Corrosion Protection Study for some alloys in Saline water using Sputtering Deposition by Silicon Carbide as protective coating

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Abstract : Thin films of silicon carbide were grown on three types of alloys (C.S1045, C.S1137, Al 5083) substrates using DC glow discharge sputtering technique. The morphological analysis was carried out using atomic force microscopy (AFM). The corrosion protection efficiency inspection of each specimen in saline water (3.5%NaCl) at different temperatures (298, 308, 318 & 328K) have been evaluated using potentiostatic techniques with three electrodes cell. the results obtained showed that the rate of corrosion of all alloys increased with increasing the temperatures from 25^oC to 55^oC, the results showed that deposition of SiC caused to protection efficiency reached 92.14 % for C.S1045, 96.27% for C.S1137 and 89.91% for Al 5083 respectively in 25^oC. Change in the enthalpy of activation & entropy were evaluated. Apparent energies of activation have been calculated for the corrosion process of uncoated and coated alloys by DC glow discharge sputtering technique in saline water (3.5% NaCl).

KEYWORDS: Carbon steel, Corrosion , Sputtering , SiC , Polarization, Aluminum.

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1. Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment. Corrosion is a serious environmental problem in the oil, fertilizer, metallurgical and other industries[1] . Carbon steel and Aluminum alloys are the most commonly used in corrosive environments due to proper resistance to general corrosion. However, due to auto passivation properties, they undergo local corrosion in chloride ion containing medias[2]. Silicon carbide SiC films have been the subject of intensive research in the past few years because of their combination of unique physicochemical, electrical and mechanical properties[3,4]. Among many other possible technological applications SiC is an interesting material to be used as a protective coating to improve the lifetime or the performance of metallic substrates when exposed to aggressive environments[5]. One acceptable explanation for these good properties could be the very strong covalent bonding between silicon and carbon and its tetrahedral coordination[6]. However, it is well known that two main requirements must be fulfilled in order to achieve a remarkable effect by a protective layer. These are a strong adhesion to the substrate and a low density of pores and cracks. Aiming to produce better films in terms of structure and adhesion up to now, studies on SiC films characterized and modified their structure under a wide range of deposition techniques and deposition parameters[7]. In particular one can find applications for SiC in many different areas, like coatings against corrosion covering fuel particles used in a high-temperature gas-cooled

reactors[8], protective layers to be used at high temperatures[9] , or corrosion resistant coatings in

biological media on metal implants[10] .

2. Materials and Methods
2.1. Materials

In this study three alloys are used a carbon steel (1045, 1137) and Aluminum alloy (5083) with a chemical composition are given in table (1). The samples of alloys were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinse with distilled water, degreased in acetone, washed again with distilled water and then dried at room temperature before used synthesized seawater. The seawater solution was prepared by dissolved 35g NaCl in 1L distilled water.

Table (1) Chemical materials composition for CS1137, CS1045, Al5083 used in this study.

Grade	%C	%Si	%Mn	%S	%P	%Ni	%Cr
C1137	0.32-0.39	<0.4	1.35-1.65	0.08-0.13	<0.04	0.11	0.16

Grade	%C	%Si	%Mn	%S	%P	%Ni	%Cr
C1045	0.43-0.50	<0.4	0.5-0.8	<0.04	<0.04	0.4	<0.4

Grade	%Mg	%Si	%Mn	%Fe	%Zn	%Cu	%Cr	%Ti	Others
Al5083	4.0-4.9	<0.4	0.4-1.0	<0.4	<0.1	<0.1	0.05-0.25	0.05-0.25	<0.05

2.2. Experimental procedures

Workpieces were placed in the sputtering unit , which operated with the D.C. bias voltage 2500 V at room temperature. sputtering unit used in this study, consists of power supply, a gas mixing device and a stainless steel vacuum chamber as shown in Fig.1. The sputtering was performed in an pure argon. Sputtering cycle was carried out by evacuation of the chamber and then followed by initialization of the glow. Sputtering process were illustrated in Fig.2. and the parameters which used to achieve sputtering process were illustrated in table (2).
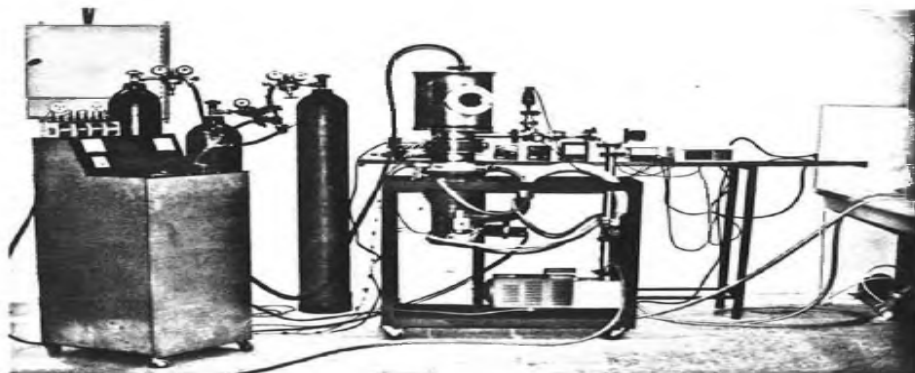

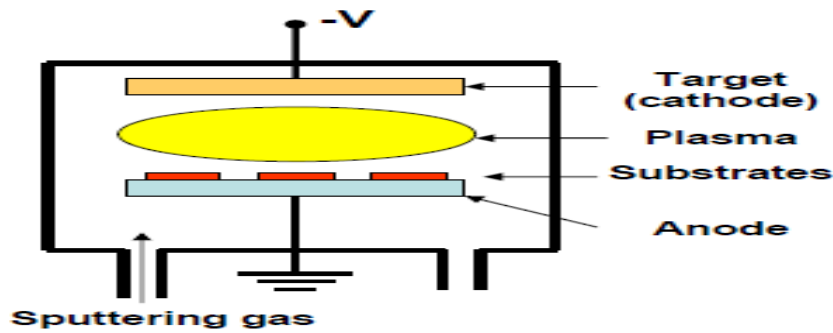**Fig.1. Illustrate DCglow discharge unit were used for sputtering process.**

Fig.2. illustrated sputtering process.

Table (2) parameters used for sputtering process

Sputtering unit	Voltage (V)	Time(hr)	Pressure	Temperature K
DC glow discharge	2500	3.00	0.3mbar	Room temp

2.3. Electrochemical Measurements

The experiments were performed in a classical three-electrode electrochemical cell. All alloys with (0.5 mm) thickness and (2.5)cm in diameter was used as the working electrode, platinum electrode as a counter electrode and silver-silver chloride electrode as a reference electrode. Prior to each experiment, the working electrode surface was polished with emery paper. The electrochemical system consists of potentiostate device (Germany, Mlab 2000), corrosion cell (1000 ml) volume and the three electrodes with a computer and MLabSci software were used for data acquisition and analysis (Srimathi, et al.2010). To determine the open circuit potential (OCP) of the specimens, the specimens have been immersed in the synthesized sea water (3.5% NaCl) at temperatures range (298-328)Kto reach the steady state between the specimen's material and electrolytic solution. The change in potential according to the current were determined during (15min), and time step equal to 60 seconds for each specimens. After reaching the steady state condition, the determined potential is known as corrosion potential or free potential or open circuit potential.

3. Results and discussion
3.1. Potentiostatic polarization
3.1.1.Potentiostatic polarization studies for uncoated alloys

The potentiostatic polarization curves for uncoated alloys in 3.5% NaCl solution at temperatures range (298-328)K are shown in figures (3,4,5). The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (ba) and cathodic Tafel slope (bc) deduced from the curves are given in tables (3,4,5). The corrosion current density values increase from (113.54)µA/cm^2 at 298K to (201.52)µA/cm^2 at 328K for C.S(1045), from (68.4)µA/cm^2 at 298K to (173.4)µA/cm$_2$ at 328K for C.S(1137) and from (16.36)µA/cm^2 at 298K to (57.08)µA/cm^2 at 328K for Al(5083) alloys. The increase in temperatures lead to increases I_{corr} values, and E_{corr} goes to more negative potential (active direction).

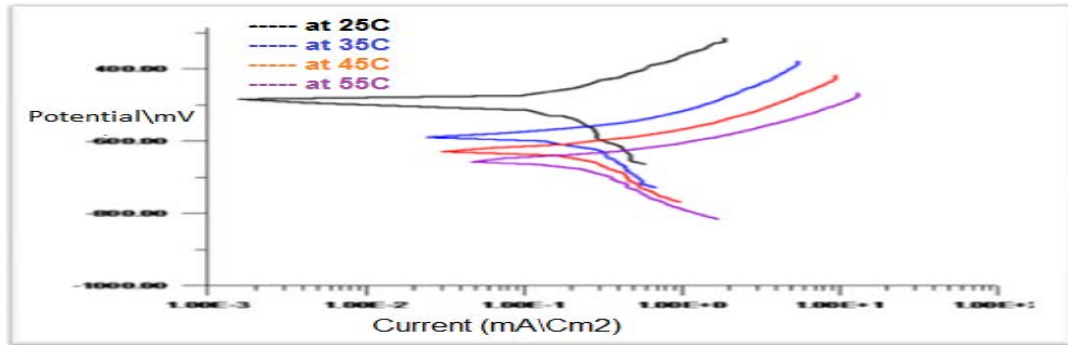$$\eta_{a,c} = b_{a,c} \log(\frac{i_{a,c}}{i_o}) \dots\dots\dots\dots(1)$$

Fig.3. potentiostatic polarization curves for uncoated carbon steel(1045) in 3.5% NaCl solution at the temperatures range (298-328)K.
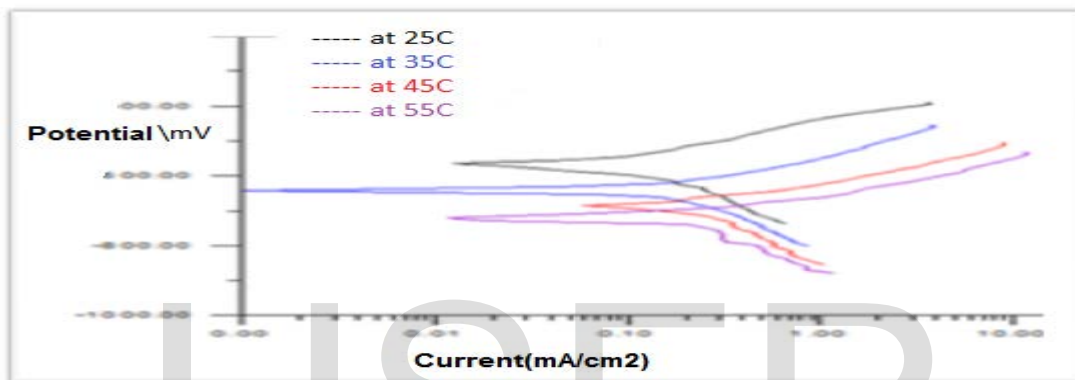

Fig.4. potentiostatic polarization curves for uncoated carbon steel(1137) in 3.5% NaCl solution at the temperatures range (298-328)K.
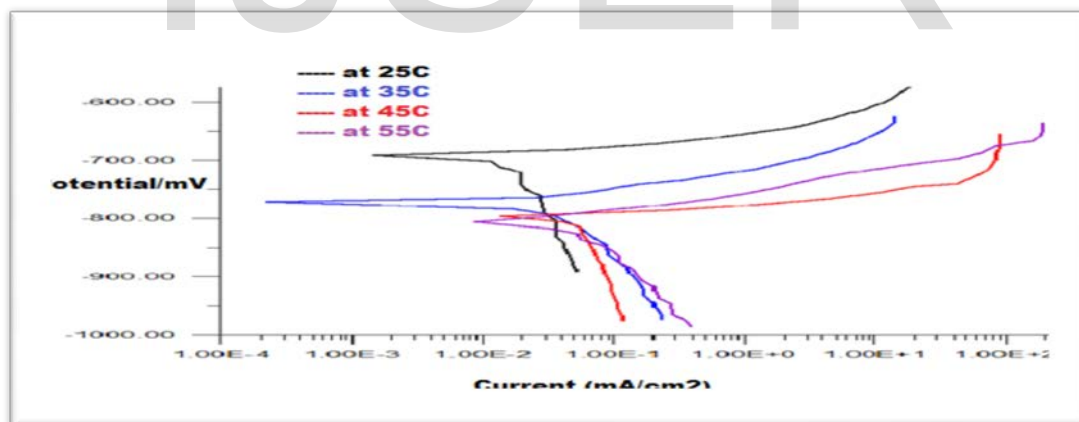

Fig.5. potentiostatic polarization curves for uncoated Aluminum(5083) in 3.5% NaCl solution at the temperatures range (298-328)K.

3.1.2. Potentiostatic polarization studies for coated alloys by SiC Sputtering

The applied SiC Sputtering deposition of carbon steel alloys (1045,1137) and Aluminum alloy (5083) showed different degrees of protection efficiency in different temperatures and with comparisons with the uncoated alloys in saline environment used (3.5%NaCl) show in figures (6,7,8).

The protection efficiency (PE) was obtained from equation (2) at temperature range (298-328)K, as

show in table (3,4,5).

$$\%PE = \frac{(Icorr)uncoated - (Icorr)coated}{(Icorr)uncoated} * 100 \; .... \; (2)$$

Table (3) corrosion kinetic parameters for uncoated and coated C.S (1045) with SiC sputtering in 3.5% NaCl at different temperature range(298-328)K.

Temp./K		Ecorr/ mV	Icorr/μ A .cm^{-2}	bc/mV. Dec^{-1}	ba/Mv. Dec^{-1}	w.l/g. m^{-2}.dl^{-1}	Pentration loss/mm.a^{-1}	Protection efficiencies%	Rp
Uncoated	298	-483.7	113.54	-217.2	114.7	28.4	1.32	----------	286.97
	308	-588.0	157.58	-172.4	86.8	39.4	1.83	---------	159.08
	318	-628.0	173.46	-160.7	80.2	34.4	2.01	---------	133.92
	328	-656.1	201.52	-191.5	74.5	50.4	2.34	---------	115.56
Coated	298	-396.1	8.92	-86.1	86.5	2.23	0.10	92.14%	2100.4
	308	-499.6	25.53	-71.3	62.8	6.38	0.29	83.79%	567.9
	318	-526.9	29.26	-78.7	57.9	7.31	0.34	83.13%	495.0
	328	-550.5	43.65	-99.5	65.7	10.9	0.50	78.33%	393.64

Table (4) corrosion kinetic parameters for uncoated and coated C.S (1137) with with SiC sputtering in 3.5% NaCl at different temperature range(298-328)K.

Temp./K		Ecorr/mV	Icorr/μ A .cm-2	bc/mV. Dec^{-1}	ba/mV. Dec^{-1}	w.l/g . m^{-2}.dl^{-1}	Pentration loss/mm.a^{-1}	Protection efficiencies%	Rp
Uncoated	298	-564.9	68.41	-134.3	100.9	17.1	0.79	----------	365.69
	308	-604.3	114.19	-138.5	88.8	28.5	1.32	----------	205.75
	318	-683.3	160.65	-156.6	80.1	40.2	1.86	----------	143.23
	328	-718.5	173.4	-188.4	76.8	44.2	2.05	----------	136.62
Coated	298	-435.6	2.55	-67.7	52	0.63	0.02	96.27%	5007.9
	308	-507.5	12.3	-73.1	57.6	3.07	0.14	89.22%	1137.2
	318	-526.5	25.73	-117.2	59.7	6.43	0.29	83.98%	667.48
	328	-531	29.57	-110.8	49.6	7.39	0.34	82.94%	503.12

Table (5) corrosion kinetic parameters for uncoated and coated Al (5083) with with SiC sputtering in 3.5% NaCl at different temperature range(298-328)K.

Temp./K		Ecorr/mV	Icorr/μ A .cm^{-2}	bc/mV. Dec^{-1}	ba/mV. Dec^{-1}	w.l/g. m^{-2}.dl^{-1}	Pentration loss/mm.a^{-1}	Protection efficiencies%	Rp
Uncoated	298	-703.7	16.36	-307.7	27.7	1.32	0.178	------	674.47
	308	-768.7	30.23	-175.4	34.2	2.43	0.329	-------	411.08
	318	-801.7	48.60	-313.9	18.7	3.91	0.529	-------	157.68
	328	-806.8	57.08	-215.5	40.4	4.59	0.621	-------	258.80
Coated	298	-672.5	1.65	-282.2	22.7	0.13	0.017	89.91%	5529.01
	308	-697.9	3.49	-199.6	33.9	0.28	0.038	88.45%	3605.04
	318	-757.1	6.36	-196.2	59.4	0.51	0.069	86.90%	3112.96
	328	-801.5	8.61	-167.1	83.4	0.69	0.093	85.00%	2805.67

The corrosion potentials were shifted to more active with temperature increasing. Corrosion

potentials, corrosion current densities determined by extrapolating the cathodic and anodic Tafel

regions, the intersect opposite the corrosion current and corrosion potential. Figures (6,7,8) shows the

polarization curve of alloys coated with SiC Sputtering in different temperatures. In compared with the

polarization curves for uncoated alloys, the corrosion potential for coated alloys goes to more noble
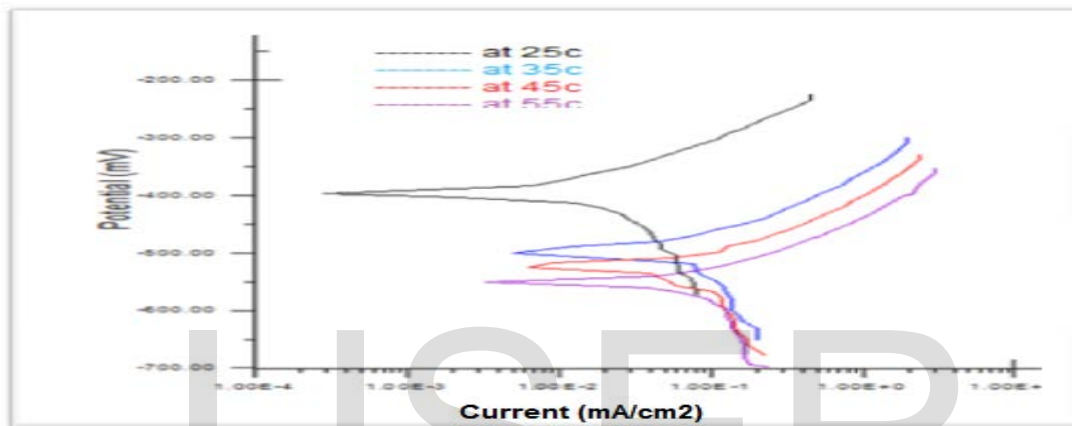
direction.

Figure (6) potentiostatic polarization curves for coated carbon steel(1045) with SiC in 3.5% NaCl solution
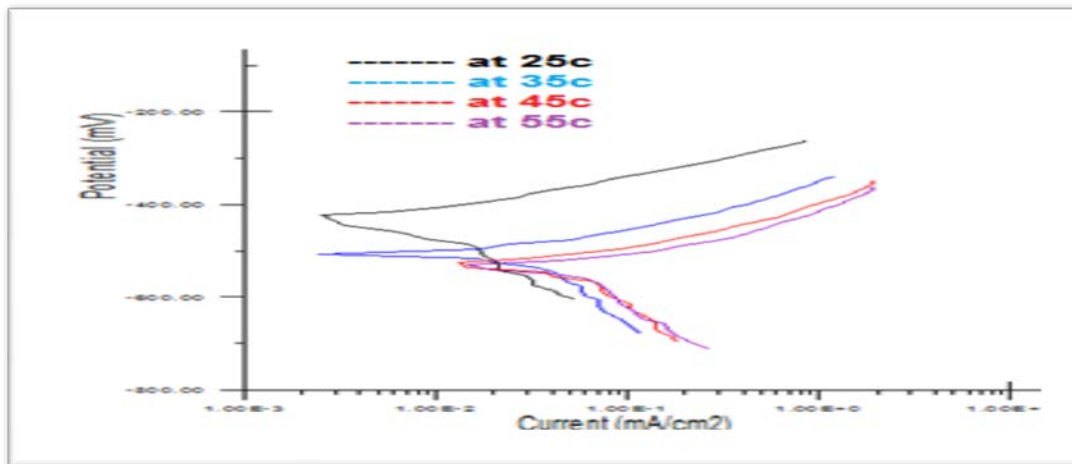at the temperatures range (298-328)K.

Figure (7) potentiostatic polarization curves for coated carbon steel(1137) with SiC in 3.5% NaCl solution
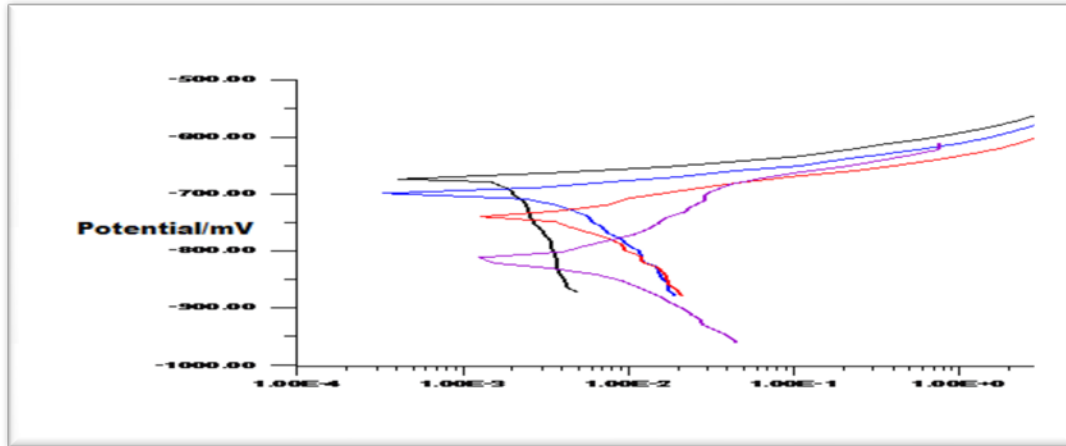at the temperatures range (298-328)K.

Figure (8) potentiostatic polarization curves for coated Aluminum (5083) with SiC in 3.5% NaCl solution at the temperatures range (298-328)K.

Two important trends are evident. Firstly , the corrosion potential shifted toward more passive value in coated with SiC Sputtering, Secondly, the corrosion current densities were significant reduced with coated by SiC Sputtering, where the protection efficiencies (PE) are ranged between (92.14%) at 298K to (78.33%) at 328K for carbon steel(1045), (96.27%) at 298K to (82.94%) at 328K for carbon steel(1137) and (89.91%) at 298K to (85%) at 328K for Aluminum(5083). Tables (3,4,5,) show the corrosion kinetic parameter deduced from these curves.

3.2. Kinetic and Thermodynamic Studies:

Thermodynamic parameters play an important protection mechanism. From Eq. (3) the values of the slopes of these straight lines permit the calculation of the similar Arrhenius activation energy (*Ea*).

$$LogI_{corr} = (-Ea/2.303RT) + Log\ A \dots\dots\dots\dots\dots(3)$$

Where R is the gas constant (R≈8.314 J K^{-1} mol^{-1}), and determine the Arrhenius factor from intercept. Moreover, transition state Eq. (4) were used.

$$Log(I_{corr}/T) = Log\ (R/\ Nh) + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad \dots\dots(4)$$

Where I$_{corr}$ is corrosion current density, T is temperature in K, h is the planks constant (6.626 x 10^{-34} J.s), N is the Avogadro's number (6.023 x 10^{23} mol^{-1}), ΔH* is the enthalpy of activation and ΔS* is the entropy of activation. Straight line were obtained from the plots of log I$_{orr}$/T vs. 1/T, with the slope of

$(-\Delta H^*/2.303R)$ and an intercept of $[\log (R/Nh) + (\Delta S^*/2.303R)]$ from which the values of ΔH^* and ΔS^*, respectively were obtained. ΔH^*, ΔS^*, Ea and A values for C.S & Al alloys before and after sputtering were illustrated in tables (6,7,8).

Table (6) the thermodynamic parameter at different temperatures for uncoated C.S (1045) & Coated with SiC in 3.5% NaCl solution.

	T/ K	E_{corr}/ Mv	I_{corr}/μA. cm^{-2}	LogI_{corr}	Log(I_{corr}/T)	-ΔH*kJ. mol^{-1}	-ΔS* J.mol^{-1}.K^{-1}	Ea/kJ. mol^{-1}	A Molecules. cm^{-2}. S^{-1}
Uncoated	298	-483.7	113.54	2.055	0.419	12.48	231.21	15.11	2.9*10^{28}
	308	-588.0	157.58	2.197	0.291				
	318	-628.0	173.46	2.239	0.263				
	328	-656.1	201.52	2.304	0.211				
Coated	298	-396.1	8.92	0.950	1.523	38.08	295.91	40.70	6.94*10^{31}
	308	-499.6	25.53	1.407	1.081				
	318	-526.9	29.26	1.466	1.036				
	328	-550.5	43.65	1.639	0.875				

Table (7) the thermodynamic parameter at different temperatures for uncoated C.S (1137) & Coated with SiC in 3.5% NaCl solution.

|	T/ K	E_{corr}/ mV	I_{corr}/μA. cm^{-2}	LogI_{corr}	Log(I_{corr}/T)	-ΔH*kJ. mol^{-1}	-ΔS* J.mol^{-1}.K^{-1}	Ea/kJ. mol^{-1}	A Molecules. cm^{-2}. S^{-1}
Uncoated	298	-564.9	68.41	1.835	0.639	23.41	263.47	26.04	1.4*10^{30}
	308	-604.3	114.19	2.057	0.430				
	318	-683.3	160.65	2.205	0.296				
	328	-718.5	173.40	2.239	0.276				
Coated	298	-435.6	2.55	0.406	2.067	64.58	374.18	67.26	8.7*10^{35}
	308	-507.5	12.30	1.089	1.398				
	318	-526.5	25.73	1.410	1.091				
	328	-531.0	29.57	1.470	1.045				

Table (8) the thermodynamic parameter at different temperatures for uncoated Al (5083) & Coated with SiC in 3.5% NaCl solution.

| T/ K		E_{corr}/ mV	I_{corr}/μA. cm^{-2}	LogI_{corr}	Log(I_{corr}/T)	-Δ$\overset{*}{H}$kJ. mol^{-1}	-Δ$\overset{*}{S}$ J.mol^{-1}.K^{-1}	Ea/kJ. mol^{-1}	A Molecules. cm^{-2}. S^{-1}
Uncoated	298	-703.7	16.36	1.21	1.260	31.67	280.29	33.967	$9.458*10^{30}$
	308	-768.7	30.23	1.48	1.008				
	318	-801.7	48.60	1.68	0.815				
	328	-806.8	57.08	1.75	0.759				
Coated	298	-672.5	1.65	0.21	3.151	36.91	262.50	45.129	$8.390*10^{31}$
	308	-697.9	3.49	0.54	2.756				
	318	-757.1	6.36	0.80	2.599				
	328	-801.5	8.61	0.93	2.547				

4. The Surface Morphology AFM studies

Surface morphology of sputtering SiC was investigated through atomic force microscopy (AFM) technique. More uniform grains may lead to more inhibition results, 2D and 3D views. AFM images for all applied layer were estimated in addition to the statically determining the particles size distribution [11]. The results of the Surface Morphology Analysis by AFM, are shown in figure (9). The average roughness of layer SiC was calculated as 57.22 nm.
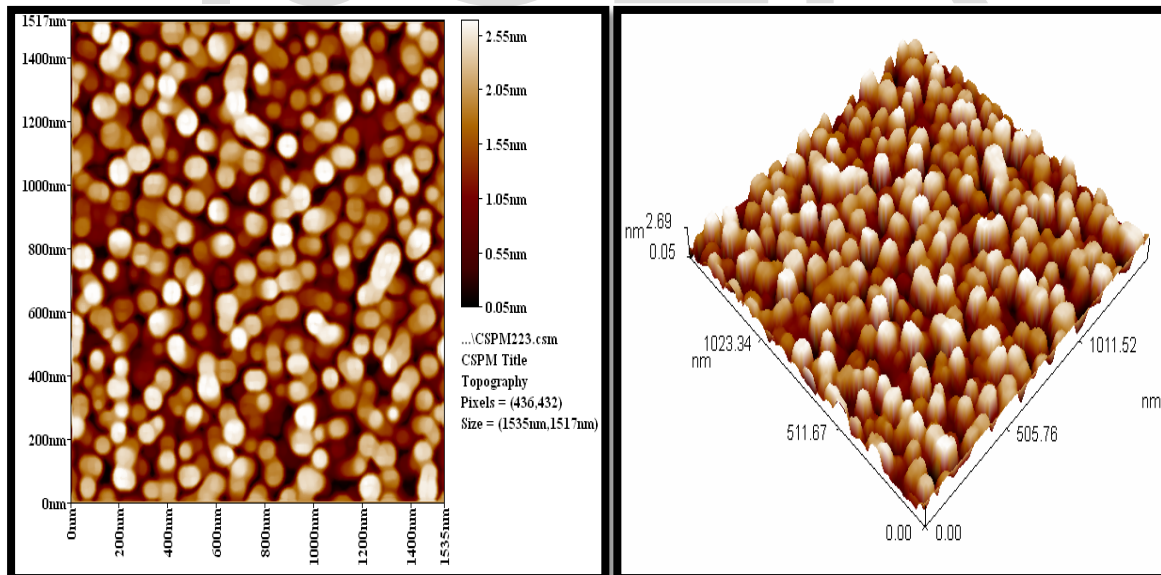
Figure(9)-2D and 3D views of AFM image of SiC by sputtering deposition.

Avg. Diameter:57.22 nm   **<=10% Diameter:40.00 nm**
<=50% Diameter:55.00 nm   **<=90% Diameter:70.00 nm**

Granularity Cumulation Distribution Chart
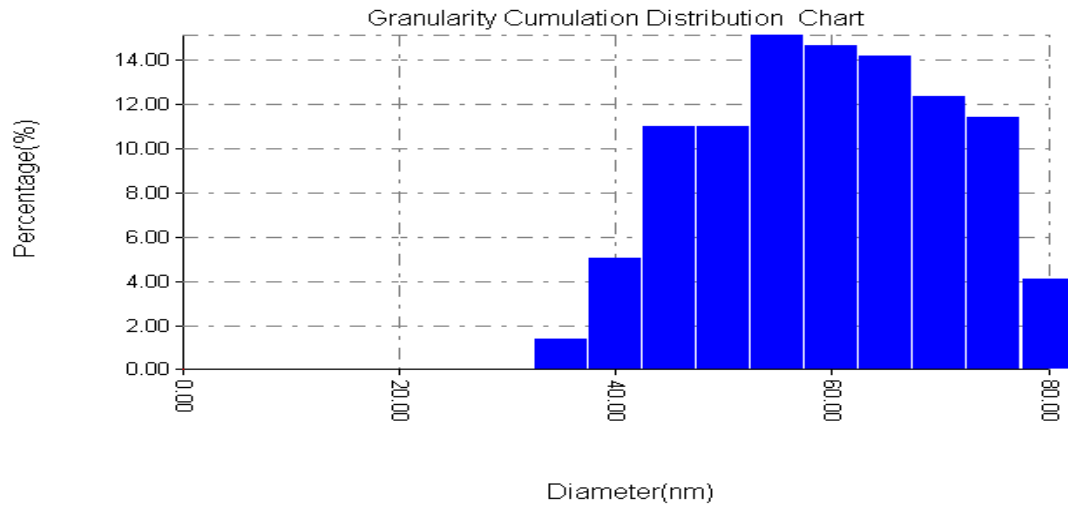
4. CONCLUSIONS

1. SiC Sputtering Deposition technique was successfully applied to coat C.S and aluminum alloys.

2. SiC film acts as good protection for the corrosion of C.S & Aluminum alloys in 3.5% NaCl solution.

3. Two important trends are evident. Firstly , the corrosion potential shifted toward more Passive value in coated alloys with SiC, secondly, the corrosion current densities were significant reduced with coated by SiC.

References

1- N.O Eddy, P.A.P. Mamza , *2009*, "*Inhibitive and adsorption properties of ethanol extract of seeds and leaves of Azadirachtaindica on the corrosion of mild steel in H_2SO_4*". Port. Electrochim. Acta *27, 4, 443– 456*.

2- Szklarska _ Smiaowska, Z., *1986*. Pitting Corrosion of Metal". Houston: National Association of Corrosion Engineers, p. *201*.

3- M. Ohring , "The Materials Science of Thin Films". Academic Press, San Diego, *(1992), p. 552*.

4- S. Ulrich, T. Theel, J. Schwan, V. Batori, M. Scheib, H. Ehrhardt, **1997**, "Formation of beta-silicon carbide, diamond and related materials". 6 *(5-7), pp.* 645 *648*.

5- C. Sella, J. Lecoeur, Y. Sampeur, P. Catania, *1993*,"Corrosion resistance of amorphous hydrogenated SiC and diamond-like coatings deposited by r.f.-plasma-enhanced chemical vapor deposition". Surf. Coat. Technol. *60, 577-583.10.1016,0257-8972(93)90156-I*.

6- J. P. Riviere, J. Delafond, P. Misaelides, F. Noli, "Corrosion protection of an AISI 321 stainless steel by SiC coatings". Surf. Coat. Technol. 100/101 (1998) 243.

7- A. Valentini, A. Convertino, M. Alvisi, R. Cingolani, T. Ligonzo,R. Lamendola, L. Tapfer, "Synthesis of silicon carbide thin films by ion beam sputtering". Thin Solid Films. Volume 335, Issues 1-2, 19 November 1998, Pages 80-84.

8- K. Minato, K. Fukuda, A. Ishikawa, N. Mita, J. "Advanced coatings for HTGR fuel particles against corrosion of SiC layer". Nucl. Mater. 246(1997) 215.

9- D.J. Kim, D.J. Cho, "High-Temperature corrosion resistance of chemically vapoure deposited silicon carbide against Hydrogen Chloride and Hydrogen gaseous environments ". Am. Ceram. Soc. 79 2(1996) 503.

10- C. Sella, J.C. Martin, J. Lecoeur, A. Le Chanu, M.F. Harman, J.P. Davidas, "Biocompatibility and corrosion resistance in biological media of hard ceramic coatings sputter deposited on metal implants". Mater. Sci. Eng. A 139 (1991) 49.

11- A. Asan , 2012, M.Sc. Thesis"A Study in Protection of Corrosion by Using Nanoparticles (TiO$_2$, SiO$_2$) for Some Metals and Alloys ",College of Science for Women University of Baghdad.