

Nitriding Based Plasma for Some Alloys for Corrosion Protection in Saline Water at Different Temperatures

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ABSTRACT

In this research a new physical deposition methods has been chosen, nitriding based plasma is an economical method to improve the corrosion resistance of three types of alloys (CS1045, CS1137 and Al5083 alloy), CS means Carbon Steel & Al means Aluminum alloys. 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 (25, 35, 45 & 55)°C have been evaluated using potentiostatic techniques with three electrodes cell. Nitride ion is deposited on the three alloys and then we studied the extent of this corrosion resistance. The results showed that deposition of N₂ gas as nitride ion caused to protection efficiency reached to 72.77% for CS1045, 61.93% for CS1137 and 90.28% for Al5083 respectively in 25°C. Change in the enthalpy of activation & entropy of activation were evaluated. Apparent energies of activation have been calculated for the corrosion process of uncoated and coated alloys by nitriding based plasma technique in saline water (3.5% NaCl).

Keywords: Carbon steel, Aluminum, Corrosion, Plasma, Nitriding, Polarization.

I. 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⁾. Plasma nitriding is an economical method to improve the hardness as well as fatigue, corrosion resistance and wear resistance of ferrous and nonferrous materials^(3,4). Nitriding technique was first introduced in the late 1930s^(5,6) and industrial acceptance began in the 1970s. plasma nitriding has become a promising nitriding method. Compared to traditional gas or salt bath nitriding, plasma nitriding imparts a hard wear resistant surface without brittleness, galling or spalling. Furthermore, plasma nitriding affects less the surface finish of the product. Salt bath and gas nitriding, which use ammonia and phosphate for activation, will roughen the polished surface. Plasma

nitriding also provides a higher surface hardness and maintains materials core properties due to lower nitriding temperatures. Finally, plasma nitriding is environment friendly because a non-toxic mixture is used. Traditional gas and salt bath nitriding use toxic gases, salts or ammonia which are hard to control and harmful to the workers and the environment^(7,8).

The first step in plasma nitriding is to generate active particles in a nitrogen environment. A considerable amount of the research activities have concentrated on N₂ and N₂-H₂ plasma Characterization and the mechanism⁽⁹⁾ although a common consensus has not been reached. Excited states of N₂⁺, N₂, NH, H, N, and N⁺ have been detected⁽¹⁰⁾. Assuming that N⁺ is the dominant ion species⁽¹¹⁾, an increased ratio of nitrogen atoms to nitrogen molecules and N⁺ to N₂⁺ when the distance from the cathode decreases has been observed⁽¹²⁾. Note that the working gases are mostly mixed gases (with hydrogen or argon) in postglow discharge nitriding experiments^(13,14) and a unified theory on the exact mechanism of plasma nitriding has

not been established. Fig.1. illustrated ion plasma nitriding mechanism.

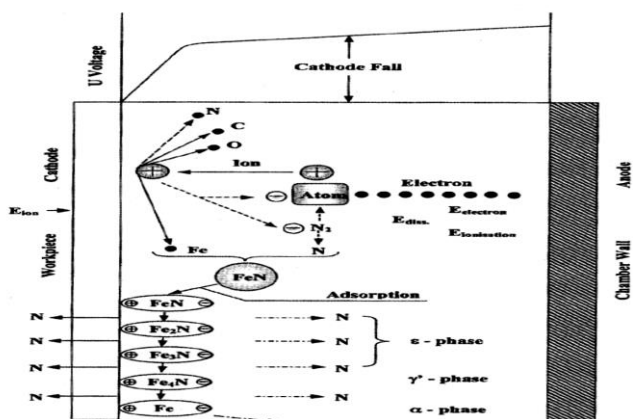


Figure 1. ion plasma nitriding mechanism[15].

II. METHODS AND MATERIAL

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	%N	%Cr
C1137	0.32	<0.04	1.35-1.65	0.08	<0.04	0.11	0.16
	0.39			0.13			

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

Grade	%Mg	%Si	Mn %	%Fe	%Zn	%Cu	%Cr	%Ti	Others
Al5	4.0	<	0.4	<0	<0	<0.0	0.0	0.0	<0.0

083	-	0.4	-	.4	.1	1	5-	05	05
	4.9	4	1.0				0.2	-	
							5	0.	
								25	

2.2. Experimental procedures

Workpieces were placed in the nitriding unit, which operated with the D.C. bias voltage 600V at room temperature. Nitriding unit used in this study, consists of power supply, a gas mixing device and a stainless steel vacuum chamber as shown in Fig.2. Plasma nitriding was performed in an pure argon firstly to etching workpieces from the oxide and other solvents which used to clean the workpieces, secondly, mixture from (20% argon & 80% nitrogen) were used to performed plasma nitriding. Nitriding cycle was carried out by evacuation of the chamber and then followed by initialization of the glow. The parameters which used to achieve nitriding process were illustrated in table (2).

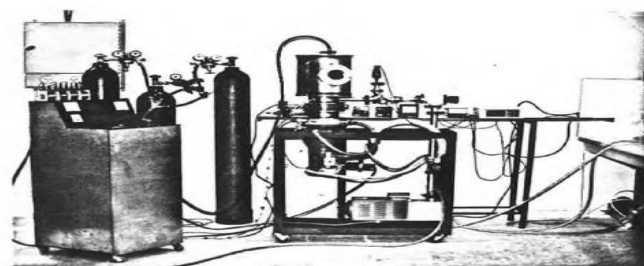


Figure 1. Illustrate DC glow discharge unit were used for nitriding process.

Table (2) parameters used for nitriding process

Nitriding unit	Voltage (V)	Time (hr)	Pressure	Temperature K	Gas mixing
DC glow discharge	600	9.00	0.3m bar	Room temp	20% Ar +80% N2

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 potentiostat 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)K 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.

III. RESULT 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 (2,3,4). 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 tables (3,4,5). The corrosion current density values increase from $(113.54)\mu A/cm^2$ at 298K to $(201.52)\mu A/cm^2$ at 328K for C.S(1045), from $(68.4)\mu A/cm^2$ at 298K to $(173.4)\mu A/cm^2$ at 328K for C.S(1137) and from $(16.36)\mu A/cm^2$ at 298K to $(57.08)\mu A/cm^2$ 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).

$$\eta_{a,c} = b_{a,c} \log\left(\frac{i_{a,c}}{i_0}\right) \dots\dots\dots(1)$$

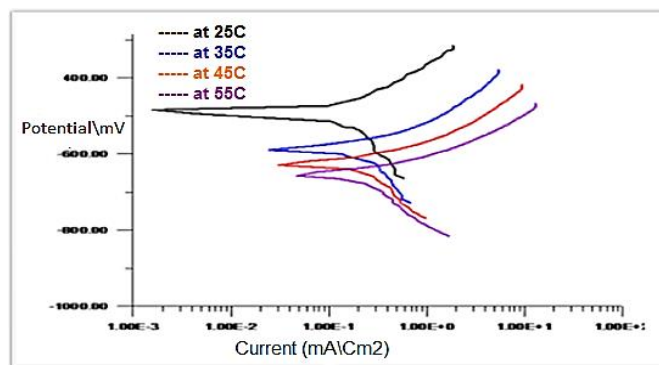


Figure 2. potentiostatic polarization curves for uncoated carbon steel(1045) in 3.5% NaCl solution at the temperatures range (298-328)K.

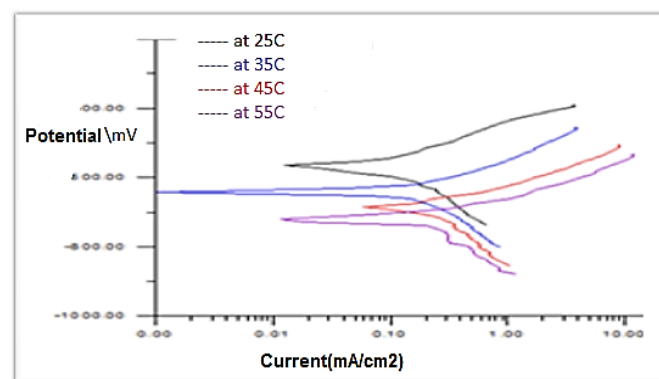


Figure 3. potentiostatic polarization curves for uncoated carbon steel(1137) in 3.5% NaCl solution at the temperatures range (298-328)K.

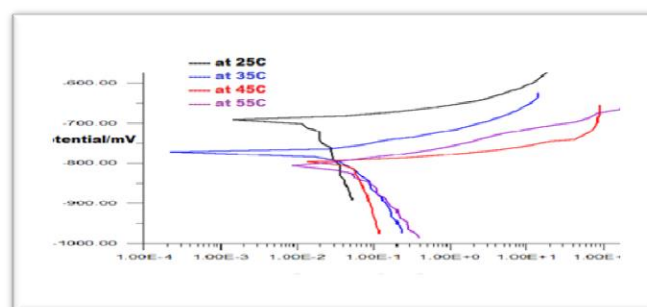


Figure 4. potentiostatic polarization curves for uncoated Aluminum(5083) in 3.5% NaCl solution at the temperatures range (298-328)K.

3.1.2. Potentiostatic polarization studies for coated alloys by plasma nitriding

The applied of plasma nitriding deposition of C.S alloys (1045,1137) and Aluminum alloy (5083) showed different degrees of protection efficiency in different temperatures and comparisons with the uncoated alloys in saline environment used (3.5%NaCl) show in figures

(5,6,7). The protection efficiency (PE) was obtained from equation (2) at temperature range (298-328)K, as show in table (3,4,5).

$$\%PE = \frac{(I_{corr})_{uncoated} - (I_{corr})_{coated}}{(I_{corr})_{uncoated}} * 100 \dots\dots\dots (2)$$

Table (7) corrosion kinetic parameters for uncoated and coated C.S (1045) with nitride ion by plasma nitriding in 3.5% NaCl at different temperature range(298-328)K.

Temp./K	E _{corr} /m V	I _{corr} /μA .cm ⁻²	b _c /mV .Dec ⁻¹	b _a /Mv. Dec ⁻¹	w.l/g. m ² .dl ⁻¹	Penetration loss/mm.a ⁻¹	Protection efficiencies%	R _p
Uncoated	298	-703.7	16.36	-307.7	27.7	1.32	-----	674.47
	308	-768.7	30.23	-175.4	34.2	2.43	-----	411.08
	318	-801.7	48.60	-313.9	18.7	3.91	-----	157.68
	328	-806.8	57.08	-215.5	40.4	4.59	-----	258.80
Coated	298	-770.0	1.59	-126.9	31.4	0.12	90.28	6874.15
	308	-816.3	3.09	-53.5	37.1	0.24	89.77	3078.55
	318	-845.1	7.40	-60.6	64.5	0.59	84.77	1833.36
	328	-865.8	10.79	-58.3	64.4	0.70	0.0954	1231.38

Temp./K	E _{corr} /m V	I _{corr} /μA .cm ⁻²	b _c /mV .Dec ⁻¹	b _a /Mv. Dec ⁻¹	w.l/g. m ² .dl ⁻¹	Penetration loss/mm.a ⁻¹	Protection efficiencies%
Uncoated	298	-514.6	116.92	-176.3	96.9	23.2	1.36
	308	-588.0	169.98	-199.2	92.1	42.5	1.97
	318	-629.1	207.49	-215.1	89.4	51.9	2.41
	328	-691.1	269.19	-220.2	78.8	68.4	3.18
Coated	298	-562.9	31.83	-52.9	51.1	7.9	0.36
	308	-648.0	53.06	-81.9	59.6	13.3	0.61
	318	-706.7	67.84	-81.1	80.1	17.0	0.78
	328	-733.5	98.05	-111.8	75.5	24.5	1.04

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. Figure (5,6,7) shows the polarization curve of alloys coated by plasma nitriding in different temperatures. In compared with the polarization curves for uncoated alloys, the corrosion potential for coated alloys goes to more active direction. 199.576

Table (8) corrosion kinetic parameters for uncoated and coated C.S (1137) with nitride ion by plasma nitriding in 3.5% NaCl at different temperature range(298-328)K.

Temp./K	E _{corr} /m V	I _{corr} /μA .cm ⁻²	b _c /mV .Dec ⁻¹	b _a /Mv. Dec ⁻¹	w.l/g. m ² .dl ⁻¹	Penetration loss/mm.a ⁻¹	Protection efficiencies%
Uncoated	298	-564.9	68.41	-134.3	100.9	17.1	0.79
	308	-604.3	114.19	-138.5	88.8	28.5	1.32
	318	-683.3	160.65	-156.6	80.1	40.2	1.87
	328	-718.5	173.4	-188.4	76.8	44.2	2.0
Coated	298	-609.4	26.04	-97.0	61.3	6.51	0.3
	308	-652.1	43.67	-81.0	41.7	10.9	0.5
	318	-674.9	77.78	-127.4	40.9	19.4	0.9
	328	-691.0	98.83	-192.1	44.5	24.7	1.1

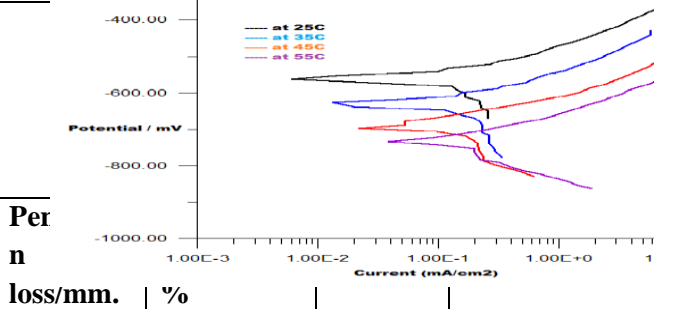


Figure 5. potentiostatic polarization curves for coated CS (1045) by plasma nitriding in 3.5% NaCl solution at the temperatures range (298-328)K.

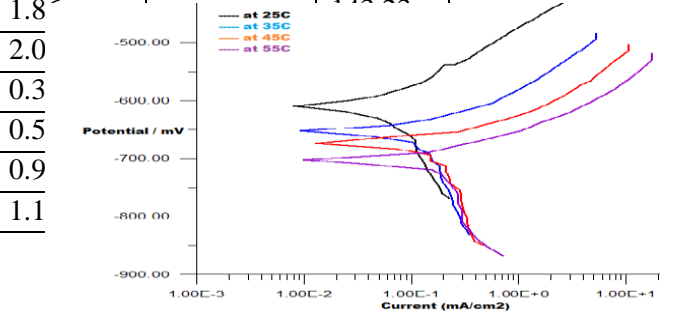


Figure 6. potentiostatic polarization curves for coated CS (1137) by plasma nitriding in 3.5% NaCl solution at the temperatures range (298-328)K.

Figure 9. corrosion kinetic parameters for uncoated and coated Al (5083) with nitride ion by plasma nitriding in 3.5% NaCl at different temperature range(298-328)K.

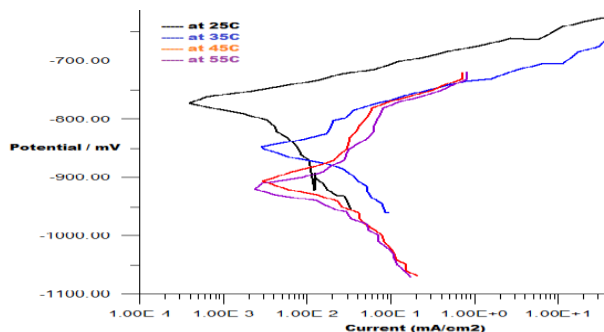


Figure 7. potentiostatic polarization curves for coated Al (5083) by plasma nitriding in 3.5% NaCl solution at the temperatures range (298-328)K.

Two important trends are evident. Firstly, the corrosion potential shifted toward more active value in coated by plasma nitriding, Secondly, the corrosion current densities were significant reduced with coated by plasma nitriding, where the protection efficiencies (PE) are ranged between (72.77%) at 298K to (63.57%) at 328K for CS (1045), (61.93%) at 298K to (43%) at 328K for CS (1137) and (90.28%) at 298K to (81.09%) at 328K for Al (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).

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

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

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

Where I_{corr} is corrosion current density, T is temperature in K, h is the planks constant ($6.626 \times 10^{-34} \text{ J.s}$), N is the Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$), ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation. Straight line were obtained from the plots of $\log I_{\text{corr}}/T$ 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 & after plasma nitriding were illustrated in tables (6,7,8).

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

T(K)	1/T(K ⁻¹)	E _{corr} /mV	I _{corr} /μA .cm ⁻²	LogI _{corr}	ΔH [*] /KJ .mol ⁻¹	-ΔS [*] /KJ.K ⁻¹	Ea/KJ .mol ⁻¹	A Molecules.c m ⁻² .S ⁻¹
Uncoated	298	0.0033	-514.6	116.92	19.39	139.99	22.459	5.45*10 ²⁸
	308	0.0032	-588	169.98				
	318	0.0031	-629.1	207.49				
	328	0.0030	-691.1	269.19				
Coated	298	0.0033	-562.9	31.83	26.88	125.58	30.137	3.1*10 ³⁰
	308	0.0032	-648	53.06				
	318	0.0031	-706.7	67.84				
	328	0.0030	-733.5	98.05				

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

T(K)	1/T(K ⁻¹)	E _{corr} /mV	I _{corr} /μA .cm ⁻²	LogI _{corr}	ΔH [*] /KJ .mol ⁻¹	-ΔS [*] /KJ.K ⁻¹	Ea/KJ .mol ⁻¹	A Molecules.c m ⁻² .S ⁻¹
Uncoated	298	0.0033	-564.9	68.41	23.05	131.67	26.040	1.40*10 ³⁰
	308	0.0032	-604.3	114.19				
	318	0.0031	-683.3	160.65				
	328	0.0030	-718.5	173.4				
Coated	298	0.0033	-609.4	26.04	34.73	101.01	38.045	5.9*10 ³¹
	308	0.0032	-652.1	43.67				
	318	0.0031	-674.9	77.78				
	328	0.0030	-691	98.83				

Table (4) the thermodynamic parameter at different temperatures for uncoated Al (5083) & Coated plasma nitriding in 3.5% NaCl solution.

T(K)	1/T(K ⁻¹)	E _{corr} /mV	I _{corr} /μA .cm ⁻²	LogI _{corr}	ΔH [*] /KJ .mol ⁻¹	-ΔS [*] /KJ.K ⁻¹	Ea/KJ .mol ⁻¹	A Molecules.c m ⁻² .S ⁻¹
Uncoated	298	0.0033	-703.7	16.36	31.93	113.78	42.123	2.2*10 ³⁴
	308	0.0032	-768.7	30.23				
	318	0.0031	-801.7	48.60				
	328	0.0030	-806.8	57.08				
Coated	298	0.0033	-770.0	1.59	51.29	68.83	56.311	3.9*10 ³⁶
	308	0.0032	-816.3	3.09				
	318	0.0031	-845.1	7.40				
	328	0.0030	-865.8	10.79				

3.3. The Surface Morphology AFM studies

Surface morphology of plasma nitriding for Al(5083) 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⁽¹⁶⁾. The results of the Surface Morphology Analysis by AFM, are shown in Fig.8. The average roughness of layer AlN was calculated as 85.94 nm.

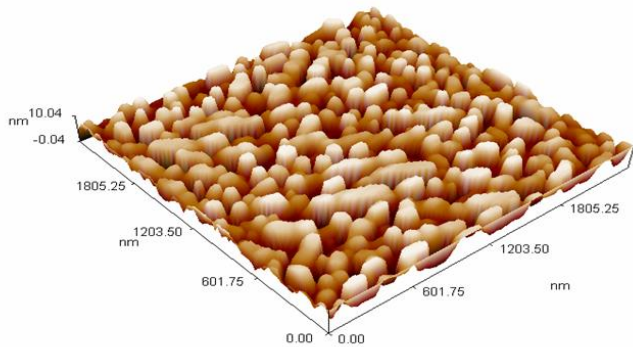
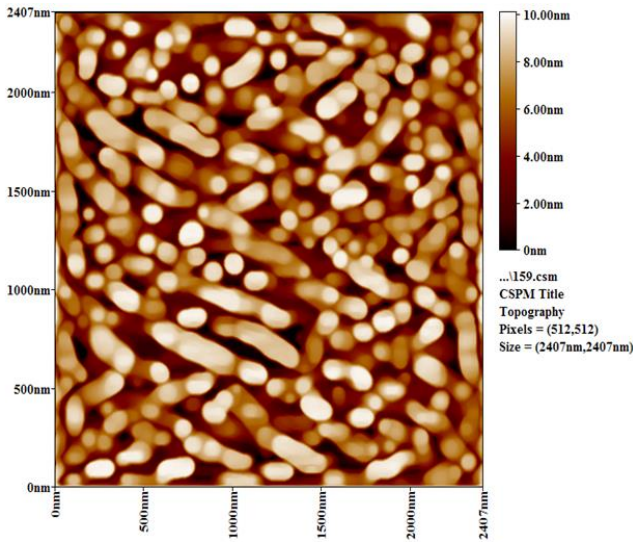
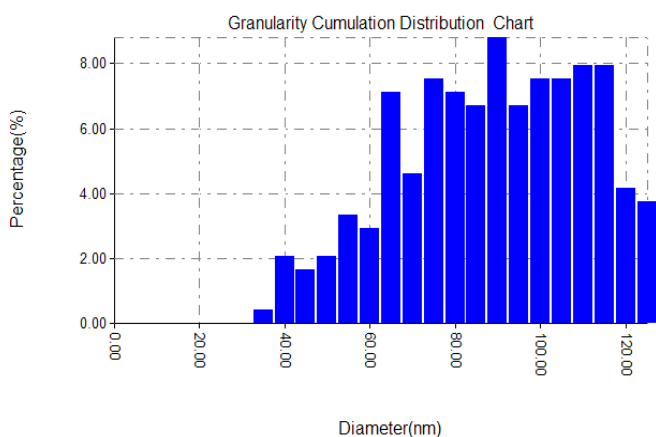


Figure 8. 2D and 3D views of AFM image Al(5083) by plasma nitriding.

Avg. Diameter:85.94 nm	<=10% Diameter:55.00 nm
<=50% Diameter:85.00 nm	<=90% Diameter:110.00 nm



IV. CONCLUSION

1. Plasma nitriding technique was successfully applied to coat C.S and aluminum alloys.
2. Nitride ion 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 active value in coated alloys, secondly, the corrosion current densities were significant reduced with coated by plasma nitriding.

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