

Anti-corrosion Performance of Engineering Mechanical Coatings Dependent on Nanotechnology

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Abstract: Corrosion is a common phenomenon. Both natural environment and industrial media may cause corrosion of metals. It is reported that every 90 seconds around the world, 1 ton of steel corrosion into rust, pipeline corrosion not only causes the transmission medium run, leakage phenomenon, bring huge waste, but also endanger health. Corrosion is not only an economic problem, but also a safety problem. The explosion caused by corrosion and the collapse of steel structures will bring accidents to people, endanger people's property and health safety. Corrosion not only affects the working accuracy of national defense facilities and equipment, but even causes the failure of key precision components, which seriously threatens national security. In this paper, the structure and properties of NM and the research status of nanomaterial complexes are introduced. It is pointed out that it is possible to improve the properties of composite coatings by adding different dimensional NP in epoxy powder coatings. It is suggested that powder coating instead of solvent coating will be a developing trend in metal AC application in the future. Through the experimental study, it was found that the main performance indexes of the nano composite epoxy powder coating prepared by the synergistic action of nano particle modification, ball milling mixing and melting mixing extrusion were improved in different degrees compared with the ordinary pure epoxy powder coating.

1. Introduction

The mechanical properties of coatings and the interfacial bond strength between coatings determine the corrosion resistance. The methods to improve the properties of epoxy powder coating are firstly to improve the properties of epoxy resin, and secondly to modify the curing agent and filler. Epoxy resin modification and curing agent modification are faced with complex technology, harsh preparation conditions, high cost, and cannot be widely promoted and utilized. Therefore, the method of blending modified NM with epoxy resin has a wider application prospect by comprehensively considering the production process, manufacturing cost and the difficulty of

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operating procedures [1].

In related studies, Kuratani et al. studied the influence of re-spraying process on the atmospheric corrosion behavior of porous plates [2]. In order to reproduce the recoating process, some pretreatments such as salt spray, sandblasting and zinc phosphate treatment were performed. In salt spray tests AFTER pretreatment and painting, corrosion increased in the case of no zinc phosphate treatment and in the case of no treatment 48 hours before painting.

Enkang et al. successfully prepared Ni-Co-Cr-Al YTa coating with excellent corrosion resistance by high-speed oxygen fuel spraying technology to protect the equipment from damage [3]. The chemical composition, mechanical properties and microstructure evolution of the coating before and after annealing treatment were studied. At the same time, the effect of annealing treatment on corrosion and cavitation properties of coating was studied. After annealing treatment, grain growth and segregation of reactive elements increase the interface strength and inhibit the formation of microdefects in the coating.

Joseph et al. mentioned that the use of anticorrosive pigments in polymer coatings is an effective way to prevent metal corrosion [4]. Therefore, Ce x Zr 1 -- x O2 NP doped with different concentrations of zirconium were prepared by co-precipitation synthesis method. X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy showed that the formation of cerium oxide - zirconia solid solution increased the density of oxygen defects. Thermogravimetric analysis showed that the oxygen storage capacity of CE-Zr solid solution was enhanced.

The matching system of two-component epoxy primer and two-component polyurethane topcoat is usually used in the coating of structural parts of construction machinery to ensure the AC and weather-resistance requirements of structural parts [5-6]. This paper aims to develop a high-performance waterborne epoxy primer suitable for construction machinery painting, replacing the existing solve-based epoxy primer, to meet the existing requirements of construction machinery painting. By systematically studying the effects of WATER-based EPOXY resin, anti-rust pigment, pigment volume concentration (PVC) and curing agent on the properties of WATER-based epoxy coatings, WATER-based epoxy coatings with similar properties to solvent-based epoxy coatings were obtained.

2. Design Research

2.1. Main Problems in the Application of Nanomaterials (NM)

To sum up, there are many researches on nano composite liquid coatings, and the dispersion methods used have improved the dispersion effect of NP in liquid coatings to a certain extent, but there are few researches on nano composite powder coatings, and a single dispersion method cannot disperse well in powder coatings. As a result, the application of NM in powder coatings is limited for three main reasons: first, the dispersion of NM in powder coatings, second, the compatibility of NM in powder coatings, and third, the proportion of NM in powder coatings [7-8]. The details are as follows:

(1) As the filler in the coating, the dispersion of NM in the coating is the key to determine whether it plays a nano effect. Due to the small size, large specific surface area, large surface free energy and high activity of NP. And the nano particles (NP) keep colliding with each other, resulting in Brownian motion, which makes the NP easy to reunite. Agglomeration reduces the dispersion effect of NM. If the dispersion is not good, the effect will not be achieved, but the coating performance will be reduced [9-10].

(2) Compatibility of NP with powder coatings. It is difficult to disperse the nano particle powder

coating uniformly, which is easy to lead to interface defects, thus reducing the overall performance of the coating. Therefore, how to improve the compatibility and stability of NP and epoxy resin and prevent further agglomeration of NP is also a problem to be considered [11-12].

(3) The proportion of NM in powder coatings. The coating formula determines the performance of the coating. The more NP are added, the better. If the amount is too large, not only the manufacturing cost will increase, but also serious agglomeration will occur, which will cause side effects and reduce the performance of the powder coating; If the amount is too small, the effect of adding NM will not be achieved. Therefore, it is also a key consideration to study the proportion of NP in the powder coating, and use the least amount to maximize its performance on the premise of ensuring the uniform dispersion of NP [13-14].

2.2. Composition of Wear-Resistant and AC Coating

The most important component of the wear-resistant and AC coating is the film-forming material. As the most basic component of the wear-resistant and AC coating, the film-forming material provides the substrate for other components of the coating and then attaches to the metal surface. The film-forming materials mainly include thermosetting and thermoplastic. Common unsaturated resin, polyurethane and epoxy resin belong to thermosetting film former, while acrylic acid belongs to thermoplastic film former [15-16].

The filler in the coating is an important component that can improve the film-forming material and endow the matrix with special functions, which can be divided into organic and inorganic. Common synthetic resin fillers belong to organic fillers, while silicate and oxide fillers such as alumina, montmorillonite and silica belong to inorganic fillers. Different micro dimensions of fillers may also affect their functionality in the matrix. For example, nano alumina and micron alumina have different modification effects on resins, because more nano alumina can be accommodated in the same scale space of the matrix, and more nano alumina can participate in the modification, so the modification effect is more obvious. At the same time, different filler micro morphology has different effects on matrix modification. Compared with rod, needle and other nano alumina morphologies, spherical nano alumina has larger specific surface area and better modification effect. One kind of filler can be selected to improve the matrix, or a variety of fillers can be selected. The most common is one component filler modification and two-component filler synergistic modification of the matrix.

If the filler and other components in the coating want to be evenly and stably dispersed in the matrix, it needs a medium, which is called dispersant. Common dispersants include water, organic solvent (such as ethanol), active agent, etc. These dispersants can properly change the viscosity of the matrix [17-18]. For example, when resin substances in the paint are used as the matrix, the filler can be uniformly and stably dispersed in it by adding an appropriate amount of ethanol.

Auxiliary agent, as the least component in the production of coatings, plays an important role in ensuring the stability of coatings. According to different requirements of functional coatings, it can be divided into thickener, defoamer, etc. When making epoxy resin coatings, a large number of bubbles will be generated during heating and mixing. If these bubbles are not removed with defoamer, not only the gloss of cured coatings will be reduced, but also their performance will be greatly reduced.

2.3. Analysis of Dynamic Polarization Curve (Tafel) of Coating

Dynamic polarization curve can reflect the change of polarization current density with electrode

potential. Generally speaking, the polarization current density is proportional to the corrosion rate. The higher the corrosion potential (Ecorr) of the coating, the lower the corrosion current density (Icorr) of the coating, and the better the corrosion resistance. The corrosion resistance of the coating can be analyzed not only by Ecorr and Icorr, but also by polarization resistance (Rp) and AC efficiency (P_E). The Ecorr and Icorr of the above samples can be obtained by linear fitting the Tafel diagram. The value of Rp can be obtained from the equation of Stearn – Geary, as shown in Formula 1:

$$R_{P} = \frac{\beta_{a}\beta_{b}}{2.303(\beta_{a} - \beta_{b})I_{corr}}$$
(1)

Where, β_a , β_b is the Tafel slope of anode and cathode respectively, Icorr is determined by $\beta_a \beta_b$ is determined.

The AC efficiency P_E is calculated according to Formula 2.

$$P_E\% = \frac{i_{corr}(uncoated) - i_{corr}(coated)}{i_{corr}(coated)} \times 100\%$$
(2)

Where Icorr (uncoated) and Icorr (coated) are the corrosion current density of bare electrode and coated electrode respectively.

3. Experimental Study

3.1. Determination of Basic Formula

Epoxy resin 1168, curing agent 969F02X, antifoaming agent Benzoin, leveling agent PV88, curing promoter 2-methylimidazole, epoxy resin: curing agent mass ratio =5:1, the basic formula is as shown in Table 1:

Preparation of NP/epoxy resin predispersions:

(1) The NP were modified, and the pre-separated particles were prepared by ball milling for 3h in a ball mill with a mass ratio of 1:100 between NP and epoxy resin at a rotational speed of 500 RPM.

(2) According to the design formula in Table 1, the pre-separated particles are doped to epoxy resin, curing agent, leveling agent, etc., and mixed in the mixer, and then fused, mixed and extruded.

(3) After cooling and pressing, it is sent to air mill for grinding, and then sieved with 120 mesh to get nano composite powder coating sample.

raw material	Relative epoxy resin content of NP (wt%)					
	0	0.1	0.2	0.5	1	
Epoxy resin (1168)	200	180	160	100	0	
Predispersed body	0	20	40	100	200	
curing agent	40	40	40	40	40	
accelerator	1	1	1	1	1	
Leveling agent (PV88)	4	4	4	4	4	
Defoamer (benzoin)	0.8	0.8	0.8	0.8	0.8	

Table 1. Formula of nano composite epoxy powder coating

Note: Modified NP/epoxy resin with different dimensions were used as pre-dispersions, and the

content of NP relative to epoxy resin was 1.0wt%. Nano-sio2 was selected for zero dimension, MWCNTs for one dimension, and MoS2 for two dimensions.

3.2. Process Flow

(1) Preparation process of nano epoxy composite powder coating





Figure 1. Preparation flow chart of nano composite epoxy powder coating

(2) Preparation process of nano epoxy composite powder coating

As shown in figure 2:



Figure 2. Preparation flow chart of nano composite epoxy powder coating

(3) Impact performance test

The impact resistance of composite coatings can greatly affect the corrosion resistance and wear resistance of the material surface. The higher the impact resistance of the composite, the closer the connection between the coating and the substrate, the more difficult the surface of the substrate is to be affected by external media, and the better the corrosion resistance is. In some extreme environments, the friction and wear degree of external fluid on the coating surface in all directions is large, the impact resistance of the coating is particularly important.

The impact resistance was tested using the XJJ-50 impact testing machine, the size of the tested coating is: length 80.0 ± 1 mm, width 10 ± 0.5 mm, thickness 4 ± 0.2 mm. The working principle of the impact testing machine is to adjust the height of the impact pendulum to make it fall freely, with gravitational potential energy impact pendulum on the sample table to test the sample deformation, according to the conservation of energy, the sample surface deformation energy is equal to the

initial energy of the impact pendulum minus the impact of the pendulum on the sample surface after the energy, Finally, the impact strength of the sample is obtained by using the calculated energy difference as a quotient of the cross-sectional area of the sample.

$$I = \frac{W_0 - W}{S} \tag{3}$$

In the above formula :I -- impact strength of the tested sample, kJ/m2; 0W -- energy before release of the impact pendulum, kJ; W is the energy of the sample deformed by the impact pendulum, kJ; S -- the cross-sectional area of the sample under test, m2.

(4) Fracture performance test

The elongation at break of composite material is an important index reflecting the fracture performance of the material. It refers to the percentage of the elongation length of the sample when the coating material is stretched by external forces in the original length. The level of elongation at break can reflect the softness of the internal tissue of the material. The higher the elongation at break, the higher the softness of the internal tissue of the material and the stronger the toughness.

The elongation at break of the composite coating was also tested by UTM4000 electronic universal testing machine. The appearance of the composite material was dumbbell-shaped, and the size was 200.0 ± 2 mm, 70.0 ± 0.5 mm, 10.0 ± 0.5 mm and 3.75 ± 0.2 mm, respectively.

$$e = \frac{L - L_0}{L_0} \times 100\%$$
 (4)

In the above formula :e -- elongation at break of the tested sample; L -- the length of the specimen when it is fractured, mm; 0L -- the initial length of the sample, mm.

4. Experiment Analysis

4.1. Basic Performance Analysis of Anti-Corrosion (AC) Coating

The basic physical properties of the prepared composite coating and the control group coating were tested. Table 2 lists the results of thickness, hardness, salt water resistance (24h immersion), adhesion (24h immersion) and water absorption respectively. As can be seen from the table, the thickness of each coating is kept at $100 \pm 3 \mu$ m. Composite test requirements. When composite materials P-f/G or P-f/G/S are added, the hardness of the coating is moderate to H. When CTGO and P-f are added separately, the hardness of the coating decreases due to the poor dispersion of these two materials in the coating. After soaking each coating in salt water for 24h, the EP coating has become discolored and foamed, and the adhesion grade is reduced to Grade 3. After immersion, CTGO-EP (C-E) and P-f-E also have discoloration, and the adhesion decreases a lot, indicating that the addition of CTGO and P-f alone has little effect on the improvement of the AC coating. However, the PANI-f/GO/SiO2-EP (P-f/G/S-E) coating has no change in appearance after 24h immersion, and the adhesion level is high. This is because the well dispersed composite P-f/G/S can form interpenetrating networks in the water-based coating. In particular, the adhesion of 0.3P-f/G/S-E and 0.4P-f/G/S-E still remained at the highest level 0.

Figure 3 also shows the water absorption values of each coating. Obviously, pure EP coating has the highest water absorption and poor water resistance. With the addition of CTGO, P-f and P-f/G composites, the water absorption decreased. These phenomena are attributed to the physical barrier

effect of NM and the interpenetrating network formed between NM and polymer emulsions. Compared with the control group, P-f/G/S-E coating has better water resistance. The addition of gaseous SiO2 and the synergistic effect of P-f and CTGO promote the dispersion of the composite in the coating, and the defects and holes in the EP coating will be filled by well dispersed P-f/G/S. More importantly, the molecular interaction between the composite P-f/G/S and the polymer emulsion forms a tight interpenetrating network, which leads to the reduction of water absorption, thus better improving the water resistance of the coating. In general, the basic performance of 0.4P-f/G/S-E is excellent.

Coating	Thickness/ µ m	Hardness	Salt water resistant	Adhesion	Water absorption%
EP	98	2B	Blistering and discoloration	3	2.45
C-E	99	HB	Discoloration	2	1.86
P-f-E	97	HB	Discoloration	2	1.53
P-f/G-E	100	Н	Unchanged	1	1.25
0.1P-f/G/S-E	101	Н	Unchanged	1	1.06
0.2P-f/G/S-E	98	Н	Unchanged	1	0.82
0.3P-f/G/S-E	99	Н	Unchanged	0	0.75
0.4P-f/G/S-E	102	Н	Unchanged	0	0.59
0.5P-f/G/S-E	98	Н	Unchanged	1	0.68

Table 2. Basic performance lesi results of each coaling	Table 2.	Basic	performance	test	results	of	each	coating
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Figure 3. Analysis chart of basic performance test results of each coating

The AC efficiency PE can directly show the AC ability of the coating. The polarization curve data of different coatings are shown in Table 3.

From the data in Figure 4, it can be found that the AC efficiency PE of composite material P-f/G/S coating is higher, and the AC capacity is 0.4P-f/G/S-E>0.5P-f/G/S-E>0.3P-f/G/S-E>0.2P-f/G/S-E>0.1P-f/G/S-E>P-f/G-E>P-f-E>C-E>EP. When 0.4 wt.% is added When P-f/G/S is added, the coating has the highest AC efficiency, and can effectively play the synergistic role of physical barrier and active passivation of composite material P-f/G/S in the coating. Excessive addition is easy to lead to the agglomeration of composite materials, and it is easy to collapse at the agglomeration point when soaking for a long time, thus reducing the protective ability of the coating.

sample	Ecorr/Vvs.SCE	Icorr/µA·m-2	βa/Vdec-1	βb/Vdec-1	$RP/k\Omega \cdot cm-2$	PE%
Q235	-0.91	6.3	0.065	-0.064	42	_
EP	-0.876	2.51	0.072	-0.081	152.6	61.1
C-E	-0.721	1.58	0.086	-0.094	221.3	74.9
P-f-E	-0.651	1.67	0.135	-0.129	376.5	73.5
P-f/G-E	-0.601	0.99	0.198	-0.153	483.2	84.3
0.1P-f/G/S-E	-0.549	0.854	0.228	-0.186	496.4	86.4
0.2P-f/G/S-E	-0.504	0.687	0.268	-0.194	512.9	89.1
0.3P-f/G/S-E	-0.452	0.529	0.289	-0.256	536.4	91.6
0.4P-f/G/S-E	-0.247	0.316	0.354	-0.267	556.5	95.0
0.5P-f/G/S-E	-0.292	0.457	0.296	-0.248	540.6	92.7

Table 3. Polarization curve data of different coatings



Figure 4. Polarization curve data analysis diagram of different coatings

4.2. Chemical Corrosion Resistance Test of Modified Nano SiO2 Composite Powder Coating

EP/0.2% m-SiO2 coating was selected for chemical reagent corrosion resistance test to further analyze the corrosion resistance of the coating. Table 4 shows the chemical reagent corrosion resistance test of composite powder coating. It can be seen from the table that after immersion in various mediums for 2000h, the surface of the coating has no phenomena such as light loss, discoloration, blistering, rust spot, peeling, etc., indicating that the EP/0.2% m-SiO2 coating has excellent chemical resistance.

Medium and concentration	Temperature	Soaking time h	Surface state	Corrosion resistance
H2SO4 30%	Room temperature	2000	Unchanged	Good
NaOH 10%	Room temperature	2000	Unchanged	Good
HCl 10%	Room temperature	2000	Unchanged	Good
NaC1 3.5%	Room temperature	2000	Unchanged	Good

Table 4. Results of chemical reagent corrosion resistance test

After the nano silica is chemically modified and ball milled, the NP can be uniformly dispersed in the epoxy resin powder, giving play to the surface effect and volume effect of the NM, and because of the small size effect of the NP, it can fill the pores formed in the curing process of the resin, enhance the density of the coating, and greatly improve the corrosion resistance of the coating.

5. Conclusion

This paper focuses on the harm caused by the corrosion of metal materials and the current status of the development of metal corrosion protection, and briefly describes the structure and performance characteristics of epoxy resin, the application status and existing problems of epoxy resin powder coatings, the structure and performance characteristics of NM, and the research status of nano material composites. It is pointed out that adding NP with different dimensions in epoxy powder coatings may improve the performance of composite coatings. It is pointed out that powder coatings will replace solvent coatings in the future metal AC applications. In a word, through experimental research, it is found that the main performance indexes of the nano composite epoxy powder coating prepared by the synergetic action of nano particle modification, ball milling mixing and melting mixing extrusion are improved in varying degrees compared with the ordinary pure epoxy powder coating, and improve the thermal stability, friction resistance, impact strength, adhesion strength and corrosion resistance of composite epoxy powder coating. Therefore, it has good application value and broad market prospects.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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