Electro-brush plating Ni-Graphene oxide composite coating enhanced corrosion resistance of fluoride ion

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Abstract
Ni-Graphene Oxide(GO) composite coating was prepared on Q235 steel plate by electro-brush plating technique to reduce the corrosion of fluoride ion. In this study, SEM, XRD and Raman tests were performed to analyze the morphologies and structures of the coatings, then electrochemical characterization was evaluated to determine the corrosion resistance. The results showed that GO provided more nucleation sites, and the surface of coatings looked more uniform and much denser because GO and Ni atoms were co-deposited on coating surface. The composite coating showed a better corrosion resistance than the pure nickel and there was an optimal addition amount of GO (Ni-GO/0.75 coating). In detail, the corrosion voltage increased from $-0.61187 \text{ V}$ to $-0.52542 \text{ V}$, and the corrosion current correspondingly decreased from $26.6 \mu\text{A}\cdot\text{cm}^{-2}$ to $6.8 \mu\text{A}\cdot\text{cm}^{-2}$, correspondingly. The charge transfer resistance was also increased from $558.6 \Omega$ to $1769.0 \Omega$. Moreover, the immersion testing demonstrated that the weight loss of Ni-GO/0.75 composite coating was only 22.2% of the pure nickel. In addition, XPS spectra indicated that the fluoride ions in the corrosive medium preferentially bonded with nickel atoms, preventing the medium from entering the active area. In conclusion, Ni-GO composite coating exhibited excellent corrosion resistance to fluoride ion due to the impermeability and high conductivity of GO.

1. Introduction

The corrosion behavior in the gas distribution system is mainly affected by the gas type, purity, cleanliness and temperature. The combination of the gas and the moisture attached to the pipe and the will cause serious corrosion to the system [1, 2]. In microelectronics industry, the cleaning of integrated circuits and ultra-large integrated circuits use standard gases like F2, HF, CHF3, CClF3, HBr and so on [3]. These gases can cause corrosion to the gas system at very low concentrations and the corrosion products with fluoride ion will affect the accuracy and precision of circuits and devices. Surface treatment technology of cylinder will affect the purity of standard gas and there were few researches for fluoride ion. Therefore, finding a new surface treatment method for standard gas cylinder was very important for the manufacturing process of the microelectronics industry [4].

In this case, surface coating has been considered as one of most effective methods to protect metal container from corrosion of fluoride ion, up to now, many surface treatment technologies have emerged, such as PVD [5], CVD [6] and electroplating [7]. Among these, Nickel-based electroplated coating has excellent tribological performance and corrosion resistance [8–12]. It was widely used in automobile, electronics, calculator and other industries. Electro-brush plating technique [13] was widely used in material strengthening and repair of large precision equipment due to its simple equipment and technology, fast deposition speed and excellent performance and has developed into the most common method for preparing composite coatings with excellent comprehensive properties. The application of electro-brush plating technique can solve the complex problem of preparation of non-metallic coating (plating) layer. The brushing operation is basically a type of mechanical stirring that can smooth the coating surface and avoid the agglomeration of nano particles, even without additional surfactants. Moreover, as the deposition only occurs at the brush-substrate contact, much less plating solution is required, which reduces potential environment impact Yan Wei et al [14] reported that a
metallic superhydrophobic coating with excellent anti-corrosion performance was fabricated by micro/nano composite electro-brush plating technology and the prepared coatings exhibited excellent abrasion resistance and the anti-corrosion performance.

In order to make single nickel plating technology meet the requirements of high performance and multifunction of products, the main way to improve the comprehensive performance of single nickel coating is to add other alloy elements or particles into the nickel based layer to form alloy coating or composite coating. Nowadays, Particles of SiC, Al2O3, SiO2, P, CNT, GO have been incorporated as second phase particles into Ni coatings to enhance their hardness, strength, high temperature inerterness, corrosion and wear resistance. Graphene oxide (GO) as an important derivative of graphene based materials, maintains the special surface properties and layered structure of graphene, which was an ideal two-dimensional nano carbon material with good physical, chemical, optical and electrical properties, as well as good hydrophobic properties, high dielectric constant and electron mobility. GO improve the corrosion resistance of materials in neutral salty solution and exhibited outstanding mechanical properties and it is widely used in the field of corrosion inhibition. K. Sai Jyotheender and Chandan Srivastava reported that Ni-Graphene oxide (GO) composite coatings were electrodeposited on mild steel substrate. Their report showed that the gradual increase in the corrosion resistance with addition of GO till the optimum concentration was attributed to the GO induced coating growth along the relatively low energy planes and impermeability of GO to corrosive media. Dan Zhang et al. reported that Ni-based nanocomposite coatings with GO were prepared by electro-brush plating technique. Their report showed that the uniform distribution of GO nanosheets in coatings is beneficial to exert a stable and permanent lubrication effect, thereby attributing to an extremely stable friction process.

Herein we present a simple and economic micro/nano composite electro-brush plating approach to create a Ni-GO composite coating on Q235 steel plates, so as to conduct a comprehensive research to discuss the influence of microstructure and surface morphology. Then 0.01M NH4HF2 solution (pH = 4 with fluoride ions) were selected as corrosive medium to study the corrosion resistance of purity GO on the brush electroplating Ni coating. In addition, the mechanism of fluoride ions corrosion should also be studied, which would promote the application of Ni-GO composite coatings in industrial production.

2. Experiment

2.1. Electrodeposition of Ni and Ni-GO nanocomposite coatings

Q235 steel plates (5 cm * 2 cm * 0.2 cm) were selected as substrate materials. Before the experiment, the materials were immersed in degreaser for 30 min and polished with 100#, 240#, 320#, 600#, 800# and 1000# sandpapers in turn, following washed by ultrasonic in anhydrous ethanol and dried in the oven.

The GO provided by Suzhou Tanfeng Tech.Inc. was prepared by oxidation-reduction method, which was characterized by FTIR, XRD, Raman and SEM.

The power supply in the brush plating experiment is Zhaoxin kxn-3030d. High-purity graphite was used as anode materials and Q235 steel plates were selected as cathode. Process and specific parameters of brush plating was shown in the table 1. Ni and Ni-GO composite coatings were produced by dispersing different amounts of GO into the electrolyte bath. Details of the bath composition and deposition parameters are provided in the table 2.

2.2. Characterization

Fourier transform infrared (FTIR) spectroscopy was measured by using Nicolet iN10 (with Pt ATR module). X-ray diffraction (XRD) profiles were obtained using the SmartLab (9KW) diffractometer with Cu Kα as x-ray source. InVia Qontor Raman spectrometer was carried out to study the degree of graphitization and disorder of the coating surface. ESEM QUANTA 450 Scanning electron microscope (SEM) coupled with energy dispersive x-ray spectroscopy (EDS) detector was used to determine coatings surface morphology and composition. The surface chemical composition of composite coating after immersion experiment was studied by XPS using ESCALAB XI from Thermo.

2.3. Electrochemical experiment

The corrosion resistance of the coating was characterized by GS350 electrochemical workstation. The measurement indexes include open circuit potential (OCP) and Tafel polarization line. The test parameters are as follows: SCE is regarded as reference electrode, platinum wire (d = 0.5 mm) is used as auxiliary electrode, sample piece is working electrode, and NH4HF2 solution with concentration of 0.01 M is considered as corrosion medium at room temperature. In order to avoid the influence of non-detection surface, the non-detection surface was sealed with epoxy resin before the experiment, and the detection area was controlled to be 1 cm². Before each test, immerse the specimen in a corrosive medium to stabilize the open circuit potential. Corrosion potential (Ecorr) and self corrosion current density (icorr) were obtained by Tafel curve epitaxy.
Table 1. Process and parameters of electro-brush plating.

| Process               | Solution                      | Voltage/V | Plating time/s | Movement velocity of plating pen/cm/s |
|-----------------------|-------------------------------|-----------|----------------|---------------------------------------|
| Electrical cleaning   | Electrical cleaning solutions | +12       | 60             | 6–8                                   |
| Intense activation    | No.2 activation solutions     | −12       | 30             | 10–12                                 |
| Slight activation     | No.3 activation solutions     | −15       | 30             | 6–8                                   |
| Preplating            | Special Ni solutions          | +10       | 30             | 10–12                                 |
| Plating               | Ni-GO composite plating solutions | +8    | 600            | 6–8                                   |

Table 2. Electrolyte bath composition and deposition parameter used for Ni and Ni-GO composite coatings.

| Sample                        | Electrolyte composition | Concentration |
|-------------------------------|-------------------------|---------------|
| Special Ni                    | NiSO$_4$·7H$_2$O         | 400 g l$^{-1}$|
|                               | NiCl$_2$                 | 25 g l$^{-1}$  |
|                               | HCl(d = 1.18)            | 20 ml l$^{-1}$|
|                               | CH$_3$COOH               | 70 ml l$^{-1}$|
| Working solution (semi-bright Ni) | NiSO$_4$·7H$_2$O | 300 g l$^{-1}$|
|                               | NaCl                     | 20 g l$^{-1}$  |
|                               | Na$_2$SO$_4$             | 20 g l$^{-1}$  |
|                               | CH$_3$COOH               | 48 ml l$^{-1}$ |
|                               | NH$_4$H$_2$SO$_4$        | 0.1 g l$^{-1}$ |

Ni-GO composite plating solutions: 0.1 g l$^{-1}$ SDS and corresponding concentration of GO

The parameters of potentiodynamic polarization curve are as follows: scanning range is $-0.25 \sim +0.25$ V, scanning speed is 5 mV s$^{-1}$, and the AC signal amplitude of electrochemical impedance is 5 mV, and the frequency response range is $10^{-2} \sim 10^5$ Hz.

2.4. Immersion testing

The consistent corrosion medium as electrochemical test was used for immersion testing at the same temperature. The area of test piece was 4 cm$^2$. In order to protect the uncoated surface, the uncoated surface is sealed with epoxy resin before immersion. The samples were soaked for 10 days in total, and were taken out every 48 h. The corrosion products on the surface were cleaned by soft brush in flowing water, then the test pieces were ultrasonically cleaned by anhydrous ethanol and dried. Finally, the corrosion weight loss was calculated by an analytical balance.

3. Results and discussion

3.1. Morphology and characterization of GO

FTIR spectrum, Raman spectrum, XRD profile and SEM bright field micro-graph of GO are shown respectively in figures 1(a)–(d). The FTIR spectrum of GO provided in figure 1(a) reveals the presence of various functional groups: 3430 cm$^{-1}$, the stretching vibration of O–H; the stretching vibration peak of C=O is at 1725 cm$^{-1}$; C=C vibrations from un-oxidized sp2 C–C bonds is at 1695 cm$^{-1}$, and 1260 cm$^{-1}$ is C–O vibrations. Raman spectrum in figure 1(b) shows there are two-bands of GO, namely the D-band at 1344–1351 cm$^{-1}$ and the G-band at 1589–1600 cm$^{-1}$, and the ratio of the intensity of the two bands (I$_D$/I$_G$) can be used to judge the surface structure of the CNMs, and prove the defects of the graphite structure in materials. The XRD diffraction pattern is shown in the figure 1(c). A sharp peak appears at 2$\theta$ angle of 10.02$, which corresponds to the (001) characteristic crystal plane of GO. Figure 1(d) is the morphology of GO obtained from scanning electron microscope (SEM). The picture shows that the GO used in the experiment is a multi-layer sheet structure.

3.2. XRD profile of composite coatings

X-ray diffraction profiles obtained from Ni and Ni-GO composite coatings are shown in figure 2. The diffraction pattern for the composite coating has three broad peaks at 44.23$, 51.8$ and 76.41$, corresponding to (111), (200), (220) of pure Ni, respectively [20]. It can be seen from the diffraction pattern that the relative intensity of
the XRD peaks vary with the addition of GO in the composite coating, the coating grows from (111) crystal plane to (220) crystal plane. The raw materials, current conditions and electrolyte bath composition will affect the plane the Nickel atoms grow [25, 26]. This preferential growth of nickel grains reduce the surface energy of the coating and make the coatings less active towards the corrosive media, thereby enhances the corrosion resistance of the composite coating [27, 28]. Apparently, no diffraction peaks of GO was detected in figure 2.

This can be explained by following reasons: one is the content of GO in the coating is lower than the detection intensity of XRD, the other is that the structure of GO in coatings changed during the electrodeposition process—a lamellate and amorphous structure.

At the same time, we also calculated the average nickel size among various kinds of nickel-based composite coatings, the Scherrer equation was used:

$$D = \frac{K\gamma}{B \cos \theta}$$

Where, D represents the crystallite size, K is the Scherrer constant: $K = 0.89$, $\gamma$ is the x-ray wavelength: $\gamma = 1.54 \text{ Å}$, $B$ is the width of diffraction peak at the half of Height, and $\theta$ is the Bragg diffraction angle.
In this calculation, three peaks \((2\theta = 44.23^\circ, 2\theta = 51.8^\circ\) and \(2\theta = 76.41^\circ\)) were used to calculate the average grain size and we have repeated the XRD experiments for three times to get the standard deviations of the average crystallite size [26, 29]. The result plotted in figure 3 shows the average crystallite sizes of all the coatings were similar around \(16.93 \pm 0.18\) nm.

The corrosion resistance of the composite coatings are determined by the grain size and the grain boundary:

1. The second phase particles (GO) are co-deposited with Ni atoms on the surface of the composite coatings, resulting in smaller Ni atoms size and larger grain area. Then the strength and ductility of samples are improved and the formability of the samples are enhanced. In addition, the finer grain size makes the corrosive medium contact more corrosion-resistant planes \((220)\), and the corrosion resistance of the sample will improved [25, 30].

2. The corrosion tendency of nanoparticles originates from grain boundaries. Coarse grains will cause uneven distribution of grain boundaries on the surface of the sample, corrosion will grow from uneven areas and spread rapidly, and refined grains will prevent this phenomenon [31].

3. The smaller the sample grain size is, the larger the crystal plane area will be. The corrosion current \((I_{corr})\) of sample will be smallest in the same corrosion medium and the corrosion will decrease. As can be seen from the figure 3, the average crystallite size of Ni-GO/0.75 is the smallest among the composite coatings.

### 3.3. Raman spectrum of composite coatings

Figure 4 is the Raman spectrum of samples. As shown in the picture, the characteristic band of graphene oxide is not observed in the pure nickel coating. The appearance of the characteristic band of graphene oxide in the composite coating indicates that GO is embedded in the composite coating, which is consistent with the XRD results [32, 33]. Table 3 gives the Raman shifts of the D-band and G-band of the Ni/GO composite coating and the corresponding \(I_D/I_G\) values. It can be seen that there is no significant change in the Raman shifts of the D-band and G-band, but there is a significant difference in the \(I_D/I_G\) value. The appearance of D-band is attributed to the disorder-induced defects of graphitic carbon and G-band is results from the vibration of \(sp^2\)-hybridized carbon atoms in rings and chains, and the intensity ratio of D band \((I_D)\) and G band \((I_G)\) shows the extent of the disorder and the graphitization in the carbon-based materials. The \(I_D/I_G\) value of GO is 0.926, and the ratio of other samples is less than 0.926, indicating that the degree of graphitization of the sample is enhanced. The Ni-GO/0.75 composite coating has the largest \(I_D/I_G\) value among coatings. This result indicates that a large amount of disordered structure exists in the Ni-GO/0.75 composite coating, which also suggests that the material is partially graphitized at this concentration. Moreover, the intensities of peaks of other composite coatings have a sharp decrease, proving that the degree of graphitization increases, the corrosion resistance decreases as well. This result indicates that GO will agglomerate because of the intermolecular forces in the plating bath and there is an optimal addition of GO in the coatings.

### 3.4. Metallographic microscope, SEM and EDS measurements

The Metallographic microscope pictures and SEM images of the samples are shown in the figure 5 and 6. From figure 6(a), the surface of the pure nickel coating is composed of a large number of grain clusters similar to...
A large number of pores exist on the surface, and even a crack of 1.547 μm. In comparison, the surface morphology of the composite coating varies from the pure nickel coating, in which no pores and cracks appear on the surface, and the grain clusters are closely connected to form a dense composite film. There are also differences between different composite coatings. A large amount of massive graphite is observed in Ni-GO/2.0. This is also due to the formation of agglomeration of GO during the brush plating process, which causes the coating surface to fluctuate dramatically. This phenomenon can be attributed to the relatively poor dispersion of GO in the brush plating solution, which affects the crystal nucleation during the brush plating process.

Table 3. Raman shifts and $I_D/I_G$ values of GO and composite coatings.

| Sample    | Peak D (cm$^{-1}$) | Peak G (cm$^{-1}$) | $I_D/I_G$ |
|-----------|--------------------|--------------------|-----------|
| GO        | 1342               | 1601               | 0.926     |
| Ni        | /                  | /                  | /         |
| Ni-GO/0.5 | 1342               | 1583               | 0.869     |
| Ni-GO/0.75| 1341               | 1580               | 0.904     |
| Ni-GO/1.0 | 1342               | 1583               | 0.879     |
| Ni-GO/1.5 | 1342               | 1583               | 0.763     |
| Ni-GO/2.0 | 1343               | 1585               | 0.770     |

‘cauliflower’. A large number of pores exist on the surface, and even a crack of 1.547 μm. In comparison, the surface morphology of the composite coating varies from the pure nickel coating, in which no pores and cracks appear on the surface, and the grain clusters are closely connected to form a dense composite film. There are also differences between different composite coatings. A large amount of massive graphite is observed in Ni-GO/2.0. This is also due to the formation of agglomeration of GO during the brush plating process, which causes the coating surface to fluctuate dramatically. This phenomenon can be attributed to the relatively poor dispersion of GO in the brush plating solution, which affects the crystal nucleation during the brush plating process.
The Ni-GO/0.75 coating was investigated by EDS to analyze its surface composition. As can be seen from figure 7(A), there are two different peaks after removing the base Fe and O elements, representing the coating which consisted of four elements: Fe, Ni, C and O, which was consistent with the chemical composition of the plating solution. The elements of C and O came from the micro-GO particles that embedded in the coating surface during the plating process [34, 35]. From the coating EDS maps of each element distribution in figure 7(B), it is indicated that the micro/nano-particles and the metal ions of the solution have co-deposited successfully. The nano-GO particles in the electrodeposition process were mainly contributing to increasing the conductivity and current density of the bath and during the nucleation of the composite coating they improved the nucleation rate. Due to the intermittent electrodeposition at a high current density, the cathode surface is

Figure 6. SEM images of electroplating layers, (a) Ni layer, Ni-GO hybrid layers with varying contents of GO, (b) Ni-GO/0.5, (c) Ni-GO/0.75, (d) Ni-GO/1.0, (e) Ni-GO/1.5, (f) Ni-GO/2.0

Figure 7. (A) EDS spectrum of the Ni-GO/0.75 coating (B) EDS map data of Ni-GO/0.75 coating chemical element distributions. (a) the SEM of scanning area, (b) element mapping distribution of Ni (c) element mapping distribution of C.
always in an unstable state, coupled with micro-nano particles is forming a smooth, dense surface, which can better isolate the corrosive medium and improve the corrosion resistance.

In order to get the thickness of samples clearly, we attached the EDS mappings of Fe element and Ni element. From the Figure 8, we got the thickness of samples, the results are shown in the table 4.

As can be seen from the table 4, the thickness of Ni-GO composites are thicker than that of pure Ni. This phenomenon can be attributed to the fact that graphene oxide(GO) provides more nucleation sites for nickel atoms, resulting in better growth of the coatings and increased thickness of the layers.

Figure 8. SEM images from cross section of the composite coatings (a1) Ni layer, Ni-GO hybrid layers with varying contents of GO, (b1) Ni-GO/0.5, (c1) Ni-GO/0.75, (d1) Ni-GO/1.0 (e1) Ni-GO/1.5, (f1) Ni-GO/2.0 and EDS map data of Fe element and Ni element, Ni-GO hybrid layers with varying contents of GO, (b2) Ni-GO/0.5, (c2) Ni-GO/0.75, (d2) Ni-GO/1.0 (e2) Ni-GO/1.5, (f2) Ni-GO/2.0.
3.5. Corrosion resistance
In order to evaluate the corrosion resistance of Ni-GO hybrid layers with different contents of GO, electrochemical property and immersion experiment were performed in 0.01 M NH$_4$HF$_2$ solutions.

3.5.1. Electrochemical characterization
The polarization curves of Ni and Ni-GO hybrid layers in 0.01 M NH$_4$HF$_2$ solutions are shown in figure 9. As shown in the picture, the cathode curve and anode curve of all samples are similar in shape and size, indicating that the dissolution rate and dissolution mechanism of samples are similar [36].

The polarization curves of different samples were fitted by the Tafel method. Corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$), corrosion rate (C.R) parameters provided by the polarization curve were shown in table 5.

The results show that the corrosion potential ($E_{corr}$) increases from Ni to Ni-GO/0.75, and decreases from Ni-GO/1.0 to Ni-GO/2.0. Similarly, the corrosion current ($I_{corr}$) decreased from Ni to Ni-GO/0.75, and increased from Ni-GO/1.0 to Ni-GO/2.0. The positive shift of the corrosion potential and the negative shift of the corrosion current mean that the inertness of the coating is enhanced. With the addition of GO, the inertness of the coating begins to increase. After adding Ni-GO/0.75, as the amount of GO increases, the inertness of the coating decreases.

The corrosion currents of Ni and Ni-GO/0.75 coatings were 26.6 $\mu$A cm$^{-2}$ and 6.8 $\mu$A cm$^{-2}$, respectively, and the corrosion rate decreased by 74%. After the amount of GO addition reached 0.75 g l$^{-1}$, the corrosion rate of the composite coating increased, but it was still lower than the original nickel coating.

These findings indicated

(a) The corrosion resistance of Ni coating will be enhanced with the addition of GO.

(b) In the coatings, there is an optimal addition amount of GO, so that the corrosion resistance of the coating reaches the optimal value.

In addition to the Tafel polarization curve, electrochemical impedance spectroscopy (EIS) is also an important tool for studying the electrochemical properties of composite coatings. EIS is a powerful non-destructive electrochemical technique used to confirm and study the corrosion behavior at the electrode/electrolyte interface, and is used to study the impedance information of sediment exposed in corrosion solutions [37, 38]. In order to obtain a complete (EIS) diagram of the sample, the samples were immersed in the corrosive medium (0.01 M NH$_4$HF$_2$) for one hour to stabilize the open circuit potential (OCP). The OCP results of each sample was shown in figure 10. Compared with the pure nickel coating, the potential of Ni-GO composite
coating is more positive, especially the Ni-GO/0.75 composite coating, indicating that the composite coating has higher corrosion resistance than the pure nickel coating.

The Nyquist diagram and Bode diagram of the sample are shown in figures 11(a) and (b). The diameter and shape of Nyquist curves can reflect the property of surface film and electrochemical process. The larger semicircle diameter, the higher corrosion resistance. As shown in figure 11(a), the diameter of the semicircle of the Ni-GO composite coating is larger than that of the pure nickel coating, indicating that the composite coating has higher corrosion resistance than the pure nickel coating. The results were similar to polarization curve test. The θ-f curves of all layers have two peaks in figure 11(b), demonstrating that the impedance spectrum has two time constants. The incorporation of GO did not change the corrosion principle of the layer.

According to the Nyquist diagram and Bode diagram, the equivalent circuit [22, 39, 40] as shown in the figure 12 is used to fit the EIS impedance spectrum. In the equivalent circuit, there are two RC circuits, Rs and Rcoat are high-frequency components, Cdl and Rct are low-frequency components. Among them, Rs is the solution resistance, Rcoat is the resistance provided by the metal oxide passivation film in the coating, charge

**Table 5.** Fitting parameters of polarization curves of Ni and Ni-GO hybrid layers in 0.01M NH₄HF₂ solutions.

| Sample       | Ecorr/V (versus SCE) | icorr/µA cm⁻² | C.R/mm·a⁻¹ |
|--------------|----------------------|---------------|------------|
| Ni           | −0.61187             | 26.6          | 0.3094     |
| Ni-GO/0.5    | −0.56767             | 14.0          | 0.1622     |
| Ni-GO/0.75   | −0.52542             | 6.8           | 0.0794     |
| Ni-GO/1.0    | −0.54689             | 11.4          | 0.1332     |
| Ni-GO/1.5    | −0.57968             | 15.2          | 0.1765     |
| Ni-GO/2.0    | −0.59439             | 20.7          | 0.2411     |

Figure 10. Open Circuit Potential of electroplating layers immersed in 0.01M NH₄HF₂ solutions.

Figure 11. (a) Nyquist and (b) Bode plot of Ni layer and Ni-GO composite coatings.
transfer resistance \( (R_{ct}) \) is a measure of the electron transfer through the surface, and is proportional to the corrosion resistance. \( C_{dl} \) is the corresponding corrosion product Chemical gradient electric double layer capacitors. Due to the non-uniformity of the coating surface, the frequency response characteristics of the double-layer capacitors of all the experimental samples did not match the pure capacitance, and a constant phase element (CPE) was required to replace the capacitor element. Which is expressed as follows:

\[
Z_{CPE, \omega} = \frac{1}{Y_0 (j\omega)^n}
\]

Among them, \( Y_0 \) is a CPE constant, often a positive number, \( j \) is an imaginary constant, \( \omega \) is an angular frequency, and \( n \) is an empirical index used to describe the surface roughness. \( n = 0 \), representing ideal resistance; \( n = 1 \), representing ideal capacitor; \( n = -1 \), representing the ideal sensor.

Zsimwin software was used to perform the sleast squares fitting on the established model. The values of \( R_s \), \( R_{coat} \), \( C_{dl} \) and \( R_{ct} \) are listed in the table 6.

The low \( C_{dl} \) value and high \( R_{ct} \) value indicate that the coating has higher corrosion resistance. The minimum \( C_{dl} \) value obtained from the Ni-GO/0.75 coating and the maximum \( R_{ct} \) value indicate that the coating has more Excellent corrosion resistance. This result is consistent with the conclusion obtained by Tafel polarization.

### 3.5.2. Immersion testing and XPS survey

The weight loss of Ni and Ni-GO coatings immersed in 0.01M NH₄HF₂ solutions are shown in figure 13. After immersion for 144 h, the weight loss of Ni coating changed suddenly, while the weight loss of Ni-GO composite coating was stable all the time, which was closely related to the fact that the thin and dense coating surface could better isolate the corrosion medium and the corrosion resistance of GO.

Similarly, it can be seen from the corrosion weight loss diagram that the maximum weight loss of the Ni coating is 14.4 mg/cm⁻² after 240 h of corrosion, while the weight loss of the Ni-GO/0.75 composite coating with the best corrosion resistance is 3.2 mg/cm⁻², only 22.2% of the Ni coating [41]. The reduction in corrosion weight loss of each Ni-GO composite coating is owing to the increased density of the coating, the corrosive media is hard to enter the active area for corrosion damage.

Figures 14 and 15 shows the morphology comparison of samples before and after immersion testing. It can be clearly observed since the pure nickel coating contains many cracks and pores during the plating process, the corrosive medium will enter the active area inside the coating through these cracks to corrode the coating. As the
corrosion time increases, the corrosive medium will penetrate the outer coating, causing the coating to peel off, and the corrosion is the most serious. Compared with the pure Ni layer, the surface rust of the Ni-GO composite coatings are significantly decreased indicating that the addition of GO particles is beneficial to improve the corrosion resistance of the Ni layer. Among these coatings, Ni-GO/0.75 coating performed excellent corrosion resistance, suggesting that there is an optimal concentration among coatings. The results are consistent with a decrease in corrosion current (figure 9) and an increase in impedance value (figure 10) as well as the XRD profile.

Figure 13. The weight loss of Ni and Ni-GO coatings immersed in 0.01M NH₄HF₂ solutions.

Figure 14. Morphologies of samples before immersion testing (a) Ni layer, Ni-GO hybrid layers with varying contents of GO, (b) Ni-GO/0.5, (c) Ni-GO/0.75, (d) Ni-GO/1.0, (e) Ni-GO/1.5, (f) Ni-GO/2.0.

Figure 15. Morphologies of samples after immersion testing. (a) Ni layer, Ni-GO hybrid layers with varying contents of GO, (b) Ni-GO/0.5, (c) Ni-GO/0.75, (d) Ni-GO/1.0, (e) Ni-GO/1.5, (f) Ni-GO/2.0.
XPS spectrum [42, 43] was used to study the chemical composition of corrosion products collected from coating surfaces after immersing in 0.01M NH₄HF₂ solution. The results are shown in figures 16 and 17. From the XPS survey in figure 16, the elements C, O, N, Ni, Fe and F was observed. The spectrum of C1s (figure 17(a)) can be divided into three peaks: C–C (284.2 eV), C–Ni (284.5 eV) and C–O–C (284.9 eV). Figure 17(b) shows the O1s peaks (about 532.7 eV) and the signal of O can be attributed to solution and GO, the peaks can be resolved into three different bands: O–H (532.8 eV), O–C (532.1 eV) and H₂O (533.7 eV). The appearance of these two element peaks indicates that GO and nickel are co-deposited well in the coating. In addition, The N1s peak at around 400 eV (figure 17(c)) can be split into two bands: the signal of N–H at (400 eV) and the signal of N–C at (398 eV). The peaks of N1s mainly comes from the corrosive medium NH₄HF₂. Additionally, from the XPS spectrum of Ni2p in figure 17(d), two peaks at 874.3 eV and 856.4 eV can be related to Ni₂P₁/₂ and Ni₂P₃/₂. And each peak accompanies with a satellite signal at 879.5 eV and 861.3 eV. The binding energy values of Co₂p prove that Co element in is in +2 oxidation state in solutions. Figure 17(e) exhibits the core-level XPS spectrum of Fe2p. The peak at 709.1 eV is related to Fe₂P₃/₂, and the peak at 723.4 eV is corresponding with Fe₂P₁/₂. Besides, two peaks (around 714.2 eV and 732.3 eV) are indexed to two shake-up type peaks of the Fe₂P₃/2 and Fe₂P₁/2 edge. In the meantime, other two peak at 711.5 eV and 724.4 eV can be related to Fe₂P₃/2 and Fe₂P₁/2. With a satellite signal at 718.5 eV and 831.3 eV. Both binding energy values of Fe2p prove that Fe element exists two oxidation states [44]. The integral area in the XPS spectrum indicates most Fe element is in +3. Moreover, from the core-level spectrum of F1s (figure 17(f)), F–Ni (685.7 eV) and F–Fe (684.9 eV) can be observed, the binding energy shows the fluorine preferentially bonds with nickel and prevent corrosive media entering the active area, furthermore, improve the corrosion resistance of composite coating. Based on the above data, we can
make assumptions that the following reactions will occur in 0.01 M NH₄HF₂ solution:

\[
\text{NH}_4\text{HF}_2 \rightarrow \text{NH}_4^+ + \text{H}^+ + 2\text{F}^-
\]

\[
\text{Ni} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2
\]

\[
\text{Ni}^{2+} + 2\text{F}^- \rightarrow \text{NiF}_2\perp
\]

Table 7 shows us that the coatings were immersed in 0.01M NH₄HF₂ solution, then XPS was used to analyze the chemical composition of the coating surface before and after the reaction. As shown in the table, before the experiment, due to the existence of pores and cracks in the pure nickel coating, the substrate element was exposed, which makes Fe element accounts for 1.9% in the coating. The C element in the coating comes from the Q235 steel plates and part of the anode graphite loss. With the addition of GO, the surface of the coating becomes smooth and dense, resulting in the decrease of Fe elements and the increase of C elements. After the immersion experiment, because of the rough surface of the pure nickel coating and the existence of pores, the corrosive medium reacts preferentially to the base element Fe, which will destroy the substrate of coating and the binding energy of coating and basement reduce. Then Ni element corroded, causing severe corrosion. As for the composite coating, the smooth and dense surface and the surface of GO has extremely strong hydrophobicity, which isolates the coating from the corrosive medium. At the same time, high conductivity of GO will hinder electron transfer, making the composite coating exhibit extremely strong corrosion resistance. The F element content on the coating surface is only 13.6% of the pure nickel coating.

In summary, GO nanoparticles are co-deposited with nickel ions on the cathode surface under the action of electric current, which provides more nucleation sites fills the pores generated during the growth of nickel atoms. This will increase the integrity of the coating surface, extend the time that the corrosive medium reach the substrate, then improve the corrosion resistance of the coating. In addition, the composite coating acts as a cathode in the corrosion process, the deposition of GO on the surface can decrease the area of the cathode and avoid the corrosion model of large cathodes and small anodes.

### 4. Conclusions

In this work, Ni-GO composite coatings with different addition amount of GO were prepared on Q235 steel plates by electro-brush plating technique. The morphology of Ni-GO composite coatings were compared and the electrochemical behavior in NH₄HF₂ solutions were studied, the main findings are as follows:

1. The addition of GO can significantly improve the compactness of Ni coatings. More nucleation centers are provided, so that the crystal grains grow from the (111) crystal plane to the (220) crystal plane. When the proper addition amount is reached, GO will agglomerate and increase the degree of graphitization of the coatings.

2. The addition of GO will enhance the corrosion resistance of the composite nickel coating, which the fluoride ion preferentially bonded with nickel and prevent corrosive medium entering the active area. And there is an optimum GO content amount in Ni-GO composite coatings for achieving the highest corrosion resistance (Ni-GO/0.75 composite coating).

3. The second phase particles (GO) are co-deposited with Ni atoms on the surface of the composite coatings, resulting in smaller Ni atoms size and larger grain area. The smaller the sample grain size is, the larger the crystal plane area will be. The corrosion current (Icorr) of sample will be smallest in the same corrosion medium and the corrosion will decrease.

4. The improvements of corrosion resistance are attributed to the strong impermeability of GO, which isolate the coatings from the corrosive medium, and its high conductivity will hinder the transfer of electrons, thereby slowing down the corrosion of the coating.
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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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