Preparation and Properties of Chromium-Free Corrosion-Resistant Coatings for Oriented Silicon Steel

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Abstract. An environmentally friendly chromium-free insulating coating suitable for oriented silicon steel was prepared by using aluminium dihydrogen phosphate, silica sol, water-based resin, sodium tetraborate and graphene aqueous dispersion as main raw materials. The morphology of the insulating coating was characterized by scanning electron microscopy. Corrosion resistance was investigated by neutral salt spray test and electrochemical test. Magnetic properties and surface insulating resistance were measured. The results showed that the surface of the insulating coating was flat; the addition of graphene could effectively improve the corrosion resistance and magnetic properties of the coating. The corrosion rate in the salt spray test was less than 10% after 120h, and the core loss was reduced by 9.57%. The addition of the graphene did not destroy the insulation properties of the coating. The surface insulation resistance per side of the coating was 269.51 Ω·mm².

1. Introduction
Oriented silicon steel is a soft magnetic alloy. It has high magnetic induction and low iron loss since the crystal grains are regularly oriented in the production process and is commonly used as material for various transformers in the industry especially stacked as laminated cores¹-³. In order to reduce the eddy current loss between the laminations, the surface needs insulating coatings with good corrosion resistance, high insulation resistance and excellent magnetic properties⁴.

At present, the most widely used silicon steel insulation coatings are various types of chromium-containing coatings⁵-⁸. The chromic anhydride or chromate seriously endanger the human body and the environment, and are difficult to recycle and dispose of waste silicon steel products leading to secondary pollution of chromium. With the implementation of the RoHS Directive, the development of chromium-free environmentally friendly coatings has become an urgent problem. To solve this problem, we mixed the water-based organic resin, silica sol, aluminum dihydrogen phosphate and sodium tetraborate to replace the coating with chromic anhydride or chromate, and added graphene to improve the properties of the coating, then prepared an organic-inorganic
composite chromium-free insulating coating suitable for oriented silicon steel. This composite chromium-free insulating coating could eliminate the harm of silicon steel products to the environment and the human body.

2. Experiment

2.1 Materials and measurements
Water-based resin (AC-8190, Shanghai Shurui Technology Chemical Co., Ltd.), amino curing agent (AC-300, Shanghai Shurui Technology Chemical Co., Ltd.), sodium tetraborate (AR, Shanghai Aibi Chemistry Preparation Co. Ltd), silica sol(Shandong Fuso Chemical Co., Ltd.), aluminum dihydrogen phosphate(AR, Shanghai Aladdin Bio-Chem Technology Co., Ltd), alkylphenol ethoxylate(AR, Shanghai Shansu Chemical Co., Ltd.), γ− (2,3 − epoxypropyl)- propyltrimethoxysilane(AR, Dongguan Changping Yuxin Plastics Business Department) and graphene aqueous dispersion(SE4101, The Sixth Element Materials Technology Co., Ltd) were used.

Morphologies of the uncoated sheet and coating were observed by using scanning electron microscopy (SEM, Philps, Philps-XL30 TMP). Corrosion resistance of the coated sheet was evaluated by neutral salt spray test in a salt spray chamber (Xiamen Guangqi Testing Instrument Co., Ltd. GQ-60B) and electrochemical test with electrochemistry workstation (Ametek, PRASTAT2273). Magnetic properties were tested by a soft magnetic material tester (Brockhaus measurements, MPG-100D). Surface tension of the sheets were calculated after contact angle between the surface and two kinds of liquid respectively were measured by contact angle measuring instrument (Kruss, DSA100). Surface insulation resistance of the coating was measured by electrical steel surface insulation resistance test system (Changsha Tianheng Measurement and Control Technology Co., Ltd., TD8560).

2.2 Preparation of chromium-free corrosion-resistant coatings
The mass fraction of the components of the coating and the preparation method were as follows. First, 1% sodium tetraborate was added to deionized water and stirred until completely dissolved. Secondly 1% aluminum dihydrogen phosphate was added to it and stirred until completely dissolved. Thirdly 20% silica sol was added. Fourthly 0.5% alkylphenol ethoxylate and 1% γ− (2,3 − epoxypropyl)-propyltrimethoxysilane were added while stirring respectively. Fifthly 20% water-based resin and 1% amino curing agent were added in sequence. Finally, 1% graphene aqueous dispersion were added to the mixture and stirred until uniform.

Coating without graphene aqueous dispersion was prepared by following the first to fourth steps above as the control group.

Before coating, it was necessary to clean the surface of the oriented silicon steel sheet. The cleaning step was, washing the floating dust with distilled water, washing with ethanol, washing ethanol with distilled water, and washing with 5% sulfuric acid. The cleaning is finally washed with distilled water and blown dry with a blower. The coating was applied by roll coating to a thickness of 3μm and cured in air at 300-400 °C for 30s [9]. Oriented silicon steel sheet coated with no graphene coating was referred to as G0, and oriented silicon steel sheet coated with the coating containing the graphene aqueous dispersion was referred to as G1. In addition, one piece of oriented silicon steel sheet was treated in the same way without coating as a blank plate.

3. Results and discussion
When observed by SEM to magnify 1000 times, rolling traces could be observed clearly on the surface of the blank plate and G0. However, the surface of G1 was smoother and flatter and there was no obvious rolling trace (figure 1).
Corrosion resistance of the coated sheet was evaluated by neutral salt spray test and electrochemical test. Neutral salt spray test was acceleration corrosion according to the test method of GB/T 10125–2012 with a neutral NaCl aqueous solution using continuous spraying. The NaCl used in this experiment was analytical grade and dissolved in deionized water to prepare an aqueous solution with a mass concentration of $50\pm 5$g/L. The sedimentation of salt spray was 1.6mL/80cm$^2$·h. The smaller the percentage of corrosion area in the test, the better the corrosion resistance was. Figure 2 shown the photos taking in neutral salt spray test. The blank plate was very corrosive, corrosion occurred after 0.5h (figure 2a), and corrosion had exceeded 10% after one hour (figure 2b). G0 showed corrosion after 12h (figure 2c), and the corrosion area reached 5% after 48h (figure 2d). G1 had the best corrosion resistance, corrosion occurred after 36h (figure 2e), the corrosion area reached 5% after 108h (figure 2f), and the corrosion area was still less than 10% after 120h (figure 2g).

Since the corrosion area in the neutral salt spray experiment was mainly calculated by the grid method, the corrosion resistance of the coating and the blank plate needed to be evaluated by electrochemical test. The electrochemical performance of the insulating coating was determined on an Ametek PRASTAT2273 electrochemistry workstation. The three-electrode system was used, the platinum electrode was the auxiliary electrode, the Ag–AgCl electrode was the reference electrode, the test sample was the working electrode, the test area of the sample was 1cm$^2$, and the electrolyte was 3.5wt% NaCl aqueous solution. At the beginning of the test, the open circuit potential was taken as the starting potential, and the scanning test was started after the open circuit potential was stable. Polarization curve was collected in a rate of 1 mV/s and scanning interval of -0.3V—0.3V.

Figure 3 showed the results of polarization curves of the blank plate and G1. The polarization parameters were presented in the table 1. As can be seen from figures and table 1, the self-corrosion potential and corrosion current density of blank plate were -0.59169V and 6.6474μA · cm$^2$. Compared with the blank plate, the self-corrosion potential of G1 was greatly positively shifted to 0.90317V, and the corrosion current density was lowered to 0.093854μA · cm$^2$. This indicated that the presence of the silicon steel coating effectively retarded the corrosion of the substrate, inhibited the entire electrochemical process, and slowed the infiltration of the corrosive medium [10-13], thereby improving the corrosion resistance. In figure 3 there was another thing noticeable that a relatively large fluctuation of current occurred in the anode and cathode curve region of the Tafel plot of G1, which is most likely due to chloride ions penetrating the coating. Since the self-corrosion current was always less than 10$^{-9}$A, it indicated that penetrating chloride ions were rare and didn’t destroy the overall corrosion resistance of the coating.
Figure 3. Tafel Polarization of blank plate(left) and G1(right)

Table 1. Tafel polarization parameters.

|           | Ec (V)  | Ic (µA·cm⁻²) |
|-----------|---------|--------------|
| Blank plate | -0.59169 | 6.6474       |
| G1         | 0.90317  | 0.093854     |

Magnetic properties were evaluated by an MPG-100D soft magnetic material tester from Brockhaus measurements. Table 2 showed the saturation magnetic induction B₈₀₀ and core loss P₁.₇ of the blank plate and G1. The B₈₀₀ was measured at 800 A/m magnetic field strength and 50Hz frequency. The P₁.₇ was measured at 50 Hz frequency and 1.7T magnetic induction intensity. It turned out that although the saturation magnetic induction was only increased by 1.23%, the core loss was reduced by 9.57%.

Table 2. B₈₀₀ and P₁.₇ of the blank plate and G1.

|       | B₈₀₀ (T) | P₁.₇ (w/kg) |
|-------|----------|-------------|
| Blank plate | 1.783     | 2.843       |
| G1    | 1.805    | 2.571       |

Since the effect of the coating on the saturation magnetic induction was not obvious, and the coating tension was one of the factors directly affecting the loss of the oriented silicon steel core¹⁴, it was necessary to calculate the tension of the coating by the contact angle test. The calculation of the coating tension required measuring the contact angle between the surface of sample and two different kinds of liquid (here were water and diiodomethane), then the surface tension could be calculated by solving the Young's equation. The contact angle of the blank plate with water was 91.6° (figure 4a), and was 74.5°with diiodomethane (figure 4b). The contact angle of G0 with water was 40.9° (figure 4c), and was 38.2° with diiodomethane (figure 4d). The contact angle of G1 with water was 23.9° (figure 4e), and was 31.4°with diiodomethane (figure 4f). By calculating, the surface tension of the blank plate, G0 and G1 was 24.36 mJ/m², 63.38 mJ/m² and 72.52 mJ/m² respectively.
According the calculation results, the addition of graphene increased the surface tension of the coating, making the surface of the oriented silicon steel sheet more hydrophilic than the magnesium silicate underlayer on the blank plate. Although the increase in tension was beneficial to reduce the core loss \cite{15,17}, this also mean that the corrosive medium, like water, could spread on the surface and be in contact with a larger area of oriented silicon steel sheet. However, the neutral salt spray test and the electrochemical test all proved that G1 had better corrosion resistance. Combined with the Nyquist spectrum, it inferred that graphene can fill the gap inside the coating and hinder the passage of the corrosive medium through the stack, thereby delaying the occurrence of corrosion and slowing down the corrosion process.

Since graphene is conductive material, the surface insulation resistance of the coating with the graphene aqueous dispersion was concerned and was measured by an electrical steel surface insulation resistance test system. When adding 2% graphene aqueous dispersion, the surface insulation resistance was 269.51Ω·mm² per side. And the surface insulation resistance of currently produced oriented silicon steel with chromium-containing coating was generally higher than 20Ω·m², indicating that the prepared coating with graphene had excellent insulating properties. And it was noticeable that the content of graphene aqueous dispersion was 4%, which means only few graphene was needed to get a huge improvement on corrosion resistance and reduction on core loss.

4. Conclusion
A chromium-free corrosion-resistant coating for oriented silicon steel was prepared successfully. The coating was smooth, flat and had excellent corrosion-resistant. In neutral salt spray test, there was less 10% area corroded after 120h. The results of electrochemical tests led to the same conclusion. With the coating, the saturation magnetic induction B_{600} was improved by 1.23% and core loss P_{1.7} was reduced by 9.57%, which was believed connected with the surface tension. The surface tension of the coating was 72.52mJ/m², which was 2.98 times that of blank plate. And the addition of graphene didn’t damage the insulation resistance, which was 269.51Ω·mm² per side.

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