Research Article

The Effect of Chlorine Ion on Metal Corrosion Behavior under the Scratch Defect of Coating

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Received 8 October 2018; Revised 15 November 2018; Accepted 13 December 2018; Published 23 January 2019

Academic Editor: Michael J. Schütze

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The influence of chloride ion on the corrosion of metal under coating with scratch defects was researched by wire beam electrode (WBE) technology and electrochemical impedance spectroscopy (EIS) technology. The results showed that the current of metal surface could be characterized by the WBE technology. In the case of scratches on the coating, the location of the damage always showed an anodic current, and the cathodic reaction took place adjacent to the damaged location. The cathode area surrounded the defect and migrated to the far end over time. With the increase of Cl− concentration, the corrosion reaction speeded up, the rate of cathode migration also increased, and the speed of coating stripping did as well. Combined with electrochemical impedance spectroscopy, uniform laws were obtained.

1. Introduction

So far, oil and natural gas are still irreplaceable energy source. Meanwhile, with the development of the economy, the demand for oil and natural gas is also increasing in many countries. There are huge challenges for ensuring a stable supply of oil and natural gas and national energy security for the oil and gas industry. Metal pipe corrosion has always been one of the most important issues for the oil and gas industry, especially offshore oil exploration. At present, in the offshore oil exploitation and transportation, pipeline coating anticorrosion is the most common and practical method, which operation process is relatively simple [1]. However, Chen Yalin [2] applied WBE technology and EIS technology to study the peeling behavior of the damaged coating in the waterline area of the damaged coating at the water/liquid interface waterline in the 3.5% (mass fraction) NaCl solution, which proved that both the damaged area and the inherent defect area could accelerate the cathode stripping process of the nearby coating, thereby accelerated the corrosion rate of the metal. Nemeth Z [3] confirmed that chloride ions could pass through the coating into the coating metal interface through radioisotope methods. He Juan [4] studied the corrosion of chloride ions in metal solutions in aqueous solution. It was found that chloride ions in aqueous solution could destroy the passivation film of metal in the process of competing with hydrogen and oxygen ions in the adsorption process, thus led to the occurrence of pitting corrosion, hole corrosion, and crevice corrosion, and made the metal equipment more susceptible to corrosion. Hornus [5] studied the effect of chloride ion concentration on the crevice corrosion of aluminum alloy. It was found that when the chloride ion concentration was 0.1~1 mol/L, the crevice corrosion products increased, and after the chloride ion concentration improved from 1 mol/L to 10 mol/L, the crevice corrosion products were reduced. Ma Yunlin [6] showed that, with the increase of chloride ion concentration in the solution, the pitting potential of stainless steel decreased, while the blunt current density became larger; it indicated that the metal was more prone to crevice corrosion with increasing chloride ion concentration. Oldfield and Sutton [7, 8] believed that crevice corrosion would happen when the chloride ion concentration reached a critical value. Therefore, the change of chloride ion concentration in the gap could indirectly reflect the development process of crevice corrosion. Nishimoto [9] used chloride ion indicator to characterize the distribution...
of chloride ions in the gap during the crevice corrosion process. It was found that the distribution of chloride ions in the gap was uneven. The concentration of chloride ions in the vicinity of local corrosion sites was relatively high. With the development of the corrosion process, the change of chloride ion concentration in the gap corresponded to the change of corrosion current density. Studies in China have also shown that the formation, growth, and dissolution of chloride ion salt membranes played an important role in the failure process of aluminum alloy/epoxy powder coating systems. Therefore, the harm of chloride ions could not be ignored, and it would have a direct impact on equipment life and production safety. In particular, Q235 steel had a carbon content of about 0.17% and belonged to low carbon steel. The equilibrium structure was subanalytic organization, ferrite + partial pearlite. Its corrosion resistance to chloride ions was not high, so epoxy powder coating was used as a primer in general oil and gas transportation pipelines. However, there were still many problems about the influence of chloride ion on the metal corrosion in epoxy powder coating with scratch defect [10]. Chen Jiejing et al. [11] found that the wire beam electrode (WBE) technology is one of the optimal choices in the study of under-deposit corrosion. Zhang Xia et al. [12] used WBE technology to study the corrosion potential and current distribution on the interface of biofilm and metal as well as their relativity with the distribution of hydrogen peroxide in the artificial biofilm and found that it could gain the electrochemical information of the electrode surface rapidly and exactly. Therefore, this paper aimed to explore the corrosion law of chloride ions on the metal under the epoxy powder coating with scratch defects, in order to find a corresponding effective protection method.

2. The Test

2.1. Test Devices and Methods. The organic glass sheets are machined into an array of 10 ∗ 10 through CNC technique, and the diameter of each hole is 2 mm; the spacing between each two holes is 0.5 mm. Insert the steel wire of Q235 material with diameter of 2 mm into the hole and pour it with epoxy resin to make it fully filled between the steel wires and ensure the mutual insulation between each steel wire. When the current is measured, the saturated calomel electrode is used as the auxiliary electrode. The measured tow is connected to the reverse end of the zero-resistance galvanometer of the current scanner. The remaining 99 roots are connected to measure the coupled current between them, and then the current density distribution is switched successively.

2.2. Sample Preparation. According to the requirements of SYT-0315-2013 «Technical Specifications for Steel Pipe Fusion Epoxy Powder Overcoat», the anchor depth of the metal surface should be controlled at 40 ~ 100μm before the epoxy powder coating is prepared. According to the comparison between sandpaper specification and roughness, the electrodes in the experiment are polished step by step with sandpaper of 60#, 180#, and 280#, respectively, and then washed and dried with acetone and alcohol in turn. The grinding good electrode array in the heating furnace of 200°C temperature preheating after 10 min adopts the method of electrostatic spraying in the array electrode surface coating epoxy powder. In 200°C temperature curing furnace when spraying is completed, take out after 20 min. When the surface temperature drops, the thickness is measured with a coating thickness gauge. 20 points are selected as measurement points for each coupon, and the average is taken as the coating thickness of the coupon after measurement. According to the requirements of GB/T 23257-2009, the three-layer PE structure adopts epoxy powder coating as the primer, the thickness should be not less than 120 μm, and the thickness of the control coating is 150±10 μm. The finished coated coupons are placed in a dry box for use.

2.3. Test Methods. As shown in Figure 1, artificial scratch damage treatment is performed at positions (6,5) and (6,6). The specific method is as follows: the coating on the surface of the two electrodes is subjected to the same degree of damage treatment by a paper cutter, and the coating is completely destroyed to expose the metal substrate to avoid introducing irrelevant variables. Array electrode edges, scratch damage, are sealed with beeswax. They are immersed in distilled water, 1% NaCl, 3.5% NaCl, 6% NaCl, and 8.5% NaCl, respectively. Three parallel samples are used for each experiment. Conduct current sweep test at regular intervals with wire beam electrode potentiometric current scanner. The standard three-electrode system is used for AC impedance measurement. During the measurement, the frequency is selected from 0.1 Hz to 100 kHz, and the amplitude is 20 mV.

3. Results and Discussion

3.1. Current Density Distribution Results and Analysis. Figure 2 shows the corrosion current density distribution of the damaged coating system after soaking in distilled water for different times. In the figure, the X axis corresponds to the row in Figure 1, the Y axis corresponds to the column in
Figure 2: Current density distribution diagram of the scratch damage system immersed in distilled water for different days.
It can be seen from Figure 2 that a corrosion reaction occurs at the damaged position at the initial stage of the immersion. In the reaction, one of the two electrodes at the location of damage showed an anode current and the other a cathode current. The corrosion current is small, and the peak current density is about 2 $\mu$A·cm$^{-2}$; this phenomenon indicates that if there is no chloride ion, although it can quickly induce electrochemical corrosion of Q235 steel, the reaction rate is relatively small. The current density of the coating area is about $10^{-3}$ $\mu$A·cm$^{-2}$, which means that no electrochemical reaction at these locations, and it shows that the coating has good protection for the electrode. With the extension of soaking time, the peak current of yin-yang electrode fluctuates slightly, and the corrosion develops slowly. When the immersion time reaches 40d, it is found that both electrodes become anode current at the damaged position. The cathode current appeared at the points (6,4), (6,7), and (5,5), which were relatively close to the location of damage. At this time, the dissolution reaction of the metal continues to occur at the location of the damage, and the cathode region of the electrochemical reaction has progressed to the adjacent coating at the location of the damage. When the experiment proceeds to the 50th day, it can be found that the anode current remains in the damaged position and the cathode current has further spread, except for the previous points (6,4), (6,7), (5,5), (5,7), (7,5), and (7,6) also showed a relatively obvious cathode current at these positions, which proved that the cathode had spread from the damaged position to the periphery.

It can be seen from Figure 3 that, in the 1% NaCl solution, the anode and cathode currents still appear at the damaged position at the initial stage of immersion, each occupying one electrode, but the corrosion current density is significantly increased and the peak value has reached about 12 $\mu$A·cm$^{-2}$. With the addition of NaCl, the immersion position has been converted to anode current when immersed for 15 days and the cathode current begins to appear under the coating (6,4), (6,7), and (5,6). This indicated that the cathode developed faster towards the intact area under the coating with the addition of NaCl. After that, the anode remained in the damaged position and the area where the cathode current appeared gradually expanded as the soaking time extended. At 50 days, significant cathode currents appeared at the 11 tow electrodes around the fracture location. In addition, the current value at the location far away from the damaged location also increased significantly, such as (5,3), (5,8), and so on. It can be seen from Figure 4 that the evolution of the current density of the system in the 3.5% NaCl solution shows a similar pattern. At the beginning of the immersion, the anode current and the cathode current appear, respectively, at the damaged position. However, as the immersion time going, the two tows at the breakage are transformed into the anode region and the position where the original current around the defect is almost zero appears as the cathode reaction region, what is more, the cathode region gradually spreads with time. This indicates that the principle of the reaction does not change as the concentration of chloride ions increases. However, the increase in the anode current density increases the rate of corrosion reaction and the rate of outward diffusion of the cathode also increases significantly with increasing chloride ion concentration. Taking the experimental time of 50 d, 15 electrodes in the coating of 3.5% NaCl solution showed obvious cathode current, including the (5,8) point far from the damage position, and the cathode diffusion speed was much faster than distilled water and A sample in a 1% NaCl solution. 

As can be seen from Figure 5, the anode current density continues to increase as the concentration of the NaCl solution increases, which has exceeded 20 $\mu$A·cm$^{-2}$ in a 6% NaCl solution. It can be found from Figures 4 and 5(d) that with the low concentration of NaCl solution, the cathode region has spread to a region far away from the damage position, and a larger cathode is also detected at positions (2, 3), (2, 9). The cathode region developed to 27 electrodes and the range of diffusion increased significantly. An anodic current appeared at (6, 7) and (7, 6) near the breakage position, which may be due to the severe peeling of the coating near the break position as the reaction progressed. A large amount of corrosive solution is in contact with the (6,7) and (7,6) electrodes, resulting in a situation in which the two positions are similar to the complete immersion in the solution and the cathodic reaction is converted into an anodic reaction.

Initially, electrochemical corrosion occurs only at the location of the damage, which is manifested by the presence of anode current and cathode current for the two electrodes. As the reaction progresses, the cathode region of the damaged position gradually changes and remains as the anode region because the oxidation reaction and the reduction reaction are simultaneously performed on each electrode in the initial stage of the reaction. One of the electrodes has an oxidation reaction rate higher than the reduction reaction rate and finally shows an oxidation reaction, showing an anode current; the other electrode has a reduction reaction rate higher than the oxidation reaction rate and exhibits a cathode current. As the reaction progresses, the damage location is gradually covered by the rust layer, which prevents the diffusion of oxygen to a certain extent, and the formation of the half-occluded anode zone tow does not easily obtain oxygen. The area around the broken location is more conducive to the ingress of oxygen. Therefore, the oxygen absorbing reaction occurring at the cathode tends to occur in a region where oxygen is easily obtained under the coating; that is to say, the peeling front end serves as a cathode region, and the broken portion performs a metal dissolution reaction.

As the reaction progresses, chloride ions destroy the integrity of the rust layer and accelerate the transfer of the material. In addition, chloride ions form a soluble chloride with ferrous ions. Hydrolysis of the chloride reduces the pH of the surrounding environment, which further promotes dissolution of the anode. Therefore, under this autocatalysis, the anode reaction is gradually enhanced. This phenomenon shows an increasing trend as the chloride ion concentration.

Figure 1, and the Z axis is the current density axis with units of $A\cdot cm^{-2}$.
Figure 3: Current density distribution of smear damage system in 1% NaCl solution at different days.
Figure 4: The current density distribution of the scratch system is immersed in a 3.5% NaCl solution for different days.
Figure 5: Current density distribution diagram of smear damage system in different days in 6% NaCl solution.
increases. Oxygen reduction reaction takes place in the cathode area and generates a lot of OH−. This process will break the bond between the coating and metal in the adjacent area, reduce the wet adhesion of the coating, cause the coating to peel off, and the cathode continues to develop further away from the damaged location. In addition, the increasing of corrosion products near the anode area will accelerate the peeling of the coating. The stripping rate increases with the increase of chloride concentration. This is mainly due to the existence of an electrical couple formed by the defective coating and the complete coating at the defect location, which provides power for the stripping of the coating. To maintain this pair you need a threshold ion concentration of C∗. And C∗ is related to the concentration of ions in solution ontology [10]. The specific relationship is as follows:

\[ C^* = KC_{bulk} \cdot \left[1 - \text{erf} \left( \frac{x_{del}}{2 \left(D_{cation}^t_{del}\right)^{1/2}} \right) \right] \]  

(1)

In the formula,
- \( K \): equilibrium constant of coating metal interface and bulk solution ion concentration;
- \( x_{del} \): the distance from the front end to the defect position;
- \( D_{cation}^t_{del} \): cation diffusion coefficient;
- \( t_{del} \): stripping time.

It can be seen from Figure 6 that the current density distribution of the damaged coating system in the 8.5% NaCl solution changes with time similar to the previous one. The anode of the electrode reaction remains in the damaged position for a long time, the cathode gradually diffuses, the coating gradually peels off, and the peeling speed increases as the chloride ion concentration increases. At the same time, the degree of cathodic migration was the most severe in the 8.5% NaCl solution. As shown in Figure 6(e), after soaking for 50d, 36 metals under coating showed obvious cathode current, including (8,2), (9,3), (6,10), and other positions far away from the damaged position. In addition, in Figures 5(e), 6(d), and 6(e), in addition to the damage location appears obvious anode current, under a good coating metal wire electrode covered have appeared in the anode current, especially in Figure 6(e), (5, 3), (5, 8) and (7, 9) in the anode current peak, it may be that as the degree of corrosion reaction increased, damage location offer the excessive corrosion products, lead to defect metal corrosion, the coating the metal is dissolved. What is more, in a highly corrosive environment, corrosive ions permeate through the coating to the metal interface of the coating. Some of the positions that had been shown to be cathode currents had undergone a polar transformation into an anode reaction area.

3.2. Analysis of Impedance Test Results. So describe the migration behavior of the cathode under the damaged coating system, and determine the consistency of the impedance and corrosion current density on the metal corrosion law under the damaged coating that some points in the 8.5% NaCl solution were selected and the impedance test was performed. Select the points at different depths from the damage location and perform impedance tests on the five positions (6,6), (6,7), (6,8), (6,9), and (6,10) from near to far. The cathode migration behavior was studied by comparing the impedances at different points in each time period. The electrochemical impedance spectra of initial, intermediate, and final stages of the coating failure process under the influence of chloride ions were simulated successively by circuit R (CR), R (CR (CR)), and R (CR (Z)), respectively.

It can be seen from Figure 7(a) that the impedance is a complete semicircular arc at a point far from the damage position and the radius of the impedance arc is larger at the initial stage of immersion, which indicates that no interface reaction occurs at the point under the coating coverage. The coating acts as a good barrier to protect the metal. The impedance at the point (6,6) is markedly different from the other locations, where the arc radius of the impedance is very small at only 2×10^4 and the metal is being dissolved.

As can be seen from Figure 7(b), the impedance of the damaged position of the immersed 15d coating hardly changed. The result is still a small arc with a small radius which indicates that the corrosion location is still going smoothly. The radius of the impedance arc is significantly reduced at the point (6, 7) near the damage location, and interfacial corrosion behavior occurs. This also indicates that the coating around the damaged location peeled off with the immersion time and caused interfacial corrosion. The electrodes (6, 8), (6, 9), (6, 10) metal far from the damaged position are still in good protection. These locations still appear as a large single impedance arc, indicating that the coating peel does not spread to these locations.

It can be seen from Figure 7(c) that the electrode impedance arc at the (6, 7) position is further reduced as the immersion time is extended, and the low-frequency impedance modulus is less than 10^4 [13]. It shows that the interface corrosion at this position is further developed, and the protection of the coating for this point is basically invalid. The phenomenon of peeling of the coating has not progressed to a farther position (6, 8), and the impedance of the remaining points hardly changes greatly. This is in good agreement with the results of the previous current density analysis, which also shows that the two methods have good consistency.

It can be seen from Figures 7(d) or 7(e) that the impedance at the damaged location of the scratch did not change significantly during this period, and it is always manifested as the impedance arc with a radius of about 10^4. The radius of the circular arc did not change much, indicating that the position is always subject to the solution of carbon steel in solution. With the extension of the immersion time, the impedance characteristics of the interface corrosion reaction appear in the near and far distance according to the distance of the damage. It indicates that the coating gradually peels away from the distal end away from the damaged location.
Figure 6: Current density distribution of scratch damage system immersed in 8.5% NaCl solution for different days.
Figure 7: Nyquist diagrams of part of the point soaking for 1d, 15d, 30d, 40d, and 50d.
position, and the cathode of the electrochemical corrosion reaction gradually migrates away from the defect position with time. The impedance changes are large at points (6, 9) and (6, 10) in Figures 7(d) or 7(e), which may be due to the penetration of the corrosion solution at the location after the immersion for a long time. External longitudinal infiltration interacts with the coating, causing the coating to decrease in impedance.

4. Conclusion

WBE technology was used to study the effect of chloride ions on the corrosion of metals under epoxy powder coatings with scratch defects. By analyzing the distribution of corrosion current density, the following rules were found:

(1) In the initial stage of immersion, the anode and cathode of the corrosion reaction appear in the damaged position. One electrode in the damaged position appears as the anode current and the other electrode appears as the cathode current.

(2) As the immersion time is prolonged, the damaged position is completely converted into an anode and the anode of the corrosion reaction is maintained at all times; the cathode reaction occurs around the damaged position and continues to expand towards the periphery as the coating peels off.

(3) The anode current density and corrosion rate increase with increasing chloride ion concentration. The migration rate of the cathode under the coating is accelerated, and the peeling speed of the coating is also the same.

(4) Combining the AC impedance technique to study the migration behavior of the cathode under the coating, it is proved that the AC impedance and the corrosion current density have a good consistency with the research results of the process.

Data Availability

The research data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

The research work was supported by Civil Aviation Safety Capacity Building Fund (Construction of Safety Evaluation System for Multi-Branch Complex Annular Apron Pipe Network) and Airport Engineering Research Base Open Fund (Study on the Optimization of Cathodic Protection Model in the Apron Area Based on BEASY).

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