Roughness Effect on Corrosion of Gr-Cu -Ni Coated Steel in Saline Water

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Abstract: *Effect of surface roughness on corrosion behavior for carbon steel was coated by metallic layers Cu- Ni Reinforced with Gr layers. Surface finishing P320, P600 and P1200 mesh used until a mirror shiny surface before metallic coated with Gr layers at consecrations 0.25, 0.5, 1and 2 g/l of Gr. First, X-ray diffraction), electron microscopy associated for carbon steel & Gr and Microscopic test for coated specimens. The techniques were performed to study the effect of saline water (3.5%) on the corrosion behaviors, Open circuit potential, Tafel polarization and impedance spectroscopy tests. At P320 Equivalent Circuit elements were decreasing but, Corrosion reaction's Rp was increased at 5 min and 0.25 g/l. And also, coating's Rpore with Electrolyte's Ru were increasing at 30 min for 0.5 g/l, and also coating's Rpore and Electrolyte's Ru were increased at 20 min for 1 g/l, At P600 ECE's were decreasing but, corrosion reaction's Rp was increased at 30 min 1 g/l, and also, coating's Rpore and Electrolyte's Ru were increased at 20 min for 1 g/l, and At P1200 ECE's were decreasing but, Coating's Ccoat was increased at 5 min 0.25 g/l, and also coating's Rpore and Electrolyte's Ru were increased at 0.5g/l, 30 min.*

***Keywords:* Carbon steel; Electrolyte; Cu –Ni -Graphene oxide coating; Corrosion**

behavior

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1. Introduction:

The multilayer metallic coatings lead to the proposal's enormous potential for improvement in performance relative to single-layer coating. [1], and corrosion is a significant reason for decay in industrial parts. So the advanced coatings improve in properties in their morphological, electrical, thermal, and mechanical characteristics [2],[3], Gr is applied as a corrosion inhibitor for metals. where a monolayer and multilayer graphene-coated onto metal surfaces have excellent barriers to oxygen diffusion, that renders the underlying metal inert from environmental oxidation [4]–[8].So, graphene-based anti-corrosion coatings are used to improving surface properties of a substrate [9], [10]. Gr consists of carbon atoms that are strongly bonded to form a hexagonal network, graphene has been generating sustained interest for many fields [11], [12].Cu- plating is used with both Ni and Cr plates and is considered to be the most preferable coating surface due to its ability to be spreader in a uniform layer and ductile with no pores with the advantage of polishing capability if several layers are used [13].Ni-plating can be used as a protecting agent against corrosion that can in the abrasion applications, resisting agent against the corrosion also as smoothing substance for other materials [13], [14].Multilayer chromium, nickel, and copper on the carbon steel, lead to copper and nickel are initially anodic versus chromium and become cathode versus carbon iron, when the electrolyte reaches the inner layer, galvanic corrosion take place [15].Resistance of a metal to electrochemical degradation was increasing by a coating of Cu with Gr. So, electrochemical characterization in aggressive CL environment shown changes in development of anti-corrosion coatings by using graphene layers [16]–[18]. Ni-graphene coatings provide corrosion resistance, which solves corrosion protection problems in the oil and gas industry [19],[20],[21]. Electrochemical for coating multilayer graphene improve the corrosion resistance of a Cu-Ni alloy [15], [22]–[24].

2. Materials and Methods:

2.1. Materials:

2.1.1. Specimens of carbon steel ST37-2

Carbon steel ST37-2 is produced by the Arab Company for Special Steel (Arkosteel) in Saddat City –Egypt with the following characteristics, Chemical analysis is measured at SPECTRO MAXX at EVACO Co. in 10th of Ramadan city, Egypt. which is shown in the following table 1

Table 1. Chemical Composition of Steel (37.2)

Chemical elements	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al	Co	Fe
%	0.12	0.3	0.42	0.014	0.01	0.04	0.003	0.02	0.05	0.02	0.003	99

- Scanning electron microscope (SEM) of carbon steel fig.1.
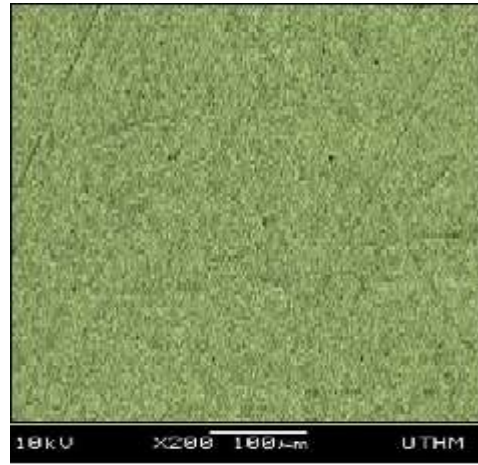
2.1.2. The characterizations of graphene oxide:

Graphene oxide was purchased from the company "Graphene laboratories ,Inc., indiamart , India " Color : broan,Thickness : 1 atomic layer- at least 60 %,Flake size : 0.5 – microns, Composition : Carbon 97%,Oxgen (20 %),Single layer graphene oxide solution ,Item no: sgraphene -001 ,which, it is prepared by Hummer's method which is oxidized graphene formed from oxidizing crystal graphite with a mixture of sulfuric acid, sodium nitrate, and potassium permanganate. Graphene Oxide is represented in fig.1., (b) graphene oxide characteristics as FE-SEM image, (c) graphene oxide characteristics as EDX spectroscopy analysis, and (d) graphene oxide characteristics as XRD pattern.

(a)
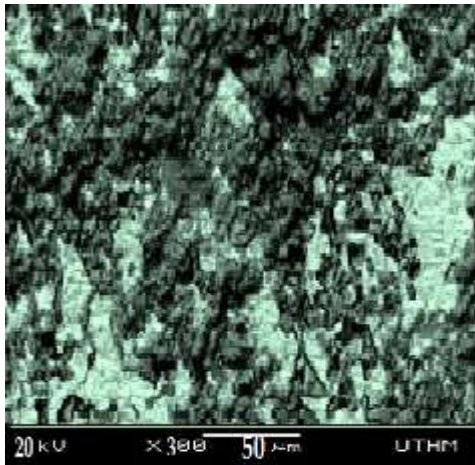
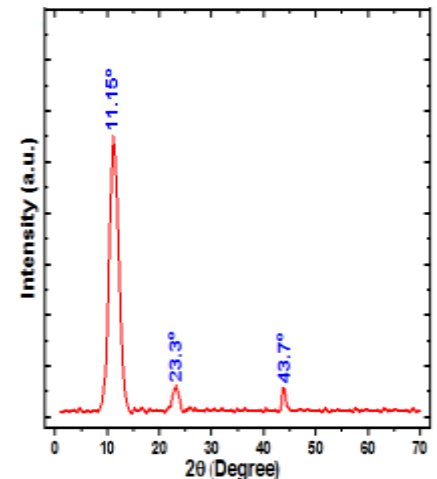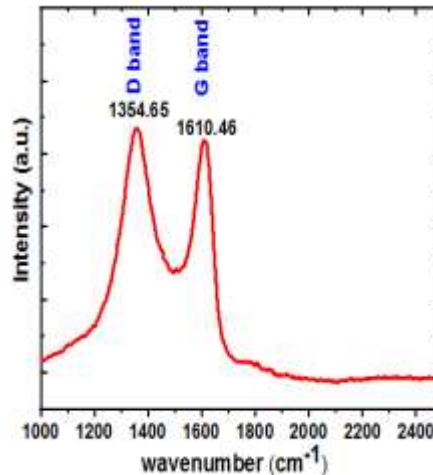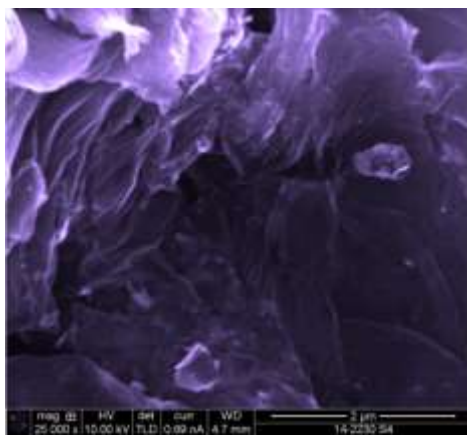(b)   (c)   (d)

Figure 1. a- Scanning Electron Microscope (SEM) of Carbon Steel ,b–d; Graphene Oxide Characteristics as, (b) FE-SEM Image, (c) EDX Spectroscopy Analysis, and (d) XRD Pattern of Graphene Oxide.

2.2. The schematic diagram of research sequence for metallic layers coated with graphene:

The searches can be summarized in the following preparation of specimens of the substrate, preliminary 5 samples for metallic coating, electroplating of graphene oxide, testing morphology of coating, and potentiodynamic scan all are represented in fig.2.The schematic diagram of the research sequence for metallic layers coated with graphene.

2.2.1. Cu- Ni- Metallic coating with Gr preparation processes

Preparations of specimens of substrate take place with the operations cutting, holing, grinding, emery, polishing, removal of grease, oxides and salts. Prior to the deposition of the coatings on Carbon steel 30X100X3mm dimensions were polished with struers® papers silicon carbide grades 320, 600 and 1200 mesh until a mirror shiny surface, Preliminary 5 samples were used to identify the suitable Cu, Cu and Ni plating conditions fig.2. for reach the appropriate conditions for the research five samples to reach the research, Electroplating of graphene oxide coating is achieved by 44 ml of

deionized water and 308 ml of acetone to dissolve the graphene oxide for 90 min in the ultrasonic 100 watt – 40 kHz to activation then added to electrolytes with different ratio 0.25,0.5,1and 2 g/l . Therefore, the graphene oxide is coating by electroplating between the coated metallic layers of Cu, Cu and Ni with two similar electrodes by the cell is represented in fig.2.
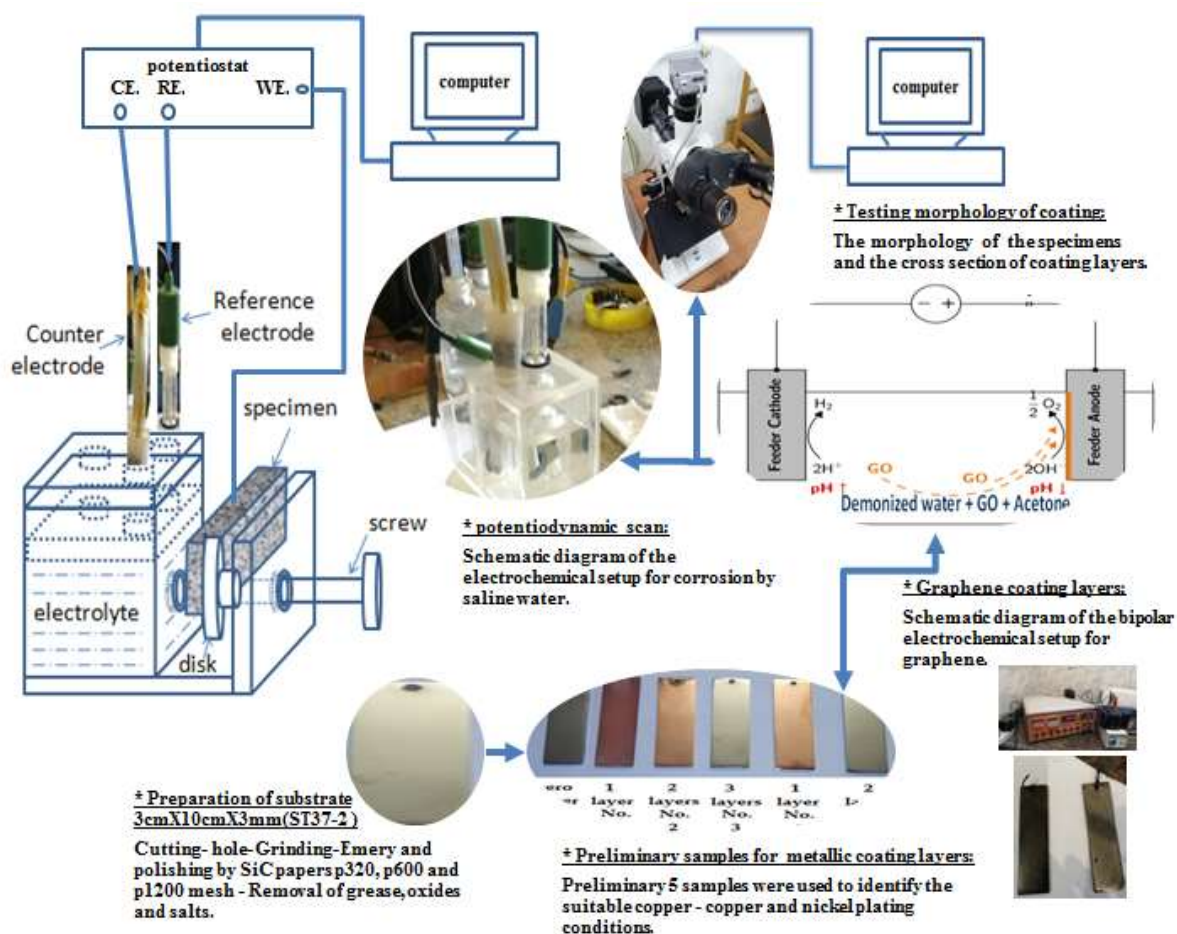

Figure 2. Schematic Diagram of Research Sequence for Metallic Layers Coated with Graphene.

2.2.2 Experimental setup design for testing morphology of coating:

z The morphology of the prepared specimens are tested by the optical microscope CIM® with digital camera moticam 2300 – 3.0MPixel USB 2.0 ,U S A shows morphology of the specimens and the cross section in fig.2.

2.3. Electrochemical measurements:

2.3.1. Experimental setup design for testing corrosion of coating

The corrosion of prepared specimens are tested by the designed cell which consists from three electrodes reference calomel electrode Rf (HI 5412), Pt counter electrode and specimen. They are immersed in saline water as electrolyte as shows in the Figure 2.

2.3.2. The corrosion techniques

An electrochemical process is electrochemical corrosion monitoring techniques are based on the corrosion of metals in solutions of electrolytes. Where, the electrochemical techniques are suitable for

corrosion of metals in media with high electrical conductance. And also, if corrosion reactions have an electrochemical nature, electrode potential, electric current and electrical resistance formed on the metal surface are the main characteristics of corrosion. So, we measure these three parameters characterize and monitor the corrosion of metals in electrical conductive media[24].

The corrosion techniques were tested by Gamry (PCI4/300®) instrument ,U S A where, the various factors were achieved on the corrosion behavior of carbon steel 37-2 coated by metallic layers (copper-copper-nickel) reinforced with graphene by the following techniques:

2.3.2.1 open circuit potential, Eoc:

For gamry's software, the open circuit potential, Eoc is the equilibrium potential assumed by the electrode in the absence of electrical connections to the electrode. So, all potentials are specified as the potential of the working electrode with respect to the reference electrode "vs. Eref"or this open circuit potential "vs. Eoc". So, the equations used to convert from one form of potential to other shown in following:

E vs. Eoc = (E vs. Eref) - Eoc

E vs. Eref = (E vs. Eoc) + Eoc

The potentials are versus Eref or versus Eoc, the sign is used positive a potential, which, more anodic it is.

2.3.2.2 The Tafel polarization test:

Potentionstat records an applied current to cell that provides an increase in potential. Where, potential drives a reaction at the anode or cathode, is observed a current. That is, a potential where a total anodic current equals a total cathodic current is an open-circuit potential (Eoc), a potential swept across a range and a current is measured. [25].

Corrosion occurs at a rate specified by the equilibrium between opposing electrochemical reactions. First is the anodic reaction, metal oxidizes, releasing electrons into the metal. Second is the cathodic reaction, a solution form (usually O_2 or H^+) is reduced, removing electrons from the metal. By equilibrium of two reactions, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. The two reactions can happen on one metal or on two dissimilar metals (or metal sites) that are electrically connected [26].

2.3.2.3 The electrochemical impedance spectroscopy (EIS):

By, applying an AC potential to an electrochemical cell and then measuring the current through the cell to get electrochemical impedance [27], [28].

The impedance attitude of coating is explored where most paint coatings degrade with time, resulting in an attitude more complex. After certain of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can happen with the new interface. According to the simple equivalent circuit elements are Ccoat, the capacitance of coating, its value is much smaller than CdL, a double layer capacitance, with, units that are pF or nF, not μF. Rpore, pore resistance, and is the resistance of coating for ion-conducting paths develops in. The paths may not be physical pores full of electrolytes. On the metal side of the pore, an area of the coating has divided and a bore filled with an electrolyte solution has formed. with, very different than the bulk solution outside of the coating.Ru, electrolyte resistance, Rp, polarization resistance[28]–[30].

2.3.3. Corrosion Rate Measurement (mpy)

The rate of corrosion (C_R) is directly proportional with its corrosion current density (i_{corr}) in a given environment in according the relation [3], [31] :

$$C_R = 0.13 \times i_{corr} \times \left(\frac{e}{\rho}\right) \qquad (1)$$

This equation calculates C_R in (m/y), e and ρ are equivalent weight and density of carbon steel, respectively. The data of corrosion rate indicate that the nanoparticle coatings led to decreasing in corrosion rate of carbon steel.

The applied coatings were evaluated by corrosion current densities for uncoated and coated specimens which, used to calculate protection efficiencies (PE%) as follows [32]:

$$PE\% = \left[1 - \frac{i_{corr_{coated\ specimen}}}{i_{corr_{uncoated\ specimen}}}\right] \times 100 \qquad (2)$$

The best efficiency was for Cu-Ni-Gr coating. Surface porosity fraction evaluated by both potentiodynamic polarization and indentation measurements. and, the porosity percentage (PP%) is calculated by the following equation [32]:

$$PP\% = \left[\frac{R_{P_{uncoated\ specimen}}}{R_{P_{coated\ specimen}}}\right] \times 10^{\frac{-\Delta E_{corr}}{b_a}} \times 100 \qquad (3)$$

So, the polarization resistances of the uncoated R_p, uncoated, the polarization resistances of the coated R_p, coated samples, the corrosion potential difference between them, ΔE_{corr}, and b_a is the anodic Tafel slope of the uncoated sample. The lowest porosity was found for Cu-Ni-Gr coating [32].

2.4. Microstructural characteristics of surface analysis:

This was shown in the XRD diffractograms of GO/Cu-Ni coatings with concentrations; (a) 0.0, (b) 0.5, (c) 1.0 and (d) 2 (g/l) of GO on carbon steel fig.3.
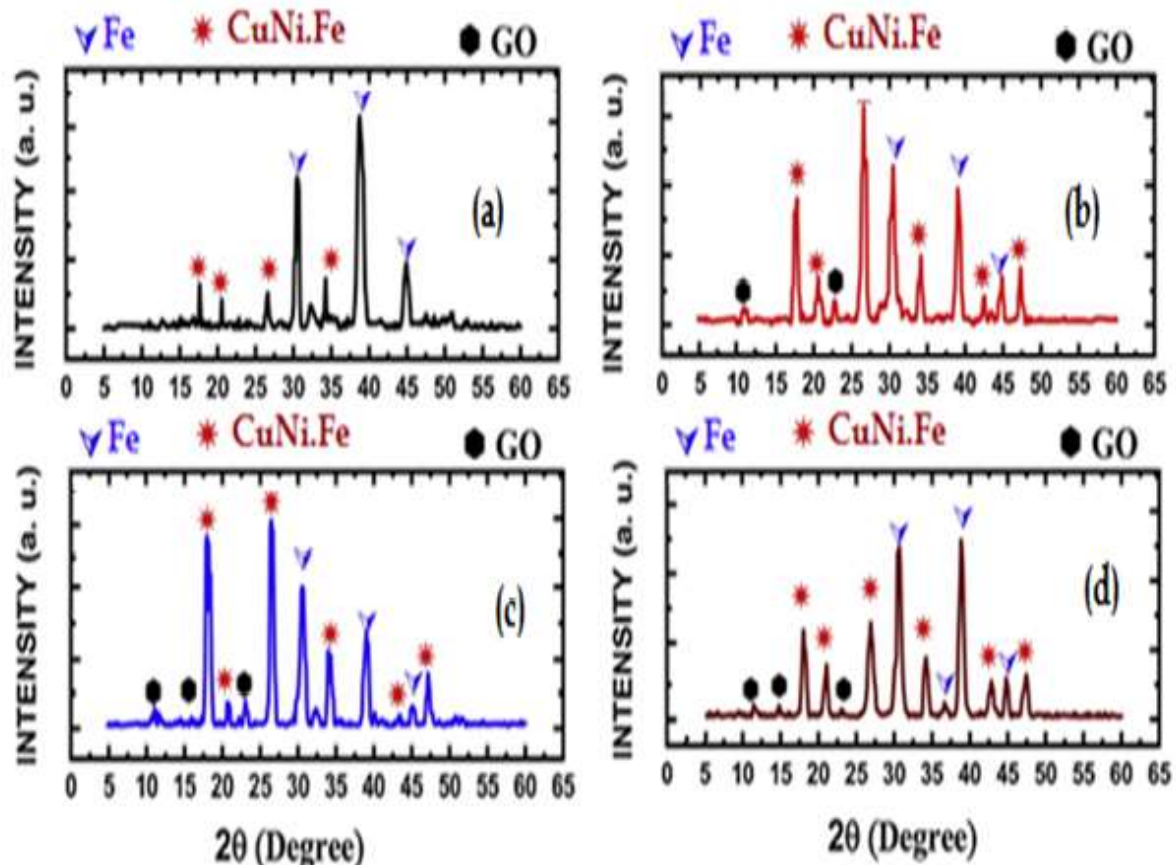

Figure 3. a–d; the XRD Diffractograms of GO/Cu-Ni Coatings with Concentrations; (a) 0.0, (b) 0.5, (c) 1.0 and (d) 2 (g/l) of GO on Carbon Steel.

3. Results and discussions:

3.1 Optical Observations of cross section and morphology for coating:

3.1.1 Cross-sections and morphology of electroplating for 1, 2 gr / L of Graphene at 10, 20 min for P320, P600and P1200:

For cross-section, the first layer was soft next to the substrate; the two layers Cu – graphene were hard spongy form, the two layers Cu – graphene brittle spongy form and Ni – graphene hard high strength spongy form with thickness 430.9 um, and For morphology, there were spongy form and had few cavities on surfaces of the coating fig.4.
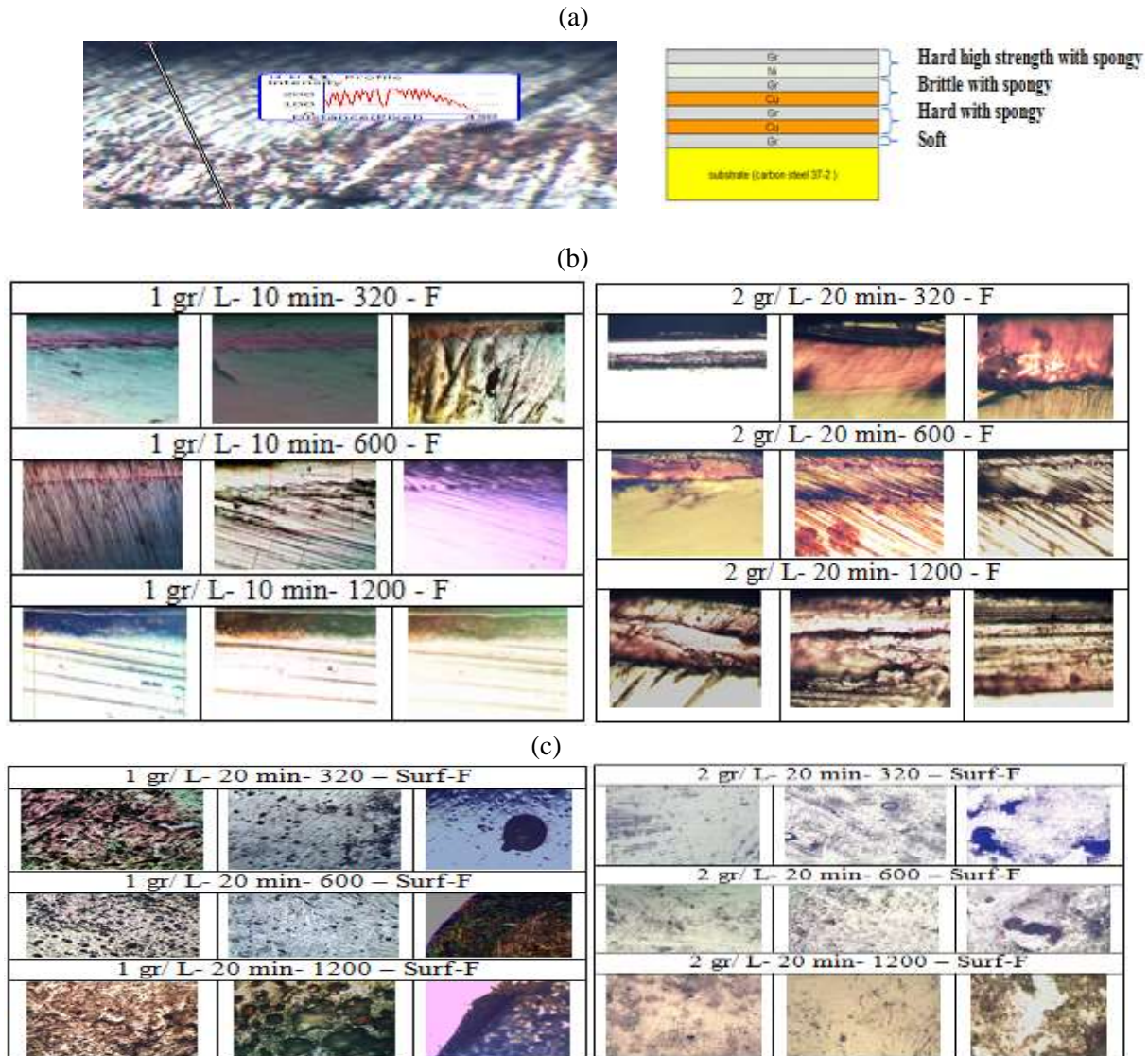
(a)

(b)

(c)

Figure 4. Cross-Section and Morphology of Coating (a) Sketch of Layers with Fatures, (b) Cross-Section and (c) Morphology of Coating for 1, 2 g/l Graphene with P320, P600 and P1200

3.2 The open circuit potential, Eoc:

The electrochemical measurements took place by Gamry PCI300/4 Potentionstat with a computer, three-electrode cell, a specimen as a working electrode with an active area of 1 cm2, a counter electrode, P_t, and reference electrode, SCE, used for our test.

3.2.1 Effect of layers coating on open circuit potential, Eoc of carbon steel:

Eoc measured for the substrate, Cu-Ni coated, and Cu-Cu-Ni coated in fig.5.(a),The three layers located in region between No corrosion to corrosion and substrate located in corrosion.

3.2.2 Effect of P320, P600and P1200 on open circuit potential, Eoc at 1 gr/L graphene:

In fig.5. (b) that with 1 g/l Gr at 20 min on P600 surface finishing at 20 min. rising from uncertainty regarding corrosion activity $V \leq -0.20$ towards no corrosion occurred $V > -0.20$ and, with P320 still in uncertainty regarding corrosion activity region $-0.35 \leq V \leq -0.20$ within 300 (S).
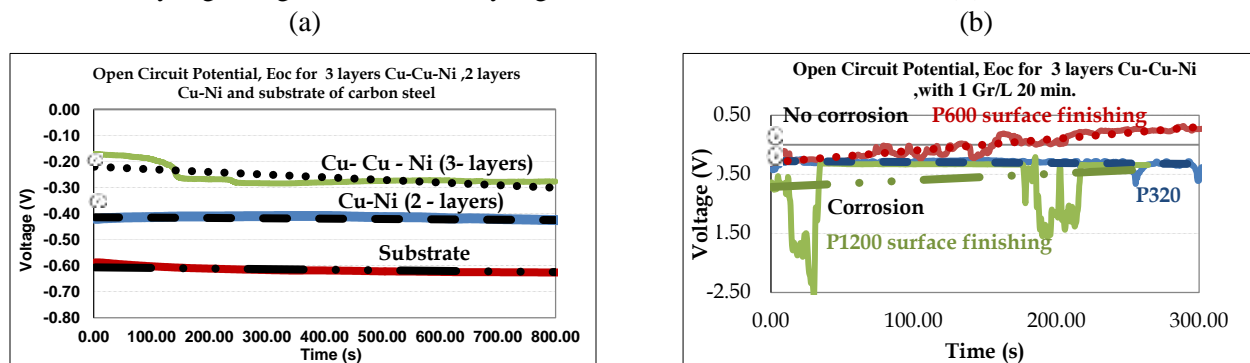
(a)   (b)

Figure 5. The Relation between Voltage (V) and Time(S) for Saline water (a) Multilayer of Cu-Ni & Carbon Steel, (b) Effect of the P320, P600and P1200 at 1 gr/L Gr

3.3 The Tafel polarization test:

3.3.1 The effect of layers coating on tafel polarization test of carbon steel:

Tafel polarization test measured for the substrate, Cu-Ni coat, and Cu-Cu-Ni coat. The voltage of corrosion goes from -884 to -404 volt by coating as shown in Figure 6 (a).

3.3.2 Effect of P320, P600and P1200 on tafel polarization at 1 g/l graphene 20 min:

Tafel polarization test measured for Cu-Cu-Ni coated by 1 g/l Gr 20 min. P600 and P320 achieved for less corrosion than P 1200 where, shown in Figure 6.(d) and table 2.

Table 2. Tafel Polarization Resistance Results for 1 g/l of Graphene 20 min. between 3 Layers Cu-Cu-Ni Coating in Saline Water.

Tafel polarization Resistance	1 g/l 320	1 g/l 600	1 g/l 1200
Lower Fit Limit (mV vs. Ref. (Pt))	-1139	-924.7	-1268
Upper Fit Limit (mV vs. Ref. (Pt))	1179	1473	1115
Beta A (V/decade)	1.33	1.24	0.56
Beta C (V/decade)	0.98	0.76	0.28
Icorr (uA)	0.1408	0.001546	956
Ecorr (mV)	-374	-271	-751
Rp (ohms)	1738000	132400000	84.84
Corrosion Rate (mpy)	0.1072	0.001178	728.1
Protection efficiencies (PE %)	100	100	98.5
The porosity percentage (PP %)	0.0001	0.000001	1.82

3.3.3 Effect of P320, P600, and P1200 on corrosion rate (mpy) and protection efficiencies PE (%) with 1 and 2 g/l graphene

The corrosion rate and protection efficiencies for a specific time of Gr's coating calculated as an explanation to the equation (2.8), where the results shown increase in protection efficiencies laded to decreasing in the corrosion rate, at 1 g/l Gr at 20 min, Corrosion rate for P600 was the least 0.001 mpy with the biggest protection efficiencies 100 %, where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement ,at2 g/l Gr at 10 min. corrosion rate for P600 was the least 48.95 mpy with protection efficiencies 67.42 %.
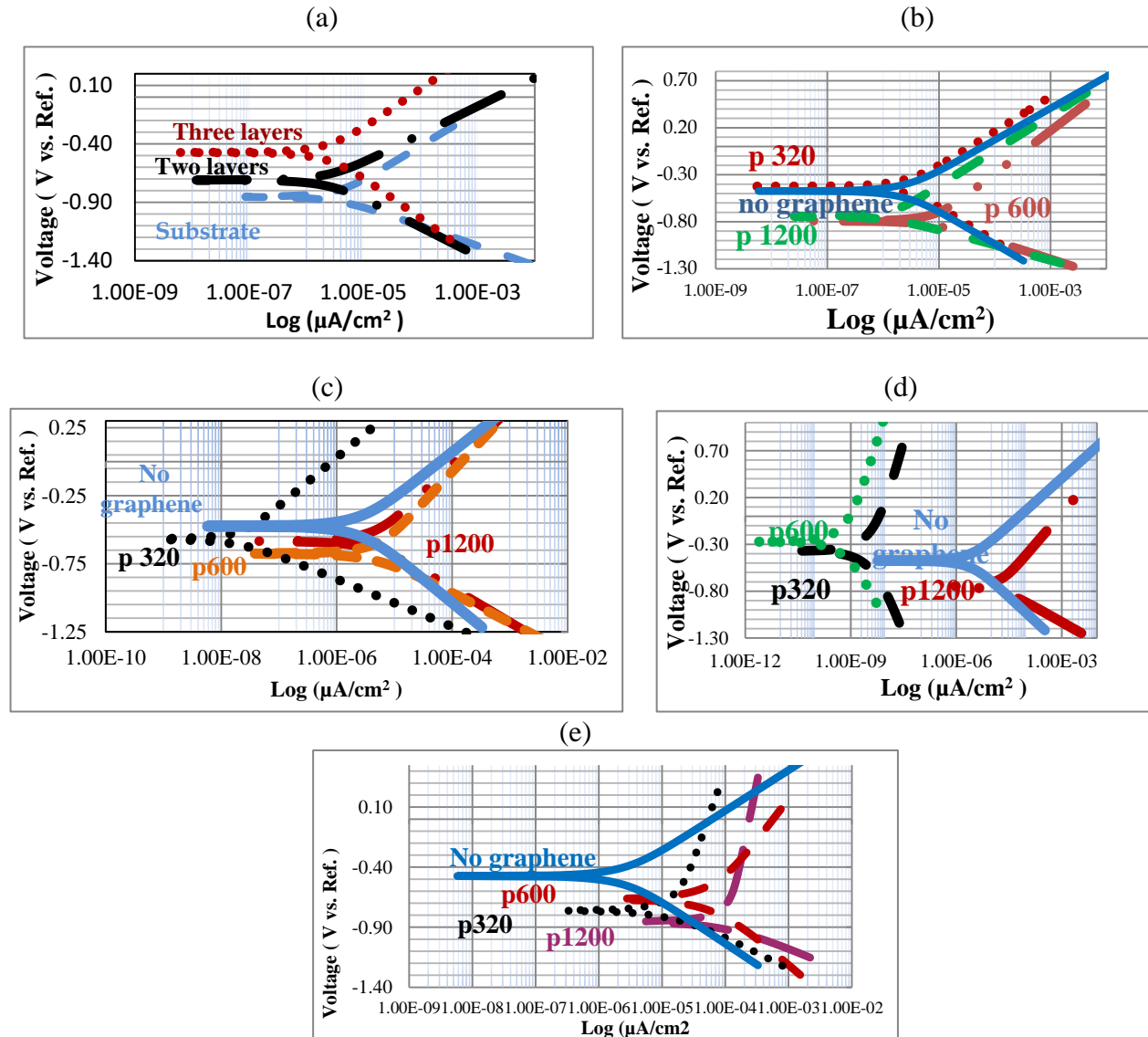

Figure 6. The Tafel Plot Relation Between Voltage (V) and Log (μA/cm²) for Saline Water of Measured for (a) Multi-Layers Coating on Carbon Steel,(b) Concentration 0.25 Gr /L,(c) Concentration 0.5 Gr /L,(d) Concentration 1 Gr /L ,and (e) Concentration 2 Gr /L Electroplating on Cu-Cu-Ni Coated Carbon Steel with & without Graphene.

3.4 The electrochemical impedance spectroscopy (EIS):

3.4.1 Effect of coating Cu-Cu-Ni on carbon steel on electrochemical impedance spectroscopy (EIS):

EIS measured in Figure 7. (a) The values of ECE's for Nyquist plot with no Gr, Where, total R 1.73E+04 ohm. And also, Ccoat was 4.98E-06 (F) and CdL was 4.38E-05 (F).

3.4.2 Effect of P320, P600, and P1200 in Cu-Cu-Ni at 0.25, 0.5, and 1 g/l Gr on steel by EIS:

EIS for P320, P600, and P1200 with 0.25 ,0.5 and 1 g/l Gr on steel in saline water shown in Figure 7.(b)-(d) ,where the values of ECE's were respectively **at 0.25 g/l Gr**, at P320the highest total R 2.20E+04 ohm,C 1.60E-5 F. **At 0.5 g/l Gr** , the highest total R 2.20E+04 ohm at P320 the lowest total R 5.94E+03 ohm at P600 , the highest total R 1.07E+12 ohm , C 7.30E+2 F at P600 the lowest total R 1.00E+02 ohm at P320, C 5.17E-08 F at P1200.**At 1 g/l Gr**, at P600, the highest total R 2.19E+04 ohm at P600, C 1.29E-5 F at P1200and the lowest total R 1.28E+04 ohm at P1200, C 6.03E-6 F at 320.
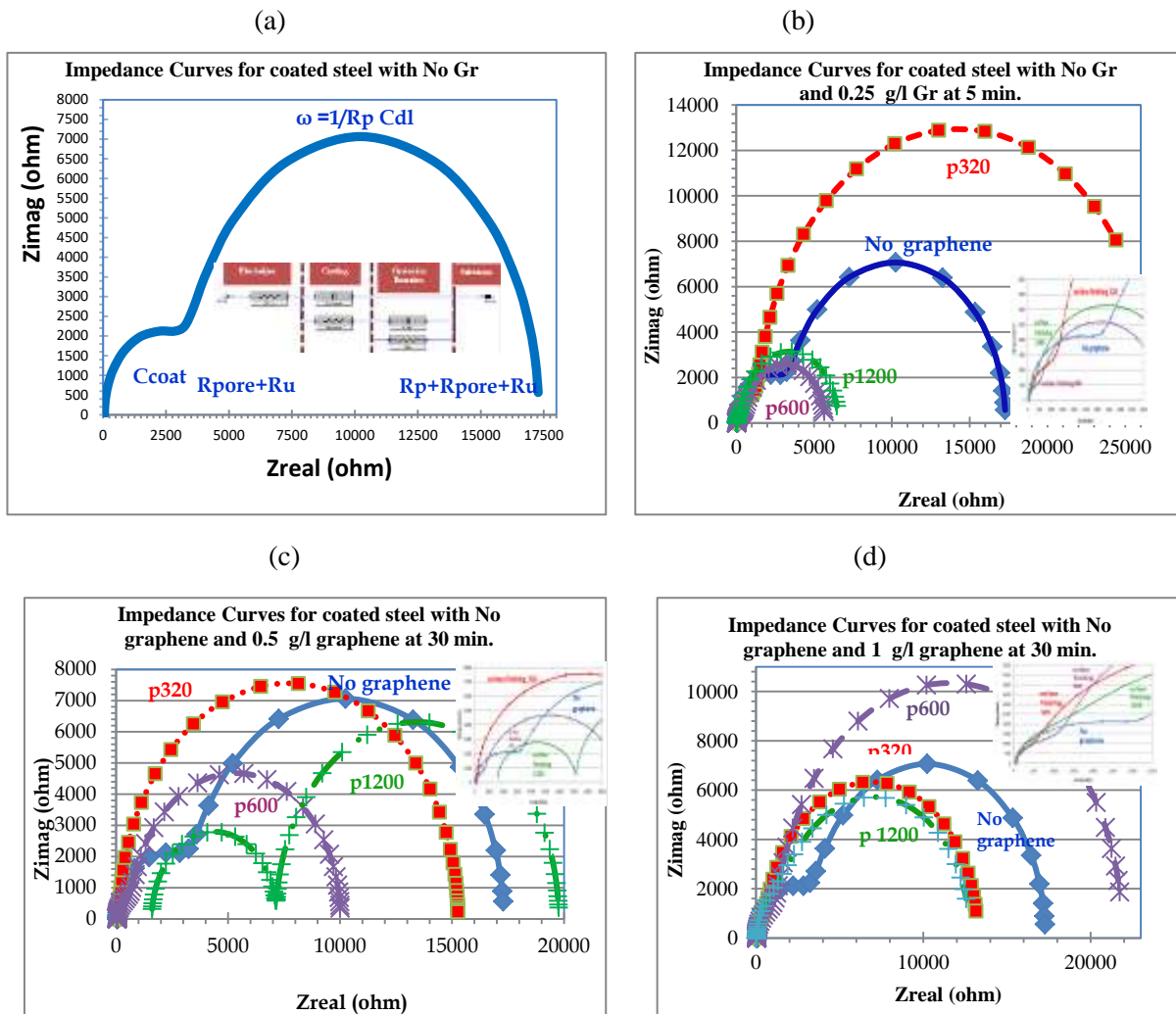
(a)

(b)

(c)

(d)

Figure 7. EIS Nyquist Plot Between –Zimag (ohm)and Zreal (ohm) (a) Coating Cu-Cu-Ni on Carbon Steel,(b)-(d) P320, P600, and P1200 in Saline Water ,(b)with 0.25 g/l Gr,(c) with 0.5 g/l Gr ,and (d) with 1 g/l Gr.

4.Conclusions:

The effect of studying different concentrations of graphene with different times and different surface on coated steel leads to the following conclusions:

1. The morphology of coating was spongier as shown in microscope in the inner faces than the outer faces of electrodes of the cells coating.

2. The protection efficiencies were decreasing by 99.6, 99.2, 95.1and55.4 % with increasing concentration of graphene coating 0.25, 0.5,1 and 2 g/l respectively between layers. The corrosion rates were increasing by 0.6, 1.1, 6.9 and 67 mpy with increasing concentration of graphene coating 0.25, 0.5,1 and 2 g/l respectively between layers.

3. The types of corrosion were pitting corrosion, where the highest protection against corrosion were at concentration 1 g/l at 20 min Gr coating with P600 and P320 mesh surfaces finishing were corrosion rate 0.001178 and 0.1072 mpy, PE % 100,100,PP % 0.000001, 0.0001,Rp 132400000, 1738000 ohm respectively in saline water. where The obtained experimental results are compared with results of K. Ollik and M. Lieder [10] with a good agreement .The next protection against corrosion were at concentration 0.5 g/l at 30 min Gr coating with P320 mesh surfaces finishing were corrosion rate 0.1615 mpy,protection efficiencies 99.7 %,porosity percentages 0.4 %,polarization resistances 444.5 ohm .

4. The protection achieved by increasing the pore resistance R_{pore} ohms of coating accompanied with decreasing of C_{coat} F, R_p ohms and C_{dl} F, with increasing of R_u. For ECE's were <u>At P320:</u> All elements decreasing but, Rp increasing at 5 min and 30 min ,and Rpore increasing at 0.5,1g/l, 20 min and 30 min, <u>At P600:</u>All elements decreasing but, Rp increasing at 5 min and 30 min by increasing concentration, and Rpore increasing at 0.5,1g/l, 20 min and 30 min. and <u>At P1200:</u>All elements decreasing but, Rp increasing at 5 min and 30 min 0.5 g/l by increasing concentration, and Rpore increasing at 0.5,1g/l, 20 min and 30 min.

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