Thermodynamic and Kinetic Study for Corrosion of Al-Si-Cu/Y₂O₃ Composites

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This study involves the effect of yttria with three wt. % (1, 2 and 3 %) on the corrosion behavior of Al-Si-Cu alloy in 0.1 N NaOH solution by potentiostat at four different temperatures 303, 313, 323 and 333 K. Corrosion parameters for these composite materials were determined by Tafel extrapolation method such as corrosion potentials E_{corr}, corrosion current densities i_{corr} and Tafel slopes b_c and b_a. The results of electrochemical study indicates that Al-Si-Cu/1 % yttria gave the lowest corrosion rate due to behaviour of yttria as protective layer which cover the metallic surface and enhances the passive film of Al_2O_3, while 2 and 3 % yttria may be behave as sufficient cathode leading to increasing the corrosion of base alloy because of the inhomogenous structure of an metal matrix composite which must be considered in designing a corrosion protection system. Thermodynamic study was achieved to estimate thermodynamic quantities of corrosion process ΔG, ΔS and ΔH. The results show spontaneous the corrosion in 0.1 N NaOH through the negative values of Gibbs free energy for composites and the lowest spontaneous process was for Al-Si-Cu/1 % yttria, the change in entropy values were positive and the lowest value was for Al-Si-Cu/1 % yttria. Also the change in enthalpy values was positive referring to endothermic nature of corrosion process. Kinetic study was applied using Arrhenius equation to estimate activation energies and the highest activation energy was for Al-Si-Cu/1 % yttria, this means that this composite need most energy to surmount the energy barrier. The relationship existed between values of the activation energy (E_a) and logarithm of pre-exponential factor (log A) for different material suggesting the operation of a compensation effect in kinetics of corrosion. This suggests that, the corrosion reaction proceeds on surface sites, which were associated with different energies of activation.

Keywords: Corrosion, Composite material, Thermodynamic quantities, Kinetic study.

INTRODUCTION

The actual corrosion of composite materials quite often begins with reaction of the reinforcement material and especially with any interface material (called the interphase) used to coat the reinforcement for debonding. One property that exacerbates is a mismatch in thermal expansion coefficients between the reinforcement and matrix, leading to microcracks. These microcracks allow the ingress of corrosive gases (*e.g.*, oxygen)[1]. Actually, a large amount of the literature on composites is concerned with an evaluation of the internal reactions that take place among the various reinforcement, interphase and matrix materials. The seawater corrosion of SiC/Al was found to be more resistant than graphite/Al by Aylor and Kain[2]. This was attributed to a lack of a galvanic driving force between the SiC and the aluminum matrix, although both composites exhibited similar mechanisms of corrosion, essentially pitting of the metal matrix around the reinforcement material.

Budruk *et al.*[3] studied the corrosion behavior of pure magnesium, Mg-Cu (0.3, 0.6 and 1 vol. %) and Mg-Mo (0.1, 0.3 and 0.6 vol. %) composites in 3.5 % NaCl solution by weight loss

and polarization methods. The corrosion rate increased with increasing volume fraction of reinforcement in Mg-Cu and Mg-Mo composites. Jamaludin *et al.*[4] studied the influence of heat treatment on the corrosion behavior of two Al-Cu matrix composites (15 vol % Al_2O_{3p} and 20 vol % SiC_w) in 3.5 % sodium chloride solution by gravimetric measurements. Nickel *et al.*[5] studied the effect of plastic deformation on the corrosion and wear behavior of composites based on an Al-Cu alloy. Al_2O_3 or SiC particles in two different fraction (5 or 15 vol. %) by potentiodynamic polarization in NaCl solution. Bobic *et al.*[6] studied the corrosion behavior of metal matrix composites metal matrix composites with aluminium alloy matrix and they reviewed of boron-, graphite-, silicon carbide-, alumina- and mica- reinforced aluminium metal matrix composites. The reinforcing phase influences on metal matrix composites corrosion rate as well as on various corrosion forms (galvanic, pitting, stress corrosion cracking, corrosion fatigue, tribocorrosion). El-Sayed *et al.*[7] fabricated a series of different aluminum-graphite composites (Al-Gr), namely pure Al, Al-1%Gr, Al-2%Gr and Al-3%Gr. The surface of these composites was investigated using optical microscopy to examine the distribution of exfoliated graphite within aluminum in 3.5 % NaCl solution using many techniques.

Hamasha and Mayyar[8] studied the effect of copper and silicon carbide content on the corrosion resistance of of Al-Mg alloys in acidic 1 M HCl and alkaline 1 M NaOH solution using weight loss method to evaluate corrosion resistance, the results show that copper and silicon carbide have a negative effect on the corrosion resistance of monolithic aluminium.

The aim of present work involves evaluation the thermodynamic and kinetic study for corrosion of Al-Si-Cu/yttria composites in 0.1 N NaOH solution over temperatures range of 303-333 K by electrochemical method.

EXPERIMENTAL

Preparation of specimens: Al-Si-Cu alloy was fabricated with chemical composition is shown in Table-1 using atomic absorption spectroscopy. The reinforcement particles Y_2O_3 with grain size (50-75 μm) were added to produce composite materials with three weight percentages (1, 2 and 3 %) and then measured amount of the matrix alloy was melted at 700 °C in an electrical furnace at 300 rpm for 3 min to make a vortex in order to disperse Y_2O_3 particles in the melt. The melting temperature was controlled and checked with thermocouple (K type) before pouring into a carbon steel die.

The cylindrical specimens (d = 1.3 cm and h = 0.5 cm) were cut, polished, degreased with acetone and rinsed with distilled water and then mounted by hot mounting using formaldehyde (Bakelite) at 138 °C for 8 min to insulate all but one side (with surface area 1.327 cm²) and made a hole on one side to electrical connection.

0.1 N NaOH solution was used as corrosive medium to study the corrosion behavior of Al-Si-Cu/Y_2O_3 composites. This solution was prepared by dissolving 4 g of NaOH (M. wt = 40 g mol⁻¹, purity > 99.5 %, obtained from FERAK) in 1000 mL distilled water.

Electrochemical measurement: Potentiostatic measurements were carried out using WINKING MLab 200 Potentiostat from Bank-Elektronik with electrochemical standard cell. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV sec⁻¹. Polarization experiments were started when the rate at which open circuit potential (E_{ocp}) changed was less and more 200 mV. SCE was used as reference electrode and Pt as counter electrode, while working electrodes were Al-Si-Cu alloy and composite materials.

RESULTS AND DISCUSSION

Electrochemical measurements: Most of the commercial work on metal matrix composites metal matrix composites has focused on aluminium and aluminium alloys as the matrix metals. The combination of light weight, environmental resistance and favorable mechanical properties has made aluminium alloys very popular for use as a matrix metal. However, the addition of the reinforcement particles could significantly alter the corrosion behavior of these materials. In this study we tried to study the effect of Y_2O_3 particles as reinforcement for Al-Si-Cu alloy in corrosive medium represented by 0.1 N NaOH solution.

Fig. 1 shows the Tafel plot of specimens in 0.1 N NaOH solution at four temperatures. This figure shows the anodic and cathodic behavior of experimental specimens. At anodic sites the following reactions can occur:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2 \qquad (I)$$
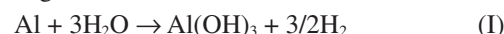
This is then followed by the reaction

$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O \qquad (II)$$
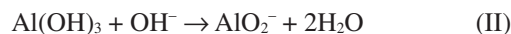
While at cathodic sites, reduction of oxygen takes place as follow:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (III)$$

						TABLE-1		
					CHEMICAL COMPOSITION OF EXPERIMENTAL ALLOY			
Element	Si	Cu	Fe	Zn	Mg	Mn	Ti	Al
Wt. %	12-12.5	0.83-1.2	0.65-0.9	0.45-0.83	0.27-0.5	0.2-0.4	0.02-0.1	Remaining

TABLE-2
CORROSION PARAMETERS OF Al-Si-Cu/Yttria COMPOSITES IN 0.1 N NaOH AT FOUR TEMPERATURES

| Specimens	Temperature (K)	-E_{oc} (mV)	-E_{corr} (mV)	i_{corr} (mA cm⁻²)	-bc (mV dec⁻¹)	+ba (mV dec⁻¹)	C_Rx10 mm/y
Al-Si-Cu alloy	303	1302	1284.0	3.79	91.8	141.5	4.13
	313	1216	1225.0	1.99	40.3	53.7	2.16
	323	1173	1193.3	5.19	70.0	464.5	5.65
	333	1137	1159.6	3.96	55.3	193.6	4.31
Al-Si-Cu/1%Y_2O_3	303	374	410.0	0.0207×10^{-3}	162.6	193	2.25×10^{-5}
	313	385	387.0	0.00171	109.6	203.4	1.86×10^{-3}
	323	487	443.0	0.0514×10^{-3}	51.0	48.6	5.59×10^{-5}
	333	495	388.0	0.00223	64.7	51.7	2.42×10^{-3}
Al-Si-Cu/2%Y_2O_3	303	1278	1272.2	0.6063	70.4	60.7	6.6
	313	1207	1205.7	1.020	93.1	106.2	1.11
	323	1162	1166.3	4.920	80.7	73.6	5.36
	333	1131	1132.8	3.340	55.0	96.5	3.63
Al-Si-Cu/3%Y_2O_3	303	1253	1242.5	3.940	78.1	111.1	4.29
	313	1211	1204.0	2.330	140.5	154	2.53
	323	1157	1163.4	6.270	61.4	174.9	6.82
	333	1108	1107.1	8.330	79.3	272	9.66
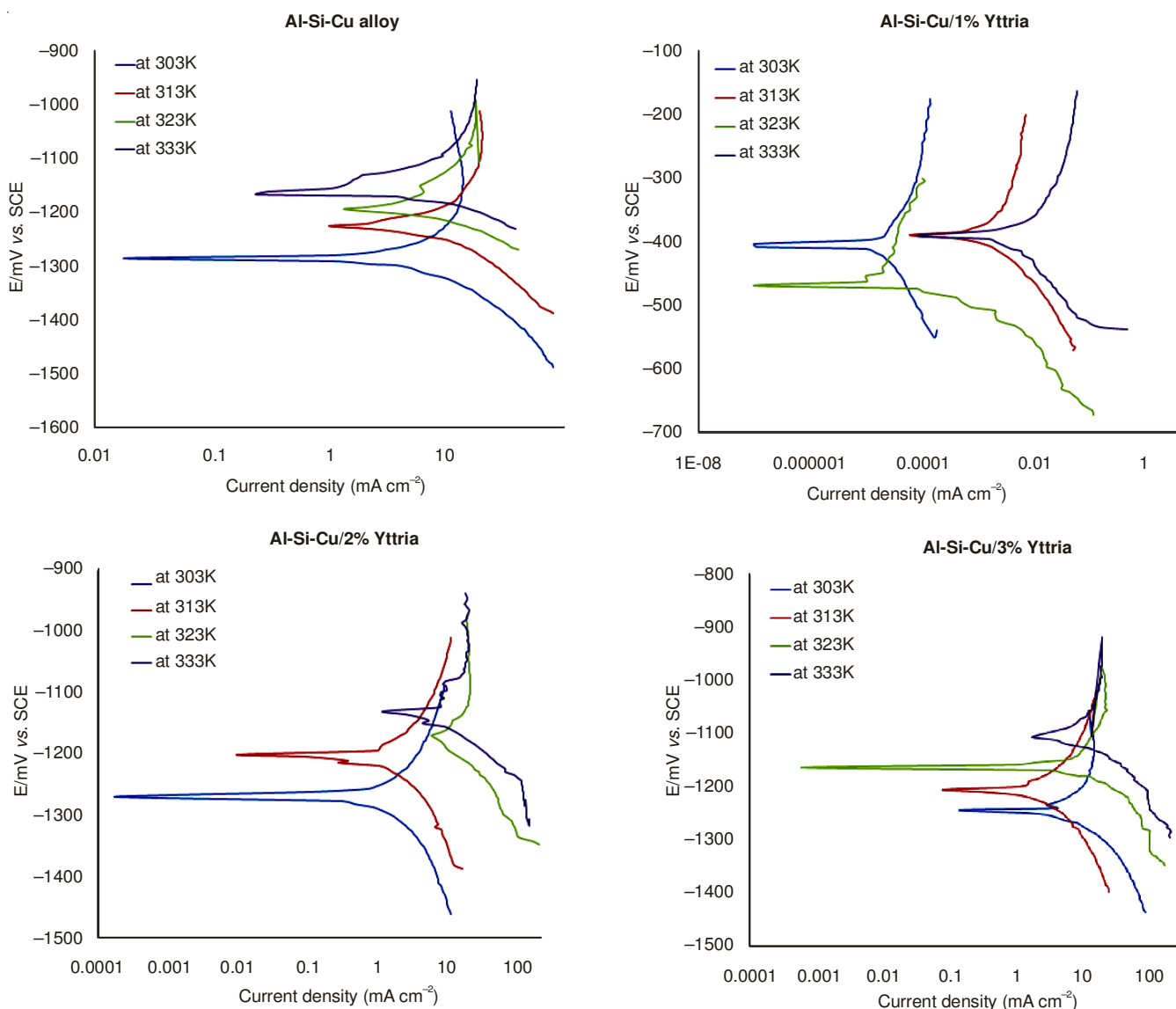
Fig. 1. Polarization curve of Al-Si-Cu/Y₂O₃ composites in 0.1N NaOH at four temperatures

From the data in Table-2, can be finding that Y₂O₃ particles shift the open circuit potentials to more positive values especially with 1 % Y₂O₃. This test was recorded after immersion in electrolyte for 300 sec *versus* SCE. The potential of the sample was followed as a function of time in order to study the evolution of the film chemistry as it came to equilibrium with solution, the more noble potential for composites may be due to cover the alloy surface by Y₂O₃ at electrical double layer. By increasing the temperature, the open circuit potential shifts to noble direction.

The corrosion parameters were calculated by Tafel extrapolation method. These data show that the corrosion potentials, in general, shift toward noble direction with increasing temperature, while the corrosion current densities gave different behavior. This behavior can be due to the difference in anodic and cathodic sites on the metallic surface because of presence of porosities in the bulk material. Cathodic and anodic Tafel slopes enhanced the different behavior of sequences of corrosion current density, *i.e.* dissolution of metals at anodic sites and reduction reactions at cathodic sites.

The presence of the reinforcing fibers and particles and the processing associated with aluminium metal matrix composites fabrication can cause accelerated corrosion of the metal matrix compared to corrosion of the unreinforced matrix alloy. Accelerated corrosion may originate from electrochemical and chemical interaction between metal matrix composite constituents, microstructural effects and from problems related to processing.

The published literature on the corrosion of aluminium based composites is often contradictory. This is due to the fact that there is a variety of aluminium alloy matrices and reinforcement type combinations which may exhibit completely different corrosion behavior. In general, the composites are more susceptible to corrosion attack than the matrix alloy. The effectiveness of all anodizing methods studied decreases with increasing reinforcement concentration. In general, corrosion resistance of surface-modified, aluminium based metal matrix composites has been found inferior to that of the corresponding matrix alloys. Simply transferring protection methods routinely used for an aluminium alloy will not be effective without considering the nature of that aluminium alloy based metal matrix composite surface.

On comparison of the behavior of composite material reinforced by yttria with base alloy (Al-Si-Cu alloy) at constant temperature can be seen than the corrosion rate of metal matrix composite with 1 % Y_2O_3 better than 2 % Y_2O_3 and these two composite materials better than the base alloy and the later better than the alloy reinforced by 3 % Y_2O_3 which may be due to the inhomogenous structure of an metal matrix composite which must be considered in designing a corrosion protection system. Surface treatments applied to metal matrix composites will encounter reinforcement particles that may disrupt any protective coatings and hinder effectiveness of passive coatings. The sequence of decreasing in corrosion rate (C_R) arranged as follow:

C_R: Al-Si-Cu/1%Y_2O_3 < Al-Si-Cu/2%Y_2O_3 <
Al-Si-Cu alloy < Al-Si-Cu/3%Y_2O_3

Possible mechanisms include microgalvanic coupling between the matrix and reinforcement or between the matrix and intermetallics, failure of the protective oxide film due to micro-segregation of the alloying elements or micro-crevices at the matrix-reinforcement interface[9].

Thermodynamic of corrosion: Thermodynamics has been widely applied to corrosion studies for many years. The change in free energy (ΔG) is a direct measure of the work capacity or maximum electric energy available from a system. Chemical and corrosion reactions behave in exactly the same fashion. Thermodynamic laws tell us that there is a strong tendency for high energy state in a system to transform into low energy state. This tendency of metals to recombine with components of the environment leads to the corrosion[10]. The free-energy change accompanying an electrochemical reaction can be calculated by the following equation.[11]:

$$\Delta G = -nFE \qquad (1)$$

where ΔG is the free energy change, *n* is the number of electrons involved in the reaction, F is the Faraday constant and E equals the cell potential.

From the value of ΔG at several temperatures, the change in the entropy (ΔS) of corrosion process could be derived according to the well-known thermodynamic relation:

$$\Delta S = - \frac{d(\Delta G)}{dT} \qquad (2)$$

Values of ΔG are usually plotted against temperature (T); thus at any temperature the value of $-d(\Delta G)/dT = \Delta S$ which corresponds to the slope of the $(-\Delta G)$ *versus* (T) plot at that temperature (Fig. 2).
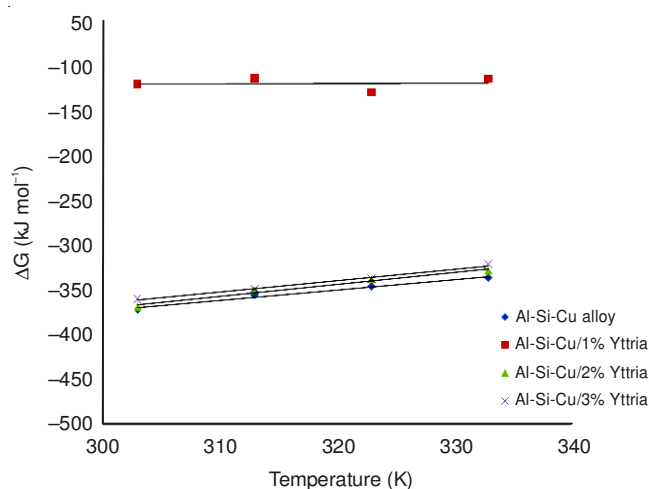

Fig. 2. Variation of ΔG with temperature for Al-Si-Cu/yttria composites in 0.1N NaOH solution

The change in free energy (ΔG) is related to change in the enthalpy (ΔH), the change in the entropy (ΔS) of the corrosion reaction at a constant temperature (T), by the equation:

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

Table-3 gives values of the thermodynamic quantities for the corrosion of Al-Si-Cu/yttria in 0.1N NaOH solution at four temperatures.

When a metal undergoes corrosion there is a change in Gibbs free energy (ΔG) of the system, which is equal to the work, associated with the corrosion reaction.

The performance of such a work is accompanied usually by a decrease in the Gibbs free energy of system. The results in Table-3 indicate that the spontaneous decreases in the composites material compared with base alloy, the results may be summarized in the following:

$-\Delta G$: Al-Si-Cu/1%yttria < Al-Si-Cu/3%yttria <
Al-Si-Cu/2%yttria < base alloy

TABLE-3
THERMODYNAMIC QUANTITIES FOR Al-Si-Cu/Ytrria COMPOSITES IN 0.1 N NaOH SOLUTION AT FOUR TEMPERATURES

Specimens	T (K)	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔH (kJ mol^{-1})
Al-Si-Cu alloy	303	-371.718		355.1722
	313	-354.638	1.172186	366.8941
	323	-345.460		378.6159
	333	-335.704		390.3378
Al-Si-Cu/1% Y_2O_3	303	-118.087		8.77185
	313	-111.747	0.02895	9.06135
	323	-128.249		9.35085
	333	-156.620		9.64035
Al-Si-Cu/2% Y_2O_3	303	-368.302		401.3999
	313	-349.050	1.324752	414.6474
	323	-337.644		427.8949
	333	-327.946		441.1424
Al-Si-Cu/3% Y_2O_3	303	-359.704		391.9263
	313	-348.558	1.293486	404.8611
	323	-336.804		417.7960
	333	-320.505		430.7308

This sequence indicates that Al-Si-Cu/1%yttria gives less spontaneous corrosion that good agreement with the results of electrochemical study.

Values of ΔS reflect the change in the order and orientation of the solvent molecules around the hydrated metal ions in the corrosion medium when metal atoms were corroded and subsequently hydrated in the solution. Values of ΔS were positive due to negativity of ΔG, this suggests a lower order in the solvated states of the metal ions as compared with the state of metal atoms in the crystal lattice of the corroding electrodes.

Table-3 indicates that ΔS values follow the sequence:

ΔS : Al-Si-Cu/1%yttria < base alloy < Al-Si-Cu/3%yttria < Al-Si-Cu/2%yttria

This result shows that the most order in solvated states obtained in corrosion of Al-Si-Cu/1% yttria which has lowest corrosion rate values.

Values of the enthalpy of corrosion (ΔH) reflect the enthalpy changes associated with the corrosion reaction and ranged from negative to positive values indicating exothermic or endothermic nature of corrosion reaction. The value of (ΔH) may be estimated from such relation as:

$$\Delta H = S + I_M - W_{M^{Z+}} - (\tfrac{1}{2}D_{H_2} + I_H - W_{H^+}) \quad \ldots\ldots(4)$$

where S is the heat of sublimation of the metal M; I_M is the ionization potential of the metal M; $W_{M^{Z+}}$ is the heat hydration of M^{Z+} ions in the solution; D_{H_2} is the bond-dissociation energy of the hydrogen molecules; I_H is the ionization potential of hydrogen atoms; W_{H^+} is the heat of hydrogen of hydrogen ions.

When comparing the enthalpy changes accompanying various metals in the same medium, the factors affecting the values of ΔH should be confined to:

$$S + I_M - W_{M^{Z+}} \quad \ldots.(5)$$

These three quantities play an important role in deciding the extent of variation in ΔH values for the metal and for its alloys in the same medium.

Table-3 indicates that ΔH values were positive for corrosion of composite materials and arranged in the following sequence:

ΔH: Al-Si-Cu/1%yttria < base alloy < Al-Si-Cu/3%yttria < Al-Si-Cu/2%yttria

This means that Al-Si-Cu/1%yttria need lowest heat due to lowest corrosion and don't need to heat for debonding.

Kinetic of corrosion: The increasing values of (i_{corr}) with a temperature follow Arrhenius equation, it is reasonable as:

$$i_{corr} = A\exp(-E_a/RT) \quad \ldots\ldots(6)$$

where A and E_a are the pre-exponential factor and energy of activation of the corrosion process, respectively.

Values of E_a were derived from the slopes of the (log i_{corr}) *versus* (1/T) linear plots as in Fig. (3), while those of (A) were obtained from the intercepts of the plots at (1/T = zero). Table-4 shows the results of activation energy (E_a) and (log A) for corrosion of composites. The highest activation energy was for Al-Si-Cu/1% yttria, this means that this composite need most energy to surmount the energy barrier.

The relationship existed between values of the activation energy (E_a) and logarithm of pre-exponential factor (log A)

TABLE-4
VALUES OF ACTIVATION ENERGY (E_a) AND PRE EXPONENTIAL FACTORS (A) FOR Al-Si-Cu/Yttria COMPOSITES IN 0.1N NaOH SOLUTION AT FOUR TEMPERATURES

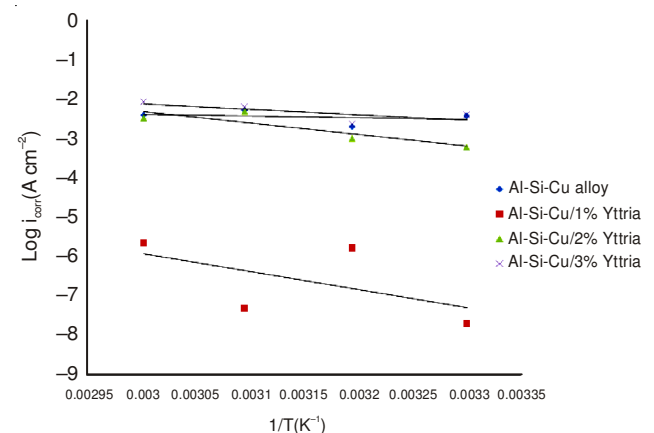| Specimens	E_a (kJ mol^{-1})	Log A
Al-Si-Cu alloy	3.877818	-0.983
Al-Si-Cu/1% Y$_2$O$_3$	38.52732	+7.992
Al-Si-Cu/2% Y$_2$O$_3$	24.56841	+6.555
Al-Si-Cu/3% Y$_2$O$_3$	11.59195	+2.060

Fig. 3. Arrhenius plots for corrosion of Al-Si-Cu/ yttria composites in 0.1 N NaOH solution

for different material suggesting the operation of a compensation effect in kinetics of corrosion. This suggests that the corrosion reaction proceeds on surface sites, which were associated with different energies of activation. The corrosion reaction is assumed to start on sites with lower (E_a) and (log A) values first, spending thereafter to those sites on which (E_a) and (log A) were higher.

The results of Fig. (4) indicate the existence of a linear relationship between the values of (log A) and the corresponding values of (E_a) which may be expressed as[12]:

$$\log A = mE_a + I \quad \ldots\ldots(7)$$

where m and I are, respectively the slope and intercept of the plots, such a behavior is referred to as "compensation effect" which describes the kinetics of a great number of catalytic and tarnishing reactions on metals[13,14].
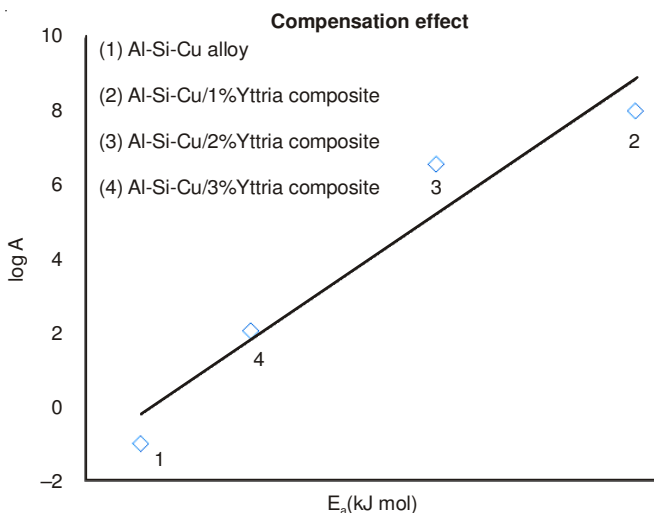

Fig. 4. log A values plotted against E_a for Al-Si-Cu/yttria composites in 0.1N NaOH solution

Eqn. (7) indicates that the simultaneous increases or decreases in (E_a) and $(\log A)$ for a system tend to compensate from the standpoint of the reaction rate.

A number of interpretations[15] have been offered for the phenomenon of the compensation effect in surface reaction, among which the effect could be ascribed to the presence of energetically heterogeneous reaction solution. A decrease in (E_a) at constant $(\log A)$ implies a higher rate, while an increase in (E_a) at constant $(\log A)$ implies a lower rate. Simultaneous increase in (E_a) and $(\log A)$ therefore tend to compensate from the standpoint of the corrosion rate. When such compensation operates, it is possible for striking variations in (E_a) and $(\log A)$ through a series of surface sites on a metal or an alloy to yield only a small variation in reactivity.

Conclusion

Study the corrosion behavior of Al-Si-Cu/Y_2O_3 composites in 0.1 N NaOH at four temperatures 303, 313, 323 and 333 K was carried out to estimate the corrosion resistance of these composites compared with Al-Si-Cu alloy. The data of corrosion measurements show that Al-Si-Cu/1%Y_2O_3 more resistance than Al-Si-Cu/2%Y_2O_3, Al-Si-Cu/3%Y_2O_3 and base alloy due to the inhomogenous structure of an metal matrix composite which must be considered in designing a corrosion protection system. Surface treatments applied to metal matrix composites will encounter reinforcement particles that may disrupt any protective coatings and hinder effectiveness of passive coatings. Thermodynamic and kinetic study was achieved to evaluation the exactly role of yttria on the corrosion behavior. The lowest negativity of free energy change was for Al-Si-Cu/1%Y_2O_3, also the lowest value of ΔS was for Al-Si-Cu/1%Y_2O_3 indicating the most order in solvated states. The highest activation energy was for Al-Si-Cu/1%Y_2O_3 which means the required more energy to surmount the energy barrier for corrosion take place.

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