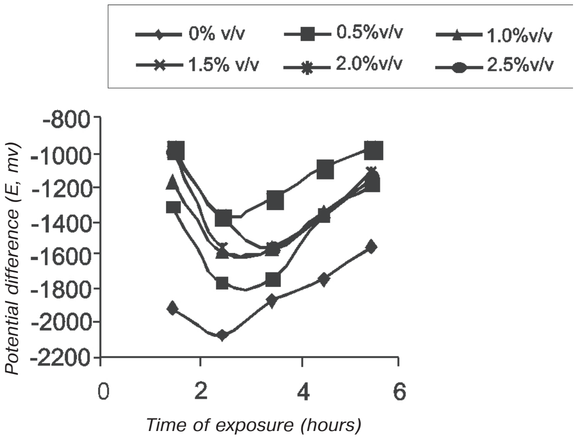

Fig. 7. Variation of potential with time of exposure at 70 °C.

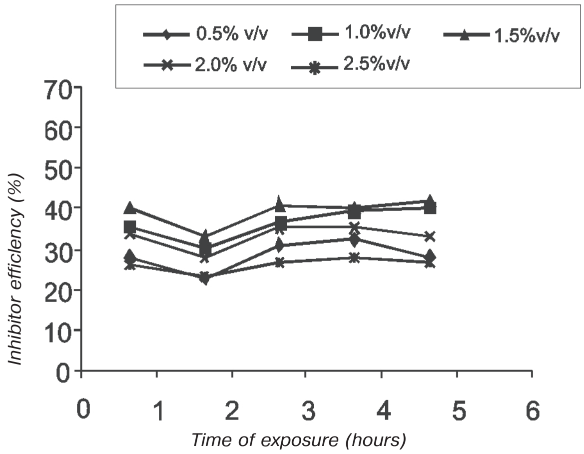

Fig. 8. Variation of inhibitor efficiency with time of exposure at 30 °C.

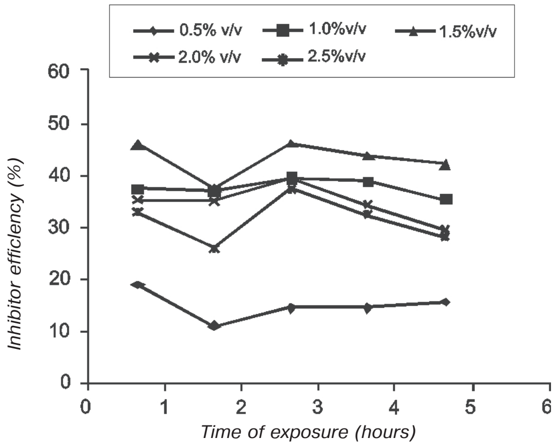

Fig. 9. Variation of inhibitor efficiency with time of exposure at 50 °C.

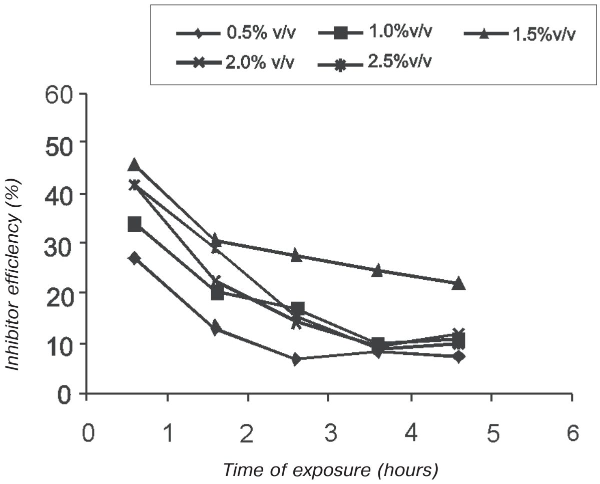

Fig. 10. Variation of inhibitor efficiency with time of exposure at 70 °C.

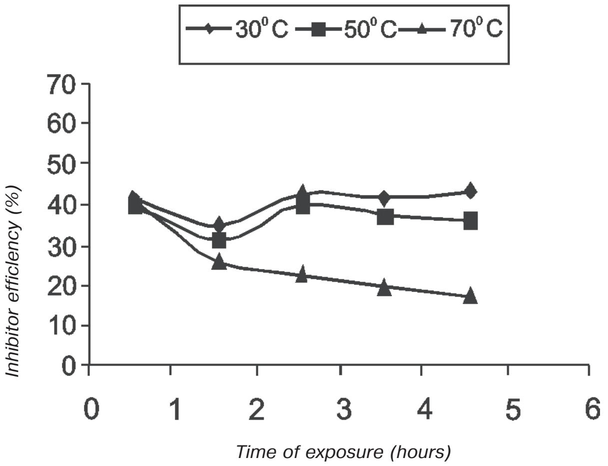

Fig. 11. Comparison of inhibitor efficiency for the various temperatures used.

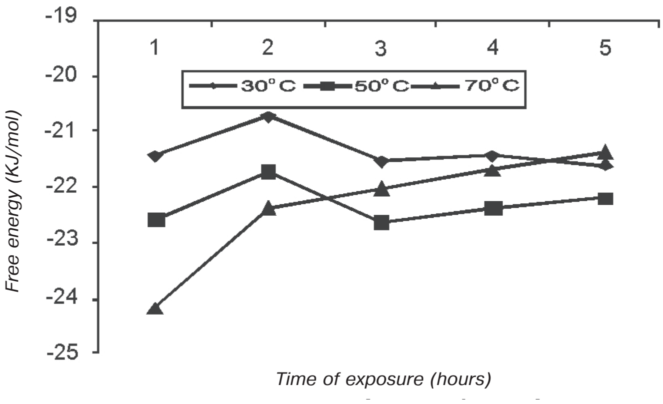

Fig. 12. Variation of free energy with time of exposure.

Effect of inhibitor concentration and time on inhibitor efficiency

Figures 8 – 10 show the variation of inhibitor efficiency with time. The maximum inhibitor efficiencies were obtained at a concentration of 1.5% v/v. however the highest inhibitor efficiency of 59.23% was obtained at 30°C and the least inhibitor efficiency of 32.89% was obtained at 70°C. this is also in line with the results obtained from gravimetric and potential measurements.

Corrosion inhibition of Propargyl

The corrosion inhibition of propargyl is attributed to the presence of multiple bond in its molecular structure which enhance the deposition of its molecules on the surface of the composite.

Effect of temperature on inhibitor efficiency

Figures 11 show the variation of inhibitor efficiency with temperature. The graph shows that the highest inhibitor efficiency is obtained at 300C while the least obtained at 700C, showing that the inhibitor acts best at 300C. The decrease in inhibitor efficiency with increase in temperature is attributed to the fact that at lower temperature the inhibitor molecules absorb onto the composite surface, while at a higher temperature desorption of the molecules from the composite surface occur as a result of dissociation of constituents of the inhibiting substance.

Reaction kinetics

The free energy of adsorption (ΔGads), the heat of adsorption (ΔHads), and activation Energy (Ea) were calculated. Figure 12, tables 1 and 2 show the results obtained respectively.

Table 1.

Heat of Adsorption (ΔHads) for Propargyl

Concentration of propargyl	Heat of adsorption(ΔHads) (J/mol)				
v/v %	1hr	2hr	3hr	4hr	5h
0.5	-6638.90	-16449.32	-32110.75	-30908.66	-28696.03
1.0	-7164.45	-15123.25	-24360.22	-34603.85	-34714.63
1.5	-810.99	-8174.41	-17766.48	-19597.79	-23466.27
2.0	1055.04	-10860.38	- 19643.49	-32129.69	-27240.84
2.5	7729.68	-1007.57	-17418.72	-26346.07	-23315.39

Table 2.

Activation Energy (-Ea)

Concentration of propargyl	Activation energy (-Ea) (J/mol)				
v/v %	1hr	2hr	3hr	4hr	5hr
0.0	23566.35	20578.84	18548.03	15009.69	14065.38
0.5	26344.87	25771.39	28724.33	25272.14	22911.66
1.0	27067.25	26502.00	28365.60	28021.52	27440.03
1.5	24035.73	24332.40	27135.27	24048.07	24830.96
2.0	23030.05	24833.39	28439.62	26358.32	23754.48
2.5	19856.99	20986.27	24622.23	23262.24	21435.98

The negative values of the free energy of adsorption (see figure 12) indicates a strong interaction of the inhibitor molecules on the surface of the composite.

Table 1 show the values of heat of adsorption (ΔHads) obtained in this work. The nature of adsorption depends on the values of ΔHads: thus if │ΔHads│< 10KJ/mol the adsorption is physical adsorption and if │ΔHads│> 10KJ/mol the adsorption is chemical[13]. From the values obtained in this work, both physical and chemical adsorption is attained.

The activation energy of the inhibited system were higher than those of the uninhibited system (see table 2), this indicates that the presence of the inhibitors caused a change in the values of the apparent activation energies, this indicates a change in the rate determining step brought about by the adsorption of propargyl onto the surface of the composite.

Conclusions

1. There was uniform and pitting corrosion on the surface of the composite, but pitting is the major form of corrosion associated with Al-5%Si/ 15% SiC in 0.5M sodium hydroxide
2. Propargyl can serve as a moderate corrosion inhibitor for Al-5%Si/ 15% SiC in 0.5M sodium hydroxide solution for temperatures up to 50 °C. with optimum concentration of 1.5% v/v.
3. The adsorption of the propargyl onto the surface of the composite was by physical and chemical (combined) adsorption.

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