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Study on Corrosion Resistance of Polyurea Coating in Marine

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Abstract

The change of corrosion resistance of Q235B steel plate protected by polyurea coating in accelerated corrosion process with scratch was studied by electrochemical test method. Meanwhile, the whole field displacement of Q235B steel plate protected by polyurea coating in 5% (mass fraction) NaCl solution in simulated seawater environment was studied by digital image correlation technology. The results show that when there is a scratch on the surface of Q235B steel plate, the corrosion resistance of Q235B steel plate in seawater solution decreases first and then increases slightly. This phenomenon can also be verified by digital image correlation technology.

Keywords

Polyurea Coating; Electrochemical Test; Digital Image Correlation.

1. Introduction

The ocean is an extremely severe and comprehensive corrosive environment, which combines a variety of damage factors such as strong sun exposure, tidal impact, salt spray, wind, and waves. Therefore, the ships in it and the submarine transportation pipelines are usually protected by coatings. The coatings play the role of anti-corrosion, anti-wear, drag reduction and anti-fouling [1-4]. In actual service, the coatings will fail quickly due to the severe corrosion of seawater and the marine atmospheric environment, as well as the combined effects of hot weather, aging, fluid erosion, and biological fouling. With the rapid development of the worldwide marine economy and the acceleration of the process of using marine space [5-7], more and more attention has been paid to the research of marine protective coatings[8]. The failure of the protective coatings is a complex evolution process from quantitative change to qualitative change due to many factors. During the service of the coating, the study found that water, oxygen, and corrosive media are the main factors which cause its debonding failure [9]. They will penetrate the coating through the micro or macro defects such as pinholes, structural pores, cracks in the coating [10]. When water molecules and corrosive media reach the metal surface, it will cause metal corrosion, which will reduce the adhesion between the coating and the substrate significantly. The formation and accumulation of corrosion products will increase the local internal pressure and cause the coating to blister and lose its protective function. More and more studies show that the debonding failure behavior of organic protective coatings has an important relationship between the adhesion failure of the coatings and the substrate [11-13]. However, most of the current researches on anticorrosive coatings in the marine environment focused on the improvement in their components, the laws of macro performance changes, and the application of concrete protection. The research on the failure behavior of debonding deformation when used in metal protection is still in preliminary exploration stage. Therefore, the research on the corrosion characteristics of the anticorrosive coating system during the service in the marine environment is extremely significant for understanding the failure mechanism of the coatings and evaluating the service life of the coatings.

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When water, oxygen, and corrosive media in the marine environment penetrate and diffuse through the anticorrosive coatings to the surface of the metal substrate, the bonding force between the coating and the substrate is called wet adhesion. At this time, the following local galvanic reactions will occur on the interface. As corrosion products accumulate gradually, the internal pressure on the interface will increase gradually, and the wet adhesion between the coating and the substrate will continue to decrease until it lost completely. Eventually, the coating will blister and fail [1,14,15]. In order to evaluate the protective performance of the coatings in this process quantitatively, a method of marine environmental corrosion experiments combined with coating performance characterization is usually used. On the basis of environmental corrosion experiments, characterize the coatings ' mechanical properties, gloss, water absorption, adhesion, impact strength, etc. With the development of modern experimental technology, FTIR, Raman, EIS, AFM, SKP are also commonly used to study the corrosion protection performance of coating metal systems. Le Thua et al. studied that the peeling behavior of the coating would lead to a sudden decrease in coating resistance and a sudden increase in coating capacitance[16]. Kittel used electrochemical AC impedance technology to separate the inner impedance at the coating metal interfaced with the outer impedance at the solution coating interface and studied the failure behavior of the coating, found failures of a the coating [17] .The behavior is very different, and the wet adhesion between the coating and the metal substrate has a great effect on the performance of the coatings.

Digital Image Correlation(DIC)was proposed By Yamaguchi [18] and Peters [19] in the early 1980s. DIC is a non-contact, non-interference, full-field deformation optical metrology method based on computer vision principles, digital image processing, and numerical calculations[20]. It reads the un-deformation and deformation images of the experimental specimen and tracks the movement towards the external marking points to obtain the displacement field and strain field of the experimental object surface. And DIC has also been proven to be an ideal tool for a wide range of applications, including the identification of mechanical material behavior, structural health monitoring[21]. Due to its advantages of non-contact, non-interference, and full-field deformation, many scholars used DIC to study the corrosion damage, displacement, and damage of concrete. Yudan Jiang et al used the DIC measurement technique and classical strain gauges to indicate that the DIC technique is an efficient measuring tool for obtaining displacements and analyzing strain fields during corrosion of reinforced concrete. However, the research on the corrosion characteristics of marine anticorrosive coatings based on DIC is still scarce[22].

With the aim of monitoring the strain field developments and the blistering process of the anticorrosive coatings under accelerated corrosion,the Digital Image Correlation technique is used in this research. The results of this research are useful for understanding the coating failure mechanisms and evaluating the coating’s life. Besides, it’s significant for exploring the high-performance anticorrosive coatings and improving the protection of the coatings.

2. Experiment and materials

2.1 Materials and specimen preparation

Considering the requirement of random texture on the sample surface based on the Digital Image Correlation coating deformation monitoring technology, this experiment uses a two-component polyurea coating spray technology. Two-component polyurea coating, including pure polyurea a component and pure polyurea b component in a volume ratio of 1: 1. The main component of component A is the isocyanate functional group of the semi-prepolymer, and its mass percentage is 18% to 23%. The main component of component B is amino-terminal amino ether, whose mass percentage is 40% ~ 75%. The two components are sprayed under high temperature and pressure using a PHX-40 sprayer from Polyurethane Machinery Corporation, USA. Preparing a carbon steel Q235 with a size of 10 mm × 10 mm × 1 mm, sanding it with the 120# sandpaper, derusting treatment, rinse with deionized water and dry. Clean the surface of carbon steel with ethanol and acetone, then dry it for use. Mix the A and B components according to a predetermined ratio, spray it on the surface

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of the treated carbon steel Q235, and the sample is cured in a dry environment until completely cured. Pay attention to controlling the temperature, spraying speed and gun moving speed to ensure that each sample has the consistent thickness and physical properties. Control the coating thicknesses in 0.5mm. In order to ensure the imaging quality of the image, select a suitable labeling dye and make sure that the speckle particle size is 10 μm. The cured sample is cured for 4 weeks and the back surface was cured for 7 days under standard conditions of epoxy resin distribution to form a coating sample with a random speckle pattern on the surface. As shown in Figure 1, it is the schematic diagram of the sample.

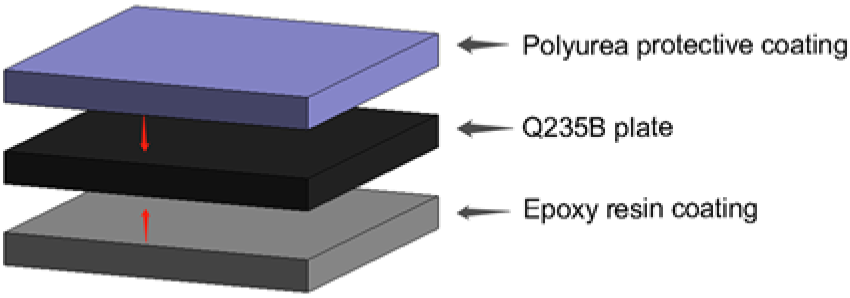

Fig. 1 Coating diagram

2.2 Accelerated corrosion of marine anticorrosive coatings.

The corrosion process of marine anticorrosive coatings exposed to the marine environment is long-term and difficult to detect in a short time. Therefore, in this experiment, a constant potential accelerated corrosion system was used to study the corrosion damage process of the anticorrosive coating and make a 5cm scratch in the center of the sample. The previous investigation and analysis showed that the main environmental factors for the failure of anti-corrosion coatings are water, oxygen and corrosive media in the ocean. In order to simulate the actual situation and accelerate the corrosion process in this experiment, the prepared anti-corrosion coating sample was horizontally fixed in a WeChat test chamber, where the NaCl concentration was 5%, and an external electric field was applied to drive water, oxygen, and corrosion in seawater The sexual medium penetrates into the coating. A wire connection was set at one corner of the sample to link with the negative pole of the DC stabilized power supply. The carbon rod was connected to the positive pole of the DC stabilized power supply and placed in seawater to form a closed circuit. In addition, the potential of the regulated power supply is maintained at a constant 1V and checked each hour.

2.3 AC impedance

The cs350h electrochemical test system produced by Koster company is used. The test frequency range is 10^5-10^{-2}hz, and the amplitude of AC sine wave signal is 20mV. A three electrode system was used, with platinum electrode as auxiliary electrode, saturated calomel electrode as reference electrode, coating substrate sample as working electrode. The working area was 100 cm^2 and the electrolyte solution was 5% NaCl solution.

2.4 Digital Image Correlation for the study

The principle of digital image correlation technology is an optical measurement method to obtain the surface deformation data of the measured object by collecting the image information before and after the deformation of the measured object, and calculating the collected image information. In the collected reference image, a square pixel sub region is selected and the center point of the sub region is taken as the research object. By tracking the position of the center point in the sub region of the target image, the displacement vector value of the center point can be calculated. By calculating the displacement vector values of the center points of a series of square sub regions in the reference image, the displacement field information of the whole image can be obtained. As shown in Fig. 2, the coordinates of the pixel center point of the selected reference sub region before deformation are

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U(x_0, y_0), The coordinate of any point near it is V(x_i, y_i), after the deformation, the coordinates of the center pixel in the target sub region become $U'(x_0', y_0')$. The coordinate of any point near it becomes $V'(x_i', y_i')$. In this experiment, two-dimensional digital image correlation technology of monocular camera is used. The computer image acquisition frequency is set at 9hz, and 9 images can be collected in one second. In order to make the image data collected in the process of experiment clear enough and high precision as far as possible, during the installation of industrial camera, make it face the sample and parallel to the sample surface, keep the distance between the camera and the sample within the maximum imaging distance range, adjust the focal length and aperture to make the imaging quality reach the highest value, lock the bolt, and fix the camera position unchanged. In case of insufficient illumination in the test environment, stable and uniform illumination shall be added outside.

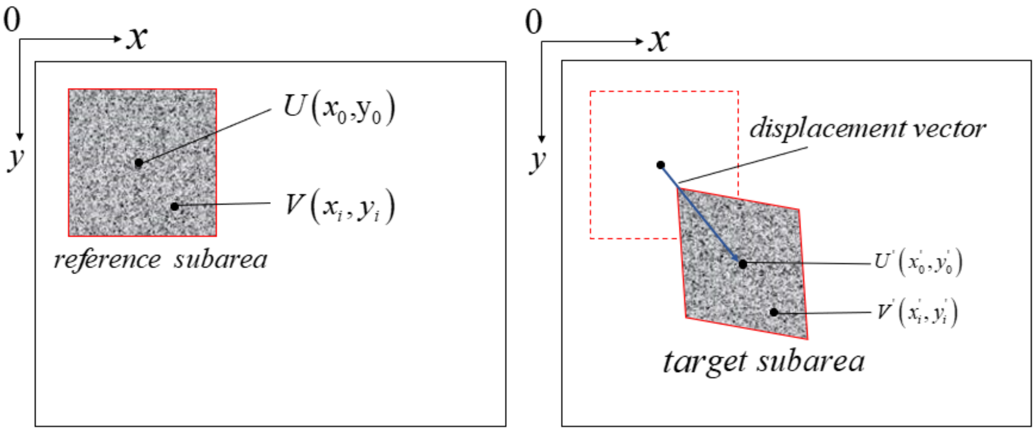

Fig. 2 Deformation subarea diagram

3. Conclusion and discussion

Fig. 3 shows the corrosion current versus time curve of polyurea coating accelerated by DC power supply in 5% salt water. It can be seen that with the increase of time, the current appears a maximum value. Before that, there was a linear correlation between current and time, which indicated that the corrosion resistance of polyurea coating decreased with the corrosion process.

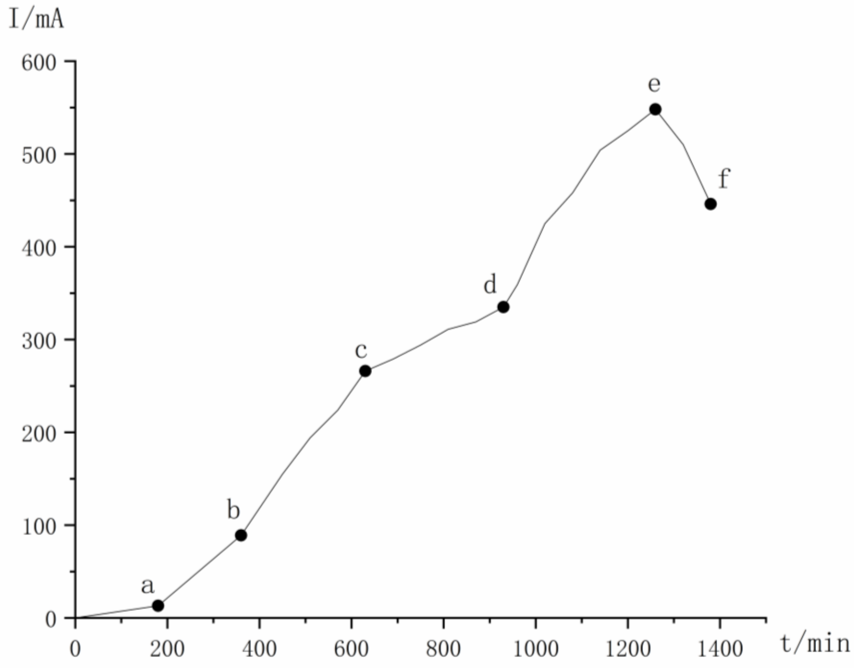

Fig.3 Corrosion current versus time curve

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Fig. 4 and Fig. 5 show the Nyquist diagram and Bode diagram of polyurea coating. It can be seen from Fig. 4 that the polyurea coating shows two time constants, and the radius of arc becomes longer and smaller with time. Combined with Bode diagram, it can be concluded that the impedance of polyurea coating decreases gradually during the corrosion process, which is consistent with the corrosion current analysis.

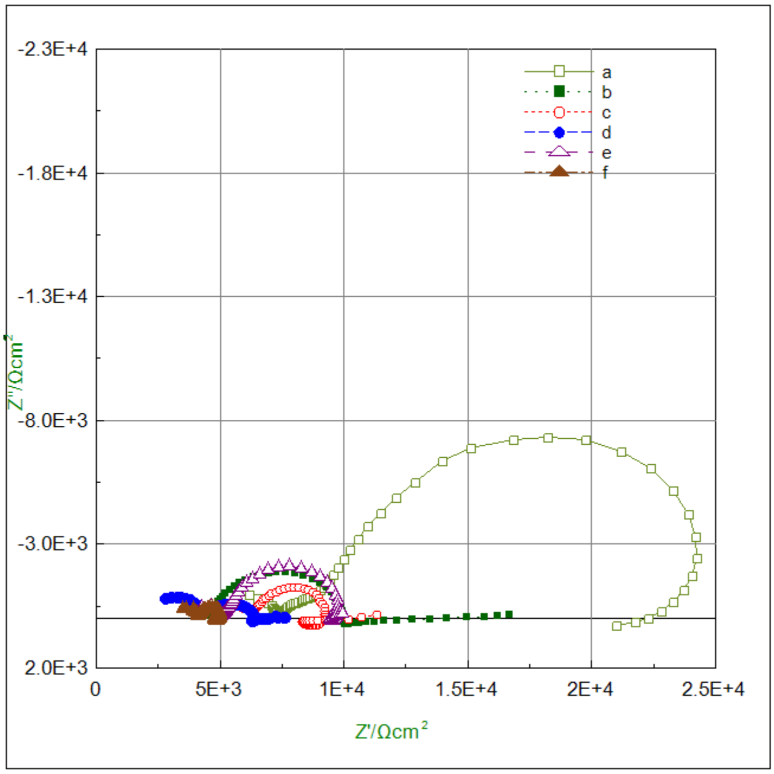

Fig. 4 Nyquist

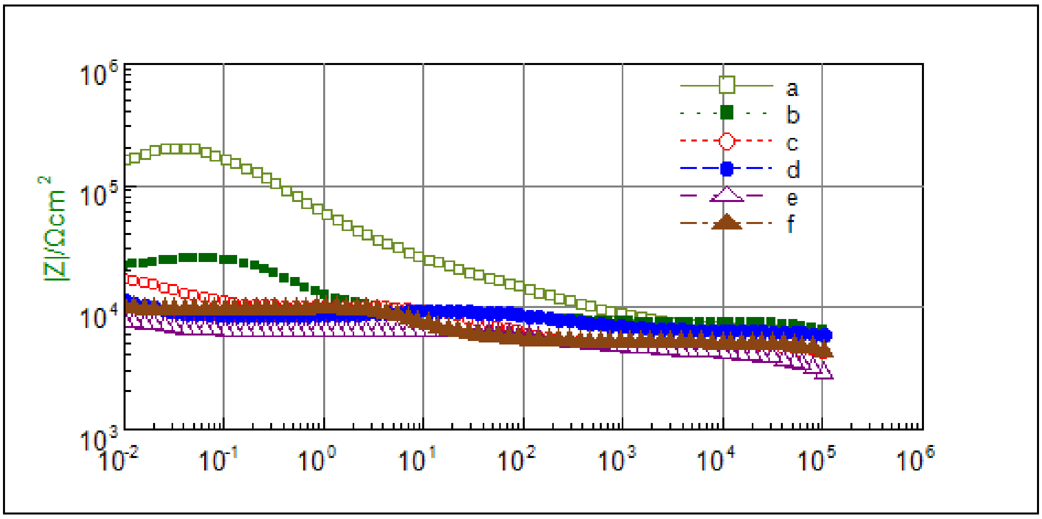

Fig. 5 Bode

Fig. 6 shows the surface displacement field analysis diagram of polyurea coating changing with time during the corrosion process. It can be seen that the displacement of the coating at the scratch gradually increases with the corrosion, and reaches the maximum displacement value at time g, which is consistent with the above analysis.

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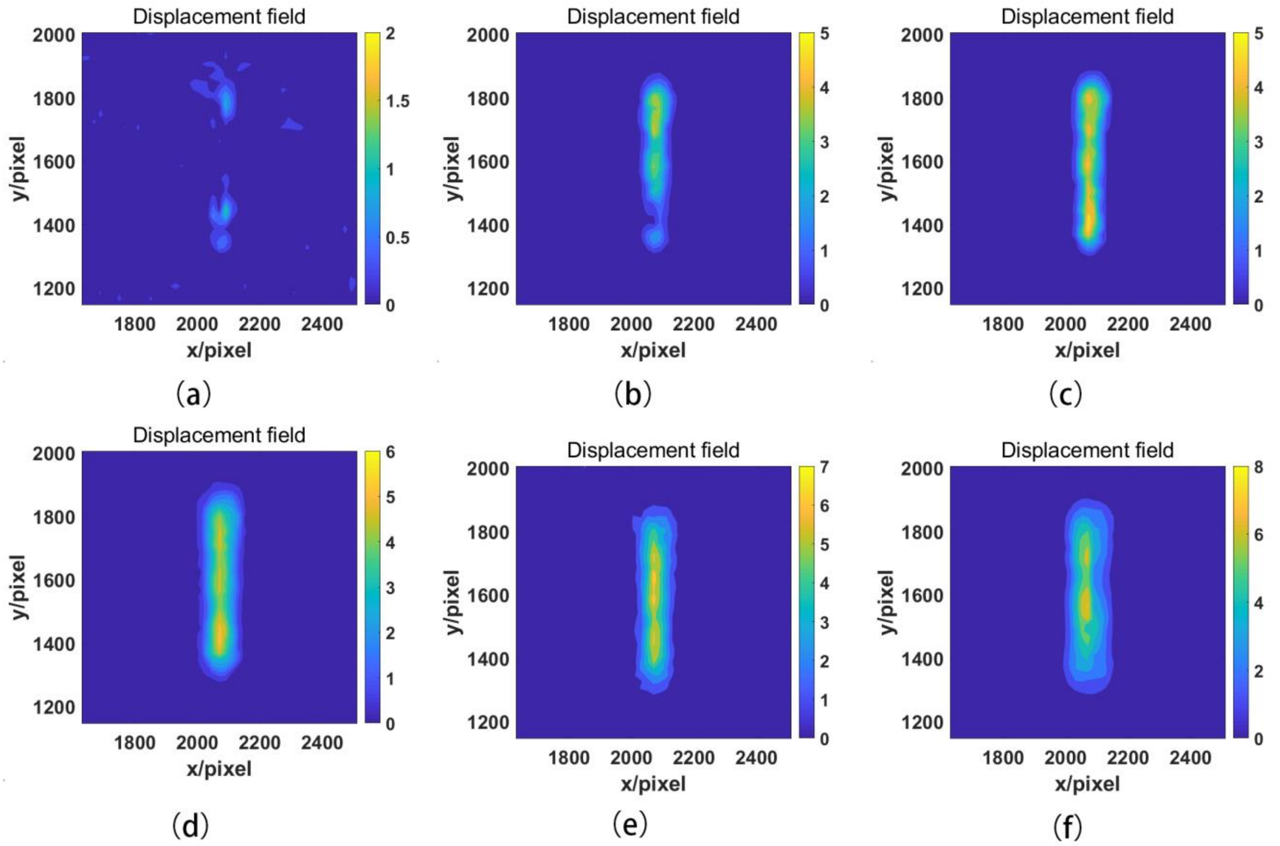

Fig. 6 Displacement nephogram

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