Study on AC Impedance Spectra of Ceramic Modified Epoxy Coatings Used for Crude Oil Storage Tank

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Abstract. The bottom of the crude oil storage tank is eroded by the sedimentary water for a long time, the main source of which is the ballast water in the ship's transportation. In this paper, sedimentary water was simulated with 3.5% NaCl solution.The structure of self-made ceramic particles modified epoxy coating was analyzed with scanning electron microscopy and the distribution of ceramic components in the coating was tested by EDS spectra, which showed that Al_2O_3 particles dispersed in the epoxy resin well;SiO_2 particles dispersed in the epoxy resin with poor performance. Using electrochemical impedance spectroscopy (EIS) to study the electrochemical behavior of the ceramic modified epoxy coating / carbon system in 3.5% NaCl solution.The coating's corrosion process is divided into three stages.The coating's AC impedance spectra of each period has been analyzed carefully and the corrosion mechanism of ceramic modified epoxy coating in 3.5% NaCl solution was revealed, which provides a reference for the maintenance of crude oil storage tanks.

Introduction

Crude oil is mainly transported by sea. When the tanker leaves our country for the destination, the ship will carry seawater to maintain the stability of the ship. When it reaches its destination, seawater in the cabin will be drained for storage. As the cabin volume is huge, can not be 100% seawater discharge, a small amount of sea water will be deposited in the bottom, along with crude oil shipped back to the crude oil storage tanks on the land. To sum up, the bottom of the crude oil storage tank by the long-term erosion of sedimentary water, its composition is mainly seawater.

Epoxy resin not only has good physical properties (high hardness, good flexibility, etc.) and chemical properties (chemical structure and stability, good dielectric properties), but also owns strong adhesion to metal, high resistance to acid, alkali and oil. All of these made it the main resin in the field of anti-corrosion[1-3]. Studies have shown that the addition of ceramic particles can make comprehensive improvement of epoxy coating heavy anti-corrosion ability and wear resistance[4-6]. Al_2O_3 and SiO_2 powder have been much concerned for its high chemical inertness and excellent anti-corrosion properties[7-9]. Studies show that the best properties of the composite coatings are obtained by the addition of l: l of 400 mesh active silicon powder and 1250 mesh alumina ceramic powder. This is due to the fact that the 1250 mesh alumina powder tends to fill the voids formed between the 400 mesh particles of the active silica fine powder, which is denser than any of the two fillers[10-12].

In this study, self-made ceramic modified epoxy coating was used as the object of study. The deposited water was simulated with 3.5% NaCl solution. Based on the anticorrosion requirements of the crude oil storage tank, the ceramic modified epoxy coating’s electrochemical impedance spectroscopy (EIS) spectra was obtained by immersing the electrochemical impedance spectra in 3.5% NaCl solution for different time and the results were analyzed combining with coating structure. The corresponding equivalent circuit model was established and the equivalent element parameters were analyzed. The failure process was analyzed quantitatively in 3.5% NaCl solution, which can reflect the corrosion mechanism of the coating when used in reality, which provides a reference for the maintenance of crude oil storage tank.

Experiment

Reagents and Materials.

Metal electrode substrate: 1cm×lcm×l cm of Q235 carbon steel(homemade); Epoxy resin: E51 and E21 (Jining Baiyi Chemical Co., Ltd.); Diluen: ethyl acetate and acetone (Tai Mau Chemical Reagent Factory); Fillers: 400 mesh Fluorine-modified active silicon powder and 1250 mesh alumina powder (Shanghai Liangjiang Chemical Products Co., Ltd.); Curing agent: polyamide resin(Zhenjiang Danbao Resin Co., Ltd.); Fluorine-modified Silica Coupling Agent); Deionized water (homemade).

Coating/Carbon Steel Electrode Preparation.

The surfaces of the electrode were enclosed with epoxy resin besides the working surface. The surface of the coated carbon steel was polished with 120 ~ 400 mesh sandpaper to expose the surface of steel substrate with metallic luster. After ultrasonic cleaning, it was degreased with acetone for 2 h and immediately dried. To E51 and E21 epoxy resin(the ratio of E51 and E21 is 2:1), 20% ~ 30% filler(the ratio of silicon and alumina is 1:1) was added and the appropriate amount of ethyl acetate and acetone were followed. The mixture was dispersed by ultrasonic for 2 hours. The curing agent polyamide resin(the mass ratio of epoxy resin and curing agent is 1:1) was added last. The ceramic modified epoxy resin was evenly coated on the carbon steel electrode surface with a coater. After one week of curing at room temperature, the thickness of the coating was measured by TT230 digital coating thickness gauge, which values 87±2μm.

Determination of Coating Structure.

KYKY1000B scanning electron microscope was used to observe the morphology of the coatings.

Determination of AC Impedance Spectrum.

The electrochemical impedance spectroscopy (EIS) test of the coating / carbon steel system was performed on the CHI604B electrochemical workstation. The electrode was used as the reference electrode, the corrosive medium was 3.5% NaCl solution, and the frequency range was 10^5-10^{-2}Hz. The classic three-electrode system was used in the test: coating / carbon steel electrode worked as the working electrode, platinum electrode worked as the auxiliary electrode and saturated calomel electrode worked as the reference electrode. The potential of the open circuit was -660mV and AC sine wave signal amplitude is 5mV. Solution was replaced once a week. The experimental data was sent to ZSimpWin for fitting processing[13].

Result and Discussion

Coating Structure Analysis.

Figure 1 shows the cross-section SEM image of the ceramic-modified epoxy coating. It can be seen from the figure that the film-forming materials such as resin and filler did not show obvious delamination, which indicates that Al_2O3 and SiO_2 particles in the epoxy resin of the dispersion is uniform. In order to further study the distribution of Al_2O_3 and SiO_2 particles in the coating, the area of Fig. 1 was scanned by EDS to analyze the composition. Fig.2, fig.3 and fig.4 are distribution maps of carbon, aluminum and silicon respectively, which can reflect the distribution of epoxy resin, Al_2O_3 and SiO_2 particles in the coating. Comparing Fig.2 and Fig.3, it can be concluded that the distribution area of Al_2O_3 particles overlaps with the distribution area of epoxy resin, which indicates that the Al_2O_3 particles can be well dispersed in the epoxy resin; Comparing Fig.2 and Fig.4, the overlap rate between epoxy resin and SiO_2 is lower, indicating that the dispersion of SiO_2 particles in the epoxy resin is uneven relatively; Comparing Fig.3 and Fig.4, the effect of mutual dispersion between Al_2O_3 and SiO_2 is ideal.

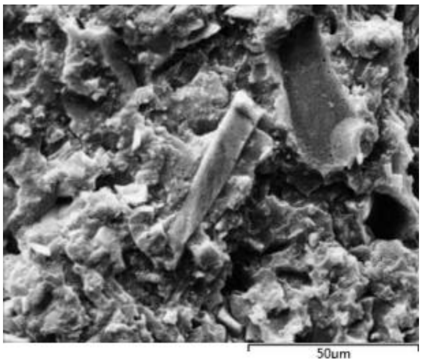


Fig.1 Sectional shape of the coating

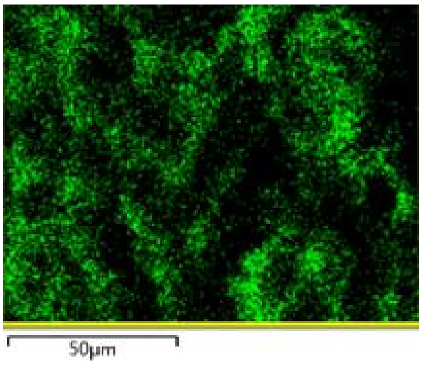


Fig.2Distribution of C

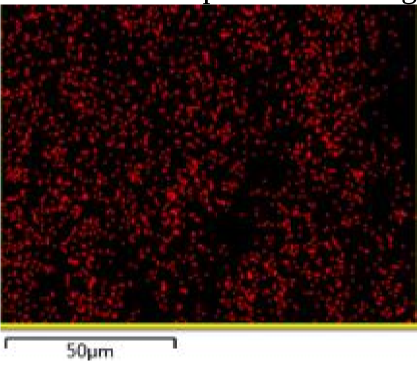


Fig.3Distribution of Al

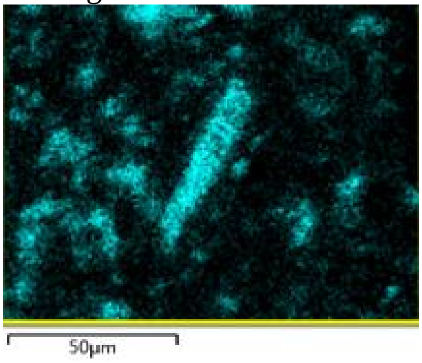


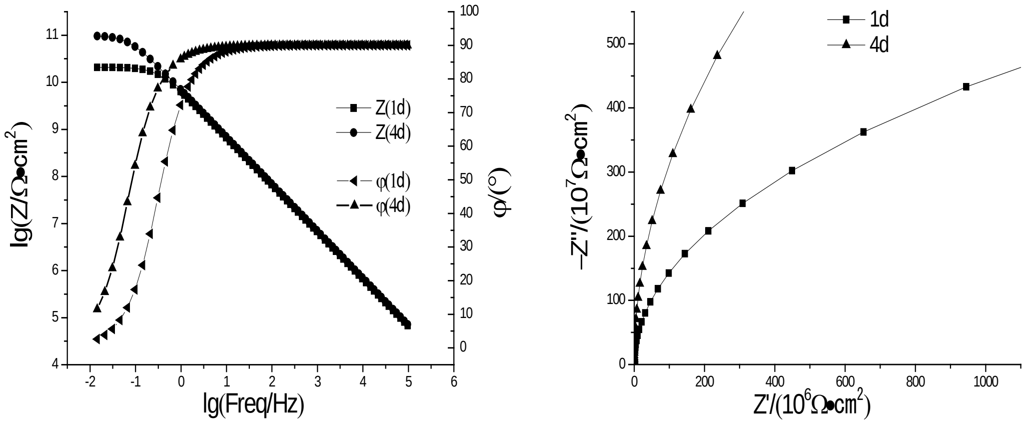
Fig.4 Distribution of Si

Electrochemical Impedance Spectroscopy (EIS) Evolution of Ceramic Modified Coating/Carbon Steel Electrode.

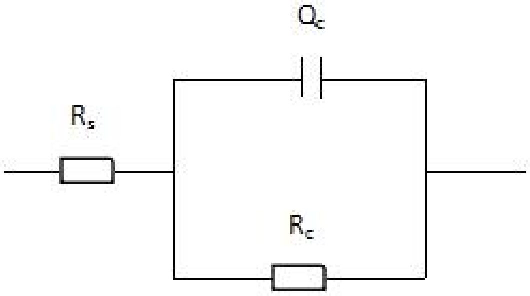
The electrochemical impedance spectroscopy (EIS) is an important method to study the mechanism of corrosion of coating / carbon steel system based on the small-amplitude sinusoidal wave potential, which can measure the impedance spectrum in a wide frequency range and obtain more dynamic information and electrode interface structure than other methods. Also, the electrochemical impedance can be used to estimate the state variables influencing the electrode process through the number of time constants and their numerical values contained in the impedance spectrum. Electrochemical impedance data of the coating / carbon steel system can also be analyzed via the equivalent circuit, which including layer capacitance Qc, coating resistance Rc, coating / carbon steel interface double layer capacitance Qdl, charge transfer resistance Rct, in order to conduct the quantitative study of coating / carbon steel system failure process.

1) Pre-soaking

At the beginning of the immersion, the ceramic-modified epoxy coating is equivalent to an insulating layer which prevents the NaCl solution from penetrating the surface of the carbon steel electrode to protect the base metal from corrosion. Fig.5 (a) and Fig.5 (b) show the EIS patterns of the coating / carbon steel system in NaCl solution at the beginning of immersion.From the Bode diagram in the early immersion (1-4d), figure line between lgZ and lgF is a slash in a very wide frequency range and the phase angle in the high-frequency range close to -90 ° , indicating that at this time Ceramic modified epoxy coating is equivalent to a isolation layer with large resistance value and small capacitance value. The corresponding equivalent circuit is shown in Figure 5 (c), in which Rs is solution resistance, Qc is the coating capacitance, Rc is coating resistance [13].



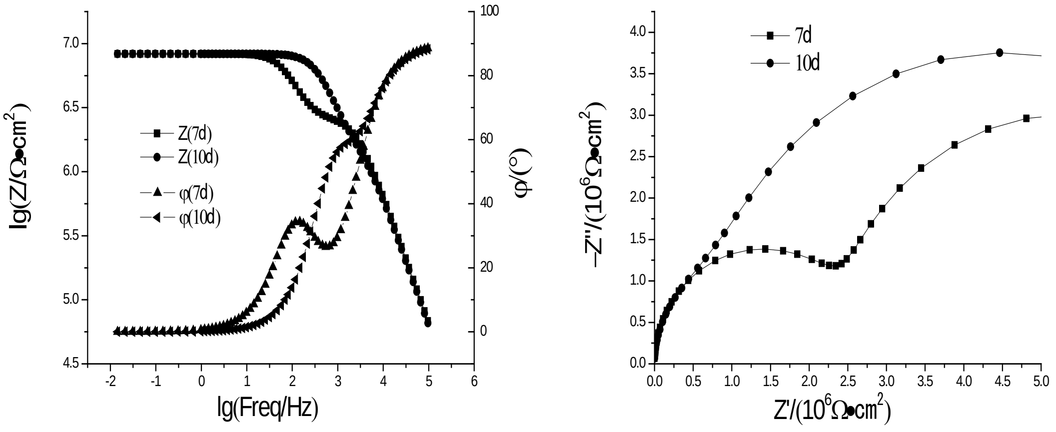
（a）Bode plot （b）Nyquist plot



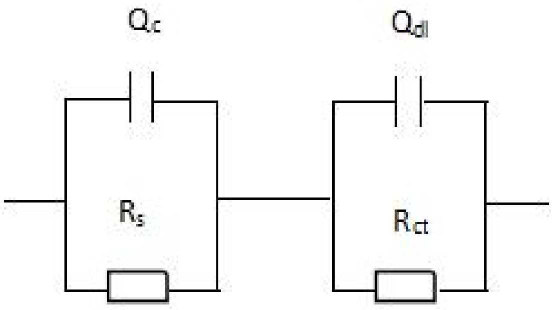
（c）Equivalent plot

Fig.5 EIS plots and their equivalent circuit for ceramic modified epoxy coating/carbon steel immersed in seawater in early stage（1-4d）

With the immersion time prolonged, the curve of Nyquist changed from straight line to arc, and the trend of capacitive arc radius decreased gradually. The corresponding degradation process was the seepage stage of the coating during this time (7-10d). Equivalent circuit shown in Fig6 (c), in which Rct is the charge transfer resistance of the ceramic particles and Qdl is the electric double layer capacitance of the ceramic particles. On the 7th day, the impedance spectrum responsed from a capacitive arc rapid transition to two-capacity arc, began to appear two time constant characteristics. Micropores formed by solvent evaporation led to the gradual penetration of the solution and the corrosion reaction in substrate surface was continuing, this time stands for the progress of base metal corrosion and gradual failure stage of the coating. In the early stage (1-10d), the magnitude of coating resistance Rc decreased from 10 to 7, which indicated that the protective performance of the coating was decreased.The fitting results are shown in Table 1.



(a) Bode plot (b)Nyquist plot

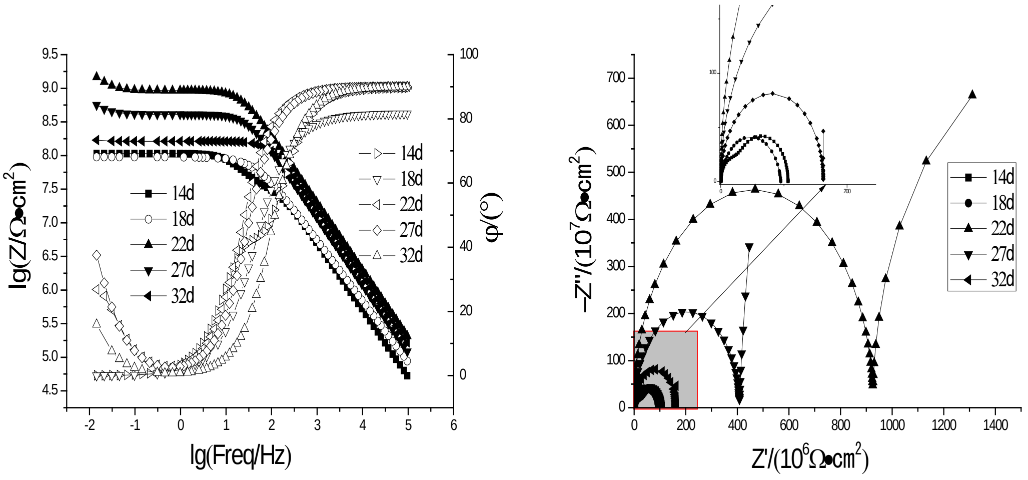


(c)Equivalent plot

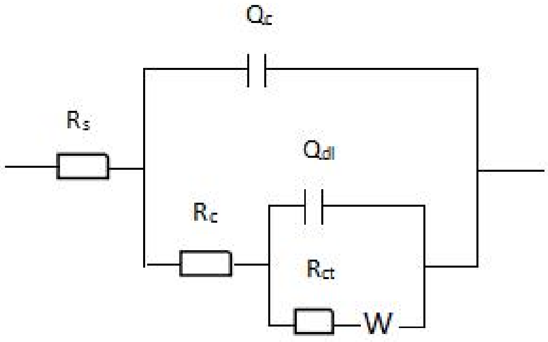
Fig.6 EIS plots and their equivalent circuit for ceramic modified epoxy coating/carbon steel immersed in seawater in early stage（7-10d）

2) Med-soaking

When the ceramic-modified epoxy coating was immersed in 3.5% NaCl sulution for 14-32 days, as the result of the hydrolysis products of alumina deposited in micropores, the coating owned a blocking effect to the NaCl solution. Therefore, in the low frequency region of the EIS spectrum, a semi-infinite diffusion Warburg impedance characteristic caused by the diffusion process, the corresponding evidence is that a semicircular arc and a diffusion tail are formed in the Nyquist diagram. As time goes by, the arc radius of high-frequency capacitance is decreasing and the the magnitude of coating resistance Rc increased to 9. At this point, the equivalent circuit of Figure 7 (c) was used to fit the EIS data and the fitting results are shown in Table 1.



(a)Bode plot (b)Nyquist plot

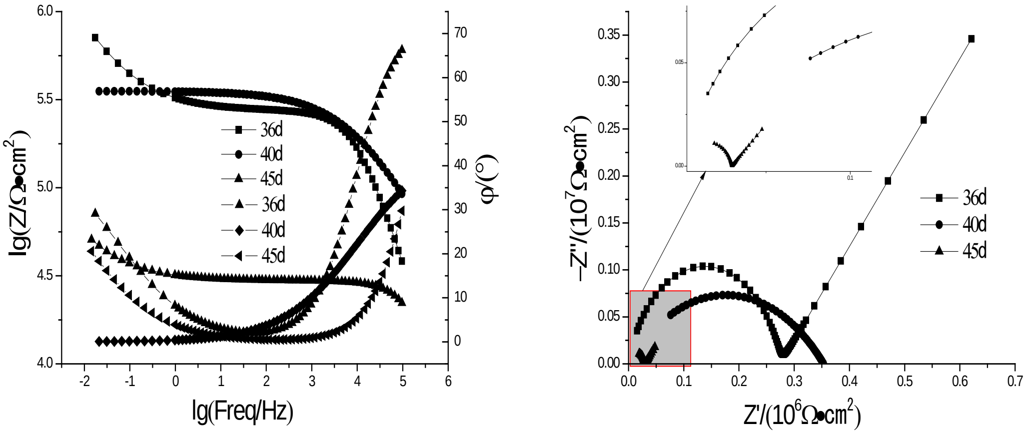


(c)Equivalent plot

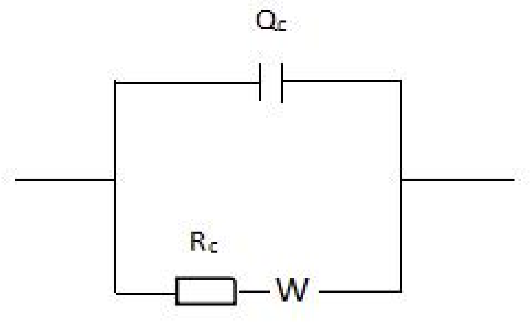
Fig.7 EIS plots and their equivalent circuit for ceramic modified epoxy coating / carbon steel immersed in seawater in early stage（14-32d）

3) Late-soaking

Period when rust point showed in the surface of the coating is known as the late soaking. Because of the presence of macroscopic pores in the coating, the concentration gradients that originally existed in the coating disappeared and the porosity of the ceramic-modified epoxy coating and foaming at the coating / carbon steel interface were both large. The formation of new open channels led to failure which overcomes the sealing effect of the corrosion products on the coating. The coating has lost the protective effect on the substrate. The magnitude of the Rc is reduced to 5 and the EIS characteristic is determined by the electrode process of the carbon steel matrix reaction. At this period, there is only one time constant in the EIS spectrum, corresponding to the coating capacitance Qc and the coating resistance Rc. The corresponding equivalent circuit is shown in Fig. 8 (c), and the fitting results are shown in Table 1.



(a) Bode plot (b) Nyquist plot



(c) Equivalent plot

Fig.8 EIS plots and their equivalent circuit for ceramic modified epoxy coating / carbon steel immersed in seawater in early stage（36-45d）

Table1 Electrochemical parameters of ceramic modified epoxy coating/carbon steel electrode immersed in seawater for different time

T/d	R_s/(Ω⁄cm^2)	Q_c/[(F⁄cm^2)·Hz^{1-n1}]	n_1	R_c/(Ω⁄cm^2)	Q_{dl}/[(F⁄cm^2)·Hz^{1-n2}]	n_2	R_{ct}/(Ω⁄cm^2)	R_w/(Ω⁄cm^2)
1	0.01541	2.768E-11	0.97	2.744E9				
4	0.01081	2.302E-11	0.95	9.844E10				
7		8.795E-8	0.64	3.963E6	2.528E-11	0.87	2.783E6	
10		6.316E-11	0.97	7.45E6	4.511E-11	1	8.68E5	
14	0.02297	1.72E-10	0.99	4.476E5	3.779E-11	0.78	3.55E7	8.916E-7
18	0.01888	3.005E-11	0.90	1.546E7	1.26E-10	0.87	5.338E7	9.769E-7
22	0.01422	1.253E-9	0.85	1.259E9	7.973E-12	0.76	8.914E8	1.152E-6
27	0.01345	1.35E-11	0.92	3.554E8	9.265E-9	0.87	5.316E8	1.621E-7
32	0.02703	2.41E-9	0.91	1.023E8	9.938E-10	0.90	1.639E8	5.252E-7
36		4.365E-10	0.82	2.751E5				6.187E-6
40		1.052E-10	0.85	3.161E5				0.002803
45		2.944E-9	0.84	2.974E4				0.000132

Conclusion

(1) EDS surface scan pattern shows that Al_2O_3 particles can be well dispersed in the epoxy resin and SiO_2 particles; Dispersion of SiO_2 particles in the epoxy resin is to be improved.

(2) According to the evolution character of EIS, the corrosion of ceramic modified epoxy coating / carbon steel electrode in 3.5% NaCl was divided into three stages: pre-soaking stage, med-soaking stage and late-soaking stage. The corresponding Bode and Nyquist plots of each stage are analyzed by the corresponding equivalent circuit to simulate the EIS in different periods and obtain the electrochemical parameters. The results show that the coating resistivity Rc does not change greatly and the resistance is high at the initial stage of immersion (1-4d), which indicates that the coating is an insulator and the carbon steel matrix is isolated from the solution, which is due to the good dispersibility of Al_2O_3 powders;The Rc was decreased from 10 to 7 in the seepage stage, and the solution had penetrated the coating to reach the surface of the substrate. During the mid-immersion (14-32 d), the magnitude of Rc was gradually increased to 9, which was due to the continuous accumulation of corrosion products at this stage blocked the channel for solution to contact matrix; During the late stage of immersion (36-45d), because of the further erosion of the solution, Rc’s magnitude gradually reduced to 5, the physical barrier properties of the coating have been lost and the coating lost its function.

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