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Anticorrosion Behavior of Deposited Magnetite on Galvanized Steel in Saline Water Using RF-Magnetron Sputtering

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Abstract:

Thin films of Magnetite have been deposited on Galvanized Steel (G-S) alloy using RF-reactive magnetron sputtering technique and protection efficiency of the corrosion of G-S. A Three-Electrodes Cell was used in saline water (3.5 % NaCl) solution at different temperatures (298, 308, 318 & 328K) using potentiostatic techniques with. Electrochemical Impedance Spectroscopy (EIS) and fitting impedance data via Frequency Response Analysis (FRA) were applied to G-S alloy with Fe_3O_4 and tested in 3.5 % NaCl solution at 298K.Results taken from Nyquist and Bode plots were analyzed using software provided with the instrument. The results obtained show that the rate of corrosion of G.S alloy increased with increasing the temperatures from 298 to 323K; and showed that deposition of Fe_3O_4 caused protection efficiency to reach 79.76% for G-S in 318K. In addition the enthalpy & entropy of activation were evaluated. Apparent energies of activation have been calculated for the corrosion process of uncoated and coated G.S alloy by sputtering technique in saline water (3.5 % NaCl). The morphological analysis was carried out using Scanning Electron Microscopy (SEM) technique.

Keywords: Corrosion protection, Electrochemical Impedance, Magnetite Nanoparticle, Polarization, Sputtering.

Introduction:

Corrosion can be defined as the chemical or electrochemical reaction when a material is exposed to an environment that causes the subsequent deterioration of the material. It causes serious damage to all engineering applications and infrastructure and becomes a threat to public safety and has a huge economic impact (1).
Galvanized steel involves aZinc (Zn) coating on steel to prevent an underlying steel substrate from rusting. Zinc is anodic to steel: thus it protects steel via the mechanism called sacrificial protection. American Galvanizers Association (AGA) conducted tests of corrosion that is Galvanized Steel in water collected from marine environments all over the USA. It was found that soft water, tropical sea water, and high oxygen content caused higher corrosion in a Zn coating of galvanized steel (2).
Galvanized steel is used in aqueous environments in many indoor and outdoor applications where rust resistance is needed. It is used in applications such as under sea water, underground pipelines, frames to build houses, household appliances, automotive body parts, telecommunication industry, power transmission lines and thermal power plants, to name a few (3).

A new generation of anticorrosion materials that both possesses passive matrix functionality, and actively responds to change in a local environment has prompted great interest from material scientists. The Nanometer Scaled Materials were gained much attention, due primarily to novel properties induced via their high surface to volume ratio (4). Nanomaterials are commonly defined as particles with the size of at least one dimension ranging from 1– 100nm, which serve as a bridge between atoms, molecules and bulk materials (5). There are many techniques that had been already employed to produce protective coating, such as dip coating, plasma spraying, physical vapour deposition and electroplating methods. Nowadays, nanomaterials have many applications due to their versatile characteristics, which are further improved via means of obtaining uniform dispersion of nano coatings using various techniques. Sputtering process is a well-established surface modifying process that involves deposition of a variety of materials, either metal, ceramic or a combination of both at any in nanometric level over various substrates (6).Magnetite Fe_3O_4 exhibits unique

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physical properties including relatively high conductivity, high magnetic characteristics, and high ratio of spin polarization. Fe_3O_4 is also known as a stable, common and biocompatible mineral of very low toxicity (7). Beginning in the 1970s, research electrochemists and materials scientists began to discover the power of electrochemical impedance spectroscopy (EIS) as a tool for studying difficult and complicated systems. The physical barrier was evaluated via Electrochemical Impedance Spectroscopy (EIS), which had many advantages in comparison with other electrochemical techniques. During EIS experiments, a small amplitude AC signal was applied to the system being studied with different frequencies. By analysis of these responses of frequency domain, different corrosion process may be deduced & studied. An equivalent electrical circuit of a corrosion system was often used in analysis of EIS measurements (8). This paper reports, the results of an investigation of corrosion resistance of nanostructure deposited used RF sputtering techniques. The aim of the work is deposit nanomaterials, magnetite Fe_3O_4 as thin films by RF magnetron sputtering technique to protect G-S from corrosion in saline water. Nyquist and Bode Plots were analyzed for the prediction of corrosion performance of nonmaterial coatings. SEM analysis of the specimen was also performed.

Materials and Methods:

The chemical composition of G-S composites are given in Table1.Other chemicals include iron oxide NPs, magnetite Fe_3O_4 (30-40) nm USA with purity 99.8%, acetone, and ethanol were purchased from BDH with purity not less than 99%.Samples of galvanized steel were cut into circles with a diameter of 2.5 cm and 1.5 mm thickness and ground until mirror like surfaces was achieved using a series of grits of increasing fineness up to 2000. The samples were washed with acetone, distilled water, ethanol and finally dried and stored in desiccators till use.

Table 1. Chemical material composition of Galvanized Steel (G-S)

Element	Fe	Zn	Co	Mn	Mo	Cr	Mg	Zr	Pb	Other
Wt%	71.93	25.73	0.714	0.278	0.200	0.127	<0.03	<0.02	0.013	<0.03

Experimental procedures:

Work pieces have been placed in the sputtering unit, which operated with the power 110 V at room temperature. The sputtering unit consists of power supply, a gas mixing device and a stainless - steel vacuum chamber as shown in Figure1.The sputtering was performed in a pure argon. Sputtering cycle was carried out by evacuation of the chamber and then followed by initialization of the glow. The sputtering process was illustrated in Fig.2 and the parameters which used to achieve sputtering process were illustrated in Table 2.

Figure 1. System of RF-sputtering.

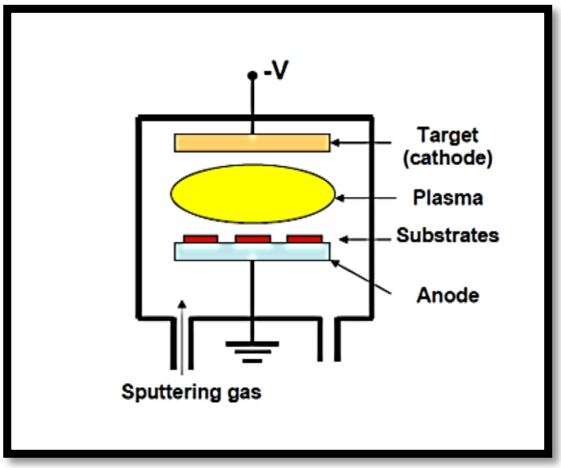

Figure 2. Illustrate sputtering process.

Table 2. parameters used for sputtering process

Sputtering unit	Power(W)	Time(hr)	Pressure(torr)	Temperature K
RF magnetron	110	1	10^{-5}	Room temp

Electrochemical Measurements:

The experiments were performed in a classical three-electrode electrochemical cell. All alloys with 1.5 mm thickness and 2.5 cm diameter have been used as working electrode, a platinum electrode as a counter electrode, silver-silver chloride electrode as a reference electrode. Before each experiment, the working electrode surface is polished with Emery Paper. Electrochemical system consists of Potentiostate device (Germany, Mlab 2000) corrosion cell with 1000 ml volume, three electrodes with a computer with; MLabSci software used for data acquisition. To determine the Open Circuit Potential (OCP) of specimens, the specimens were immersed in synthesized sea water (3.5 % NaCl) at a temperatures range of 298-328 K to reach the steady state between specimens material and electrolytic solution. The changing in potential according to a current study has been established as 15min, with the time step equal to 60 seconds for each specimen. After reaching the condition of steady state, the determined potential is known as corrosion potential (open circuit potential).

Electrochemical Impedance Spectroscopy (EIS) Tests:

A behavior of the corrosion of specimens has been monitored using Electrochemical Impedance Spectroscopy (EIS) during immersion in 3.5% NaCl Solution open to air and at room temperature. Three - Electrode set-up has been used to record corrosion potential of coating. Saturated Calomel Electrode (SCE) has been used as reference electrode. It has been coupled capacitive to a Pt wire to reduce phase shift at higher frequencies. Electrochemical Impedance tests have been carried out by using Auto lab type-III, provided with frequency response analyzer, frequency in range from 1mHz up to 100 KHz to collect data with a total number of 40 readings for the whole range. An amplitude of sinusoidal voltage signal has been 50 mV.Data has been collected via means of Frequency Response Analyzer Software developed by Princeton Applied Research instruments has been in form of Nyquist Plots.

Results and Discussion:

Potentiostatic polarization studies for Galvanized Steel uncoated:

The potentiostatic polarization curves for G-S uncoated in 3.5 %NaCl solution for temperatures ranging frob 298-328 K are shown in Figure 3. Corrosion kinetics parameters such of corrosion potential ($E_{corr.}$), corrosion current density ($i_{corr.}$), anodic Tafel line (b_a), cathodic Tafel slope (b_c) were deduced from the curves are given in Table 3. Corrosion current density values increased from (65.00 $\mu A/cm^2$) at 298K to (207.31 $\mu A/cm^2$) at 328K .The increase in temperatures led to an increase in $i_{corr.}$ and $E_{corr.}$values.

$$\eta_{a,c} = b_{a,c} \text{ Log } \left(\frac{ia,c}{io}\right) \ldots\ldots \ldots(1)$$

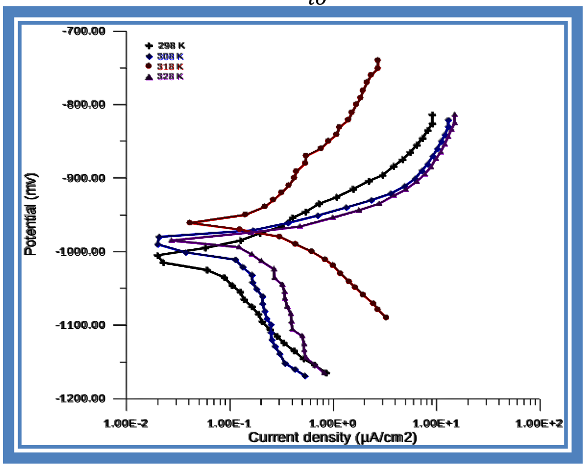

Figure 3. Potentioatatic polarization curves for uncoated G-S in 3.5% NaCl solution at various temperatures.

Table 3. Corrosion parameters for the uncoated G-S alloy in 3.5 % NaCl solution at various temperatures.

Temp/ K	-OCP/ mV	$-E_{corr}$ / mV vs SCE	I_{corr} / $\mu A.cm^{-2}$	-bc / mv .dec^{-1}	ba / mv.dec^{-1}	W. L/ g m^{-2}d^{-1}	P.L/ m m.y-^{1}	Rp/ $\Omega.cm^2$	R/ mpy
298	998	1012.2	65.00	157.6	72.6	19	0.974	332.03	38.62
308	972	985.6	93.23	222.7	40.1	27.3	1.40	158.27	55.39
318	949	961.4	196.42	79.9	188.2	58.8	3.01	123.99	116.69
328	971	984.2	207.31	368.9	45.4	60.7	3.11	84.67	123.16

The data in Table3. show that the corrosion current density ($i_{corr.}$) values increase with temperature increase, whereas corrosion potential ($E_{corr.}$) shifts negative with temperature increases, The G-S Uncoated became more active toward corrosion process with temperature increase, weight loss W.L, penetration low P.L and rate of corrosion R increased with increasing temperature. Polarization Resistance Rp, decreased with increasing temperature.

Potentiostatic polarization studies for Alloy coated by RF magnetron sputtering technique:

The applied Magnetite deposition on G-S showed different degrees of protection efficiency in different temperatures. The protection efficiency (PE) was obtained from equation (2) at temperature range 298-328 K, as shown in Table-4. Comparisons with the polarization curves of uncoated G.S alloys is shown in Fig.4

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

Table 4.Corrosion parameters for the G-S Coated by the Sputtering –Fe_3O_4 at 1hr in 3.5 % NaCl at various temperatures.

Temp/ K	-OCP/ mV	-$E_{corr.}$ / mV	$I_{corr.}$ / A. cm^{-2}µ	-bc/ mv dec^{-1}	ba/ mVdec^{-1}	W. L/ $gm^{-2}d^{-1}$	P.L/ mmy^{-1}	Rp/ $\Omega.cm^2$	PE%	R/ mpy
298	993	1006.7	36.55	157.3	37.9	0.107	0.547	362.83	43.77	21.71
308	1000	1012.1	36.75	139.1	38.3	0.108	0.550	354.83	60.58	21.83
318	981	995.7	39.76	205.1	34.9	0.116	0.596	325.72	79.76	23.62
328	964	977.1	46.61	198.1	48.8	0.136	0.698	364.76	77.52	27.69

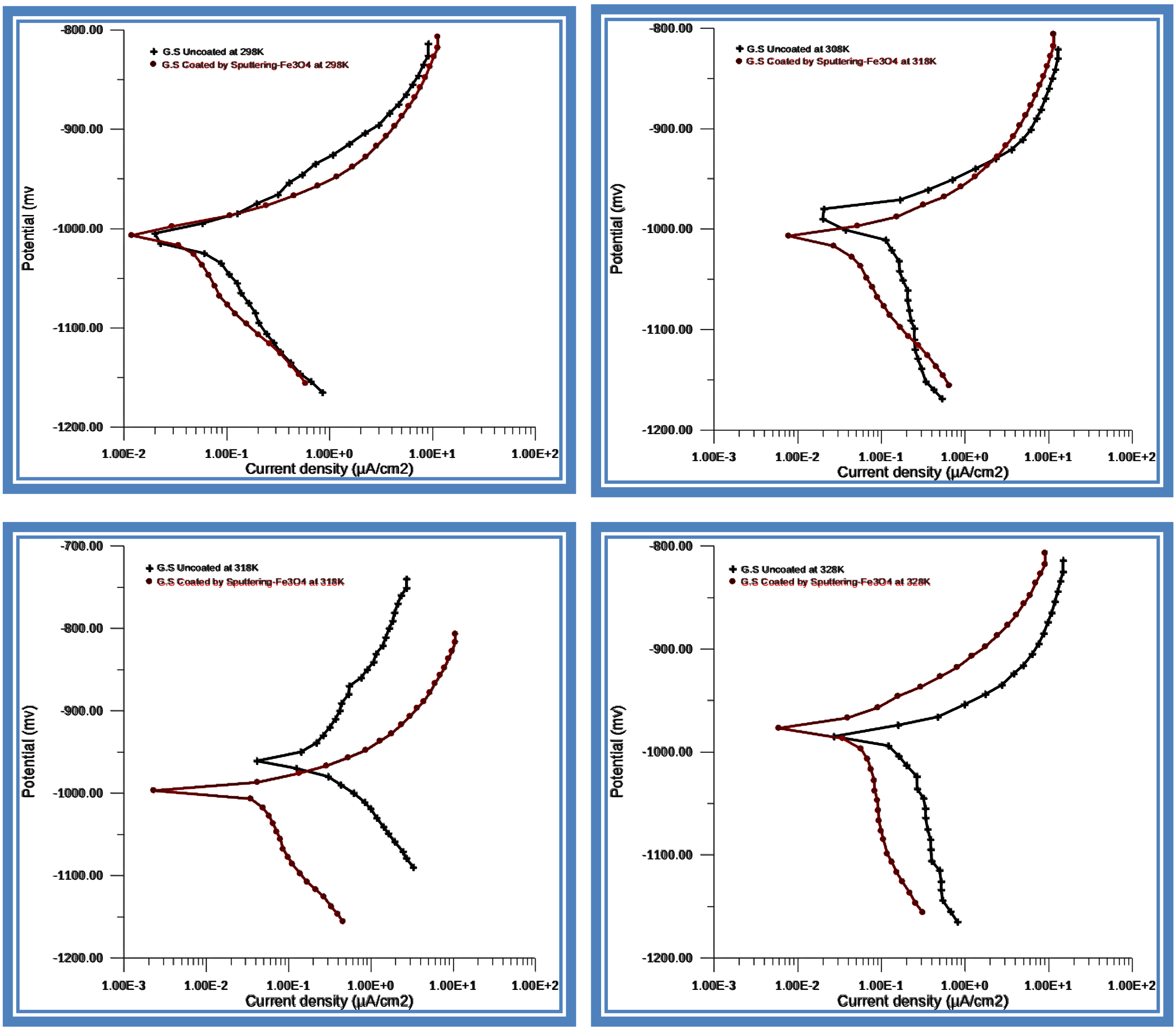

Figure 4. Polarization curves for the corrosion of G-S Coated by the sputtering –Fe_3O_4 at different temperature as compared with the polarization curves for Uncoated G.S.

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 (9):

$$LogI_{corr.} = \left(\frac{-Ea}{2.303RT}\right) + Log\ A \quad \ldots\ldots (3)$$

Where R is the gas constant (R=8.314 $JK^{-1}\ mol^{-1}$), and determine the Arrhenius factor from intercept. Moreover, transition state Eq. (4) was used:

$$\text{Log}\left(\frac{Icorr.}{T}\right) = \text{Log}\left(\frac{R}{Nh}\right) + \frac{\Delta S*}{2.303R} - \frac{\Delta H*}{2.303RT} \quad \ldots (4)$$

Where $I_{corr.}$ is corrosion current density, temperature in K,h the Planck's constant(6.626 × 10^{-34} J.S),N is the Avogadro's Number (6.023 ∗ 10^{23} mol^{-1}),ΔH^* is enthalpy of Activation , ΔS^* is Entropy of Activation, A straight line was obtained from the plots of $I_{corr.}$/T Vs. 1/T, with the slope of (-ΔH^*/2.303R), an intercept of [log(R/Nh) + ΔS^*/2.303R)], from which the values of $\Delta H^*$and ΔS^* were obtained, respectively. For GS Alloy uncoated and coated, by using the estimated values of $\Delta H^*$and ΔS^*, it was possible to calculate the values of the change in Gibbs free energy ΔG^* of activation for corrosion process from the relation:

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \quad \ldots\ldots (5)$$

ΔH^*, ΔS^*, Ea and A values for Cs45 alloy before and after coating were illustrated in Table 5.

Table 5. The thermodynamic parameter at different temperatures for Uncoated G-S & coated with Fe_3O_4 by Sputtering in 3.5 % NaCl solution.

	Temp/ K	1/T/ K^{-1}	$i_{corr.}$/ $\mu A.cm^{-2}$	Log $i_{corr.}$	Log ($i_{corr.}$/T)	ΔG*/ $KJmol^{-1}$	ΔH*/ $KJmol^{-1}$	ΔS*/ J. mol^{-1}	Ea/ $KJmol^{-1}$	A/ Molecules $Cm^{-2}S^{-1}$
Uncoated	298	0.0033	113.92	2.057	-0.418	61.34	12.64	-163.42	8.45	2.23E+27
	308	0.0032	148.37	2.171	-0.317	62.97				
	318	0.0031	163.36	2.213	-0.289	64.61				
	328	0.0030	171.29	2.234	-0.282	66.24				
Coated	298	0.0033	76.96	1.8862	-0.5879	62.30	4.57	-193.73	7.23	8.11E+26
	308	0.0032	82.50	1.9164	-0.5720	64.34				
	318	0.0031	91.27	1.9603	-0.5420	66.18				
	328	0.0030	99.41	1.9974	-0.5184	68.11				

Electrochemical Impedance Spectroscopy (EIS) Tests for uncoated Alloy:

G-S Uncoated:

We see from EIS measurement that the behavior of G-S is ideal, Fig.5 and Fig.6 Represent Nyquist and Bode plots for impedance of specimen was tested after Immersion In 3.5 % NaCl solution at 298K, where the equivalent circuit refers to Randle circuit.

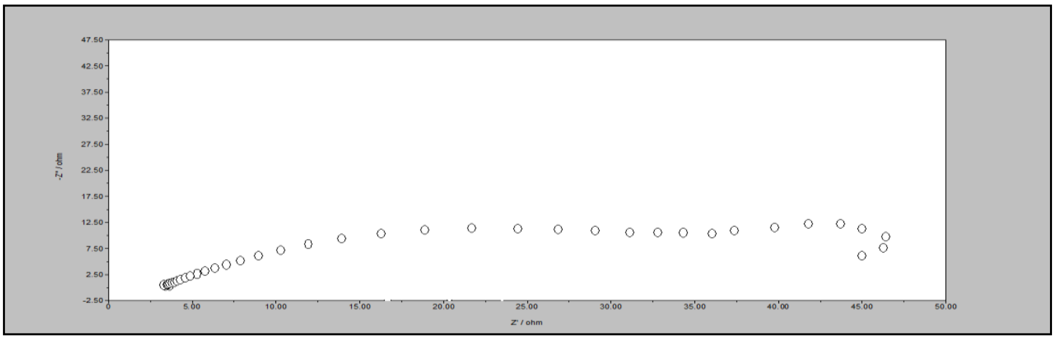

Figure 5. Nyquist plot of the G-S uncoated in 3.5% NaCl solution at 298K.

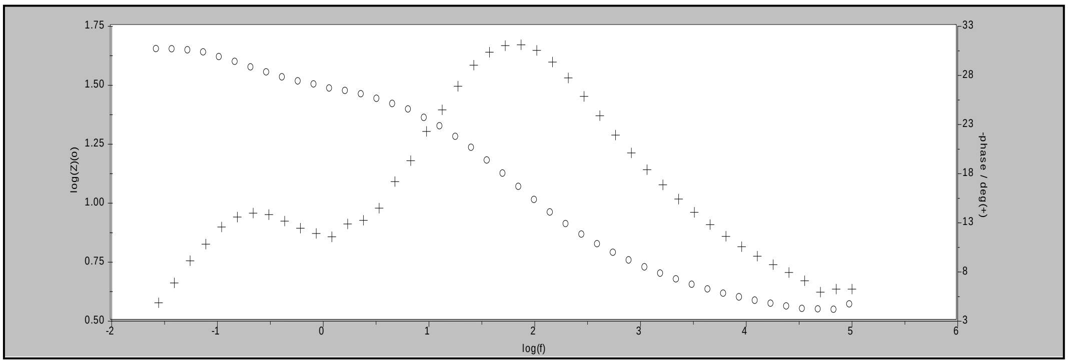

Figure 6.Bode plot of G-S Uncoated in 3.5% NaCl solution at 298K.

Where the Equivalent circuit for G-S Uncoated refers to Randle circuit,which can be represented via a model as shown in Fig.7, where R_s is solution resistance, R_z is Resistance of Zinc layer,

R_{ct} is Charge Transfer Resistance of Steel/Solution Interface, Cz is capacitance of Zinc layer, Cdl is Double Layer Capacitance.

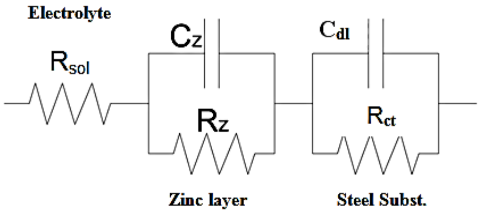

Figure 7. Equivalent Circuit diagram, model: R (CR) (CR) at G-S uncoated in 3.5% NaCl Solution at 298K.

G-S coated with Fe_3O_4 by RF-Sputtering:

We notice that there is an obvious change in the behavior of Nyquist and Bode plots, the nanomaterial affects the corrosion as shown in Fig.8 and Fig.9. Behavior takes the shape of part of semicircle with up resistance, from which the ability to predict which Magnetite coating possess good corrosion resistance properties. Other parameters are recorded in Table 6.R_c gives an indication about corrosion process at the steel surface. Those parameters can be used for study effectiveness for coating of protection for metal.

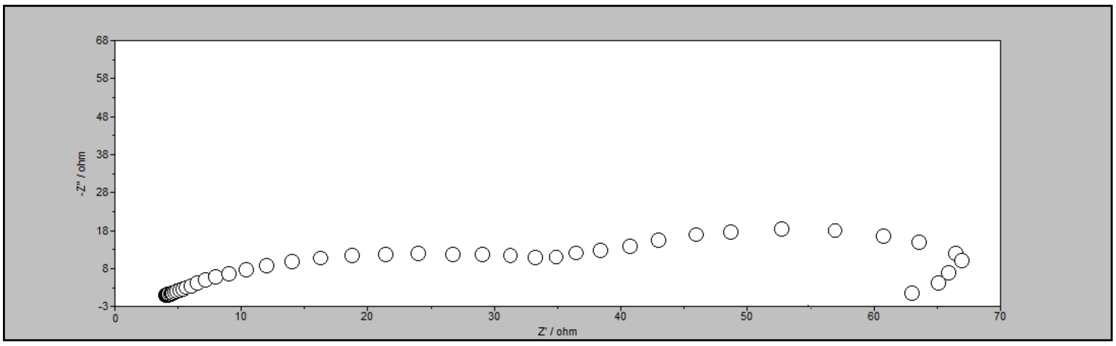

Figure 8. Nyquist plot of G-S coated with Fe_3O_4 by RF-Sputtering in 3.5% NaCl solution at 298K.

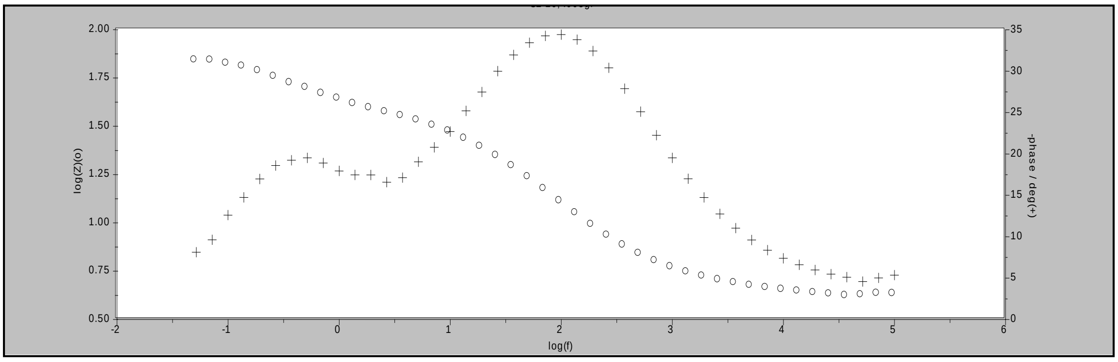

Figure 9.Bode plot of the G-S Coated with Fe_3O_4 by RF-Sputtering in 3.5% NaCl solution at 298K.

Where the Equivalent circuit for G.S coated can be represented via model shown in Fig.10, where R_s is solution resistance, R_c is resistance of coating, R_z is resistance of zinc as layer, R_{ct} is charge transfer resistance of steel/C_c is the capacitance of the coating, capacitance solution interface, C_z is capacitance of zinc layer, and C_{dl} is double layer capacitance.

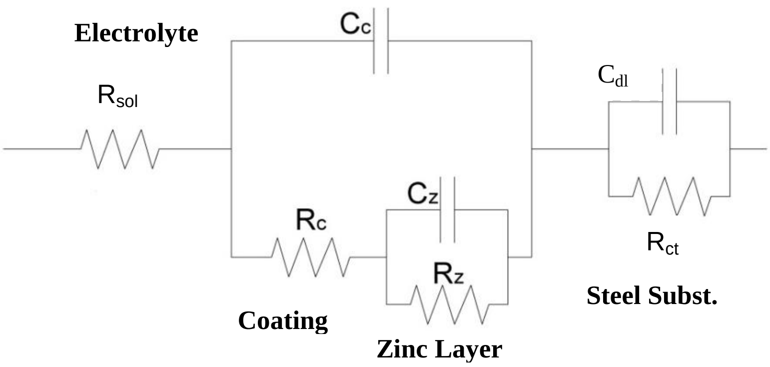

Figure 10. Equivalent circuit diagram, Model R(C(R (CR))) (CR) for G.S Coated by Fe_3O_4 in 3.5% NaCl Solution at 298K.

Table 6. Electrochemical Parameter for Equivalent Circuits acquired of bestead fitting for impedance datum of G-S Uncoated and Coated by RF-Sputtering in 3.5% NaCl solution at 298K

Stat	R_S (Ω)	Rc (Ω)	R_Z (Ω)	R_{CT})Ω(	R_{Total} (Ω)	Cc (F)	C_Z (F)	C_{dl} (F)	n_1	n_2	n_3
G.S uncoated	3.1	------	32.7	6.3	42.1	------	1.3E-3	4.5E-3	0.8631	0.8524	------
Coated with Fe_3O_4	4.5	18	30.1	20	72.6	1.1E-3	1.2E-3	1.4E-3	0.8745	0.8617	0.8582

Morphological Study of Sputtering:

SEM is a technique which uses electromagnetic lenses and an electronic beam to illuminate samples under vacuum (10, 11). Scanning Electron Microscope scans a focused an electron beam upon the surface of a specimen to create imagery. Electron interaction with atoms of surface, produced various signals which allows the user obtain information about surface topography, composition, and surface morphology ,the thickness of sputtering Technique for galvanized steel using Magnetite Fe_3O_4 have been studied using scanning electron microscopy (SEM) technique was a Hitachi S4160.More uniform grains may lead to more protection results, via the surface morphologies. Cross section have been analyzed via a Zeiss Supra 55VP PGT/HKLSystem, which offers that ultra-high resolution at a relatively lower voltage. The results of the Surface Morphology Analysis by SEM of RF sputtering by magnetite Fe_3O_4 are shown in Figures 11 & 12, respectively.

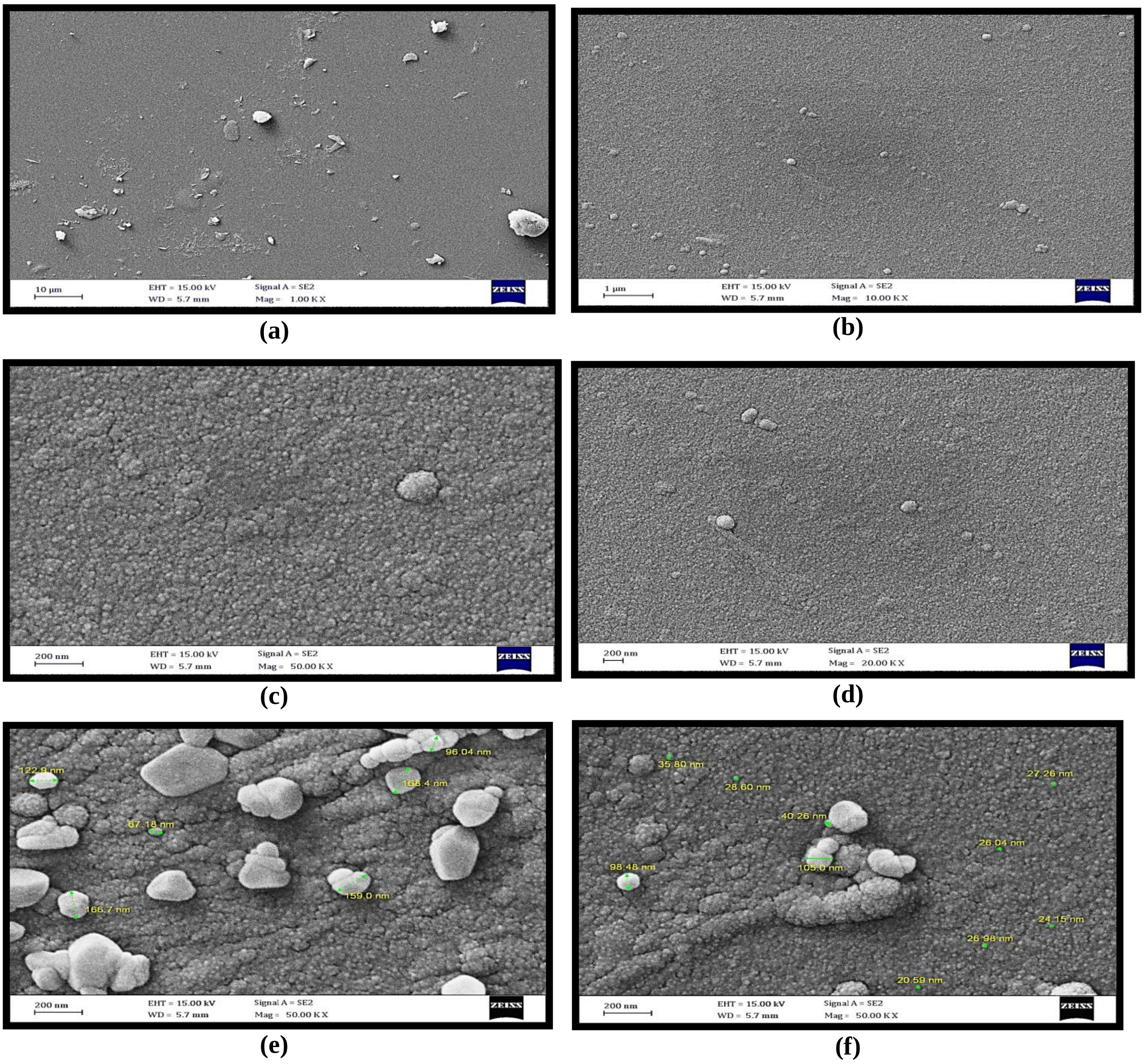

Figure 11. SEM image of Magnetite Fe_3O_4 coating (a/10µm), (b/1µm), (c/200nm), (d/200 nm), (e&f Particle Size).

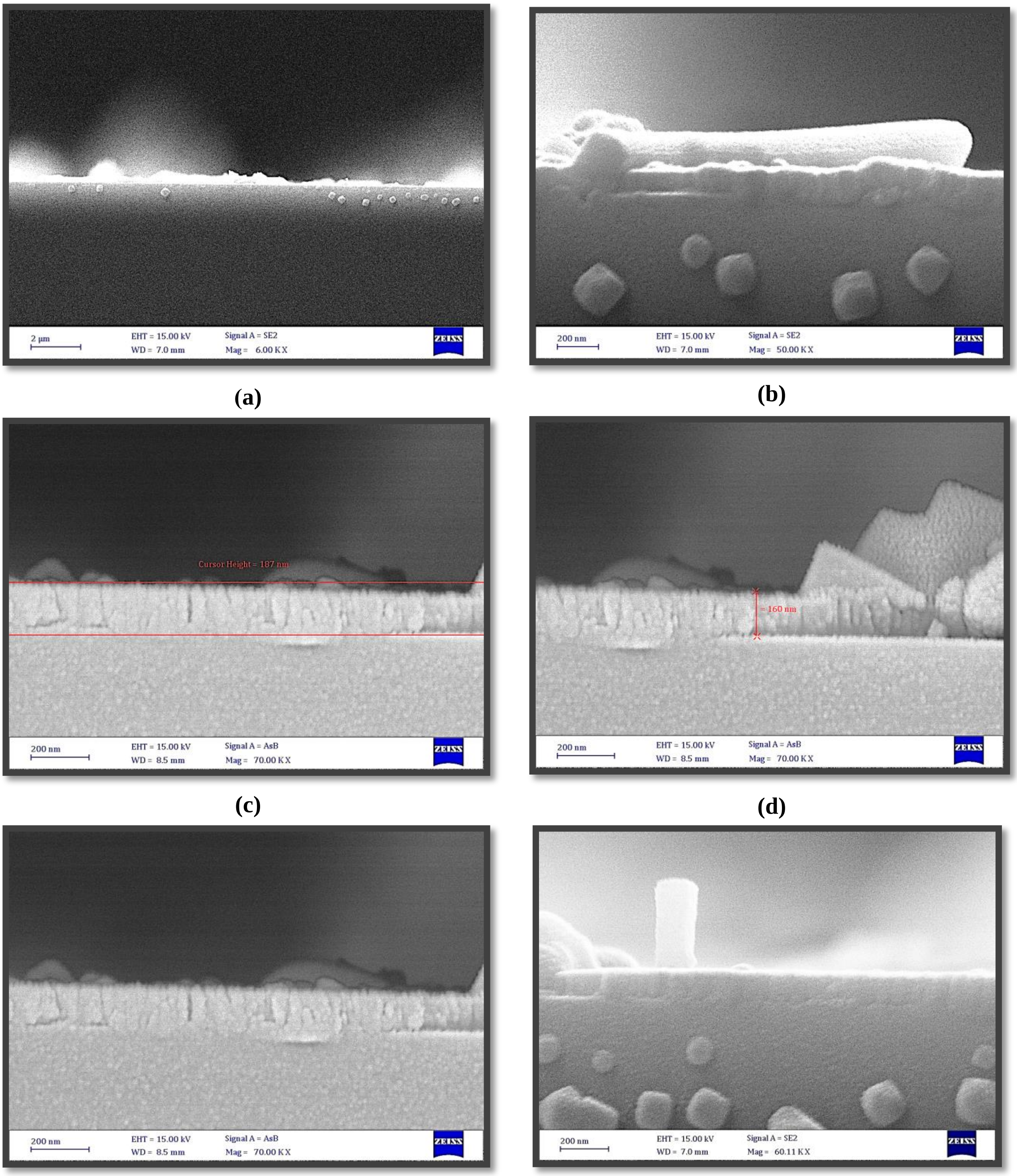

Figure 12. SEM images of Magnetite Fe_3O_4 film .(a\2µm),(b\200nm),(c\Cursor High = 187nm), (d\Cross Sectional outlook of Magnetite Fe_3O_4 film coating indicate that thickness about 160 nm), (e&f 200 nm).

Conclusions:

The corrosion protection efficiency of G-S alloy using RF-reactive magnetron sputtering technique in 3.5% NaCl by thin films of Magnetite has been investigated using electrochemical measurement.

Thin films of nano Magnetite Fe_3O_4 at a thickness of 160 nm acted as good protections for corrosion of galvanized steel alloy in 3.5 % NaCl solution.The coated galvanized steel with Magnetite by magnetron sputtering reduced corrosion rate compared to uncoated alloy. Their values were obtained from the Polarization method and electrochemical impedance, and the data obtained are in good agreement, RF- magnetron sputtering technique was successfully applied to coat Galvanized Steel alloy. In Conclusion, EIS data will be very useful in predicting the corrosion resistance coated and the adsorption processes.

Conflicts of Interest: None.

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السلوك المضاد للتآكل من ترسيب المغنتايت على الحديد المغلون في المياه المالحه بأستخدام الموجات الراديويه-الترذيذ الماكتروني الفعال

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الخلاصة:

تم في هذا البحث ترسيب غشاء رقيق من المغنتايت على سبيكة الحديد المغلون بأستخدام الموجات الراديويه – تقنية الترذيذ الماكتروني الفعال كطلاء حمايه،و درست كفاءة حماية التآكل للحديد المغلون في المياه المالحه (3.5% كلوريد الصوديوم)بأستخدام جهاز مقياس الجهد الساكن مع ثلاثة اقطاب، وبأستعمال جهاز قياس الممانعه الكهروكيميائيه الطيفي تم تحليل النتائج. أظهرت النتائج أن معدل سرعة التآكل للحديد المغلون بدون طلاء زاد بزيادة درجة الحراره (298-328) كلفن، و اظهرت النتائج أن ترسيب المغنتايت الناجم عن كفاءة حمايه بلغ 79.76% في درجة حراره 318 كلفن ،تم حساب قيم التغير في الانثالبي وطاقة التنشيط،حيث قدرت قيم الطاقات الظاهريه من التنشيط لعملية التآكل لسبيكة الحديد المغلون المطليه وغير المطليه في المياه المالحه (3.5% كلوريد الصوديوم)، تم أجراء التحليل المورفولوجي بأستخدام تقنية المجهر الضوئي الالكتروني.

الكلمات المفتاحية:حماية التآكل، نانومغنتايت، الترذيذ، الأستقطاب، مطيافية المعاوقه الكهروكيميائيه.