Performance of Modified Nano-SiO2 Composite Phosphating Coating on the Surface of Steel

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Abstract: In order to enhance the corrosion resistance and the quality of the phosphating film, nano-SiO2 was used in the phosphating solution. The structure and properties of the phosphating film were evaluated by SEM, electrochemistry, cupric sulfate drop corrosion test and film thickness measurement. The results show that the thickness of the phosphating film increases with the increase of nano-SiO2 content. The nano-SiO2 modified with vinyl triethoxy silane possessed good dispersibility in the phosphating solution, the phosphating solution with the addition of modified nano-SiO2 could greatly improve the corrosion resistance of the phosphating film.

1. Introduction

Phosphating is almost a standardized pretreatment mode for cathodic electrophoretic coating. Phosphating can enhance the corrosion resistance of metal, provide more fixing points for paint film and increase the adhesion of paint film[1]. Most phosphating solutions contain nickel ions. Adding nickel ion can not only speed up phosphating treatment, but also improve film compactness, adhesion and corrosion resistance[2-3]. However, nickel is a heavy metal ion, which is harmful to human body and environment. The emission standard of nickel ion has been reduced from 1.0 mg / L to 0.5 mg / L due to increasingly strict restrictions[4]. It is still an important research direction of phosphating industry in the future to explore the phosphating process with little or no nickel. In recent years, with the development of nanotechnology, nano materials are widely used in traditional surface treatment fields, such as solid coating, organic coating, passivation[5-7]. However, there are relatively few applications of nanomaterials in phosphating processes, and related research is still in its infancy. For example, R. Mohammad Hosseini et al. [8] studied the phosphating solution added with nano-Al₂O₃ and found that the phosphating film has strong wear resistance and lubricity. M. Tamilselvi et al. [9] prepared phosphate coatings on the surface of a steel plate, and found that the phosphate coating containing nano ZnO had better corrosion resistance. S.M.A. Shibli[10] reviewed the film-forming process of phosphating solution containing nano-TiO² on the surface of galvanized steel plate. It was noted that the addition of nano-TiO² could improve the electrochemical stability and corrosion resistance of the film.

In this study, the nano-SiO₂ was added into the phosphating solution instead of nickel ion. A phosphating solution containing no nickel ions was prepared.
2. Materials and experiments

2.1 Nano-SiO₂ preparation
Add 50ml of sodium silicate solution of a certain concentration to the three mouth flask, put it on the mixer, adjust the rotating speed to 100 r/ min, and slowly raise the temperature to 60 ℃, put the flask into a constant temperature water bath at 60 ℃, slowly add 1mol / L sulfuric acid to the flask, and quickly stir it to make it mix evenly until white precipitate appears.

Weigh 0.3 g of nano-SiO₂ and dissolve it in ethanol solution, stir it at room temperature and disperse it in ultrasonic cleaner for 15 min to obtain uniform and transparent suspension. In addition, 0.3g vinyl triethoxysilane (A151) was hydrolyzed in 3g deionized water at room temperature under acidic conditions, and pH = 3-4 was adjusted with phosphoric acid until the hydrolysis was complete.

2.2 Phosphating process
The mild steel is first sanded with 60# sandpaper to remove the surface deposits, and then the surface of the steel bar is completely exposed by grinding with 120# sandpaper. After polishing, rinse with water and rinse for 1 min; Rinse the steel bar with a dilute hydrochloric acid solution with a mass concentration of 5% to activate the steel bar metal for 30 s; then rinse with water for 30 s to remove residual acid on the surface; The steel bar is placed in the phosphating solution for 5 to 10 minutes; the cleaning is carried out for 1 min to remove the residual phosphating solution and dried at room temperature. The above test procedures were all carried out at room temperature.

2.3 Preparation of phosphating solution
The basic test phosphating formula is obtained through preliminary orthogonal test, as shown in Table 1.

| composition | ZnO | H₃PO₄ | Mn(NO₃)₂·4H₂O | NaNO₃ | NaF | citric acid |
|-------------|-----|-------|---------------|-------|-----|-------------|
| mixture ratio | 1.5 | 18.0 | 9 | 16 | 0.8 | 1.2 |

The composite modified nano-SiO₂ phosphating solution was prepared by adding the modified nano-SiO₂ dispersion, stirring and dispersing, and then ultrasonic treatment for 15 min. After the phosphating solution is prepared, adjust its acidity to the process range with 1 mol / L NaOH solution.

2.4 Instruments and analytical methods

2.4.1 Morphology analysis. The morphology of phosphating film was observed by JSM-6700F scanning electron microscope (jeol company of Japan)

The thickness of phosphating film was measured by thickness gauge. Take three points of the same sample for measurement, and calculate the arithmetic mean value, which is the thickness of the phosphating film.

2.4.2 Cupric sulfate drop corrosion test. Take a drop of copper sulfate solution (40ml 0.1mol/L copper sulfate solution + 20ml 10% sodium chloride solution + 0.8ml 0.1mol/L hydrochloric acid) and drop it on the phosphating film. Observe the time from blue, light green, yellow to red. Take more than three points to calculate the average value.

2.4.3 Electrochemical characteristics of steel fiber phosphating film formation process. The test material is a steel fiber sample. The sample for the Et (potential-time) curve is made into a working electrode of 1 cmx0.1 cm, the electrolyte is a phosphating solution, and the electrochemical test uses a three-electrode system. The specific electrode is a saturated calomel electrode, the auxiliary electrode is a platinum wire, and the test instrument adopts a CP-6 type potentiostat. The temperature of the phosphating solution is maintained at 20±1℃ in a constant temperature water bath during the test.
2.4.4 Neutral salt spray test (NSST) corrosion. The corrosion solution is 50g/L NaCl solution, the solution pH = (7+0.5), the temperature inside the salt spray box is (35+2)℃, the settlement is 2ml/(80cm²·h), the sample is placed at 30 degrees in the vertical direction of the salt mist rack, and is continuously sprayed with 8h for 1 cycles. The corrosion area was tested and the corrosion resistance of phosphating film was evaluated after different cycles.

3. Results and discussion

3.1 Scanning electron micrograph
Through the analysis of the surface morphology after phosphating and corrosion (1500 times), it can be found that the appearance of the phosphated steel fiber is dark gray, continuous and uniform, as shown in Figure 1. It can be seen from Figure 1 that the generated phosphating film completely covers the metal substrate and is continuously distributed in blocks with large surface area and completely covers the metal surface.

3.2 Effect of nano-SiO₂ on phosphating film thickness
It can be seen from Figure 2 that the film thickness of the phosphating film increases with the increase of the concentration of nano-SiO₂.

3.3 Effect of Nano-SiO₂ on corrosion resistance of phosphating film
It can be seen from Figure 2 that the corrosion resistance time of copper sulfate in phosphating solution increases first and then decreases with the increase of nano-SiO₂ content. When the content of nano-SiO₂ is 1g/L, the corrosion resistance time of the phosphating film is the best, more than 115s.

3.4 Electrochemical analysis
In order to simulate the corrosion resistance of phosphated steel, unphosphorized steel and stainless steel in the corrosive environment, adjust the mass fraction of sodium chloride in the solution to 3.5%, and the measured potential changes are shown in Figure 3. It can be seen from Figure 3 that the potential of the modified phosphating film is the highest, and its rise range with the change of time potential is the smallest.

3.5 Neutral salt spray performance
Figure 4 shows the corrosion area curve of steel before and after phosphating in different neutral salt spray cycle tests. It can be seen from Figure 4 that the corrosion area of unphosphorized steel is about 80% after the second salt spray cycle, and it is completely corroded after the third salt spray cycle. However, the corrosion area of galvanized steel plate after phosphating treatment is significantly
smaller than that of unphosphorized steel plate. After five cycles of salt spray, the corrosion area of the composite modified nano-SiO$_2$ phosphating film is about 38%, while the corrosion area of the basic phosphating film is about 60%, which shows that the corrosion resistance of galvanized steel after the composite modified nano-SiO$_2$ phosphating treatment is greatly improved on the basis of the basic phosphating treatment.

3.6 Mechanism analysis

As the nano-SiO$_2$ still has the characteristics of nano particles, the specific surface area is large, the surface activity is high, and it is easy to adsorb on the steel surface. In the process of phosphating, when the galvanized steel is immersed in the phosphating solution, these particles will be adsorbed on the surface of steel, which not only increases the number of micro cathodes on the surface of the substrate, but also becomes a better crystal nucleus when the phosphate crystal is crystallized. In the process of film formation, such a large number of nuclei can change the extension direction of phosphate crystal crystallization, and make the crystal grow along its extension direction. With the progress of phosphating reaction, when the crystallization and dissolution of phosphate crystal reach equilibrium, these modified nano-SiO$_2$ particles can be adsorbed on the surface of the film and filled in the gap, which makes the porosity of the phosphating film reduce and the corrosion resistance increase.

![Figure 3. Potential change diagram in NaCl solution with different treatment methods](image1)

![Figure 4. Corrosion area curve in different neutral salt spray cycle tests](image2)

4. Conclusion

The thickness of the phosphating film increases with the increase of the concentration of nano-SiO$_2$. Adding nano-SiO$_2$ to the phosphating solution can enhance the corrosion resistance of the phosphating film. When the amount of nano-SiO$_2$ is 1g / L, the thickness of the film is 7.81 μm, and the corrosion resistance of the phosphating film is the best.

The composite modified nano-SiO$_2$ phosphating film on the steel surface has excellent corrosion resistance, which can effectively prevent the corrosion of the film by the medium.

5. References

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**Acknowledgments**

This work was supported by Shandong Provincial Natural Science Foundation (ZR2017LEE029).