Comparative Study on the Corrosion Resistance of Inorganic Zinc-Rich Coating and Thermal-Spray Zinc Coating

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Comparative Study on the Corrosion Resistance of Inorganic Zinc-Rich Coating and Thermal-Spray Zinc Coating

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Abstract: The corrosion resistance of two steel coatings (inorganic zinc-rich coating and thermal-spray zinc coating) was studied in detail by using the electrochemical and salt spray test, and the salt spray corrosion thickness was calculated by the time-varying equation established from the mathematical fitting method. The result show that the corrosion mechanism of the two types of coatings was the same that based on the sacrificed of zinc through anodizing phenomenon. The main reason for the difference of corrosion resistance between the two anticorrosive coatings was that the coating density and shielding effect of corrosion products were different. The 7500-hours salt spray test showed that the corrosion rates and microstructure characteristics of both types of zinc coatings were homogeneous on the premise of ensuring coating reliability. The time-varying equation can be used to evaluate the service life of the zinc coatings and judge their corrosion resistance quickly, that providing theoretical support for the maintenance of steel structures as well as the accelerated selection and design of coating formulations.

Keywords: corrosion resistance, inorganic zinc-rich coating; salt spray test; anodizing phenomenon, mathematical fitting

1 Introduction

In generally, the service life of large-scale steel structures, such as the offshore oil

production platform facilities, ship hulls and nuclear power plant, are designed to 70~110 years. Due to prolonged exposure to the marine or industrial atmosphere high corrosive environments for a long time, they must be protected by the anticorrosive coating system to further extend the service life [1,2]. At present, the period of anti-corrosion coating system is about 25~35 years and protected by the long-acting coating is the most effective and common path. In the case of comprehensive consideration of product life cycle, manufacturing cost, maintenance costs and other factors [3-5]. The industry practice has proved that the life of thermal spraying zinc coating can reach more than 20 years on the basis of guaranteeing the reliability of the coating [6,7]. It is a kind of heavy anticorrosive coating with excellent performance, and its life period is widely recognized in the field of heavy anticorrosive coating [8]. As a new coating technology, the inorganic zinc-rich coating has better corrosion resistance performance than the thermal spraying zinc coating in laboratory evaluation system [9]. However, due to the lack of long-term service life verification, its promotion and application in the field of heavy corrosion protection is affected to some extent [10-12].

The coating life prediction concerning the service life and safety is an important index that can be used to evaluate the coating durability. At present, the domestic and foreign scholars' research on zinc anticorrosive coating mainly focuses on the preparation method, synthesis process of resin and performance improvement of coating, while the research on coating life prediction is relatively few [13-15]. The method of coating life prediction mentioned in literatures was put forward by the National Aeronautics and Space Administration Center in the 1980s. This prediction model of service life method was limited in the laboratory conditions. Based on this prediction model, the Weibull life prediction model, fatigue curve model, theoretical prediction model and other new prediction methods have emerged [16]. However, these new prediction models are all based on the fact that thermal stress and interfacial oxidation are the key factors to determine the coating failure. The life prediction model of thermal barrier coatings was quite different from the zinc anti-corrosion failure mechanism of coatings under actual working conditions [17,18]. Therefore, it is difficult to predict the life of inorganic zinc-rich coating simply according the above

model [19,20]. The coating failure will affects the safety function of equipment and drilling platform as well as the normal operation of the system. It is necessary to demonstrate and analyze the service life and microstructure of the coating in the corrosion process that providing guidance for the technical research and optimal selection of the matched engineering coating [21-24]. The homogeneous corrosion rate and microstructure characteristics of the zinc coating are important parameters for life evaluation that providing critical support for the steel structures maintenance and rapid selection and design of coating formulations [25]. The nature of corrosion resistance of zinc coating is to sacrifice anode material to protecting the steel structure [26]. Therefore, the coating life depends on the thickness of zinc layer and dissolution rate of zinc, namely the oxidation rate of the zinc coating on the premise of the reliability of the coating [27-30]. The essence of inorganic zinc-rich coating is still to prevent the corrosion of metal components through oxidation process of sacrificing zinc anode [31].

In this paper, the corrosion micromorphology and corrosion rate of hot-sprayed zinc coating and inorganic zinc rich coating were studied by the electrochemical and long-term salt spray tests. The correlative corrosion mechanism was discussed and the factors affecting the corrosion rate were determined. The interfacial corrosion thinning weight loss equation was established by mathematical fitting method and the service life of inorganic zinc-rich coating was predicted by comparing with that of hot-sprayed zinc coating through 7500-hours salt spray test. The research has practical guiding significance for the rapid selection and design of the matching scheme, and can also provide reference for the life prediction of other types of anti-corrosion coatings.

2 Experiments and measurements

2.1 Materials and Instruments

The coated steel samples were provided by CNOOC Changzhou Paint and Coatings Industry Research Institute Co., Ltd. All the interfaces of the steel plate were covered with a zinc coating. The sample of thermal-spray zinc coating and inorganic zinc-rich primer were obtained by self-produced. The sample specification was 90×50×6 mm and 90×50×6 mm and the thickness of coating was 80-150 μm and 200-

350 μm , respectively. The reagents needed in the experiment (Distilled water, Ammonium chloride, Acetic acid and Ammonium acetate) were all at industrial grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The electrochemical performance of coating were measured using a electrochemical workstation (Auto Lab PGPSTA302, Eco.chemine company). The test conditions are as follow: pH=7(5 wt. % NaCl aqueous solution adjusted by 0.5 M NaOH solution); temperature: 25 ± 2 $^{\circ}\text{C}$; sweep rate: 1 mVs^{-1} ; scanning range: $-400 \text{ mV} \sim +400 \text{ mV}$. The corrosion resistance performance of coating was tested by the salt spray test chamber (ATLAS BCX3000(850L), ATLAS Engineering Machinery Co., Ltd.). The relevant test conditions are: testing area: $191 \times 74 \times 63 \text{ cm}$; pressurized gas flow: $0.1 \text{ m}^3/\text{min}$; pressure of dry and oil-free pressurized gas: 103 kPa. The phases identifications and micro-structures of thermal-spray zinc and inorganic zinc-rich coating were observed by using the X-ray diffractometer (D8 Focus, Bruker company of Germany) and scanning electron microscope (SU3500/X-act, Hitachi company of Japan), respectively.

2.2 Accelerated corrosion test

Before spraying, the steel plate was pretreated by sandblasting roughening. The technological parameters of sandblasting are as follows: sandblasting pressure: 0.5-0.8 Mpa; quartz sand size: 12-24 mesh. After sandblasting, the surface must be clean and free of moisture, iron oxides and other dirt, and meet the requirements of Sa2.5. A zinc wire (purity>99.9%) with a diameter of 3 mm was used as thermal-spray zinc, while an inorganic zinc-rich coating was made by the high-pressure airless spraying technology. After coating formation, the zinc content was>80%, while the content of other organic and inorganic substrate (ethyl silicate, silica powder, etc.) was<20%.

Accelerated cyclic corrosion tests according to procedure ASTM B 117. The salt solution pH stayed between 6.5 and 7.2. The original size and mass of each test block was measured and recorded before testing. Changes in the mass of the test blocks were also monitored before and after the test.

After they were placed well according to the regulations, the thermal-spray zinc coating and inorganic zinc-rich coating samples underwent a salt spray test for intervals of 500 h, 1200 h, 2000 h, 3500 h, 5000 h, and 7500 h, respectively. Test blocks were taken out at each specified time point, with 5 test blocks for testing, 3 for an experiment and 2 for later use. The corrosion products were removed, and 2 samples taken out at each time point were weighed. After the removal of the corrosion products, mass

monitoring was performed and the change in the mass of each test block was recorded.

The corrosion products were removed at each salt spray time point. After sampling, the corrosion test blocks were weighed and recorded. Then, the corrosion products on the test blocks were removed on the specialized cleansing table. After being cleaned, the test blocks were dried left idle for 10 min. The test blocks were then weighed again with the weight data recorded. The corrosion weight loss per unit area at each sampling time point was calculated by comparing with the initial mass and the corrosion area of the test blocks. Finally, the corrosion weight loss rate of each test block was calculated. The calculation method of corrosion rate of the salt spray sample is as follows formula [32,33]:

$$v = (w_1 - w_2) / (s \times t) \quad (1)$$

Where the v , w_1 , w_2 , s and t represents the corrosion rate of the sample, mass loss of the salt spray and blank sample, surface area and salt spray time, respectively. According to the calculation formula, the weight loss data and thinning thickness at each time point were calculated and fitted for plotting. The whole accelerated corrosion test process was shown in Fig.1.

Fig.1 Interfacial corrosion thinning and weight loss test process

2.3 Removal process of corrosion product

A corrosion product removal technique was selected prior data acquisition (stripping refers to removing the salt stains, rust, and other corrosion products on the coating without damaging the coating or matrix themselves). To ensure the reliability of the data, the test was conducted repeatedly until the weight loss was minimized and stabilized [34,35]. After repeated tests, the sodium-hydroxide method was selected as the corrosion product removal method for the thermal-spray zinc coating, while the

ammonium chloride method was selected as the corrosion product removal method for the inorganic zinc-rich coating. The optimal process parameters determined for the above stripping technique were adopted for cleaning. This test was also conducted based on reference to HB 5257-1983 (the determination of the weight loss from the corrosion test results and the removal of corrosion products) and GB/T 16545-2015” (the removal of the corrosion products on the metal and alloy corrosion samples).

(1) The Removal process of the corrosion products of thermal-spray zinc coating are as follow:

- 1) Gently brush the test blocks to remove corrosion products weakly attached to the surface.
- 2) Soak all test blocks in distilled water, then remove them after five minutes.
- 3) Mixing 100 g of sodium hydroxide (NaOH) with distilled water, producing a 1000 mL solution.
- 4) Place the test plates vertically into 10% NaOH solution, and take them out 10 min later (specific soaking duration may be extended or shortened depending on the length of salt spray).
- 5) Rinse the test blocks with running water while gently cleaning the surface of the blocks with a soft brush to remove the residual NaOH solution and corroded materials from the surface.
- 6) Soak the test blocks in distilled water for 30s, then remove them.
- 7) Bake the test blocks in an air-dry oven for 15min at 80°C.
- 8) Weigh the dried test blocks and record the results.
- 9) Repeat steps 3-8 until the corrosion weight loss approaches a minimum and fluctuates steadily. Based on our tests, the number of washing iterations varied between 5 and 8.

(2) The Removal Process of the corrosion products of inorganic zinc-rich coating are as follow:

- 1) Gently brush the test blocks to remove corrosion products weakly attached to the surface.
- 2) Soak all test blocks in distilled water and remove them 5min later.
- 3) Mix 100g of NH_4Cl with distilled water to produce a 1000 mL solution.

- 4) After heating to the NH_4Cl solution to 50°C , place the test blocks vertically in the solution and remove them 10min later (specific soaking duration may be extended or shortened depending on the length of salt spray).
- 5) Rinse the test blocks with running water while gently cleaning the surface of the blocks with a soft brush to remove the residual NaOH solution and corroded materials from the surface.
- 6) Soak the test blocks in distilled water for 30s, then remove them.
- 7) Bake the test blocks in an air-dry oven for 15min at 80°C .
- 8) Weigh the dried test blocks and record the results.
- 9) Repeat steps 3-8 until the corrosion weight loss approaches a minimum and fluctuates steadily. Based on our tests, the number of washing iterations varied between 5 and 8.

Weight loss test data were obtained for both types of zinc coatings through the above corrosion product removal techniques. Meanwhile, a blank sample was used to correct the test sample.

3 Results and Discussion

3.1 Reliability tests and appearance of corrosion samples

It is obvious that after the salt spray acceleration tests, both types of coatings show flat surface, but salt stains are more prone to adhering to the thermal-spray zinc coating surface, while the inorganic zinc-rich coating had a smoother surface, where there are only a few salt stains.

3500/5000/7500 hours of salt spray (from left to right respectively; the upper part of the pictures shows the thermal-spray zinc coating, while the lower part of the picture shows the inorganic zinc-rich).

As can be seen from Fig.3, after the salt spray test and the removal of the corrosion products from the surface, corrosion stains appear on the surface of the thermal-spray zinc coating, which was whitened, while there were basically no changes on the surface of the inorganic zinc-rich coating, whose color remains unchanged. The surface of the two zinc coatings is free of defects such as bubbles, cracks, rust, etc., and the coating

samples are intact, meeting the requirements of coating reliability.

(a) Rush samples of the thermal-spray zinc coating

(b) Rush samples of the inorganic zinc-rich coating

Fig.2 Pictures of coating appearance after 1200-hour salt spray test (the rightmost one is a primary rush sample)

Fig.3 Appearance of the coating after corrosion product removal following

3.2 Electrochemical characteristics

As shown in Fig.4, the corrosion potential of the steel substrate is -0.563V, while the corrosion potential of the thermal-spray zinc and inorganic zinc-rich coating is -

1.078V and -0.971V, respectively. The corrosion potential of both coatings is much lower than that of the substrate, suggesting that it can provide cathodic protection for the substrate. The corrosion potential of zinc coatings is mainly determined by the Zn/Fe area ratio. The thermal-spray zinc coating has a loose surface and high roughness, and compared with the inorganic zinc-rich zinc coating, its specific surface area is larger. Due to the addition of a polymer to the inorganic zinc-rich coating, the electrical conductivity is deteriorated, and the Zn/Fe area ratio also decreases. From the perspective of corrosion tendency, the inorganic zinc-rich coating is more resistant to corrosion.

Fig.4 The corrosion potential-time curves of the steel substrate and two zinc coatings

According to the self-corrosion current data in Fig.5, at the early stage of salt spray, uniform corrosion occurred on the surface of thermal-spray zinc coating, and the corrosion dissolution rate was high. After 1200h of salt spray, the self-corrosion current decreased sharply. At the same time, the self-corrosion current data is discrete owing to the instability of the corrosion products, but it just fluctuates within a certain range. In general, the self-corrosion potential of the thermal-spray zinc coating shifted positively in a continual way with the extension of the salt spray time, while the corrosion dissolution rate showed a downward trend. It might be because new corrosion products generated on the surface of the thermal-spray zinc coating after zinc dissolution, preventing the internal zinc from further dissolving.

Fig.5 Polarization curve of the thermal-spray zinc coating

The Nyquist curves of AC impedance in Fig.6 and Fig.7 show that the samples after salt-sprayed for different durations have basically the same trend. The Nyquist charts are composed of a high-frequency single-capacity reactance arc and a low-frequency Warburg impedance diffusion arc. The high-frequency impedance spectroscopy reflects the coating information, while the low-frequency impedance spectroscopy reflects the diffusion process of dissolved oxygen in the corrosion products or coating pores. The presence of the Warburg impedance diffusion tail indicates that the electrolyte solution penetrated into the coating/metal interface at the very beginning of the salt spray test, with an electrochemical reaction occurring at the interface. As the metal corrosion reaction or thermal-spray zinc dissolution reaction proceeded at the interface, the corrosion products would block the coating pores, thus rendering the corrosion reaction subject to the influence of the dissolved oxygen within the corrosion products. However, since corrosion occurred on part of the surface, the phase angle of some diffusion tails were 45° off. As the salt spray time progressed, the radius of the capacity reactance arc in the high-frequency region increases, indicating that the corrosion rate of the thermal-spray zinc coating decrease, with the effect of galvanic anode protection on the matrix being gradually reduced. There are three time constants at 5000h, which may be caused by the formation of new corrosion products covering the coating surface.

Fig.6 Nyquist chart of the 0-2000h AC impedance of the Thermal-spray zinc coating

Fig.7 Nyquist chart of the 3500-7500 h AC impedance of the thermal-spray zinc coating

As can be seen from Fig.8, the self-corrosion potential and self-corrosion current of the inorganic zinc-rich coating show similar change trends compared with those of the thermal-spray zinc coating. With the passage of salt spray time, the self-corrosion potential shifts positively while the self-corrosion current decreases. The difference is

that the positive shift of self-corrosion potential of the inorganic zinc-rich coating is small, from -1.2 V to -0.8 V; within the test time range, the self-corrosion current changes slightly, indicating that the effect of cathodic protection with sacrificial anode is relatively stable, and there is no rapid decline in the coatings' protective performance.

Fig.8 Polarization curve of the inorganic zinc-rich coating

As can be seen from Fig.9 and Fig.10, at 0h, since the inorganic zinc-rich coating shows a single capacitance arc, indicating that the inorganic zinc-rich coating is more compact, and at the initial stage, the electrolyte solution can't pass through the coating to the surface of the coating/metal. After 500h of salt spraying, a Warburg impedance diffusion arc appears at low frequency end, indicating that the electrolyte solution penetrates into the coating/metal interface, with an electrochemical reaction occurring at the interface, leading to an increase in the corrosion dissolution rate of the coating^[18-19]. With the extension of salt spray time, the capacitance arc radius of the coating increases significantly after 2000h. The oxidation reaction of metallic zinc in the interface area would generate corrosion products, which would cover the coating surface, thereby restricting the diffusion of dissolved oxygen in the corrosion products, finally leading to a decrease in the dissolution rate of the coating. This is consistent with the results of the polarization curve.

Fig.9 Nyquist chart of the 0-2000 h AC impedance of the inorganic zinc-rich coating

Fig.10 Nyquist chart of the 3500-7500 h AC impedance of the inorganic zinc-rich

According to the comparison of electrochemical test results between the thermal-spray zinc coating and the inorganic zinc-rich coating, the self-corrosion potential of the thermal-spray zinc coating decreases more subsequently than that of the inorganic zinc-rich coating, indicating that the performance of the thermal-spray zinc coating decline faster than that of the inorganic zinc-rich coating. The self-corrosion current of the thermal-spray zinc coating was higher than that of the inorganic zinc-rich coating,

indicating that the reaction rate of the inorganic zinc-rich coating was lower than that of the thermal-spray zinc coating. In short, the inorganic zinc-rich coating featured better performance than the thermal-spray zinc coating in terms of galvanic anode protection.

3.3 Coatings microstructure and corrosion products identification

As shown by the results of SEM and EDS, in the blank sample applied with thermal-spray zinc coating, due to the construction principle and technology, zinc failed to form a continuous and homogeneous coating in the cooling process, resulting in uneven coating surface. After formation, the inorganic zinc coating was continuous and uniform. As can be seen, spherical zinc is closely arranged and flat, with very low roughness. The computer grayscale method was used to measure the porosity of the zinc coatings. The porosity of the thermal-spray zinc coating is 6.3% while the porosity of the inorganic zinc-rich coating is 1.6%. The high density of the inorganic zinc-rich coatings might be due to the presence of Si-OH in the coating, complexing with zinc atoms, forming a highly dense physical cross-linking network. Therefore, for thermal-spray zinc coatings, permeable corrosive media, such as chloride ions, can quickly penetrate into the thermal-spray zinc coatings and even to the surface of the substrate through the pores, thus accelerating corrosion and increasing damage to the coating; for the inorganic zinc-rich coating, owing to its low porosity, chloride ions are difficult to reach the surface of the substrate quickly. This further confirms the conclusion of the AC impedance Nyquist curve, i.e., the thermal-spray zinc began to undergo an oxidation reaction at the interface when the test had just started, while for the inorganic zinc-rich coating, corrosion wasn't observed until 500h later. After salt spray, there were obviously more corrosion defects in the thermal-spray zinc coating, and the contact surface became larger, making the coating more susceptible to corrosion. After the salt spray test, the spherical zinc powder on the surface of the inorganic zinc-rich coating disappeared, while the coating remained flat and there were only a few wrinkles on it. According to the results of EDX, after salt spray, new elements, such as aluminum and chlorine, came into being, suggesting that new, insoluble corrosion products are indeed formed during the accelerated salt spray test.

Fig.11 Analysis of the surface microstructure of the thermal-spray zinc coating
 (On the left side of the figure is a stereoscan (SEM) photograph, while on the right side is an X-ray energy spectrum analysis (EDS); the upper part of the figure provides an analysis without salt spray while the lower part shows a salt spray analysis at 7500 h)

Fig.12 Analysis of the surface microstructure of the inorganic zinc-rich coating

(On the left side of the figure is a stereoscan photograph, while on the right side is an X-ray energy spectrum analysis (EDS); the upper part of the figure provides an analysis without salt spray while the lower part shows a salt spray analysis at 7500 h)

To further analyze the change in the material structure on the coating surface before and after salt spray treatment, we analyzed the substance composition of the two coatings before and after corrosion. Fig.13 and 14 show XRD spectra of the untreated surface of the thermal-spray zinc and inorganic zinc-rich coatings. According to the results of a comparison with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) Database, as shown in Fig.13, the position and relative intensity of the diffraction peaks that appeared at $2\theta=43.2^\circ$, 36.3° , and 39.0° are consistent with the three strong peaks of pure zinc, respectively corresponding to the (101), (002), and (100) crystal planes of pure zinc. Bruker Corp.'s XRD pattern analysis software DIFFRACEVA was used to provide a semiquantitative reference value for the substance content, with the approximate content ratio of the two substances being as follows: pure zinc: zinc oxide=95: 5. The position and relative intensity of the diffraction peaks that appear at $2\theta=36.3^\circ$, 31.8° and 34.4° are consistent with the three strong peaks of zinc oxide, respectively corresponding to the (101), (100), and (002) crystal faces of zinc oxide. The position and relative intensity of the diffraction peaks that appear at $2\theta=26.6^\circ$, 20.9° and 50.1° are consistent with the three strong peaks of quartz, respectively corresponding to the (101), (100) and (112) crystal planes of quartz. The approximate content ratio of the three substances being as follows: pure zinc: zinc oxide: quartz=90: 5: 5. It also contains a small amount of impurities ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$, $\text{C}_{30}\text{H}_{14}\text{N}_4\text{O}_4\text{Zn}$, etc.). This is because the inorganic zinc-rich coating can react with the water and CO_2 in the air, generating a new chemical compound or complex during its own solidification.

Fig.13 XRD pattern of thermal-spray zinc coating without salt spray

Fig.14 XRD pattern of the inorganic zinc-rich coating without salt spray test

Fig.15 and 16 show the results of XRD analysis of the two coating samples after 7500 h of salt spray with the salt stains freely soluble in water and corrosion products on the coating surface removed lightly with water and a brush. According to the results of a comparison with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) Database, the position and relative intensity of the diffraction

peaks that appeared at $2\theta=36.3^\circ$, 31.8° , and 34.4° are consistent with the three strong peaks of zinc oxide, respectively corresponding to the (101), (100), and (002) crystal planes of zinc oxide. 2θ is 11.234, 16.557, 22.094, 24.851, 28.127, 30.378, 31.094, 32.840, 33.511, 34.454, 37.867, 44.763, and 58.155, which are the characteristic peaks of $\text{Zn}_5(\text{OH})_8\text{Cl}_2$; 2θ is 12.819, 17.340, 23.901, 27.947, 30.917, 32.655, 34.331, and 35.892, which are the characteristic peaks of $\text{Zn}_4\text{CO}_3(\text{OH})_6$. The diffraction peak intensity at $2\theta=34.4^\circ$, corresponding to the (002) crystal plane of zinc oxide, greatly differs from the theoretical value. There are two possible reasons for this, as follows: 1) a new substance with a crystal structure similar to zinc oxide might be generated during this process; 2) when the coating surface is formed, the grain orientation is not randomly distributed, but preferentially arranged around some special orientations, forming a preferred orientation and resulting in an increase in the diffraction peak intensity at $2\theta=34.4^\circ$. The content ratio of the two substances is as follows: pure zinc: zinc oxide=20:80. It contains a little new corrosion product. The position and relative intensity of the diffraction peaks appearing at $2\theta=33.5^\circ$, 32.8° and 37.9° in Fig.16 are consistent with the three strong peaks of chemical compound $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$, corresponding to the (202), (021) and 205) crystal planes of the chemical compound, respectively. 2θ is 11.234, 16.557, 22.094, 24.851, 28.127, 30.378, 31.094, 32.840, 33.511, 34.454, 37.867, 44.763, and 58.155, which are the characteristic peaks of $\text{Zn}_5(\text{OH})_8\text{Cl}_2$. The content ratio of the three phases is as follows: pure zinc: Quartz: $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$ / $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ =65:25: 10.

Fig.15 XRD pattern of the thermal-spray zinc coating after 7500 h of salt spray test

Fig.16 XRD pattern of inorganic zinc-rich coating after 7500 h of salt spray test

According to the XRD analysis results of thermal-spray zinc and inorganic zinc before and after salt spray, new corrosion products were formed on the surface of both coatings after the accelerated salt spray test. Despite a slight difference in the products, the nature of coating oxidation isn't changed, i.e., zinc remained oxidized into zinc ions, which are combined with dissolved hydroxide ions and chloride ions, forming insoluble salt. Therefore, the corrosion of the two coatings is the same in essence, and the service life of the inorganic zinc-rich coating can be judged by comparison with that of the thermal-spray zinc coating. Owing to the introduction of Si-O bond into the inorganic zinc coating formulation, whose bond energy is higher than C-C bond, suggesting high stability of the inorganic zinc coating. At the same time, a highly dense chelate is formed on the coating and adhered to the surface of the steel structure, not only reducing the electric conductivity of the system, but also suppressing the diffusion of chloride ions together with the corrosion products, exerting a shielding effect, thus reducing the corrosion rate of zinc and improving the service life of the coating. According to the electrochemical analysis, the corrosion tendency and rate indicate that the coordination among the corrosion products, porosity and other relevant factors change the micro-current coupling capability and exert a shielding effect on the diffusion of chloride ions, thereby reducing the corrosion rate of zinc, with the corrosion resistance of the coating

improved.

3.4 Thinning rate comparison and service life prediction

Considering that the two coatings are the same in corrosion mechanism, it is the difference in their composition and structure that caused a difference in the corrosion rate. Although the previous SEM and electrochemical analysis show that the inorganic zinc-rich coating has higher corrosion resistance, more detailed data remain required for the prediction of its service life. After 7500 h of salt spray test, the thinning rate of the two coating samples was compared, the relevant data are shown in Table 1.

Tab.1 Weight loss data and thinning rate of thermal-spray zinc coating and inorganic zinc-rich coating at each time point

Name of test item	500 h	1200 h	2000 h	3500 h	5000 h	7500 h
Mass loss per unit area of thermal-spray zinc coating (mg/cm ²)	16.71	23.81	29.38	39.47	43.42	50.99
Thinning rate of thermal-spray zinc coating (μm)	25.47	36.30	44.79	60.17	66.19	77.73
Mass loss per unit area of inorganic zinc-rich coating (mg/cm ²)	1.14	2.56	4.59	5.8	8.78	9.67
Thinning rate of inorganic zinc-rich coating (μm)	2.73	6.14	11.00	13.91	21.05	23.18

Based on the buoyancy method in the Archimedes principle, according to GB/T 9272-2007 (the nonvolatile substance volume fraction of the paint and varnish was determined by measuring the density of the dry coating), the density of the dry thermal-spray zinc is 6.56 g/cm², while the density of the dry inorganic zinc-rich coating is 4.171g/cm². This data can be used to calculate the coatings' thinning rate. These data points are lineally fitted by mathematical methods based on the thinning data at each time point in Tab.1 (the nonlinear least square method based on the Levenberg-Marquardt algorithm (LMA) was adopted for curve fitting). The sets of data were fitted, deriving corrosion rate equations for the two coatings, as shown in Fig.17.

Fig.17 Fitting curve of the salt spray time-varying corrosion thickness loss per unit area

The thinning rate of thermal-spray zinc coating was fitted as the following:

$$y = 31.45 * \ln(x + 1118.27) - 207.21 \quad [R^2 = 0.995] \quad (2)$$

The thinning rate of inorganic zinc-rich coating was fitted as the following:

$$y = 13.46 * \ln(x + 1339.11) - 98.67 \quad [R^2 = 0.989] \quad (3)$$

As can be seen from the fitting equation in Fig.17, the thinning data show that under the same accelerated corrosion condition, the thinning rate of the inorganic zinc-rich coating is much lower than that of the thermal-spray zinc coating. According to the data from the heavy-duty anti-corrosion industry, after 4200 h of accelerated salt spray test, if the coating is intact and reliable, the coating is basically approved to have a service life of 15-20 years. As shown by the results of the calculation made according to the equation, the thickness of the thermal-spray zinc coating is reduced by 56.04 μm while the thickness of the inorganic zinc-rich coating is reduced by 17.34 μm. The thickness of the conventional thermal-spray zinc coating is about 250 μm and decreased by 22.4% after corrosion. The design thickness of the inorganic zinc-rich coating is about 100 μm and decreased by 17.3% after corrosion. The thinning data indicate that the requirements of heavy-duty anti-corrosion are easily met. According to the results of prediction made in the prediction equation, if accelerated salt spray treatment is adopted on the basis of high coating reliability, it takes about 40 years for the thermal-

spray zinc coating to be thinned by 200 μm , while it takes about 40 years for the inorganic zinc coating to be thinned by 75 μm . So, the service life should be greater than 40 years in the actual working environment.

4 CONCLUSIONS

Based on coating reliability, the corrosion mechanism of the thermal-spray zinc and inorganic zinc-rich anti-corrosion coatings was compared using analytical methods including electrochemical testing, XRD, SEM, etc., concluding that insoluble corrosion products are generated in both coatings during the corrosion process. The corrosion products at the interface changes the micro-current coupling capability and exerts a shielding effect on the diffusion of chloride ions, thereby reducing the corrosion rate of zinc and improving the service life and corrosion resistance of the coating. Due to its denser structure and the existence of Si-OH, the corrosion rate of the inorganic zinc-rich coating is further decreased. After 7500 h of salt spray test, the corrosion rate equations of the two coatings were fitted, and according to the known service life of the thermal-spray zinc coating, the inorganic zinc-rich coating proves to have much better corrosion resistance, i.e., its service life is more than 40 years under the same condition.

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