Preparation of reduced graphene oxide and its application in chromium-free inorganic insulating coating for oriented silicon steel

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Abstract—In the fields of military industry, national defence and major engineering, oriented silicon steel is an indispensable material, but the chromium-containing insulating coating coated on its surface is harmful to the environment and humans. Due to poor performance, the industrialization of chromium-free inorganic coating is hindered. To improve the corrosion resistance of chromium-free inorganic insulating coating for oriented silicon steel, reduced graphene oxide (rGO) was prepared by the hydrothermal reduction method and added to the basic chromium-free inorganic insulating coating composed of small-particle silica sol, large-particle silica sol and aluminium dihydrogen phosphate to obtain rGO-containing coating. Scanning electron microscopy (SEM) and Raman spectroscopy were used to analyse the microscopic morphology and structural characteristics of rGO. Electrochemical impedance spectroscopy (EIS) and Tafel polarization curves were used to test the corrosion resistance of the coating. The results show that the prepared rGO has a multi-layer structure with a smaller size than graphene oxide (GO) and can be dispersed in water-based coatings. And rGO can reduce the corrosion current density of the coating by two orders of magnitude, and improve the corrosion resistance of the coating.

1. Introduction
As an important magnetic material, the properties of oriented silicon steel will be greatly affected by the insulating coating. The commonly used insulating coating for oriented silicon steel are chromium-containing, and the chromate contained is toxic to the human body and the environment, especially as the long-term negative impact on the ecosystem \cite{1}. Therefore, relevant laws have been issued worldwide to prohibit the use of chromium-containing coatings and encourage the research and development of chromium-free coatings. The chromium-free coatings in the research can be divided into three categories: organic coatings, semi-inorganic coatings and inorganic coatings \cite{2}. Organic coatings are a mixture of...
various organic resins. And organic coatings have been eliminated by the market due to problems such as organic volatiles and poor heat resistance. The semi-inorganic coatings are a mixture of organic resin and inorganic salt. Although there have been related reports on chromium-free semi-inorganic coatings with good performance [3,4], the thermal decomposition of organic components resulting in coating performance loss is still the main obstacle to their industrialization. In contrast, the good heat resistance of inorganic coating makes it have a better application prospect in the field of oriented silicon steel, and it’s also the development trend of chromium-free insulating coatings in the future. However, inorganic coatings still have problems such as poor corrosion resistance. To improve the corrosion resistance of the coating, adding functional fillers is a common approach. Nanomaterials such as graphene are regarded as promising functional fillers of anti-corrosion coating for their good chemical stability, thermal stability and anti-permeability [5-7]. However, the structure of graphene makes it difficult to disperse stably in an aqueous system. In contrast, graphene oxide (GO), which is soluble in water, doesn’t have excellent performance as graphene. The reduced graphene oxide (rGO) has an adjustable structure and its properties are between the graphene and GO. Therefore, it’s still necessary to find a suitable method to prepare rGO with various properties that meet the requirements of coatings. The hydrothermal reduction method is characterized by simple operation, with no need for additional reducing agents. And the surface of the rGO prepared has more oxygen-containing functional groups like hydroxyl groups than other methods. Moreover, this method can effectively avoid the agglomeration of products and is often used in the preparation of rGO/nanocomposites [8,9].

To solve the above problems, rGO that can be well dispersed in water-based coatings was prepared by the hydrothermal reduction method and used as a functional filler of a chromium-free inorganic coating. The microscopic morphology and structural characteristics of rGO were characterized. And the corrosion resistance of the rGO coating was tested by electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. The results show that rGO improves the corrosion resistance of the coating.

2. Materials and Methods

2.1. Preparation of rGO
First, 20 g of GO aqueous dispersion with 1% mass fraction was mixed with 20 mL deionized water in the hydrothermal reactor and stored at 120 ℃ for 3h. Second, the product was centrifuged at 12000 r/min for 10 min. Third, the centrifuged product was separated into the upper liquid and lower sample. And the upper liquid was filtered. Fourth, the filtered product was mixed with the lower sample, washed with ethanol three times, and washed with deionized water until the filtrate was neutral. Fifth, the sample was vacuum-dried to a constant weight in a vacuum drying oven at 60℃ to obtain the rGO.

2.2. Preparation of rGO coating
First, rGO was ground, mixed with deionized water and ultrasonically dispersed to obtain an aqueous dispersion of rGO with a mass fraction of 1%. Second, the rGO aqueous dispersion was added into a basic chromium-free inorganic insulating coating [10] composed of small particles of silica sol, large particles of silica sol and aluminium dihydrogen phosphate, etc. After being stirred evenly, the rGO coating was prepared. The mass fraction of rGO in the coating is 0.1‰. Third, the rGO coating was coated on the oriented silicon steel sheet, cured at 475℃ for 10 s and sintered and 800℃ for 40 s. Then, the sheet would be ready for the performance test. For comparison, the plates with the basic coating and uncoated blank plates were also prepared.

2.3. Characterization and Measurement
Scanning electron microscopy (SEM, Apreo S HiVac and Nova Nano SEM 400, Thermo Fisher) was used to characterize the micromorphology of rGO. Raman spectroscopy (inVia Qontor, Renishaw) is used to analyse the structural characteristics of rGO. The laser used in Raman analysis was 532nm.

An electrochemical workstation (CH 760E, CH Instruments) was used to test the corrosion resistance by EIS and Tafel polarization curves. The working electrode is a sample plate. The reference electrode
and auxiliary electrode are a silver-silver chloride electrode and platinum electrode respectively. And the electrolyte solution is the 3.5wt% NaCl solution. The EIS was carried out with applied 5mV sinusoidal amplitude in the range of $10^{-2}$-$10^5$ Hz. The Tafel polarization curve was adopted in the voltage range of -0.5 - 0.5 V with the open circuit potential as the midpoint, and the scan rate is 0.01 V/s.

3. Results and Discussion

3.1. Structural analysis of rGO

Fig. 1 shows the microscopic morphology of GO and rGO. It can be found that the size of the layer structure in the GO is larger. When magnified by 1000X (Fig.1(a)), no significant fracture edges are observed in the area. And the morphology of GO is reticulated. Furthermore, the image of GO at 30000X (Fig. (b)) revealed that the reticulated morphology is formed by the wrinkles of the GO sheet, not structural damage. As for rGO, the image of it at 50000X (Fig. 1(c)) shows obvious and more lamella fracture edges and proves that the size of its layer is smaller than GO. And further magnification to 100000X (Fig.1(d)) can reveal that there are more wrinkles.

Fig. 2 Raman spectrum of GO and rGO

Fig.2 is the Raman spectrum of GO and rGO. The peaks at 1350 cm$^{-1}$, 1585 cm$^{-1}$ and 2700 cm$^{-1}$ corresponding to graphene D peak, G peak and 2D peak respectively are observed in both GO and rGO. This indicates that the basic structure of rGO prepared is the same as GO. The 2D peak in rGO is broad, and the value of $I_D/I_G$ is over 1, indicating that the structure is multilayer. Furthermore, the value of $I_D/I_G$ in GO is 1.05, and the value of $I_D/I_G$ in rGO is 1.06. It’s a slight increase, while the intensity of D and G peaks in rGO decreases obviously. It can be inferred that rGO has more edge defects \(^{11}\), which is consistent with the result of smaller flakes and richer wrinkles of rGO in the SEM observation. It indicates that the reduction process of GO leads to the fracture of the carbon ring and the peeling of
oxygen-containing functional groups. The increase of defects could provide more sites for the combination between rGO and other components of the coating, and the smaller size is also conducive to the dispersion of rGO in water-based coatings.

3.2. Corrosion resistance of rGO coating
The colour of the rGO coating is uniform and there is no solid precipitate, indicating that rGO is successfully dispersed in the coating. To test the effect of rGO on the anti-corrosion performance of the chromium-free inorganic insulating coating, the uncoated blank plate and the sample plates with basic coating and rGO coating respectively were prepared. The EIS test and Tafel polarization curve test were carried out by an electrochemical workstation. The test results are shown in Fig.3 and Fig. 4.

Fig. 3 (a), (b) and (c) are the EIS of the uncoated blank plate, basic coating plate and rGO coating plate respectively. It can be found that the capacitive reactance radius of the rGO coating is the largest, the capacitive reactance radius of the base coating is the middle one and that of the blank film is the smallest. This indicates that the basic coating can improve the corrosion resistance of oriented silicon steel, and rGO can effectively improve the corrosion resistance of the basic coating. Fig. 3(d) is the Bode plot of three kinds of samples. The impedance modulus value in the low-frequency area is considered to represent the ability of the coating to prevent the penetration of corrosive media and delay the corrosion. It can be found that the impedance modulus value of rGO coating is the largest. Moreover, rGO increases the impedance modulus value by an order of magnitude, which also showed that the addition of rGO improved the corrosion resistance of the coating.

![Fig. 3 EIS of different sample sheets: (a) blank plate; (b) basic coating; (c) rGO coating; (d) the Bode plot of three kinds of samples](image1)

![Fig.4 Tafel polarization curve of basic and rGO coating](image2)

Tab.1 Tafel polarization parameters of basic and rGO coating

| | Basic coating | rGO coating |
|---|---|---|
| $E_{corr}(V)$ | -0.1990 | -0.2260 |
| $I_{corr}(μA·cm^{-2})$ | 0.1150 | 0.0086 |

To explore the influence of rGO on the corrosion resistance of chromium-free inorganic insulating coatings, a Tafel polarization curve test was performed on the basic coating and rGO coating. Fig. 4 shows the Tafel polarization curve test results of two samples, and Tab. 1 is the parameters of the Tafel polarization curve. It can be found that rGO makes the corrosion potential ($E_{corr}$) negatively shift. It may be caused by the pores of the coating relatively increase after the addition of rGO, which makes the coating more permeable to corrosive medium and then the self-corrosion potential decreases. However, the corrosion current density ($I_{corr}$) decreases significantly by two orders of magnitude. The corrosion current density is generally considered to be positively correlated with the corrosion rate, which means rGO can significantly reduce the corrosion rate. Therefore, it may make corrosion more likely to occur,
but ultimately the comprehensive effect of rGO improves the corrosion resistance of the coating.

4. Conclusions
rGO with good dispersion stability in water-based coating systems were prepared by hydrothermal reduction method. And the chromium-free inorganic insulating coating for oriented silicon steel was prepared with rGO, small-particle silica sol, large-particle silica sol, aluminium dihydrogen phosphate and so on. The results show that rGO has a multi-layer structure, and its size is smaller than that of GO. EIS test and Tafel polarization curve test have proved that rGO can improve the corrosion resistance of the coating. Specifically, rGO can greatly reduce the $I_{corr}$ of the coating, reduce the corrosion rate, then achieve the improvement of corrosion resistance. However, the addition of rGO may increase the pores of the coating and make corrosion more likely to occur. Therefore, the optimal amount of rGO needs to be further explored.

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