Electrodeposition of Ni–GNS–TiO₂ nanocomposite coatings as anticorrosion film for mild steel in neutral environment

M.W. Khalil, Taher A. Salah Eldin, H.B. Hassan, Kh. El-Sayed, Z. Abdel Hamid

Article history:
Received 24 January 2015
Revised 19 May 2015
Accepted in revised form 21 May 2015
Available online 23 May 2015

Keywords:
Mild steel silos
Graphene nanosheets (GNS)
Nanocomposite
Corrosion
Electrodeposition technique

Abstract
In this article nanocomposites of graphene nanosheets–anatase titanium dioxide (GNS–TiO₂) were prepared via hydrothermal method. In this method graphene oxide (GO) was reduced to graphene nanosheets (GNS) simultaneously with anatase (TiO₂) growth in situ on the graphene nanosheet (GNS) surface. The resulting GNS–TiO₂ nanocomposite was characterized using X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). The percentage of TiO₂ in the prepared GNS–TiO₂ was determined by thermo gravimetric analysis technique (TGA). The fabricated GNS–TiO₂ nanocomposite was codeposited with Ni by electrodeposition technique and used as a protective film for mild steel used in construction of steel silos. Different operating conditions for the deposition process were adopted to obtain Ni–GNS–TiO₂ nanocomposite coatings with good morphological properties. The Ni–GNS–TiO₂ nanocomposite coatings were characterized using a field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDX). Moreover, Ni–GNS–TiO₂ nanocomposite coatings were subjected to different electrochemical and mechanical tests to evaluate their corrosion behavior and hardness in comparison with that of pure Ni coating. It was found that the corrosion rate of the Ni–GNS–TiO₂/mild steel electrodes decreases and the microhardness increases with increasing the wt.% of GNS–TiO₂ nanocomposite in the prepared electrodes. The best corrosion resistance value of 33.1 kΩ cm² and relatively high hardness value of 478 HV were recorded for the composite coating electrode that contains 20.4 wt.% GNS–TiO₂ compared with the other composite coating electrodes or pure Ni coatings.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

For many decades, mild steel has wide field of applications in industry and technology especially that requiring a lot of steel such as construction of steel silos due to its availability and low cost [1]. Besides, it is weldable, very hard, durable and easy to be annealed. Nevertheless it ranks high among the construction materials which undergo corrosion at high rates. Mild steel silos are subjected to different forms of corrosion due to many factors such as the presence of chloride ions in the surrounding environment or silage acids that are produced during the process of silage making such as lactic acid and acetic acid or organic acids like formic acid used as additives to inhibit the growth of microorganisms, which generally destroy the nutrient value of the grain when stored. These acids cause deterioration and failure of the metal components of structures [2]. It is well known that corrosion of metals is a serious problem that faces societies causing many difficulties to the economy, safety and health [3,4].

Corrosion control and prevention can be achieved by applying corrosion-resistant materials or materials with a corrosion allowance, applying external coatings (paints) or internal lining systems such as cement, rubber, epoxy or coatings [5]. Generally, various protective methods have been adopted to control or minimize the corrosion of mild steel; one of them is the use of protective coatings such as Ni, Cu, Zn metallic coatings and alloy coatings such as Ni–Zn [6,7] and Ni–Co [8–12]. Coating plays a vital role in improving the surface quality and providing protection for a substrate by isolating it from the surrounding environment [6–12].

Moreover, additional benefits and desirable properties are obtained by combining nanoparticles with specific properties into the metal matrix during the electrodeposition process to produce nanocomposite coatings. There is still a continuous search for improving the protective ability of the coatings by the inclusion of some nanoparticles as a reinforcement phase, such as TiO₂, SiO₂, Al₂O₃ and ZrO₂ to the coating layer during the electrodeposition; this process granted the forming composite coatings a number of advantages over the traditional coatings [9–15].

Recently, graphene which is a carbon allotrope has attracted worldwide attention due to its extraordinary and unique properties. Graphene...
n anosheet (GNS) is a single two-dimensional layer of graphite in a honeycomb lattice that has promising properties including high thermal conductivity, high electrical conductivity, high Young’s modulus and excellent biocompatibility. It is considered as a very strong material as it is ~200 times stronger than steel and has a large specific surface area. Owing to the aforementioned advantages, graphene-based materials have been widely used to design and prepare graphene-oriented electrodes for a wide range of applications in electrochemistry[16,17]. It is a very promising new generation material due to its excellent properties; it is believed that it could be used to enhance the performance of coatings significantly. Moreover, it can be used with nanoparticles to form graphene-nanoparticle composite coatings and as high quality coating materials[18].

Graphene-based material has been prepared using graphene oxide that contains functional groups such as epoxide, carbonyl, hydroxyl, and carboxyl which increase the surface ability to be functionalized with metal or metal oxide[16,17,19]. Due to its outstanding properties, graphene is reported to improve the anti-corrosion property of the coating systems[17,20].

Meanwhile, TiO2 nanoparticles that are inexpensive and nontoxic were reported as good anti-corrosion reinforcement with Ni filler[14]. Moreover, TiO2 nanoparticles have antibacterial and antifungal effects[21,22]. Modification of graphene sheets with TiO2 nanoparticles produces a GNS–TiO2 nanocomposite that will produce a promising reinforcement for Ni-based nanocomposite coatings in addition to its inhibitive effect on the growth of some microorganisms that could be produced during the storage of seeds in the steel silos.

In the present work, the issue of preparation of a promising protective coating for mild steel is presented. GNS–TiO2 nanocomposite has been prepared via one step hydrothermal method, this means that the reduction of graphene oxide (GO) to graphene nanosheets (GNS) concurrently with the formation of TiO2 nanoparticles on its surface is carried out. The synthesized GNS–TiO2 nanocomposite is co-deposited with Ni on the surface of mild steel using electrodeposition technique. Ni–GNS–TiO2 nanocomposite coatings were subjected to different electrochemical and mechanical tests to evaluate their corrosion behavior and hardness in comparison with that of pure Ni coating.

2. Experimental techniques

2.1. Chemicals and materials

Chemicals of analytical grade were used in this study. Titanium (IV) isopropoxide (Ti(OCH(CH3)2)4) (99.99% Sigma-Aldrich) was used to synthesize anatase TiO2 nanoparticles. In addition, pure ammonia solution (33% Fluka) was used for pH adjustment. Natural graphite powder (99.9995%, 200 mesh–Alfa Aesar) was used to synthesize graphene oxide nanosheets. Sulphuric acid (95–97% H2SO4–Sigma–Aldrich), sodium nitrate (NaNO3–Sigma–Aldrich), hydrogen peroxide (30% H2O2–Alpha Chemika) and potassium permanganate (KMnO4), analytical grade, were used for different preparation steps.

2.2. Preparation of graphene oxide

Graphene oxide (GO) nanosheets were prepared by Hummers method[23] with some few modifications. Briefly, 1 g of natural graphite powder and 1 g of sodium nitrate (NaNO3) were mixed with 50 ml of sulfuric acid (97% H2SO4) at 70 °C with a continuous stirring. The mixture was placed in an ice bath at 0 °C and 6 g of potassium permanganate (KMnO4) was added gradually to the mixture. Magnetic stirring is applied during the whole steps of preparation. The mixture was left over night at 35 °C, after that 92 ml of deionized water was added slowly to the solution which was kept at 98 °C, then 280 ml of hot deionized water and 10 ml of 5% H2O2 were added sequentially to the reaction mixture. A brown mixture was obtained. This was washed several times with ethanol and deionized water using a centrifuge operated at 4000 rpm for 15 min. The graphene oxide nanosheets were obtained after drying in vacuum at 60 °C for 12 h.

2.3. Preparation of GNS–TiO2 nanocomposite

0.1 g GO was dispersed in 50 ml deionized water under ultrasonic treatment for 1 h. 0.4 ml titanium (IV) isopropoxide [Ti(OCH(CH3)2)4] (TTIP) was added dropwise to the solution that was subjected to a vigorous stirring, and then the system was sonicated for 15 min. The operating pH 4 was adjusted using ammonia solution. The suspension was transferred to 100 ml Teflon-lined stainless autoclave tube and kept in an oven at 170 °C for 24 h. GNS–TiO2 nanocomposite was isolated by centrifugation and washed several times with deionized water and then dried at 80 °C for 12 h.

2.4. Electrodeposition process

Pure Ni, Ni–GNS and Ni–GNS–TiO2 nanocomposite coatings were deposited on mild steel sheets; each has dimensions of 50 mm × 40 mm × 0.6 mm using Ni bath solution. The chemical composition of mild steel used in this study is shown in Table 1. The composition of the electrolyte for the deposition and the operating conditions are given in Table 2. Pure Ni metal and mild steel plates were used as anode and cathode, respectively. Prior to the electrodeposition process, mild steel surface was polished using emery papers of different grades to get smooth and bright surface, then it was degreased in an alkaline degreasing solution consisting of NaOH, Na3PO4 and Na2CO3 at 70 °C, and it was rinsed with water, then it was immersed in 10% HCl to remove the rust, after that it was washed with deionized water and dried. Finally, the electrode was transferred to the deposition solution. The operating pH 5 of the electrolyte was adjusted using ammonia solution and/or 10% H2SO4. Different operating conditions were tested to prepare the specimens. The electrodeposition process was carried out at different current densities (c.d.) from 2.5 to 20 mA cm−2 at a constant concentration of GNS–TiO2 nanocomposite (0.4 g l−1). Other batches of Ni–GNS–TiO2 nanocomposite coating electrodes were prepared at different concentrations of GNS–TiO2 composite (0–1 g l−1), at a constant current density of 10 mA cm−2 for 60 min, and at a stirring speed of 150 rpm. Prior to the deposition process, GNS–TiO2 nanocomposite powder was added into the plating electrolyte and it was subjected to a continuous stirring by a magnetic stirrer for about 5 h for proper dispersion of GNS–TiO2 in the electrolyte. Also, a magnetic stirrer at an optimum stirring speed of 150 rpm was applied to mix the GNS–TiO2 particles and the electrolyte during the deposition process to disperse the particles in the solution and break up the agglomeration. Ni–GNS was prepared from the Ni electrolyte at the same experimental condition, in the presence of 0.4 g l−1 graphene nanosheets (GNS) and operated at 10 mA cm−2 for 60 min.

<table>
<thead>
<tr>
<th>Element %</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low carbon steel (mild steel)</td>
<td>0.15%</td>
<td>0.6%</td>
<td>0.028%</td>
<td>0.25%</td>
<td>Balanced</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration g l−1</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO4</td>
<td>26.26</td>
<td>Current density: 2.5–20 mA cm−2</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>56.81</td>
<td>Temperature: 30 °C</td>
</tr>
<tr>
<td>H2BO3</td>
<td>18.54</td>
<td>pH 5</td>
</tr>
<tr>
<td>GNS–TiO2</td>
<td>0–1</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Chemical composition of mild steel used as substrates for nanocomposite coating electrodeposition.

Table 2

Chemical composition of Ni electroplating electrolyte and the operating conditions for electrodeposition of Ni nanocomposite coatings on mild steel.
2.5. Coatings thickness test

The thickness of the coating layer was estimated using a thickness tester (Thickness gage – ElektroPhysik – MiniTest 70) that is based on the eddy current method. The thickness was measured at several places on the specimen and the average value was obtained.

2.6. The microhardness measurements

Vickers microhardness of mild steel, electrodeposited Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO2/mild steel nanocomposite coatings was determined by an indentation technique at 100 gf load with a diamond pyramid indenter technique (Tukon Series B200 microhardness tester). The hardness was measured at several different places and the average microhardness was obtained.

2.7. Corrosion tests

The corrosion performance of different samples was investigated using potentiodynamic polarization Tafel lines and electrochemical impedance spectroscopy measurements (EIS) in 0.6 M NaCl solution. The experiments were carried out in aerated solutions at 25 °C after the open circuit potential value is reached after \( \approx 30 \) min. The electrochemical measurements were performed in a typical three-electrode glass cell consisting of mild steel, electrodeposited Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO2/mild steel as working electrodes; the exposed surface area of each was 1.0 cm\(^2\). The reference electrode that all potentials are referred to was Hg/Hg2Cl2/Cl\(^-\) of \( E^\circ = 240 \) mV vs standard hydrogen electrode (SHE) and the auxiliary electrode was a platinum sheet. The electrolyte used was 0.6 M NaCl solution prepared using triply distilled water. The polarization was started from the cathodic then the anodic part, first of all the electrode was dipped in the test solution until the open circuit potential was reached (\( E_{corr} \)), the polarization was started from this point down to \(-500 \) mV in the cathodic direction, then the polarization was reversed from the open circuit potential in the anodic direction up to \(+500 \) mV. The corrosion current (\( I_{corr} \)) was calculated from the intersection of the linear parts of the anodic and cathodic lines at zero polarization. Impedance measurements were carried out in the frequency range of 35 kHz–100 mHz with an amplitude of 10 mV sinusoidal potential using ac signals at the open circuit potential. The electrode potential was allowed to stabilize for 30 min before starting the measurement. All experiments were carried out in aerated solutions at a room temperature.

2.8. Surface characterization

X-ray diffraction (XRD) patterns were obtained over the diffraction angle range (2\( \theta \)) of 4–80° using an XRD (X’Pert PRO – PANalytical, Netherlands) diffractometer with Cu K\( \alpha \) (\( \lambda = 1.5404 \) Å) radiation at a generator voltage of 45 kV and a generator current of 30 mA, with a step size of 0.02° and a scan speed of 0.05 s\(^{-1}\).

High resolution transmission electron microscopy (HR-TEM) images were obtained using an FEI (Tecnai G2 20S-Twin, Netherlands) microscope with an accelerating voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) thermo scientific K-Alpha was used to evaluate the prepared samples. The sample was irradiated with Al K\( \alpha \) monochromatic X-ray source, and the analyzer passes energy of 200 eV with a step size of 1 eV for high resolution spectra to obtain the chemical state information.

FTIR studies were performed using an AT1 Mattson model Genesis Series (USA) infrared spectrophotometer. For all prepared nanomaterials, the KBr technique was carried out approximately in a quantitative manner, as the weight of the sample and that of KBr was always kept constant.

A field emission scanning electron microscope (FE-SEM) equipped with energy dispersive X-ray system (EDX) model JEOL, JSM-5410 was used to study the surface morphology of the coatings and the elemental analysis of the deposited layer, respectively.

Thermo gravimetric analysis (TGA) test was carried out using DSC–TGA SDTQ 600, USA under N\(_2\) atmosphere, with 1000 °C and a heating rate of 10 °C min\(^{-1}\).

Porosity measurement of the coating layer was carried out by a chemical test (the classic ferroxyl test). A color change will occur in the presence of corrosion products from the substrate forming a distinctive spot at each pore. The test solution is prepared by dissolving 25 g of potassium ferrocyanide and 15 g of sodium chloride in 1 l solution. The sample is cleaned and immersed for 5 s in the test solution at 25 °C, followed by water rinsing and air drying. Blue spots visible to the

![Fig. 1. XRD patterns for graphene oxide (GO), graphene nanosheets (GNS), TiO2 (anatase) and GNS–TiO2 nanocomposite.](image-url)
naked eye will form at pore sites. Their allowable number should be specified [24].

3. Results and discussion

3.1. Preparation and surface characterization

3.1.1. GNS, TiO₂ and GNS–TiO₂

The phase structure of the as prepared graphene oxide (GO), graphene nanosheets (GNS), TiO₂ (anatase) and GNS–TiO₂ nanocomposite was determined using XRD as shown in Fig. 1. A diffraction peak at 11.7° was observed corresponding to the (001) plane of GO [19,25]. After the hydrothermal reduction of GO nanosheets, the diffraction peak at 11.7° disappeared due to the removal of the hydroxyl and epoxide functional groups that are usually located on the GO basal plane and a new diffraction broad peak appeared at around 24.5° corresponding to the (002) diffraction plane for the graphene nanosheets (GNS) [19,24]. Also, XRD pattern indicates diffraction peaks for pure anatase (TiO₂) according to the standard pattern (JCPDS 01-75-2547) at 2θ values of 25.3°, 37.8°, 48.0°, 54.0°, 55.1°, 62.7°, 68.8°, 70.3° and 75.1° which were indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes of the phase, respectively. On the other side, the diffraction pattern of GNS–TiO₂ nanocomposite showed the disappearance of the diffraction peak corresponding to GO.

Fig. 2. HR-TEM images for: a) GO; b) TiO₂; c) GNS–TiO₂ nanocomposite; d) high resolution TEM image for TiO₂ and e) EDX analysis for GNS–TiO₂.
The crystallite size of the formed anatase phase in pure TiO$_2$ and in GNS–TiO$_2$ nanocomposite was estimated from XRD patterns based on the Debye–Scherer equation [27] of the most intense peaks (101) and (200) of the TiO$_2$ (anatase). The average crystallite sizes were 5 and 4.3 nm for anatase phase in pure TiO$_2$ and in GNS–TiO$_2$, respectively.

The surface morphology and the structure of GO, GNS, TiO$_2$ nanoparticles and GNS–TiO$_2$ nanocomposite were characterized by HR-TEM. Fig. 2a shows a number of GO nanosheets. The selected area electron diffraction (SAED) pattern of these sheets as illustrated in the inset figure of Fig. 2a reveals a lattice spacing corresponding to the (001) diffraction plane of the GO phase. On the other side, TEM image of TiO$_2$ nanoparticles in Fig. 2b shows some aggregation with a clear and homogeneous particle size of a spherical shape. The selected area electron diffraction (SAED) pattern of these nanoparticles in the composites as seen in the inset figure of Fig. 2b reveals a lattice spacing corresponding to the (101), (004) and (200) diffractions of the anatase phase according to the standard pattern (JCPDS 01-75-2547). Furthermore, Fig. 2c shows many small TiO$_2$ nanoparticles that are distributed on the graphene sheet surfaces, confirming formation of GNS–TiO$_2$ nanocomposite. Fig. 2d shows the image for TiO$_2$ as the lattice structure obviously appears with d-spacing of 3.5 Å which matches the diffraction peak for the (101) plane of anatase TiO$_2$. The average particle size of the TiO$_2$ nanoparticles in pure anatase and in GNS–TiO$_2$ nanocomposite powders was found in the range from 4 to 8 nm, which is in a good agreement with the crystal size values calculated from the Debye–Scherer formula based on XRD pattern data. On the other side, the energy-dispersive X-ray (EDX) of GNS–TiO$_2$ nanocomposite as shown in Fig. 2e shows peaks corresponding to C, O, and Ti elements, confirming the existence of TiO$_2$ nanoparticles on the surface of graphene nanosheets.

The formation of GNS–TiO$_2$ nanocomposite was further confirmed by XPS as shown in Fig. 3a. It shows the full survey of XPS spectra for GO and GNS–TiO$_2$ nanocomposite. It is clear that there is a peak for Ti confirming the presence of Ti species in the composite. The high resolution XPS spectra of Ti 2p as in Fig. 3b show two peaks at 459.76 and 465.46 eV corresponding to Ti 2p$^{3/2}$ and Ti 2p$^{1/2}$ spin orbital splitting in the Ti$^{4+}$ chemical state with a red shift toward high binding energy far from the pure TiO$_2$ (459.18 and 464.88 eV) and this binding energy shifts could be due to a change in chemical state or electronic interaction between graphene surface and TiO$_2$ nanoparticles [28,29]. The other two peaks that appeared in full XPS survey spectra in Fig. 3a which are further detailed in the high resolution XPS spectra in Fig. 3c and 3d are corresponding to GO and GNS–TiO$_2$ nanocomposite, respectively. From Fig. 3c, three peaks located at 284.7, 286.9 and 288.7 eV are observed and can be attributed to C–C, C–O and C=O, respectively [30]. Fig. 3c and d illustrates the spectra of GO and GNS–TiO$_2$ nanocomposite, and it was found that the intensity of C–O and C=O in GNS–TiO$_2$ nanocomposite sharply decreased indicating that after the hydrothermal treatment most of the oxygen-containing species in GO were removed.

FTIR measurements shown in Fig. 4 were carried out to estimate the compositional and structural changes and for further confirmation of the reduction of GO. FTIR spectra for GO show peaks at 1053, 1220, 1625, 1729, and 3433 cm$^{-1}$ which are assigned to oxygen-containing functional groups, i.e., C–O stretching, C–OH stretching, C=C stretching, C=O stretching, and O–H stretching, respectively [28]. The spectrum of GNS–TiO$_2$ nanocomposite shows that the GO characteristic peaks sharply decreased, indicating a considerable reduction of GO after the hydrothermal treatment. For pure anatase TiO$_2$ spectrum, three different peaks at 499, 1630 and 3397 cm$^{-1}$ refer to Ti–O–Ti stretching vibration modes [31]. The spectrum of GNS–TiO$_2$ nanocomposite indicates a strong band at 558 cm$^{-1}$ corresponding to Ti–O–C vibration, while, the peak that appeared at 1616 cm$^{-1}$ indicates C=C for the graphene skeleton [32]. The presence of Ti–O–C bond confirms the anchoring of TiO$_2$ nanoparticles on graphene surface.
The thermogravimetric analysis (TGA) curves for GO, TiO₂ and GNS–TiO₂ shown in Fig. 5 illustrated four distinct regions; in the first region up to 100 °C, GO curve shows a weight loss of about 20%, this weight loss could be attributed to the elimination of loosely bound or adsorbed water and gas molecules [33,34]. In the region between 150 °C–300 °C, GO curve shows a weight loss of about 35%. This weight loss is due to the burning decomposition of oxygen-containing groups attached to graphene oxide layers or labile oxygen groups like carboxylate, anhydride, or lactone groups [35]. In the third region which located between 300 °C–500 °C, GO curve shows a weight loss of about 7% and it was associated with the removal of more stable oxygen groups such as phenol, carbonyl, and quinine [36]. On the other hand, in the last two regions located in the temperature range of 150 °C–500 °C, TiO₂ and GNS–TiO₂ curves show a weight loss less than that of GO, this could due to the hydrothermal treatment during the preparation of the two materials in which oxygen-containing groups have been
removed as CO and CO₂. In the last region above 500 °C, the weight loss is due to the high temperature which leads to the pyrolysis of carbon skeleton of GO [36], but in the case of TiO₂, the loss in weight is due to the removal of the carbon-containing functional groups that may present, but the percentage loss in weight is very small if it is compared with that of GO [37]. The total loss in weight for GNS–TiO₂ was 26.48% and the percentage of TiO₂ in GNS–TiO₂ was estimated to be 73.52% and this value is in an agreement with Wang et al. [38].

### 3.1.2. Ni–GNS–TiO₂ nanocomposite coatings

Ni–GNS and Ni–GNS–TiO₂ nanocomposite coatings were electro-deposited on mild steel surfaces from Ni plating electrolyte. GNS–TiO₂ nanocomposite was added to the plating solution with different concentrations ranging from 0 up to 1 g l⁻¹ at a constant current density of 10 mA cm⁻² for 60 min and at 30 °C, pH 5 and at a stirring rate of 150 rpm. The thickness of the nanocomposite films formed on mild steel substrates, as a function of GNS–TiO₂ nanocomposite concentration is depicted in Tables 3a and 3b. The data reveals that the thickness of nanocomposite coatings increases with increasing GNS–TiO₂ nanocomposite concentration in the electrolyte of up to 0.4 g l⁻¹ and beyond this concentration, the thickness decreases. The experiments were repeated at a constant concentration of GNS–TiO₂ nanocomposite reinforcement (0.4 g l⁻¹) and at different deposition current densities ranging from 2.5 to 20 mA cm⁻² for 60 min and at 30 °C, pH 5 and 150 rpm (Table 4). The results illustrated that the thickness of nanocomposite coatings increases with increasing current density up to 10 mA cm⁻² due to the increase of the deposition rate, but at higher current density beyond 10 mA cm⁻² the thickness decreases. The deposition rate is determined by initiation of real contact between the Ni²⁺ adsorbed on GNS–TiO₂ nanocomposite and the cathode surface. At the optimum current density of 10 mA cm⁻², the rate of movement of Ni²⁺ and GNS–TiO₂ nanocomposite from the bulk of the electrolyte to the cathode surface is equal to the rate of deposition (i.e. the rate of the mass transfer is equal to the rate of the charge transfer), this trend is confirmed elsewhere [39,40]. At current density above 10 mA cm⁻², the rate of the charge transfer is relatively high, as a result the reduction of Ni²⁺ is controlled by the mass transfer, consequently, the deposition rate of Ni–GNS–TiO₂ nanocomposite coatings gradually decreases due to the depletion of the metal cations in the vicinity of the cathode surface.

There are many mechanisms used to explain the formation of composite coatings where the particles are suspended in the electrolyte and co-deposited with the metal. The most popular theoretical model was suggested by Guglielmi where the co-deposition has usually been explained based on adsorption of metal ions on the particles [41]. An improvement of Guglielmi’s model was postulated by Saher and Hamid [42]: they proved that the codeposition of solid particles depends largely on the mobility and electrokinetic nature of the particles in the plating solution. Solid particles in the electrolyte are electrostatically charged by adsorbing ions on their surfaces. The sign and magnitude of the electrolytic charge are known as zeta potential (ζ). The mechanism of solid particle electrodeposition could be suggested as the positively charged Ni²⁺ in the electrolyte is adsorbed on negatively charged solid particles then migrate to the cathode where metal ions are reduced to Ni forming the coatings with the entrapped solid particles occupying a place in the metal matrix. In this work, zeta potential value of GNS–TiO₂ nanocomposite at the operating pH has a vital role in the deposition process. From Fig. 6, it is clear that the zeta potential has a negative value of −17.7 mV at the operating pH 5, the negative potential value helps in adsorption of Ni²⁺ ions on the GNS–TiO₂ nanocomposite. Under the effect of convection force (mechanical agitation), transport of the particles to the cathode surface takes place by the flowing fluids to contact the cathode. Then, they will stay on the cathode surface by the external force and be included by the deposited metal [43].

EDX analysis as in Fig. 7 has been carried out to determine the chemical composition of the electrodeposited Ni and Ni–GNS–TiO₂ nanocomposite coatings. Additionally, Table 5 shows the influence of GNS–TiO₂ nanocomposite concentrations in the plating solution on the wt.% of GNS–TiO₂ nanocomposite codeposited within the Ni matrix. It is clear...

---

### Table 3a

The thickness of Ni–GNS–TiO₂ nanocomposite coatings (prepared at different concentrations of GNS–TiO₂ in the plating electrolyte and at 10 mA cm⁻²) on mild steel and the standard deviation (σ) values for the five measured values for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GNS–TiO₂ conc. in the plating solution, g l⁻¹</th>
<th>Thickness (μm)</th>
<th>Standard deviation (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>–</td>
<td>6</td>
<td>0.172</td>
</tr>
<tr>
<td>Ni–GNS</td>
<td>–</td>
<td>13.5</td>
<td>0.332</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>0.2</td>
<td>10</td>
<td>0.172</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>0.3</td>
<td>14</td>
<td>0.172</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>0.4</td>
<td>20</td>
<td>0.354</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>0.5</td>
<td>12</td>
<td>0.412</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (V)</td>
<td>1.0</td>
<td>7</td>
<td>0.458</td>
</tr>
</tbody>
</table>

### Table 3b

The thickness of Ni–GNS–TiO₂ nanocomposite coatings prepared at different deposition current densities and at 0.4 g l⁻¹ GNS–TiO₂ in the plating electrolyte on mild steel substrates and the standard deviation (σ) values for the five measured values for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>The deposition current density, mA cm⁻²</th>
<th>Thickness (μm)</th>
<th>Standard deviation (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>2.5</td>
<td>15.8</td>
<td>0.299</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>5</td>
<td>16.4</td>
<td>0.303</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>7.5</td>
<td>18.3</td>
<td>0.256</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>10</td>
<td>20</td>
<td>0.354</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (V)</td>
<td>20</td>
<td>17.2</td>
<td>0.210</td>
</tr>
</tbody>
</table>

### Table 4

EDX analysis data of Ni–GNS–TiO₂ nanocomposite coatings prepared at different concentrations of GNS–TiO₂ in the bath and at 10 mA cm⁻² on mild steel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. of GNS–TiO₂ in the bath, g l⁻¹</th>
<th>wt.%</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>Ni</th>
<th>GNS–TiO₂ wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>0.2</td>
<td>17.48</td>
<td>1.61</td>
<td>0.55</td>
<td>80.36</td>
<td>17.48</td>
<td></td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>0.3</td>
<td>18.67</td>
<td>1.77</td>
<td>0.42</td>
<td>79.14</td>
<td>18.67</td>
<td></td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>0.4</td>
<td>20.43</td>
<td>1.66</td>
<td>0.76</td>
<td>72.95</td>
<td>20.43</td>
<td></td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>0.5</td>
<td>19.32</td>
<td>2.26</td>
<td>0.76</td>
<td>77.66</td>
<td>19.32</td>
<td></td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (V)</td>
<td>1.0</td>
<td>14.24</td>
<td>1.50</td>
<td>0.50</td>
<td>83.76</td>
<td>14.24</td>
<td></td>
</tr>
</tbody>
</table>

---

**Fig. 6.** Zeta potential measurement of GNS–TiO₂ composite vs pH.
that inclusion of the GNS–TiO₂ nanocomposite in the coating layer depends clearly on the amount of suspended particles in the electrolyte. The wt.% of GNS–TiO₂ nanocomposite in the deposits increases with increasing the concentration of GNS–TiO₂ nanocomposite in the electrolyte and attains the optimum value at 0.4 g l⁻¹, and then it decreases with further increasing GNS–TiO₂ nanocomposite up to 1 g l⁻¹ concentration in the plating solution. Farther the optimum concentration, the suspended GNS–TiO₂ nanocomposite particles appeared to agglomerate in the electrolyte, accordingly, the entrapment of GNS–TiO₂ nanocomposite into the nickel matrix decreased and accordingly the thickness also decreases and this indicates that the adsorption of GNS–TiO₂ nanocomposite in the coatings has reached the saturated state. At a relatively high concentration of GNS–TiO₂ nanocomposite suspended particles, the agglomerates themselves may prevent the incorporation and screen the surface from the stream of the incoming particles [44].

The surface morphology of the electrodeposited films of Ni, Ni–GNS and Ni–GNS–TiO₂ nanocomposite coatings containing different wt.% of GNS–TiO₂ nanocomposite is shown in Fig. 8. It can be seen that the surface of Ni coating consists of crystals of cubic shaped structure in Fig. 8a, while the surfaces of the Ni–GNS–TiO₂ nanocomposite coatings containing different wt.% of GNS–TiO₂ nanocomposite as in Fig. 8(b–d) are characterized by particulate-like structure and have more compact and fine granular morphologies homogenously distributed on the entire surface. Additionally, it is evident from the surface morphologies that as

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% GNS–TiO₂ in the coating layer</th>
<th>$E_{corr}$, V (SCE)</th>
<th>$I_{corr}$, A cm⁻²</th>
<th>$b_{an}$, V dec⁻¹</th>
<th>$b_{cat}$, V dec⁻¹</th>
<th>C.R., mm/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel</td>
<td>–</td>
<td>–0.679</td>
<td>1.55 x 10⁻⁵</td>
<td>0.113</td>
<td>0.219</td>
<td>0.181</td>
</tr>
<tr>
<td>Ni/mild steel</td>
<td>–</td>
<td>–0.325</td>
<td>4.20 x 10⁻⁶</td>
<td>0.325</td>
<td>0.516</td>
<td>0.049</td>
</tr>
<tr>
<td>Ni–GNS/mild steel</td>
<td>–</td>
<td>–0.512</td>
<td>1.53 x 10⁻⁶</td>
<td>0.191</td>
<td>0.225</td>
<td>0.0183</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>17.48</td>
<td>–0.235</td>
<td>1.42 x 10⁻⁶</td>
<td>0.245</td>
<td>0.441</td>
<td>0.017</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>18.67</td>
<td>–0.457</td>
<td>1.14 x 10⁻⁶</td>
<td>0.324</td>
<td>0.362</td>
<td>0.013</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>20.43</td>
<td>–0.410</td>
<td>3.46 x 10⁻⁸</td>
<td>0.314</td>
<td>0.433</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>19.32</td>
<td>–0.555</td>
<td>3.50 x 10⁻⁹</td>
<td>0.254</td>
<td>0.222</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Fig. 7. EDX of electrodeposited, a) Ni/mild steel and b) Ni–GNS–TiO₂/mild steel.

Table 5

Electrochemical parameters derived from Tafel lines for electrodeposited Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO₂/mild steel containing different wt.% of GNS–TiO₂ nanocomposite (deposited at 10 mA cm⁻²) in 0.6 M NaCl at 25 °C.
the wt.% of GNS–TiO$_2$ nanocomposite increases, the surface appears finer. The inclusion of GNS–TiO$_2$ nanocomposite results in the decrease of Ni crystal grain, this could be due to the adsorption of GNS–TiO$_2$ nanocomposite on the Ni grain boundary and restricts its growth and consequently result in fine grain surface and also the morphology is changed to a small spherical particle. Moreover, the distribution of GNS–TiO$_2$ with the Ni matrix deposited at the optimum condition (0.4 g l$^{-1}$ GNS–TiO$_2$, 10 mA cm$^{-2}$) is demonstrated by backscattered image as shown in Fig. 8e. The GNS–TiO$_2$ nanocomposite appears as dark spots distributed on different places on the electrode surface. On the other hand, Fig. 8f shows SEM image of Ni–GNS/mild steel electrode prepared from Ni electrolyte in the presence of 0.4 g l$^{-1}$ graphene nanosheets at 10 mA cm$^{-2}$ for 60 min (the optimum condition of electrodeposition Ni–GNS–TiO$_2$ nanocomposite coating). It is clear that a fine morphology is obtained which is similar to that obtained with Ni–GNS–TiO$_2$/mild steel (Fig. 8d).

The phase structures of electrodeposited Ni and Ni–GNS–TiO$_2$ nanocomposite coatings are estimated by XRD patterns as shown in Fig. 9. It is clear that the incorporation of GNS–TiO$_2$ nanocomposite in the nickel matrix decreases the size of Ni grains from 24 nm in case of pure Ni to 20 nm for the Ni composite coatings as calculated from the Sherrer equation [28]. As can be seen in Fig. 9 both Ni and Ni–GNS–TiO$_2$ nanocomposite coatings display nanocrystalline structures. Diffraction pattern of Ni shows sharp peaks at around 45°, 51.8°, 76.4° and, 92.9° characteristic of the (111), (200), (220) and (311) states of Ni according to the standard reference [card No. 00-004-0850]. The same sharp peaks appeared with Ni–GNS–TiO$_2$ nanocomposite coatings but with relatively low intensities.
3.2. Microhardness

Microhardness of mild steel, mild steel coated with Ni, Ni–GNS or Ni–GNS–TiO2 nanocomposite coatings containing different wt.% of GNS–TiO2 nanocomposite is shown in Fig. 10. It is obvious that the incorporation of GNS–TiO2 nanocomposite in the deposits increases the microhardness. A value of 180 HV was recorded for mild steel, 243 HV for mild steel coated with Ni and 250 HV for Ni–GNS/mild steel, while a value of 478 HV was measured for mild steel coated with Ni–GNS–TiO2 nanocomposite coatings which were prepared in the presence of 0.4 g l⁻¹ GNS–TiO2 nanocomposite in the electrolyte. In the present work the obtained microhardness value for Ni–GNS–TiO2 nanocomposite coatings which were prepared at the optimum condition is higher than that obtained with Ni–GNS prepared from Ni electrolyte in the presence of 0.4 g l⁻¹ GNS and 10 mA cm⁻². This result is consistent with that obtained by Kumar et al. [17], also, it is higher than that obtained with Ni–TiO2 nanocomposite coatings which were studied by Shao et al. [45]. Accordingly, it is obvious from our results that the synergistic effects are obtained by adding graphene and TiO2 in the Ni–GNS–TiO2 nanocomposite coatings. Additionally, the results show that the hardness of nickel coating increases with increasing the weight percent of the incorporated GNS–TiO2 nanocomposite particulates. The maximum hardness produced at 0.4 g l⁻¹ GNS–TiO2 nanocomposite in the electrolyte is a result of the dispersion hardening effect of the GNS–TiO2 and the grain fining as shown in Fig. 5c–d. The re-inforced particles in the Ni matrix obstruct the easy movement of dislocation and resist plastic flow. This resistance to the deformation is shown by an increased microhardness value for Ni–GNS–TiO2 nanocomposite coatings [46,47].

3.3. Corrosion tests

3.3.1. Potentiodynamic polarization Tafel lines

Fig. 11 shows Tafel lines for mild steel uncoated and coated with Ni, Ni–GNS or Ni–GNS–TiO2 nanocomposite coatings (that contain different wt.% of GNS–TiO2 nanocomposite) in 0.6 M NaCl. It is clear that three distinguished regions appeared in the anodic part of the polarization Tafel lines, the first one is the active dissolution region in which the current density increases with increasing the potential, the second region showed a monotonic increase in the current density with increasing the potential, and the third region indicated a large increase in the current density with increasing the potential. An obvious shift toward less corrosion current density values is observed in the anodic and cathodic Tafel lines as the wt.% of the incorporated GNS–TiO2 nanocomposite increases in the nanocomposite coatings compared to those of electrodeposited Ni–GNS, Ni–mild steel or uncoated mild steel electrode. The electrochemical corrosion parameters derived from these Tafel lines are summarized in Table 6. It illustrates the anodic Tafel slope values (b_a), cathodic Tafel slope values (b_c), corrosion potential (E_corr), corrosion current densities (I_corr) and corrosion rates in mm/y for mild steel, Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO2/mild steel electrodes in 0.6 M NaCl at 25 °C. From Table 5, a clear shift is observed of the open circuit potential value from more negative direction in case of bare mild steel toward more positive direction in case of the Ni–GNS–TiO2 nanocomposite coatings indicating the noble behavior of Ni–GNS–TiO2 coating layer. This shift toward more positive direction could be attributed to the decrease in the active surface area of the electrode and the decrease in the ionic transfer by GNS/TiO2 nanocomposite-particulates [15]. A lower corrosion current and corrosion rate are obtained for Ni–GNS–TiO2/mild steel electrodes; also, the corrosion rate decreases as the wt.% of GNS–TiO2 nanocomposite in the deposited electrode increases. This corrosion rate is much lower than that obtained with Ni–GNS/mild steel. Also, its corrosion rate is much lower than that of Ni–TiO2 composite coating that was studied elsewhere [45].

From the corrosion results it can be concluded that the corrosion performance of the mild steel coated Ni–GNS–TiO2 samples depends on the surface morphology and the wt.% of GNS–TiO2 nanocomposite. The good distribution of GNS–TiO2 nanocomposite within the nickel matrix resulted in smooth and compact surface morphology. Also, the change in the microstructure from coarse grained in case of pure Ni to fine grained granular structure in case of Ni–GNS–TiO2 nanocomposite coatings, especially that formed from a plating solution containing 0.4 g l⁻¹ GNS–TiO2 nanocomposite, produced a perfect deposit, which protects the surface and exhibited best corrosion resistance. The co-deposited GNS–TiO2 nanocomposite-particulates were distributed in the Ni matrix and reduced the surface active area of the electrode and greatly contributed to decreasing the corrosion rate. On the other hand, the presence of GNS–TiO2 nanocomposite could help in the formation of denser, compact and free pore surface than that of pure Ni coatings and is less prone to the corrosion process [48]. The porosity of the steel coated by Ni or Ni–GNS–TiO2 nanocomposite coatings was estimated using a classic ferroxyl test which causes a color change in the presence of corrosion products from the substrate, forming a distinctive spot at each pore. Our results reveal that the porosity percentage (blue spots) of steel coated with Ni is about 10% related to the total surface area (mass per unit area is 5.34 mg/cm²), while Ni–GNS–TiO2 nanocomposite coating didn’t show any blue spots which means
no appreciable pores are detected on the Ni–GNS–TiO₂ surface (mass per unit area is 17.8 mg/cm²). Accordingly, lower corrosion rates are obtained with Ni–GNS–TiO₂ coatings. This means that the corrosion resistance decreases with decreasing the porosity of the coated layer.

The corrosion performance of Ni–GNS–TiO₂ composite coatings prepared at different deposition current densities (c.d.) is represented in Fig. 12 and Table 7. From the results it is clear that the corrosion rate decreases as the deposition current densities increase up to 10 mA cm⁻².

**Table 6**

Electrochemical parameters derived from Tafel lines of Ni–GNS–TiO₂/mild steel (prepared at different deposition current densities (c.d.) and 0.4 g l⁻¹ GNS–TiO₂ nanocomposite in the plating electrolyte) in 0.6 M NaCl at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition c.d., mA cm⁻²</th>
<th>Ecorr, V (SCE)</th>
<th>Icorr, A cm⁻²</th>
<th>b₌, V dec⁻¹</th>
<th>bᵣ, V dec⁻¹</th>
<th>C.R., mm/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>2.5</td>
<td>−0.532</td>
<td>0.0011</td>
<td>0.248</td>
<td>0.169</td>
<td>12.87</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>5</td>
<td>−0.569</td>
<td>0.00015</td>
<td>0.148</td>
<td>0.190</td>
<td>1.755</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>7.5</td>
<td>−0.420</td>
<td>7.4 × 10⁻⁶</td>
<td>0.578</td>
<td>0.458</td>
<td>0.087</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>10</td>
<td>−0.410</td>
<td>3.46 × 10⁻⁶</td>
<td>0.314</td>
<td>0.433</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

**Fig. 11.** Polarization Tafel lines of mild steel, Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO₂/mild steel nanocomposite coatings (prepared at different concentrations of GNS–TiO₂ I–IV) in 0.6 M NaCl at 25 °C.

**Fig. 12.** Polarization Tafel lines of Ni–GNS–TiO₂/mild steel nanocomposite coatings (prepared at different deposition current densities (c.d.) and 0.4 g l⁻¹ GNS–TiO₂) in 0.6 M NaCl at 25 °C.
A complete surface coverage could be obtained at relatively higher deposition current density; consequently a lower corrosion rate is obtained as shown from Table 7.

### 3.3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements for Ni–GNS/mild steel and different samples of Ni–GNS–TiO₂/mild steel were carried out in a

---

**Table 7**

Electrochemical parameters derived from EIS for mild steel, Ni/mild steel, Ni–GNS/mild steel and Ni–GNS–TiO₂/mild steel (containing different concentrations of GNS–TiO₂ nanocomposite and deposited at 10 mA cm⁻²) in 0.6 M NaCl at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% of GNS–TiO₂ in the coating layer</th>
<th>$R_p$, Ω cm²</th>
<th>$R_s$, Ω cm²</th>
<th>$C$, F cm⁻²</th>
<th>$W$, Ω cm²</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel</td>
<td>-</td>
<td>3.76 × 10²</td>
<td>7.85 × 10⁴</td>
<td>1.18 × 10⁻³</td>
<td>7.61</td>
<td>0.98</td>
</tr>
<tr>
<td>Ni/mild steel</td>
<td>-</td>
<td>1.27 × 10²</td>
<td>3.44 × 10⁴</td>
<td>1.74 × 10⁻⁴</td>
<td>1.77 × 10²</td>
<td>0.98</td>
</tr>
<tr>
<td>Ni–GNS/mild steel</td>
<td>-</td>
<td>1.23 × 10²</td>
<td>3.90 × 10⁴</td>
<td>1.09 × 10⁻⁴</td>
<td>4.03 × 10²</td>
<td>0.97</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (I)</td>
<td>17.48</td>
<td>1.6 × 10⁰</td>
<td>9.27 × 10⁴</td>
<td>5.23 × 10⁻⁴</td>
<td>1.69 × 10⁴</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (II)</td>
<td>18.67</td>
<td>1.72 × 10⁰</td>
<td>4.56 × 10⁴</td>
<td>7.21 × 10⁻⁵</td>
<td>8.11 × 10²</td>
<td>0.97</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (III)</td>
<td>20.43</td>
<td>4.36 × 10⁷</td>
<td>3.31 × 10⁸</td>
<td>2.88 × 10⁻⁵</td>
<td>2.11 × 10²</td>
<td>0.94</td>
</tr>
<tr>
<td>Ni–GNS–TiO₂ (IV)</td>
<td>19.32</td>
<td>1.0 × 10⁰</td>
<td>2.0 × 10⁴</td>
<td>4.67 × 10⁻³</td>
<td>1.40 × 10²</td>
<td>0.95</td>
</tr>
</tbody>
</table>

---

Fig. 13. Nyquist plots for a) mild steel, Ni/mild steel and Ni–GNS/mild steel prepared at 0.4 g/l GNS and 10 mA cm⁻² and b) different Ni–GNS–TiO₂/mild steel electrodes (prepared at different concentrations of GNS–TiO₂ nanocomposite and 10 mA cm⁻²) in 0.6 M NaCl at open circuit potential.
Potential.

Composite deposits prepared by Kumar. So, the relatively high corrosion resistance is obtained with Ni–TiO2/mild steel than that of Ni–GNS/mild steel. The presence of such a protective coating indicates the anticorrosive nature of the prepared composite electrodes.

0.6 M NaCl solution, with the applied frequency ranging from 35 kHz to 100 mHz and the results are presented in Figs. 13 and 14 and Tables 7 and 8. EIS results indicate that a one capacitive loop is clearly observed in the high-frequency region and a straight line (Warburg) in the low-frequency region is observed in the Nyquist plots as shown in Figs. 13 and 14. The capacitive loop is attributed to the charge transfer resistance (Rt), whereas the Warburg impedance is attributed to the diffusion of the anodic and cathodic reaction products from the solution to the electrode surface. The presence of the Warburg (W) impedance in the circuit confirms also that the mass transport is limited by the surface protective film. It was found that the polarization resistance values (Rt) calculated from EIS data are much higher for the Ni–GNS–TiO2/mild steel than that of Ni–GNS/mild steel and also it increases as the wt.% of GNS–TiO2 nanocomposite increases in the composite electrodes and the highest corrosion resistance value was recorded for Ni–GNS–TiO2/mild steel electrode that contains 20.4 wt.% GNS–TiO2 nanocomposite, this implies the anticorrosive nature of the prepared composite coatings. The presence of such a protective coating film decreases the penetration of the electrolyte to mild steel surface and creates a barrier against diffusion. In comparison with Ni–GNS/mild steel electrode prepared at 0.4 g/l GNS in the electrolyte and 10 mA cm−2, a much higher corrosion resistance is obtained with Ni–GNS–TiO2/mild steel electrode. Polarization corrosion resistance values of 33.1 kΩ cm2 and 3.9 kΩ cm2 were recorded for Ni–GNS–TiO2/mild steel and Ni–GNS/mild steel electrodes, respectively. This result was confirmed by Kumar et al. [17], where the corrosion resistance value of Ni–GNS–TiO2/mild steel electrode is found to be ~15 times higher than that of Ni–graphene composite deposits prepared by Kumar. So, the relatively high corrosion resistance of Ni–GNS–TiO2/mild steel electrode could indicate the appearance of a synergistic effect due to the presence of GNS and TiO2 in the Ni–GNS–TiO2 nanocomposite coatings.

Moreover, the polarization resistance values increase with increasing the deposition current density. This electrochemical behavior is modeled with the equivalent electrical circuit model Rs(RpW)C for samples in 0.6 M NaCl as shown in Fig. 15. Rt is the solution resistance between the reference and working electrodes, Rp is corresponding to the corrosion resistance at the metal substrate/solution interface, C is the capacitive loop and W is the Warburg impedance that is attributed to the mass transport during the corrosion reactions. It is found that the Rp values increased with increasing the concentration of GNS–TiO2 nanocomposite in the plating solution and also with increasing the deposition current density. The decrease of capacity values for the Ni–GNS–TiO2/mild steel composite electrodes was attributed to the good distribution of the coatings on the electrode surface acting as a barrier against the diffusion process. The impedance parameters for the different composite electrodes as calculated by the software are shown in Tables 7 and 8. Where, N value is a parameter that was calculated by the software provided with the instrument (varying between 0 and 1) to account for the deviation from the ideal capacitive behavior and it shows if there is conformity between theoretical and experimental impedance parameters of the equivalent model. From N values, it is clear that there is a good conformity between theoretical and experimental impedance parameters for the whole frequency range, the results are in good agreement with that obtained from Tafel lines. It can be seen that the best corrosion resistance value (Rt) was recorded for the electrode containing a relatively higher wt.% of GNS–TiO2

Table 8
Electrochemical parameters derived from EIS for Ni–GNS–TiO2/mild steel (prepared at different deposition current densities and 0.4 g l−1 of GNS–TiO2 nanocomposite in the bath) in 0.6 M NaCl at 25°C

<table>
<thead>
<tr>
<th>Deposition c.d., mA cm²</th>
<th>Rn, Ω cm²</th>
<th>Rp, Ω cm²</th>
<th>C, F cm⁻²</th>
<th>W, Ω cm⁻²</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>5.37 × 10</td>
<td>1.49 × 10</td>
<td>4.04 × 10⁻⁴</td>
<td>1.51 × 10⁻⁵</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>7.07 × 10</td>
<td>2.10 × 10</td>
<td>3.84 × 10⁻⁴</td>
<td>2.85 × 10⁻⁵</td>
<td>0.96</td>
</tr>
<tr>
<td>7.5</td>
<td>1.72 × 10²</td>
<td>4.36 × 10³</td>
<td>7.21 × 10⁻⁵</td>
<td>8.11 × 10⁻⁵</td>
<td>0.97</td>
</tr>
<tr>
<td>10</td>
<td>4.36 × 10²</td>
<td>3.31 × 10⁴</td>
<td>2.88 × 10⁻⁵</td>
<td>2.11 × 10⁻³</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Fig. 14. Nyquist plots for different Ni–GNS–TiO2/mild steel electrodes (prepared at different current densities and at 0.4 g l−¹ of GNS–TiO2 nanocomposite) in 0.6 M NaCl at open circuit potential.

Fig. 15. Equivalent circuit model represents the corrosion behavior of Ni–GNS–TiO2/mild steel electrodes in 0.6 M NaCl.
nanocomposite. By inspection of the SEM images of the surfaces as seen in Fig. 8, it was found that a perfect, compact and smooth surface free from defects is obtained with Ni–GNS–TiO₂ nanocomposite coating electrode that contains a relatively high wt.% of GNS–TiO₂ nanocomposite compared with the surfaces of other electrodes. This result is consistent with the result of the porosity test.

4. Conclusions

GO is prepared by the Hammer method from graphite and reduced to graphene nanosheets (GNS) concurrently with the formation of TiO₂ nanoparticles to form GNS–TiO₂ nanocomposite. The GNS–TiO₂ nanocomposite was codeposited with Ni matrix and used as protective coatings for mild steel. The presence of GNS–TiO₂ nanocomposite with the nickel deposit changed its surface morphology to fine grained deposit and reduced the grain size from 24 to 20 nm. Also, the inclusion of GNS–TiO₂ nanocomposite in the deposits improves the corrosion resistance and increases the microhardness of the prepared electrodes. Ni–GNS–TiO₂ nanocomposite coatings that contain 20.4 wt.% of GNS–TiO₂ particulates reduce markedly the corrosion rate of mild steel and gave the highest microhardness. Owing to the abovementioned properties, Ni–GNS–TiO₂ is recommended to be used as protective coatings for mild steel used in the agriculture field.

References