Study the Corrosion and Wear properties of Al-12.5Si-3.5Cu alloy in the acidic and basic environments

دراسة التآكل وخاصية البلى لسبيكة المنيوم-12.5 سليكون- نحاس
في وسط حامضي وقاعدي

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Abstract

This research involves study the polarization behavior of Al-Si-Cu alloy in acidic and basic medium (0.1 M HCl & 2.5×10^{-3} M NaOH) by potentiostatic method and the values of Tafel slopes (b) ,corrosion rate (R_{mpy}) and the polarization resistances (Rp) were interpreted. Wear properties for this alloy in acidic and basic medium were measured at different sliding speed and different applied load and gives same results that observed in the corrosion behavior.

Keywords: Al-Si-Cu alloy ,Corrosion behavior in different media, Wear property of Al-Si-Cu alloy.

الخلاصة:

يتضمن هذا البحث دراسة السلوك ألاستقطابي لسبيكة (ألمنيوم-سليكون-نحاس) في حامض الهيدروكلوريك بتركيز 0.1 مول ومحلول هيدروكسيد الصوديوم بتركيز 2.5×10^{-3} مول بطريقة المجهاد الساكن حيث تم تفسير قيم ميول تافل ومعدل التآكل (R_{mpy}) وقيم مقاومة الاستقطاب.
تم قياس خاصية البلى لهذه السبيكة في الوسط الحامضي والقاعدي عند سرع انزلاق مختلفة وقيم مختلفة من الحمل المسلط وأعطت قياسات البلى نفس النتيجة الملاحظة في سلوك التآكل.

1- Introduction

Al-Si-Cu alloys are important as one of the aluminium casting alloys, mainly because of high fluidity, low shrinkage in casting, high corrosion resistance. Because of their applicabe importance, there is necessity to study their corrosion resistance and their mechanical properties. Corrosion normally occurs at a rate determined by the equilibrium between opposing electrochemical reactions (anodic and cathodic reaction)[1].Despite the excellent mechanical and physical properties of the Al-Si-Cu hypereutectic alloy, their corrosion resistance in aggressive environments is not yet well known. Some work has been carried out to evaluate the corrosion resistance of this alloy in alcoholic fuels [2,3]. It has been suggested that corrosion of Al-Si-Cu alloy starts at the matrix/precipitate interface [4]. Ferreira S.G., and Ensiger M.McCaffery studied the pitting corrosion resistance of 2024-T351 alloy in 3 wt% NaCl solution and for Al 2014 alloy in 0.1 M NaCl solution [5,6]. Paul.H. Chong and Thompson G. E studied the polarization behavior of Al-Si alloy in 10 wt% HCl ,5 wt% NaCl solutions, they shows that the improvement in the corrosion and wear resistance using laser surface melting (LSM) is significant potential for improving surface properties [7].

Wear is one of three most commonly encountered industrial problems,leading to the replacement of components and assemblies in engineering system, the others being fatigue and corrosion[1].

Taken to study a trajbological characteristics of the aluminum alloys, particularly aluminum-silicon alloys the largest space between the all other ferrous and non-ferrous alloys. Because of the distinctive properties of Al-Si-Cu alloys, researchers becomes introsted to study the properties of wear resistance of these alloys[8].

The mechanism of wear in those alloys involves the damage occurring on surface layers and subsurfaces, the deformation mechanism for this layer leads to break the sconed phase of more hardness (repersent silicon) to a small particles, which distribute by regular shape in subsurface region [9]. The purpose of this study is to investigate the corrosion behavior of Al-Si-Cu alloy in acidic and basic media, and its behavior effect on wear resistance.

2- Experimental Part
2-1 Corrosion Test
In this work, the Al-Si-Cu alloy was prepared by metallic cast with rod shape ,the chemical composion of alloy was(*Si-12.587, Cu -3.88, Mg*-1.168, *Fe*-0.857, *Zn-0.683*, *Ni-0.513,Mn-0.335*) which obtained by chemical analysis in Naser company for mechanical industries Baghdad-Iraq.

Al-Si-Cu alloy was cut into cylindercal shape of (1.7 cm) diameter,and electrode was formed by pressing a copper wire into a hole on one side and the other side was isolated with an epoxy resin.The open side was polished mechanically to a mirror finish ,rinsed in distilled water and stored in a desiccators.

Polarization experiments were performed by using a WENKING Mlab multi channels potentiostat and SCI-M lab corrosion measuring system from Bank Electroniks-Intelligent controls Gmbh, with electrochemical standard cell with provision for working electrode (Al-Si-Cu alloy), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with as saturated calomel electrode (SCE reference electrode).

The basic solutions of corrosion test were 0.1 M HCl and 2.5×10^{-3} M NaOH which are corresponding to pH values 1 and 11.4 respectively. This work performed at three different temperturesin the range of (20-40 °C).

Electrochemical measurements were performed with a potentiostat at a scan rate 3 $mV.sec^{-1}$. Polarization experiments were started at potential below its open circuit potential E_{ocp} (-491,-379 mV in acidic and basic media) by 250 mV and ended above it also by 250 mV.

The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) , corrosion current density (i_{corr}), cathodic and anodic Tafel slopes, in addition to calculate the corrosion rate in milli-inches per year(10) .

$$Corr.\ Rate(R_{mpy})=0.13\ i_{corr} \times e/\rho \qquad …….(1)$$

where (R_{mpy}) is the rate of corrosion in mil per year, corrosion current density (i_{corr}), (e) is the equivalent weight of the alloy and (ρ) is its density (27.68 gm/cm^3).

2-2 Wear Test Equipment

Pin-on-disc machine which belong to, tribology laboratory, department of production engineering and metallurgy was used to carry out the wear test experiment.

Wear test specimens were cut cylindrical shape specimen 10 mm in diameter and 15 mm in lenghth .the specimen were machined on a lathe, and the two end surface of each specimen were ground with (120,320,600,1000) grade silicon carbid paper. The ground surface were polished with 5 μm and 0.03 μm alumina slurry respectively.

A carbon steel disc was used as a counter face with a hardness values of 428 Hv. The disc rotational speed was 420 rpm, with a linear sliding of (1.14,2.73,3.08).

The linear speed was calculated as follows[11]:

$$V= \pi Ds\ N\ /1000 \times 60 \qquad ......(2)$$

where V is a linear sliding speed (m/sec), D_s is sliding circle diameter (mm), and N is disc rotational speed (420 rpm).

Loading was carried out normally by putting suitable weight on the specimen holder weighting (5, 10, and 15 gm).

Wear rate calculated from weight loss measurement by using sensitive balance with an accuracy of $\pm$ 0.0001 gm. Mettle type AE 200, the formula used to convert, the weight loss into rate is(11):

$$\textit{Wear rate (weight loss)} = \Delta W/S \qquad .....(3)$$
$$\Delta W = W_1 - W_2 \qquad .....(4)$$

where ΔW: weight loss of the sample (gm), W_1 : sample weight before the wear test, and W_2: sample weight after the wear test.The total sliding distance S (cm) was calculated as:

$$S = V\ x\ t \qquad .....(5)$$

where t: running time (30 min) at each test.

3- Results and discussion

3-1 Study of Corrosion

3-1-1 Polarization behavior

Polarization behavior of Al-Si-Cu alloy in (0.1 M HCl) solution (pH=1) which is shown in Figure (1) consists mainly of two clear regions, **(i)** cathodic Tafel region (abc section) and **(ii)** anodic Tafel region (cde section) curves and the results of corrosion parameters were listed in table (1).
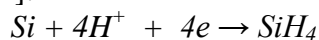
The cathodic region represents the reduction reactions that occur at cathode which include:

$$2H^+ + 2e \rightarrow H_2$$

and

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$
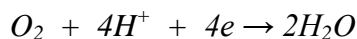
In addition to the above reaction[12]:

$$Si + 4H^+ + 4e \rightarrow SiH_4$$
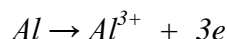
Moreover, the active dissolution of aluminium (matrix) can be partly balanced by last reaction.

The anodic region represents the dissolution of aluminium along (cde) section forming initially both Al^{3+} and Al^+ ions, the univalent ion (Al^+) then reduces water to forms trivalent (Al^{3+}) in accord with [12 ,13]:

$$Al \rightarrow Al^{3+} + 3e$$
$$Al \rightarrow Al^+ + 1e$$
$$Al^+ + 2H_2O \rightarrow Al^{3+} + H_2 + 2OH^-$$
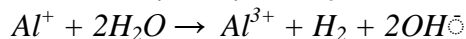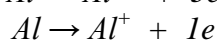
Hence, when Al is anodized some H_2 evolution are also expected at anode. H_2 evolution is also explained by the increased local corrosion during anodic dissolution.

Hamilta de Oliveira and others [14] observed that the electrochemical process of Al-Si-Cu alloy occurring at high rate is probably due to charge transfer processes associated with reduction of Si to form silicon hydride (at pH=3.3) and the anodic dissolution of the matrix can be balanced by the hydrogen evolution reaction on the intermetallic particles, and by reduction of Si and O_2.

While the polarization behavior of same alloy in (2.5×10^{-3}M) NaOH solution (pH=11.4) which is shown in Figure (2) and table (2) is consisted of three regions: **(i)** cathodic Tafel region(abc section) which represented by migration of electrons through the surface oxide films and subsequented interaction of those electrons with hydrogen ions as dissolved oxygen at film/solution interface and the reaction which occurs at this region is:

$$O_2 + 4e + 2H_2O \rightarrow 4OH^-$$
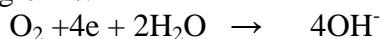
(ii) the weak passivity region(cde section) which due to formation of aluminium oxide (Al_2O_3) on the surface,where thermodynamically aluminium an unstable metal and reacts spontaneously with oxygen to give alumiium oxide according with [15]:
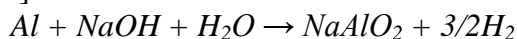
$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 800 \, Kcal$$
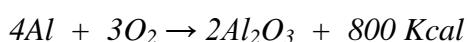
Finally **(iii)** the transpassive region along (fgh section) where the breakdown of the protective film would occur.The initial reaction in aqueous solution of sodium hydroxide may be represented as[16]:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2$$

This is then followed by the reaction

$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O$$
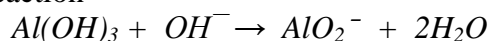
The net reaction thus being [17]

$$Al + NaOH + H_2O \rightarrow NaAlO_2 + 3/2H_2$$

3-1-2 Tafel slopes (b)

The hydrogen evolution reaction (h.e.r) has been the most widely studied electrode reaction. However, it is important to note that the discharge step involves adsorption of hydrogen atoms at available sites on the metal surface, and is followed by desorption that may be either a chemical step, or an electrochemical step in which further charge transfer occurs [12].

A value of the cathodic Tafel slope of (-0.120 mV.decade^{-1}) may be diagnostic of a proton discharge-chemical desorption mechanism in which the proton discharge is the rate-determining step (r.d.s).

On the other hand, the electrochemical desorption step is far more complex since it involves reaction between an adsorbed H atom, a hydrated proton H_3O^+ and an electron, and for desorption to occur the proton must discharge onto a hydrogen atom adsorbed on the metal surface [12].

If the discharge process is followed by rate-determining step involving chemical desorption(C.D.), the expected value of the cathodic tafel slope should be (-30 mV.decade^{-1}).

Under these circumstances the probability of collision well is low unless the coverage θ_H is high. When electrochemical desorption becomes the rate-determining step for (h.e.r) on the cathode, the expected value of b_c will be (-50 mV.decade^{-1}).

The results in the table (1) and (2) indicates that the cathodic Tafel slope values close to the values which indicate that the rate- determining step involving chemical desorption .

3-1-3 Polarization resistance (R_p)

The term (R_p) corresponds to the resistance (R) of the metal/solution interface to charge – transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed.

The polarization resistance, R_p, of according electrode is defined as the slope of a potential (E) – current density (i) plot of the corrosion potential (E_{corr}) as :

$$R_p = \left(\frac{\partial \eta}{\partial i}\right)_{T,C} \; at\, \eta \to 0 \qquad ......(6)$$

where $\eta = E - E_{corr}$.

From the polarization resistance, R_p the corrosion current density (c.d) i_{corr} can be calculated as [18]:

$$i_{corr} = \frac{\beta}{R_p} \qquad ......(7)$$

Where β is a combination of the anodic and cathodic Tafel slopes (b_a, b_c) as :

$$\beta = \frac{b_a b_c}{2.303(b_a + b_c)} \qquad ......(8)$$

For the general case, by inserting equation (7) into equation (8) one obtains the so – called the Stern – Geary equation[13,14]:

$$R_p = \frac{b_a b_c}{2.303(b_a + b_c)i_{corr}} \qquad ......(9)$$

The values of R_p have been calculated from eq.(9), which are presented in tables (1) and (3). These results indicates that the R_p of Al-Si-Cu alloy in 2.5×10^{-3} M NaOH solution more than that observed in 0.1 M HCl solution. This mean that the acidic medium more corrosive for Al-Si-Cu alloy.

3-2 Wear Property

3-2-1 Effect of Sliding Speed

The results of wear test of Al-Si-Cu alloy before and after chemical treatment at different sliding speeds and constant applied load (10 gm) were shown in Figure(3) which indicates that the chemical treatment with (0.1 M HCl and 2.5×10^{-3} M NaOH) increases the rate of wear.

As sliding speed increase, the wear resistance decrease untill it reachs aspeed at which the time for contact surface is very shart enough to increase the wear resistance again also high sliding speeds may cause the elemination of surface roughness because friction may take off the drips between the contact surfaces.

The samples of Al-Si-Cu alloy which immersed in the acidic solution gives less resistance for wear than that which immersed in the basic solution and the following sequence indicates this behavior and the results were listed in table (3):

Wear Resistance: samples without $>$ *samples immersed* $>$ *samples immersed*

$$\begin{bmatrix} treatment \end{bmatrix} \quad \begin{bmatrix} in\ basic\ medium \end{bmatrix} \begin{bmatrix} in\ acidic\ medium \end{bmatrix}$$

3-2-2 Effect of Applied Load

   Table (4) shows the applied loads effect increaced on the wear resistance for samples which immersed acidic and basic media compared with as received. The increasing of applied loads leads to increase the rate of wear because of plastic deformation of the protrusions which present in the touching surfaces and then lead to remove the particular top of protrusions.

   Figure (4) shows the effect of different applied loads in the wear resistance for Al-Si-Cu alloy before and after the chemical treatment which indicates that the rate of wear after treatment by acidic and basic media more than that of as received .

   Results had revealed that within the first few minutes of running a dark-coloured band appeared on the disc, consisting of loose particles which did not stick to the disk.

   At higher loads, increasing fraction of the particles and increase the plastic deformation of bulges which presence on the interaction surfaces lead to partial remove of drips the bulges which affect on the weight of the tested samples [7]. The increasing of loads and continoued sliding and remove the oxide layer from the surface and stronger metallic adhesivity which required higher force to eliminate the metallic boundaries of alloy crystalls and lead to increase the rate of wear resistance.

Table (1) : *Values of E_{corr} corrosion potentials, corrosion current densities i_{corr}, cathodic and anodic Tafel slopes b_c and b_a ,polarization resistances R_p and corrosion Rate(mpy) for the polarization of Al-Si-Cu alloy in 0.1 M HCl at three temperatures.*

T(•C)	Corrosion		Tafl slopes (mV.decade^{-1})		$R_p/10^{-9}$ (mΩ.cm^{-2})	$R_{mpy}/10^{-9}$
	-E_{corr} (V)	i_{corr} (µA.cm^{-2})	-b_c	+b_a		
20	308.2	28.01	16.8	17.1	0.132	3.638
30	310.4	29.60	17.2	17.3	0.126	3.844
40	315.0	31.44	17.5	17.4	0.120	4.083

Table (2) : *Values of E_{corr} corrosion potentials, corrosion current densities i_{corr}, cathodic and anodic Tafel slopes b_c and b_a, cathodic , polarization resistances R_p and corrosion Rate(mpy) for the polarization of Al-Si-Cu alloy in 2.5x10^{-3} M NaOH at three temperatures.*

T(•C)	Corrosion		Tafl slopes (mV.decade^{-1})		$R_p/10^{-9}$ (Ω.cm^{-2})	$R_{mpy}/10^{-9}$
	-E_{corr} (V)	i_{corr} (µA.cm^{-2})	-b_c	+b_a		
20	516.5	23.49	10.7	48.5	0.162	3.245
30	518.0	26.18	11.8	50.7	0.158	3.399
40	518.9	27.30	11.2	51.4	0.156	3.545

**Table (3) :** *The results of wear rate(×10⁻⁶) testing for Al-Si-Cu alloy at different sliding speed.*

Samples	Sliding Speed		
	1.14	*2.73*	*3.08*
Without treatment	*0.853*	*0.826*	*0.805*
Immersed in basic medium	*1.573*	*1.198*	*0.897*
Immersed in acidic medium	*1.980*	*1.782*	*1.190*

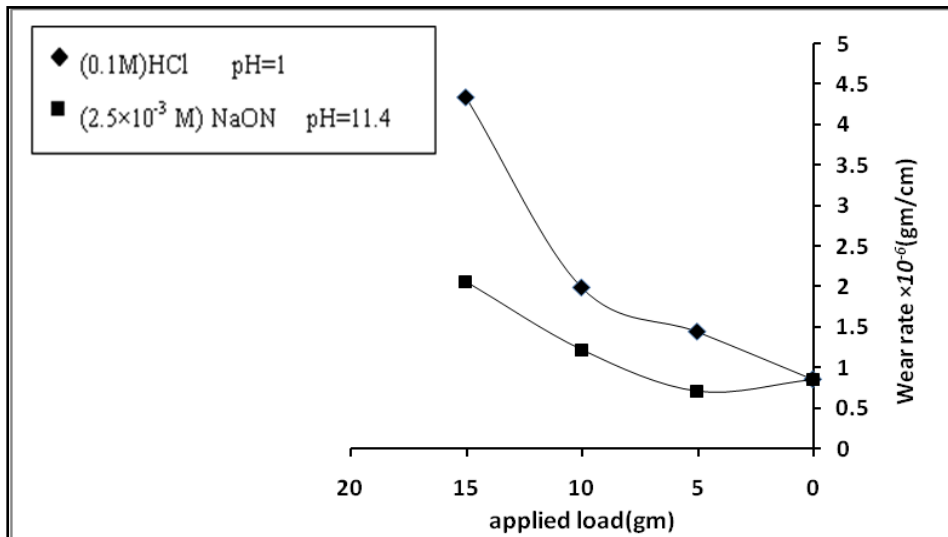**Table (4) :** *The results of wear rate(×10⁻⁶)testing for Al-Si-Cu alloy at different applied loads.*

| Samples	Applied Loads		
	5	*10*	*15*
Without treatment	*0.853*	*0.890*	*0.922*
Immersed in basic medium	*0.965*	*1.220*	*2.056*
Immersed in acidic medium	*1.442*	*1.987*	*4.336*
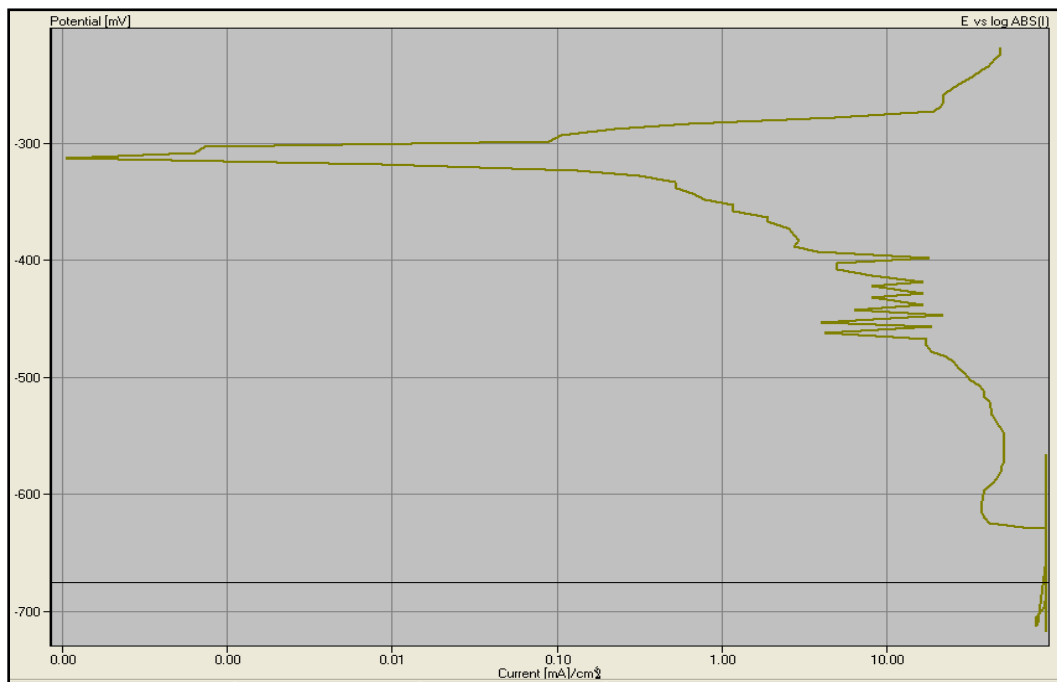
Fig. (1): polarization behavior of Al-Si-Cu alloy in 0.1 M HCl at 30 °C.
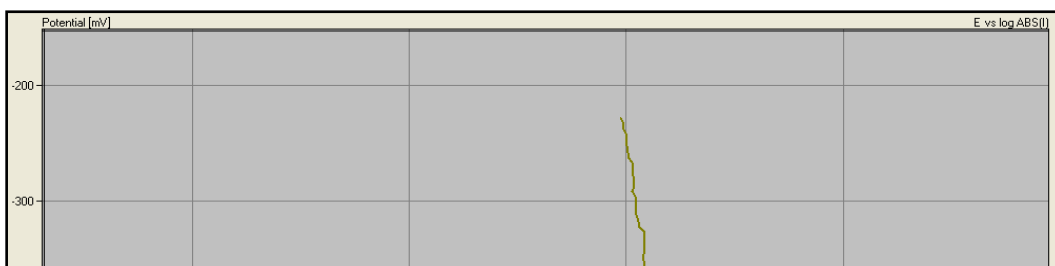
Fig. (2): polarization behavior of Al-Si-Cu alloy in 2.5×10^{-3} M NaOH at 30 °C.

Fig. (7): Effect of sliding speed in the wear test of Al-Si-Cu alloy in the acidic(0.1 M HCl)and basic(2.5×10^{-3} M NaOH) medium.
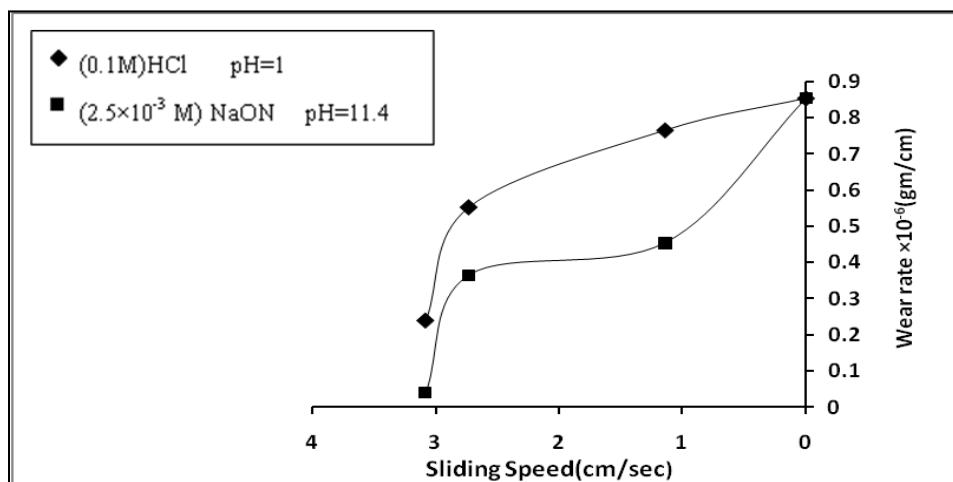
Fig. (7): Effect of applied load in wear test of Al-Si-Cu alloy in the acidic(0.1 M HCl)and basic(2.5×10^{-3} M NaOH) medium.

4- Conclusion:

1-Polarization behavior of Al-Si-Cu alloy in (0.1 M HCl) which mainly consisted of two regions, cathodic and anodic Tafel region. While in (2.5×10^{-3} M) NaOH which was consist of three regions cathodic Tafel region, the week passivity region and transpassive region.

2- Polarization resistance (R_p) of Al-Si-Cu alloy in 2.5×10^{-3} M NaOH solution more than that observed in 0.1 M HCl solution. which means that the acidic media is more corrosive for Al-Si-Cu alloy.

3- Wear Resistance for samples which immersed in the acidic and basic solution following :

Wear Resistance: $\begin{bmatrix} samples\ without \\ treatment \end{bmatrix} > \begin{bmatrix} samples\ immersed \\ in\ basic\ medium \end{bmatrix} > \begin{bmatrix} samples\ immersed \\ in\ acidic\ medium \end{bmatrix}$

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