

Corrosion and Corrosion Protection Studies of Carbon Steel alloys in Saline Water using; Zirconium Oxide, Silicon Carbide and Alumina Nanoparticles

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Abstract

In this research a new fast growing field of using nanomaterials has been chosen, that is coating carbon steel alloy surfaces with such smart materials to enhance corrosion protection capability. Silicon carbide (SiC), Zirconium oxide (ZrO₂) and alumina (Al₂O₃) nanoparticles (NPs) were used to coat specimens of carbon steel. The corrosion protection efficiency inspection of each specimen in saline water (3.5% NaCl) at different temperatures (25, 35, 45 & 55°C) have been evaluated using potentiostatic techniques with three electrodes cell. Electrophoretic deposition (EPD) was used to coat the metal surfaces by nanomaterials, the results obtained showed that the rate of corrosion of carbon steel increased with increasing the temperatures from 25°C to 55°C, the results showed that deposition of SiC, ZrO₂ & Al₂O₃ NPs by used EPD caused to protection efficiency reached to 88.48%, 82.9% & 82.1 respectively in 25°C. Change in the free energy, enthalpy & entropy. Apparent energies of activation have been calculated for the corrosion process of uncoated C.S and coated C.S by NPs in saline water (3.5% NaCl).

KEYWORDS: Carbon steel, Corrosion, EPD, Nanomaterial, Polarization.

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 (Eddy et al., 2009). Carbon steel is one of the most commonly used metals in corrosive environments due to proper resistance to general corrosion. However, due to auto passivation properties, they undergo local corrosion in chloride ion containing media (Szklaarsk et al., 1986). Nanomaterials are important due to their unique properties that may lead to new and exciting applications. Current scenario of application of nanotechnology in the field of corrosion prevention of metals (Saji et al., 2007). Nanoparticle coatings possess good thermal and electrical properties and they are resistant to oxidation, corrosion, erosion and wear in high temperature environments. These property is very important factor in the applications such as pipelines, castings and automotive industry.

A uniform nanoparticle coating has been applied on metals, using electrophoretic deposition (EPD) (Ferrari et al., 1998, Fre'de'ric et al., 1999 and Kretz et al., 2004) & sol-gel method (Kasemann et al., 1994 and Shanaghi et al., 2009). Electrophoretic deposition (EPD) is a simple method for the formation of a coating nanomaterials on an electrode using a stable suspension in a direct current (DC) field (Tang et al., 2004 and Safaa 2006)]. EPD technique was used to coat silicon carbide (SiC) particles on metal surfaces. Both sparse SiC particles and dense particle coating layers were fabricated on metal

surface. Detailed analysis shows that SiC particles are bonded and compacted well with the metal surface(Bo et al.,2012), also used Zirconium oxide (ZrO₂)(Dorian et al.,2012)& alumina (Al₂O₃)(Askari et al.,2009) nanoparticles lead to similar layers.

2. Experimental

2.1. Chemical materials:

The alloy used in this work was carbon steel (C45) with following chemical materials composition:

Table (1) Chemical materials composition for C.S used in this study.

Grade	% C	% Si	% Mn	%S	% P	% Ni	% Cr	%Mo, Cr+Mo+Ni
C45	0.42-0.50	<0.40	0.50-0.80	<0.045	<0.045	0.40	<0.40	<0.10

Table (2) Chemical materials used in this study.

Raw Material	Molecular Formula	Supplier	Purity
Alumina	Al ₂ O ₃ (20-30nm)	Hongwu nanometer	99.9%
Deionized Water	H ₂ O	University of Baghdad/ College of Science/Laboratory of service	high degree of purity/empty of additional ions
Ethanol (EtOH)	C ₂ H ₅ OH	GCC	99.9%
Iodine	I ₂	Riedel-Dehaen AG.	99.98%
Sodium Chloride	NaCl	BDH	99.5%
Silicon carbide	SiC (20-30nm)	Hongwu nanometer	99.9%
Zirconium Oxide	ZrO ₂ (40-50nm)	Hongwu nanometer	99.9%

2.2. Sample Preparation

A piece of carbon steel (C45) of (0.5 mm) thickness was mechanically cut into circular sample with dimensions of 2.5 cm in diameter then:

Carbon steel sample surface was polished with emery paper in different sizes(600, 800, 1200, 2000). Then washed by water, distilled water and finally with ethanol. The specimen were kepted in desiccator for protecting and preventing them from oxidation.

2.3. Preparation of emulsion solution

Three steps used for preparation emulsion solution as follows:

1. Emulsion solution was prepared by adding 1% nanoparticles (NPs)(Al₂O₃ or ZrO₂ or SiC) powder to ethanol as solvent (adding 1.5 g NPs to 150 ml ethanol).
2. To homogenize the solution, an ultrasonic (50W) stirrer was used to mixed the solution for 30 min.
3. The solutions were applied for coating the pieces of carbon steel (C45) by using EPD method technique.

* Some time added few I₂ to increase conductivity.

2.4. Electrophoresis of Deposition of emulsion solution (Coating Samples)

To deposit emulsion solution on a pieces of carbon steel surfaces, deposition cell device was used. The device can be used in anodic or cathodic deposition by reversing electrodes of the power supply.

The deposition cell device composed of the following components:

1. Beaker 250 ml capacity and cover contain two slit with distance between then equal 1cm.
2. Power supply used to supply constant direct current D.C voltage (0 – 20 V).
3. An electrical circuit was connected by ammeter, respectively, to measure the current generated between the electrodes.
4. Stainless steel rode used as inert electrode in deposition process cell.
5. A piece of carbon steel catch by tongs made of stainless steel.

The deposition must continue about (5 min) and the specimens thermally dried at 400 °C for 2 min.

2.5. Electrochemical measurements

The experiments were performed in a classical three-electrode electrochemical cell. Carbon steel (C45) of (0.5 mm) thickness with dimensions of 2.5 cm in diameter was used as the working electrode and 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) and 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)in different temperatures (25, 35, 45 & 55)°C to 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 carbon steel alloy

The potentiostatic polarization curves for uncoated carbon steel in 3.5% NaCl solution at temperatures range (298-328)K are shown in Figure(1). The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) deduced from the curves are given in Table (2). The corrosion current density values increase from $168.88\mu A/cm^2$ at 298K to $260.08\mu A/cm^2$ at 318K. The increase in temperatures lead to increase I_{corr} values, and lead E_{corr} goes to more positive potential (active direction).

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

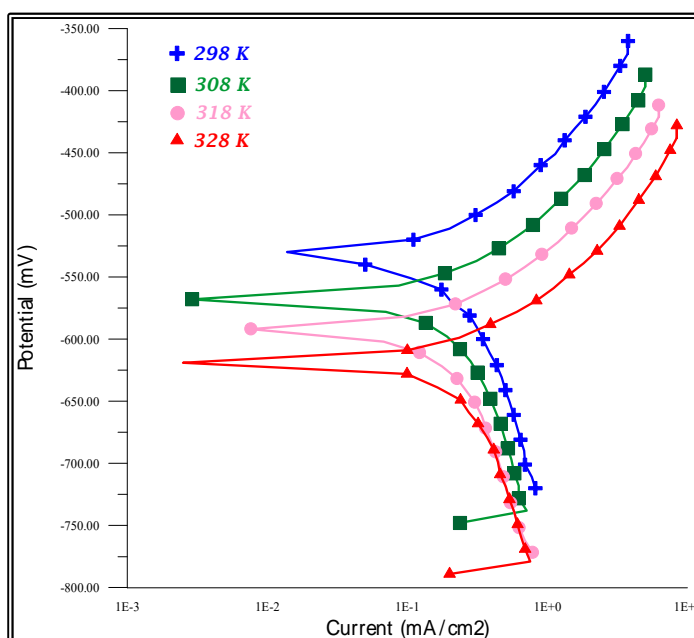


Figure (1) potentiostatic polarization curves for uncoated carbon steel in 3.5% NaCl solution at the temperatures range (298-328)K.

3.1.2. Potentiostatic polarization studies for coated carbon steel with nanoparticles

The applied silicon carbide nanoparticles coating of carbon steel alloys showed different degrees of protection efficiency in different temperatures and comparisons with the uncoated C.S alloys in the saline environment used (3.5%NaCl) show in figure (2). The protection efficiency (PE) was (88.4%) at (298K) was obtained from equation (2), as show in table (3).

$$\%PE = \frac{(C.R)_{uncoated} - (C.R)_{coated}}{(C.R)_{uncoated}} \times 100 \dots \dots \dots (2)$$

The corrosion potentials were shifted to more active with temperature increasing, they ranged between -692 and -718 mV.

Table (3) corrosion kinetic parameters for uncoated Carbon Steel and coated with SiC , ZrO₂ and Al₂O₃ alloys in 3.5% NaCl at different temperature range(298-328)K.

Temp./K	OCP/ mV	E _{corr} /m V	I _{corr} /μA .cm ⁻²	bc/ mV.Dec ₁	ba/ mV.Dec ₁	w.l/ g.m ⁻² .dl ⁻¹	Pentration loss/mm.a ⁻¹	Protection efficiencies %	
Uncoated C.S.	298	-541	-519.6	168.88	-244.2	107.2	42.2	1.96	-
	308	-568	-567.7	184.86	-253.3	98.2	46.2	2.15	-
	318	-592	-592.2	222	-351.4	104.1	55.5	2.58	-
	328	-609	-618.3	260.08	-352.8	106.7	65	3.02	-
Coated with SiC	298	-581	-691	19.45	-50	142	7.41	0.226	88.48
	308	-606	-696.5	21.87	-60.7	88.1	5.47	0.254	88.17
	318	-623	-703	31.27	-72.5	87.5	7.82	0.363	85.91
	328	-639	-718	39.13	-76.6	103	9.78	0.454	84.95
Coated with ZrO ₂	298	-631	-666.8	28.71	-71.3	57.5	7.18	0.333	82.9
	308	-664	-692.1	45.09	-79.5	48.3	11.3	0.523	75.6
	318	-677	-705.2	65.58	-85.1	50.2	16.4	0.761	70.45
	328	-681	-709.6	79.55	-97.1	53.2	19.9	0.923	69.41
Coated with Al ₂ O ₃	298	-629	-668.3	30.2	-95.7	71.8	7.55	0.351	82.1
	308	-640	-688.5	39.44	-105.4	82.4	9.86	0.458	78.66
	318	-654	-704.9	44	-99.3	93.3	11	0.511	80.2
	328	-671	-730	58.87	-86.7	89.3	14.7	0.683	77.36

The results show that the corrosion potential shifted towards more active value and the corrosion current densities reduced when coated carbon steel by silicon carbide, as shown in figure (2). Coated carbon steel by silicon carbide nanoparticle has improved the corrosion resistance by factor ranging from (88.4%) at 25°C to (84.95%) at 55°C .

The Potentiostatic polarization curves of coated carbon steel with ZrO_2 in different temperatures and comparisons with the polarization curves of uncoated C.S. is shown in Figure (2). 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 Table (3). The corrosion current density values increase from $28.71 \mu A/cm^2$ at 298K to $79.55 \mu A/cm^2$ at 328K. The protection efficiencies (PE) were ranged between (82.9%) at 298K to (69.41%) at 328K, goes to more potential active direction. The increase in temperature of the saline environment increase the I_{corr} values. E_{corr} values be little affected by the temperatures.

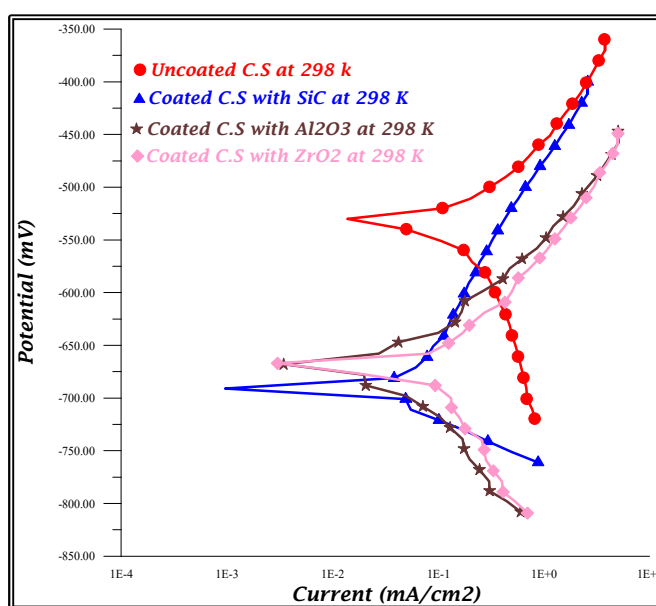


Figure (2) Polarization curves for Carbon Steel coated with NPs compared with the polarization curve for uncoated C.S alloy in 3.5% NaCl at 298 K.

Corrosion potentials, corrosion current densities determined by extrapolating the cathodic and anodic Tafel regions, the intersect opposite the corrosion current and corrosion potential. Figure (2) shows the polarization curve of carbon steel coated with Al_2O_3 in different temperatures compared with the polarization curves for uncoated C.S.

Two important trends are evident. Firstly, the corrosion potential shifted toward more active value in coated carbon steel with Al_2O_3 , Secondly, the corrosion current densities were significant reduced with coated by Al_2O_3 , where the protection efficiencies (PE) are ranged between (82.1%) at $25^\circ C$ to (77.38%) at $55^\circ C$. Table (2) show the corrosion kinetic parameter deduced from these curves.

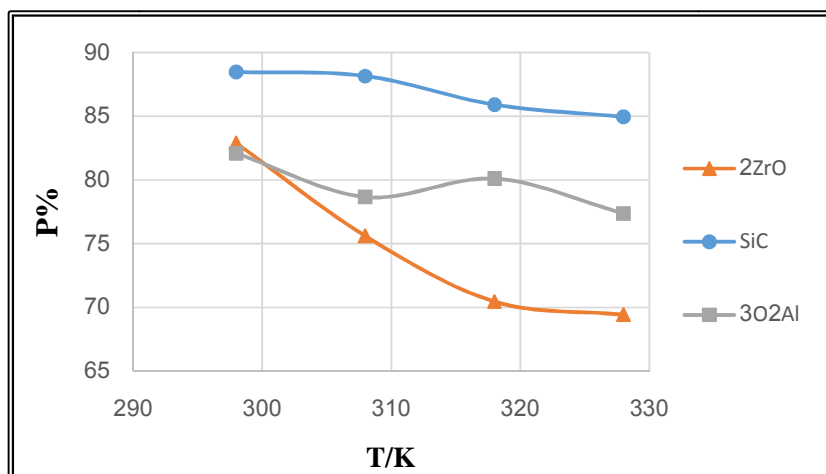


Figure (3) the relation between protection efficiency (P%) and temperature for coated C.S with different NPs.

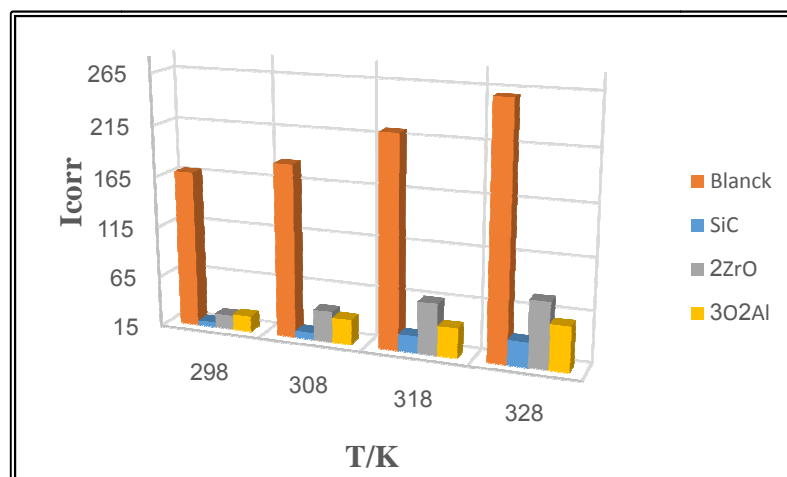


Figure (4) the relation between corrosion current density (I_{corr}) and temperature for coated C.S with different NPs

3.2. Kinetic and Thermodynamic Studies:

Thermodynamic parameters play an important role in studying the corrosion protection mechanism. The free energy (ΔG) was obtained according to the following equation :

$$\Delta G = -nFE_{\text{corr}} \dots \dots \dots (3)$$

It is worth noting that ΔS is the slop of the straight line $-\Delta G$ vs. T according to the equations:

$$\Delta G = \Delta H - T\Delta S \dots \dots (4)$$

While ΔH is obtained from eq. (4).

The thermodynamic parameters obtained are listed in table (4):

The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy (E_a).

$$\text{Log}I_{\text{corr}} = (-E_a/2.303RT) + \text{Log} A \dots \dots \dots (5)$$

Where R is the gas constant ($R \approx 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and determine the Arrhenius factor from intercept.

Table (4) the thermodynamic parameter at different temperatures for uncoated C.S & coated with SiC, ZrO₂ and Al₂O₃ in 3.5% NaCl solution.

Coating type	T(K)	1/T(K ⁻¹)	E _{corr} /mV	I _{corr} /μA.cm ⁻²	LogI _{corr}	-ΔG/KJ	ΔH/KJ	-ΔS/KJ.K ⁻¹	Ea/KJ.mol ⁻¹	A Molecules.c m ⁻² .S ⁻¹
Uncoated C.S.	298	0.0033	-519.6	168.88	2.227	100.28	83.884	0.618	12.3307	1.323E+28
	308	0.0032	-567.7	184.86	2.266	109.56	80.784			
	318	0.0031	-592.2	222	2.346	114.29	82.234			
	328	0.0030	-618.3	260.08	2.415	119.33	83.374			
Coated with SiC	298	0.0033	-691	19.45	1.29	133.36	-83.057	0.1688	20.1044	3.271E+28
	308	0.0032	-696.5	21.87	1.34	134.42	-82.429			
	318	0.0031	-703	31.27	1.49	135.67	-81.991			
	328	0.0030	-718	39.18	1.59	138.57	-83.203			
Coated with ZrO ₂	298	0.0033	-666.8	28.71	1.458	128.69	-47.306	0.2731	28.4908	1.492E+30
	308	0.0032	-692.1	45.09	1.654	133.57	-49.455			
	318	0.0031	-705.2	65.58	1.816	136.10	-49.254			
	328	0.0030	-709.6	79.55	1.9	136.95	-47.373			
Coated with Al ₂ O ₃	298	0.0033	-668.3	30.2	1.48	128.98	-12.521	0.3908	17.0409	1.587E+28
	308	0.0032	-688.5	39.44	1.59	132.88	-12.513			
	318	0.0031	-704.9	44	1.64	136.23	-11.955			
	328	0.0030	-730	58.87	1.76	140.89	-12.707			

The thermodynamic studies was showed the Gibbs free energy (ΔG) in carbon steel in saline water (3.5% NaCl) for uncoated and coated carbon steel increase in Gibbs free energy with increasing temperature.

Also observed change values of enthalpy (ΔH) from positive to negative after coated by nanoparticles (change from exothermic reaction to endothermic reaction).

While entropy (ΔS) and activation energy (E_a) values were listed table (4).

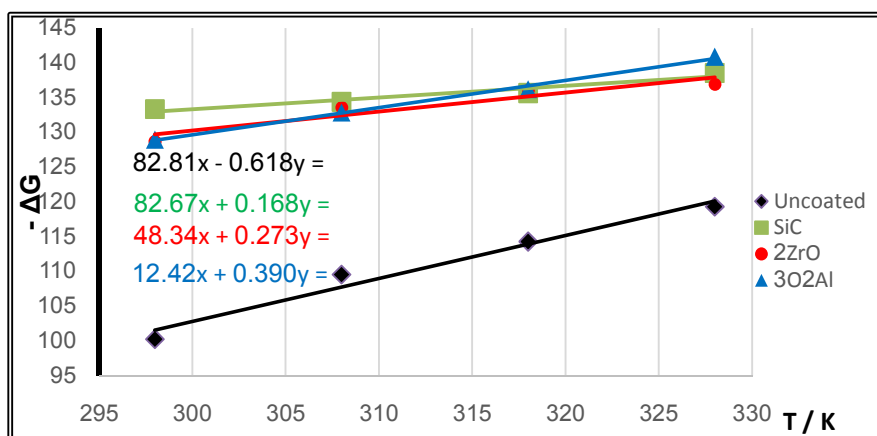


Figure (5) Plot of ΔG Vs. T for uncoated C.S & coated with SiC, ZrO₂ and Al₂O₃ in 3.5% NaCl.

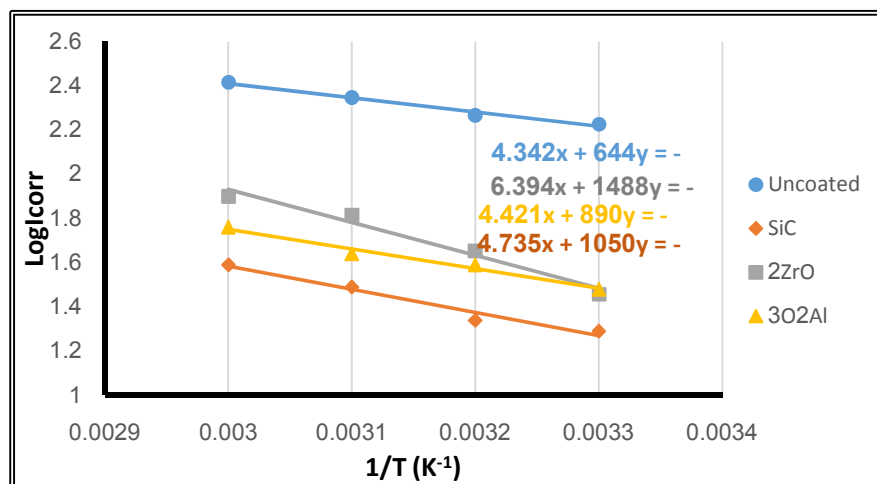


Figure (6) Plot of $\log I_{corr}$ Vs. $1/T$ for Carbon steel without and with different coated in 3.5% NaCl to determine activation energy (E_a) & Arrhenius factor (A).

4. CONCLUSIONS

1. The Electrophoretic Deposition (EPD) technique was successfully applied to coat C.S by SiC, ZrO₂ & Al₂O₃ nanoparticles.
2. Coated by nanoparticles acts as good protection for the corrosion of C.S in 3.5% NaCl solution.
3. Two important trends are evident. Firstly, the corrosion potential shifted toward more active value in coated carbon steel with NPs, Secondly, the corrosion current densities were significantly reduced with coated by NPs.
4. Coated by nanoparticles lead to change corrosion process from endothermic to exothermic process.

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