Analysis of engineering application requirements of nano coating materials

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Abstract: Coatings are the primary means to control the corrosion of marine engineering structures. It is the frontier and hot spot of nano coating materials research to use nano materials to modify anti-corrosion coatings, realize the complementary advantages between different materials, and prepare high-performance, environmental protection, energy saving and functional anti-corrosion coatings. However, with the application of nano coating materials in the atmospheric subtropical coastal environment, there are many problems of poor weatherability. Based on the environmental corrosion characteristics of the subtropical coastal zone, this paper evaluates the environmental adaptability of several nano coating materials in the coastal atmospheric environment, analyzes the engineering application requirements of nano coating materials, and puts forward the measures and suggestions for the development of nano coating materials in marine engineering in view of the main problems existing in the engineering application of nano coating materials in China.

1. Introduction
With the development of global marine resources, the major infrastructure and important industrial facilities are gradually pushed to the deep blue sea. However, the harsh service environment of the ocean has caused extremely serious corrosion of the infrastructure in the marine climate environment, which endangers the service life and safety of the marine infrastructure [1-2]. Moreover, the marine corrosion situation is complex and different service areas have different corrosion rates, bringing severe challenges in the development of corrosion-resistant materials and corrosion protection [3]. Energy chemistry in extreme environments is an important part of the national energy science and technology strategy. China is one of the few countries that have conducted deep-sea corrosion material tests [4], which provide a reliable basis for anti-corrosion research in marine atmospheric environment.

Coating is a primary means of corrosion control of marine engineering structures. Nanomaterials have become ideal materials for corrosion protection due to their excellent properties. In recent years, the research and application of new nano-coating materials have attracted a lot of attention [6]-[10]. Because of their convenient construction and widespread application, nano-coating materials have become one of the important factors that affect the service safety, life span and reliability of ships, offshore engineering, and ocean-going facilities and have attracted great attention from governments and industries all over the world [11]. Therefore, it is of great significance to develop the anti-corrosion coatings and coating technology in marine engineering and to establish the coating requirements of protective coating, which can effectively reduce the corrosion of exposed carbon steel, stainless steel, and aluminum components. In this way, the service safety and reliability of marine engineering and ships can be ensured, the occurrence of major disasters can be reduced, and the service life of marine structures can be prolonged.
Based on the characteristics of environmental corrosion in the coastal zone of the South China Sea, this paper evaluated the environmental adaptability of several nano-coating materials in the nearshore atmospheric environment and analyzed the engineering application requirements of nano-coating materials. In addition, the measures and suggestions for the development of nano-coating materials in marine engineering were put forward in view of the main problems existing in the application of nano-coating materials in marine engineering in China.

2. Characteristics of environmental corrosion in the coastal zone of the South China Sea

The high salt concentration (generally around 3.5%), rich oxygen, and numerous marine microorganisms and macroorganisms in seawater, together with the impact of waves and sunlight, resulted in severe marine corrosion environment\(^1\). The corrosion severity of seawater in typical sea areas of China was evaluated based on the metal corrosion rate, which showed that the seawater severity of Nanhai island was higher\(^{12}\). Atmospheric corrosion is classified into 6 categories in ISO 12944, with the highest corrosion grade in the marine environment. Due to the influence of sodium chloride particles contained in seawater droplets, the corrosion in the coastal land environment within 200 m also belongs to the category of corrosion in the marine environment\(^{13}\).

Hainan Island is located in the coastal zone of the northern edge of the tropics. The whole island is surrounded by the coastline. It has the climate characteristics of high temperature, high humidity, thunderstorm, heavy precipitation, tropical cyclone landing, high salt fog and strong radiation\(^{14}\). The characteristics of tropical marine atmospheric environment are obvious. The whole island of Hainan, especially the Wenchang area, has high temperature all year round. The annual average temperature is 24.1 °C, the annual average relative humidity is 86.4%, the annual average dew point temperature is 21.8 °C, and the annual average sunshine hours is 1803.6 h/a\(^{15}\).

In order to evaluate the environmental corrosion law of the northern coastal zone of the South China Sea more effectively, two environmental monitoring sites with different distances from the coastline in Wenchang area were selected. Based on the results of long-term environmental monitoring, environmental data from the southeastern China Sea region were analyzed to determine the characteristics of environmental corrosion.

![Figure 1. Temperature change curves of the two monitoring sites](image1)

![Figure 2. Material surface humidity change curves of the two monitoring sites](image2)
The changes in temperature and humidity of the two environmental monitoring sites at different distances from the coastline are basically the same. Figure 1 and Figure 2 show the temperature change curves and the material surface humidity change curves of the two sites, respectively.

The environment of the two sites was monitored for a long time by an online corrosion monitor, as shown in Figure 3. According to the ISO9223-9226 atmospheric corrosion classification standard, the environmental corrosion level of the two sites both reached level 5. The annual wetting time exceeded 6,500 hours, and the level was ζ5. As can be seen from Fig. 3, the atmospheric environment of the two sites was typical of high temperature, high humidity, high irradiation, and high chloride ion deposition environment. In this environment, the materials were continuously subjected to a drying-wetting cycle. The corrosion process was directly related to the surface wetting time.

![Figure 3. Long-term instantaneous corrosion rate curves of carbon steel and zinc alloy](image)

A comprehensive analysis of the surface wetting status of each time period in a single day shows that the temperature and humidity were basically the same in the time period of 00:00–08:00, during which the characteristics of high temperature and high humidity were maintained, and the sample surface was in a state of condensation. In the time period of 08:00–12:00, the humidity decreased rapidly and the temperature rose rapidly, which corresponded to the drying process of the sample surface. During the period from 12:00 to 16:00, the temperature and humidity were stable again and the sample surface was further dried. During the time periods of 16:00–20:00 and 20:00–24:00, the surface of the sample was wetted, which was the reverse process of the first two stages.

![Figure 4. Corrosion behaviors of zinc alloy at the two sites](image)

An online corrosion monitor based on electrochemical reaction mechanism of metal corrosion was used to analyze the instantaneous environmental corrosion degree. The corrosion law of zinc alloy at the two sites was compared, as shown in Figure 4. The annual corrosion rate of the two sites was quite different. The instantaneous corrosion rate and the average annual corrosion rate of site 1 were both half of those of site 2. It was found that the main factor affecting the corrosion rate was the deposition rate of sea salt particles at the two sites. The deposition rate of sea salt particles in site 1 was 0.1841 mg/
Wenchang launch site is located in low latitude area and close to the sea, with high annual average temperature, long sunshine time, high relative humidity, and extremely bad corrosion environment. The corrosion rate of carbon steel in the offshore field (site 1) is 0.3274 mm/a. According to the definition of corrosion environment in ISO 12944 and ISO 9223, the corrosion environment in Wenchang coastal zone belongs to the typical C5-M∼Cx harsh corrosion environment grade.

3. Comparative analysis of environmental adaptability between nano-coating materials and traditional heavy-duty anti-corrosion coatings

Anti-corrosion coatings are applied to the surface of base course. After a polymer film is formed and cured, a mysterious film is formed, which isolates the protected substrate from the external corrosive medium, so that the corrosion reaction does not occur or the corrosion rate is delayed. In recent years, more and more researchers in our country began to pay attention to the research of nanoparticles to improve the corrosion resistance of coatings, some of which have entered the engineering application stage.

3.1 Materials and experimental methods

The base sample material is Q345B steel. The specific chemical composition is shown in Table 1. The size of the sample sheet is 100 mm × 50 mm × 3 mm.

Coating samples were selected based on environmental adaptability evaluation and corrosion resistance test of 4 kinds of coating materials and traditional heavy-duty coatings. The coating systems were shown in Table 2.

Sea salt particles are chlorides, which can penetrate into the coating material and cause corrosion. Therefore, the cyclic salt spray resistance performance test was carried out referring to the cyclic A test procedure in the standard GB/T 31588.1-2015 "Paints and varnishes - Determination of resistance to cyclic corrosion conditions - Part 1: Wet (salt fog) / dry / humidity". The test was carried out in
accordance with the cycle A of artificial weathering (method 1) in GB/T 1865-2009 "Paints and varnishes - Artificial weathering and exposure to artificial radiation - Filtered xenon-arc radiation".

3.2 Analysis of coating resistance to circulating salt spray

Table 3 showed the appearance of samples at different assessment stages during the cyclic salt spray test. According to the table, after 0-720 h cyclic salt spray test, there was basically no corrosion on the surface of the sample. After 960 h cyclic salt spray test, slight stain and rust began to appear on the surface of the sample surface. Some of them even bubbled and peeled off.

| Number | Conclusion                         |
|--------|------------------------------------|
| 1      | the surface is dirty               |
| 2      | discoloration of the surface, 1 bubble, a small amount of rust and peeling on the edge, slight staining of rust |
| 3      | no corrosion, the surface is slightly stained |
| 4      | the edge is slightly rusted, peeled, bubbled, and slightly stained |
| 5      | no corrosion                      |

Table 4 shows the comprehensive rating results of the surface state of the test sample after 1440 h cyclic salt spray test. According to GB/T 1766-2008 "Paints and varnishes - Rating schemes of degradation of coats", the comprehensive ratings of the five types of test samples for cyclic salt spray resistance are level 1, level 4, level 1, level 3, and level 0 respectively. The cyclic salt spray corrosion resistance of the whole set of nano-coating materials is the worst, followed by the micro nano-coating materials. When nano-coating materials are used as primer, their performance is slightly better, but all of them are worse than the traditional heavy-duty anti-corrosion coating.

Table 4 Comprehensive rating of cyclic salt spray resistance test

| Number | Test Time | Light Loss Rate% | ΔE | Loss of Light | Discoloration | Pulverization | Pan gold | Spot | Stain | Crack | Blistering | Mold | Peel Off | Rust | Comprensive grade |
|--------|-----------|------------------|----|---------------|---------------|---------------|----------|------|-------|-------|------------|------|----------|------|------------------|
| 1      | 1440 h    | 25.5             | 2.9| 2             | 1             | 0             | 0        | 0    | 0     | 0     | 0          | 0    | 0        | 0    | 1                |
| 2      | 4.2       | 6.0              | 1  | 2             | 0             | 0             | 2        | 0    | 1     | 0     | 2          | 1    | 4        |      |                  |
| 3      | 16.9      | 2.5              | 0  | 1             | 0             | 0             | 1        | 0    | 0     | 0     | 0          | 0    | 1        |      |                  |
| 4      | 9.7       | 3.9              | 0  | 2             | 0             | 0             | 2        | 0    | 1     | 0     | 1          | 1    | 3        |      |                  |
| 5      | 0.2       | 1.4              | 0  | 0             | 0             | 0             | 0        | 0    | 0     | 0     | 0          | 0    | 0        |      |                  |
3.3 Analysis of aging resistance of coating to xenon lamp

Table 5 shows the comprehensive test results of the surface state of the five types of test samples after 720 h xenon lamp aging test. Xenon lamp aging mainly assesses the ultraviolet (UV) aging resistance of the topcoat. According to GB/T 1766-2008, the comprehensive ratings of the five types of test samples for resistance to cyclic salt spray are level 5, level 3, level 0, level 3 and level 0 respectively. The fluorocarbon topcoat exhibits the best performance and the nano-coating system shows the worst performance. The light loss rate has reached 59.7%.

| Number | Test Time | Light Loss Rate% | △E | Loss of Light | Discoloration | Pulverization | Spots | Stains | Cracks | Blisters | Mold | Peel Off | Rust | Comprehensive grade |
|--------|-----------|------------------|-----|--------------|---------------|---------------|-------|--------|--------|----------|------|----------|------|---------------------|
| 1      | 648 h     | 59.7             | 17.3| 4            | 5              | 2              | 0     | 0      | 0      | 0        | 0    | 0        | 0    | 5                   |
| 2      | 720 h     | 71.3             | 4.2 | 4            | 2              | 0              | 0     | 0      | 0      | 0        | 1    | 0        | 0    | 3                   |
| 3      |           | 10.5             | 0.3 | 1            | 0              | 0              | 0     | 0      | 0      | 0        | 0    | 0        | 0    | 0                   |
| 4      |           | 31.4             | 0.3 | 3            | 0              | 0              | 0     | 0      | 0      | 0        | 0    | 0        | 0    | 3                   |
| 5      |           | 13.1             | 0.1 | 1            | 0              | 0              | 0     | 0      | 0      | 0        | 0    | 0        | 0    | 0                   |

3.4 On-site adaptability assessment of coating system

Table 6 shows the on-site inspection results of in-service coatings of 5 types of coating systems, which evaluates the protective performance and environmental adaptability of the coating systems.

| Coating system number | Coating thickness (μm) | Comprehensive Appearance Rating | Adhesion | Electric spark leak detection | Evaluation of coating system |
|-----------------------|------------------------|--------------------------------|----------|------------------------------|------------------------------|
| 1                     | 238                    | Level 1                         | 5A(Crossing method) | There is a leak at the weld | The construction of the project was completed in September 2016. After 2 years of service, the surface of the coating was slightly stained and there were anti-rust and leakage spots at the weld. |
| 2                     | 697                    | Level 2                         | 5.32MP(Drawing method) | No leakage | The mailing sample was tested on site after 6 months of service. The coating thickness exceeded the standard and the coating surface was blistered. |
| 3                     | 637                    | Level 1                         | 5A(Crossing method) | No leakage | The test construction was completed in May 2018. After 4 months of service, the on-site test showed that the coating thickness exceeded the standard and the coating surface was slightly blistered. |
| 4                     | 371                    | Level 3                         | 5A(Crossing method) | No leakage | The test construction was completed in April 2018. After 5 months of service, the on-site test showed that the coating was obviously stained and blistered and the coating performance remained relatively good. |
| 5                     | 535                    | Level 1                         | 4A(Crossing method) | No leakage | The test construction was completed in April 2018. After 5 months of service, the on-site test showed that the coating performance remained good. |

Based on the analysis of laboratory results and on-site test results, it is found that some of the domestically produced nano-coating materials have relatively poor environmental adaptability in the Wenchang coastal zone. In particular, the aging resistance of the topcoat and the barrier performance of
the intermediate paint both showed a gap with traditional heavy-duty anti-corrosion coating materials.

4. Analysis of engineering application requirements of nano-coating materials

China's marine coatings market is almost completely occupied by foreign countries. In particular, the coatings for ocean-going vessels, offshore platforms paint, and antifouling coatings are all foreign coatings. As far as the technical level is concerned, some domestic coating technologies have reached an applicable level, but there is a lack of opportunities for practical engineering applications. This not only affects the development of relevant domestic key technologies, but also affects the application of offshore platforms built in China in foreign countries.

Traditional anti-corrosion coatings contain heavy metals and some difficult-to-degrade organics, which will harm the environment no matter in the production process or in the use process. Therefore, the current field engineering applications requires nano-coating materials with performance comparable to traditional heavy-duty anti-corrosion coating materials, focusing on environmental protection, energy saving, resource saving, high performance, and functional development. In order to expand the engineering application of nano coating materials in the South China Sea, several requirements need to be improved:

(1) Improving the barrier properties of nano-coating materials

By adjusting the composition of the nano-coating material, improving the microstructure of the coating, adjusting the combination of nanoparticles and organic solvents, a dense coating structure can be formed, which can significantly reduce the porosity of the coating and effectively block the penetration of water, oxygen, and corrosive ions such as chloride ions.

(2) Improving the weather resistance of nano-coating materials

The introduction of nanoparticles can improve the rheology, adhesion, hardness, smoothness, and anti-aging properties of coatings. However, most of the nano-coating materials on the market are sensitive to UV radiation and are prone to light loss and pulverization. The research of nano-modified topcoat is highly desired. Modified materials such as super weather-resistant topcoat-fluorocarbon resin and fluorine-containing polyurethane are excellent choices for topcoat base materials. In addition to being used for hull paint, they can also be used for interior coatings in contact with strong corrosive media.

(3) Developing environmental friendly nano-coating materials

Environmentally-friendly high-performance heavy-corrosion protective coatings and environmentally-friendly long-life marine antifouling coatings are one of the important development directions for the sustainable development of "Green Hills and Clear Waters" and "the Belt and Road Initiative". How to effectively use the characteristics of nanomaterials and improve their environmental protection is one of the practical engineering application problems that need to be solved.

(4) Investigating the compatibility between nano-coating materials and traditional coatings

5. Conclusion

In view of the slight corrosion on the surface of the in-service anti-corrosion coating of some carbon steel structures in the marine atmospheric environment, the surface paint can be polished off and directly applied to the paint brand that has passed the recoatability test to renovate the coating. Solving the compatibility between nano-coating materials and traditional coatings is an important means to improve the efficiency of material application.

In addition, promoting the formulation of advanced anti-corrosion materials and technical standards and specifications, deepening the basic theoretical research on nano-coating materials, and increasing the anti-corrosion design before use are all key steps to further promote the application of advanced nanomaterials in anti-corrosion engineering.

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