

# Study of Degradation of Organic Coatings in Seawater by Using EIS and AFM Methods

Feng Zhang,<sup>1</sup> Jingjun Liu,<sup>1</sup> Xiaoyu Li,<sup>1</sup> Ming Guo<sup>2</sup>

<sup>1</sup>College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, China

<sup>2</sup>Coating Research Department, Naval Vessel Research Institute of China, 102442, Beijing

Received 19 September 2006; accepted 23 February 2007

DOI 10.1002/app.28010

Published online 30 April 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this article, electrochemical behaviors and their topography observation for four organic coatings used in seawater, by using both electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) methods to study environment behaviors of different coatings as well as the effects of their film formation, pigments, and fillers on anticorrosion behaviors, were measured. The results show that polyurethane, epoxy, and chlorinated rubber coatings all present one capacitive loop in their tested EIS which contains phenomenally only one time constant, whereas alkyd coating presents two capacitive semicircle arcs. With two capacitive loops, the capacitive semicircle in the high frequency range represents barrier layer property, but the semicircle in the low frequency range represents corrosion reaction of metals under the film. Polyurethane coating used in seawater has well anticorrosion property in seawater immersion test. The appearance features of different layers are visible different between different layers of tested coatings at their surface topography. The property of polyurethane paint film coated on metal is better than other layers, and film of alkyd coating has many pits at its surface by observing the

layer's images. AFM photos imaged have also been used to further detail surface topography for four organic coatings, and to approve effects of topography of these coatings on its electrochemical behaviors, from two views of both height and phase modes. It is beneficial to explain deeply the environment behaviors and degradation mechanism of organic coatings. To further study failure of these organic coatings and dynamic processes of corrosion of metal under the film, two equivalent circuit models, according to these tested EIS, have been suggested to explain the corrosive kinetics of these four coatings. To polyurethane, epoxy, and chlorinated rubber coatings used in seawater which have good protection effects for substrate metal, the diffusion process for water, from their layer's surface to interface of film/metal, is mainly controlled factor for degradation. However, the electrochemical reaction process has may become a control procedure for corrosion of alkyd coated metal. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1890–1899, 2008

**Key words:** coatings; seawater; performance; EIS and AFM; degradation

## INTRODUCTION

There are mainly three types of resins that are often used for heavy duty anticorrosive paint by now, and they are the epoxy resin, polyurethane, and chloric ethylene resin.<sup>1</sup> These types of coatings are well known as efficient organic coatings to protecting metallic substrates from corrosion in various fields and corrosion protection of metals by using coating film is very important. Following wide applications of coatings in different environments, the degradation of the corrosion protection coating films for various applications has become a very important issue. Consequently, the corrosion behaviors of organic paints on metal substrate have been investigated and reviewed by many researchers.<sup>2</sup>

Someone studied the general degradation of 12 organic coatings used in seawater, and it has been

shown that anticorrosive performance of coatings is relative to the sorts of the used macromolecule resin as film formation.<sup>3</sup> Electrochemical impedance spectroscopy (EIS) is widely used to determine the performance of protective organic coatings on metals. In the literature, EIS is frequently used to elucidate degradation mechanism by studying defective areas in coating.<sup>4</sup> Marchebois et al. used EIS method to study the electrochemical performance of Zinc-rich paints in artificial seawater, and they found that Zn powder content affects performance of coating remarkably.<sup>5</sup>

Moreover, characterization of the metal-coating interface on a scale of measurement that gives little microscopic-scale information is also crucial to understand and predict the performance of corrosion protection coatings. Atomic force microscopy (AFM) has the ability to provide such information. Bierwagen et al.<sup>6</sup> in their work investigated the changes in surface morphology of some coatings with immersion time in brine and studied the performance of organic coatings by using AFM and SEM methods.

Correspondence to: X. Li (lixu@mail.buct.edu.cn).

It is possible to explain deeply the environmental behaviors and degradation mechanism for some organic coatings on metal substrate used in seawater by studying their electrochemical performance in seawater medium, and surface morphology for a defect in an organic coating.

In this article, the EIS and AFM spectroscopy of various organic coatings used in seawater were measured to study the performance of different coatings used in seawater as well as the effects of their film formation, pigments, and fillers on anticorrosion behaviors. It is beneficial to explain deeply the environmental behaviors and degradation mechanism of organic coatings.

## EXPERIMENTAL

The available experimental materials are polyurethane, epoxy, alkyd, and chlorinated rubber coatings provided by Naval Vessel Research Institute of China. The two components polyurethane coating is composed of TDI 280 curing agent, acrylic resin, fillers, etc; epoxy micaceous iron oxide (epoxy MIO) coating is composed of epoxy resin 6101, gray micaceous iron oxide, pigments, and addition agents, mixed with the amines curing agent (e.g., polyamide) in some weight ratio of 100 : 12.89, respectively; alkyd coating is composed of alkyd resin as the main substance of film formation, iron oxide, some anticorrosion pigments and fillers, and simultaneously adding agents, etc; and chlorinated rubber coating is composed of materials such as the chlorinated rubber liquid (10–20 cp) as the main substance of film formation, other modified resin, iron oxide, some pigments, and addition agents. These coatings have been used in seawater to protect the metal against corrosion in practice.

Electrochemical measurements for coatings system coated on metal were performed in aerated artificial seawater (3.5% NaCl solution, weight fraction) at the room temperature (25°C), and the electrochemical cell with three-electrode mode was shown in Figure 1. The carbon steel sheet coated with these different organic coatings including polyurethane, epoxy, alkyd, and chlorinated rubber coatings, was exposed in the tested solution, which was used as the research electrode, a saturated calomel electrode (SCE) as the reference, and platinum sheet as the counter electrode. EG and G Potentiostat/Galvanostat made up of a M273 PARC Potentiostat and a M5210 lock-in amplifier were used. The software employed was Powersuite electrochemical test system. A sinusoidal AC perturbation of 10 mV amplitude coupled with the open circuit potential was applied in the metal/coating system. The EIS test was performed in the tested frequency range from 100 KHz to 10 MHz. The working area of all tested samples is 9.23 cm<sup>2</sup>. All the imped-

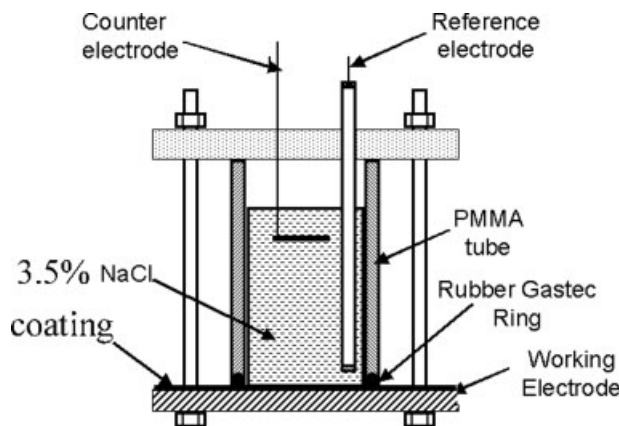


Figure 1 The diagram of used electrochemical test cell.

ance measurements were carried out for three replicate samples of each coating system. After experimental sheets were exposed in the electrolytic cell for 30 min and the open-circuit potential of research electrode reaches a steady value, electrochemical impedance measurement began to be performed.

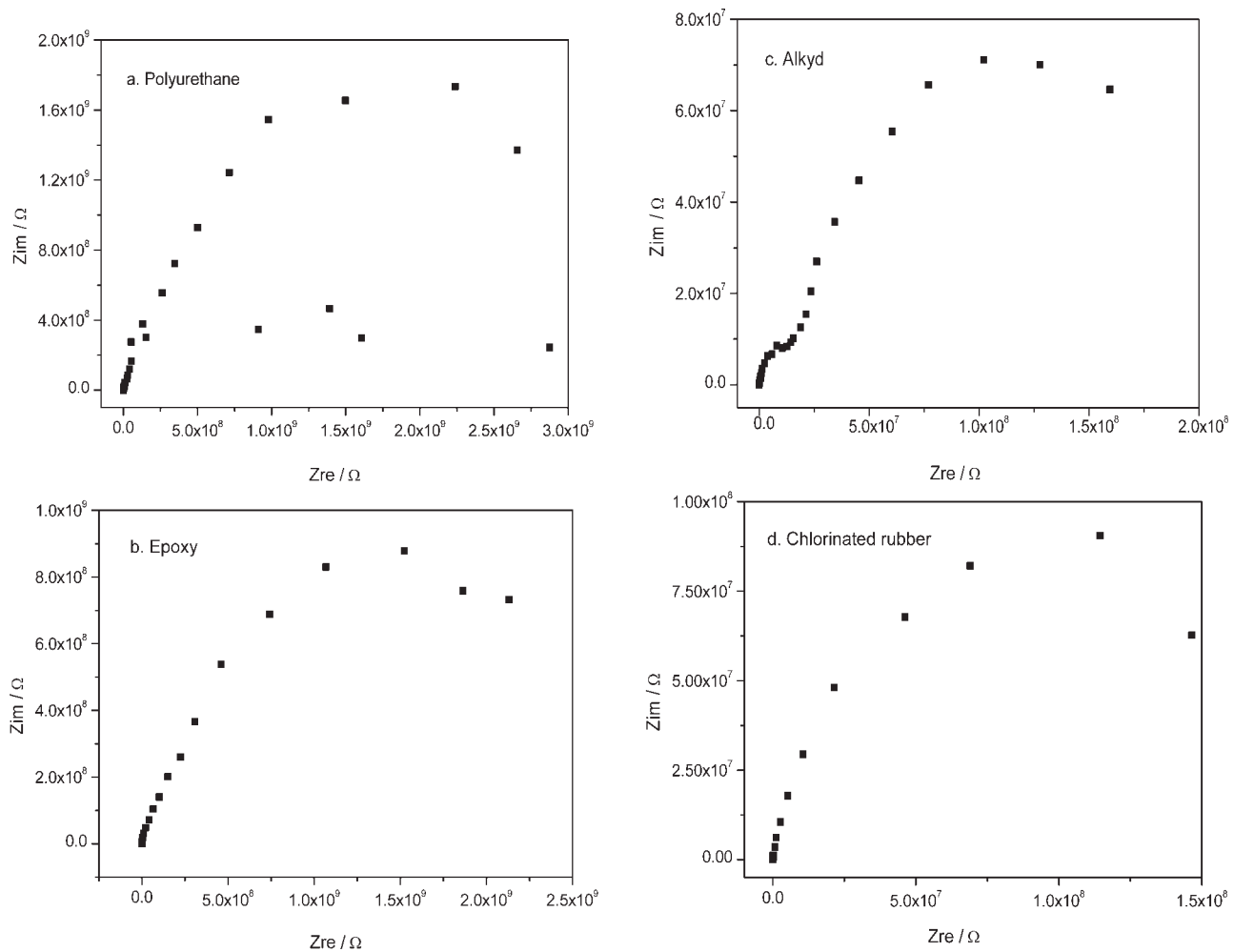
AFM and DMRM/E optical microscope were utilized to examine topography of these tested organic coatings. Experiments were performed with a commercial AFM (Digital Instruments, Nanoscope III) equipped with a J scanning head (125 μm), and Silicon nitride cantilevers (Si<sub>3</sub>N<sub>4</sub>, Tip, V-shape) were used. For the study of polymer coating, cantilevers with the lowest spring constant were preferred (0.12 or 0.06 N/m) to minimize the load force between the tip and sample surface. The surface topography was scanned by monitoring the cantilever deflection.

## EXPERIMENT RESULTS

### EIS Measurement of Various Coatings used in Seawater

To study electrochemical behaviors of various coatings used in seawater, the EIS for carbon steel sheets coated with four organic coatings polyurethane, epoxy, alkyd, and chlorinated rubber coatings in a quiescent aerated 3.5% NaCl aqueous solution at room temperature (25°C) were measured. The tested results were shown in Figure 2.

As shown in Figure 2, during the initial time of immersion, the Nyquist diagram of EIS of polyurethane, epoxy, and chlorinated rubber coatings are same for all. In this figure, one capacitive loop is found which contains phenomenally one time constant. In this case, the coatings act as a pure capacitance, and the coating resistance of each coating is regularly very large with very little coating capacitance, which means that the barrier properties of these painted film toward water are well in seawater medium. The barrier effects for seawater are very important because the presence of an aqueous solu-



**Figure 2** Electrochemical impedance spectroscopy of four coatings tested in seawater (25°C). (a) polyurethane; (b) epoxy; (c) alkyd; (d) chlorinated rubber.

tion in the film can activate the corrosion process or can cause to lose adhesion and blistering.

But, EIS of alkyd coating present two time constants in its EIS [in Fig. 2(c)], and there are two capacitive semicircle arc to be found in the same test condition, compared with other paints. In the Nyquist diagram of EIS with two capacitive loops, the capacitive semicircle in the high frequency range presents barrier layer property, whereas the semicircle in the low frequency range presents under film corrosion reaction of metals. This shows that in short time water and oxygen molecules in seawater already reach the interfacial surface between film and substrate through micropores in the coating and electrochemical reaction of substrate metal may start. It can be suggested that the coating's barrier performance against diffusion of corrosive medium is weak.

Moreover, the tested diameters of impedance semicircle of polyurethane, epoxy, and chlorinated rubber coatings in the high frequency region are much bigger than that of alkyd coating, and the diameter of polyurethane's semicircle, namely coating resist-

ance, is the biggest. The value of impedance is more than  $10^9 \Omega$ ; epoxy and chlorinated rubber coatings take second place, whose values of impedance also reach  $10^8 \Omega$ . Some studies suggested that when tested coating resistance keep in  $10^8$ – $10^9 \Omega \text{ cm}^2$ , the system of metal/organic coating has very well anticorrosion property; when coating resistance is lower than  $10^7 \Omega \text{ cm}^2$ , anticorrosion property of this system has already dropped; once coating resistance is under  $10^6 \Omega \text{ cm}^2$ , barrier ability of coating to water is already very weak, and electrochemical corrosion reaction at interface of coating/metal may take place.<sup>7</sup>

It is clearly known from the tested result that the coating resistance of polyurethane is the maximum and alkyd coating is the minimum for four tested coatings. It is concluded that polyurethane coating in seawater has good anticorrosion property in seawater in the initial time of immersion.

### Microscopic Observation of Topography

To further examine the relationship between their topography and performances of various coatings



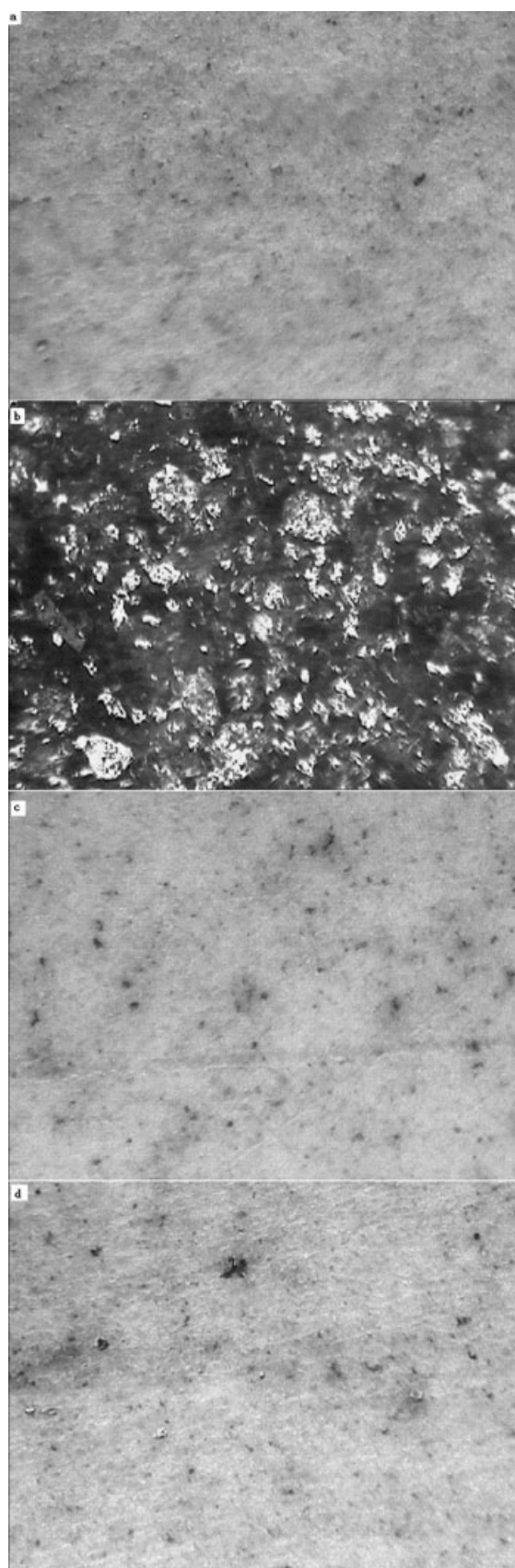
tested in seawater, with the measurements of electrochemical behaviors, microscale observation has also been used to investigate the change of surface morphology, with concomitant changes in the samples because of the sorts of coatings. The images of surface morphology of four coatings are observed by us.

In Figure 3, although the surface morphology of four types of coatings are all relatively flat, uniform, and smooth at their film surface, the appearance features of different layers are different from each other. From the view of the topography, there was readily difference on their surfaces for the different coatings.

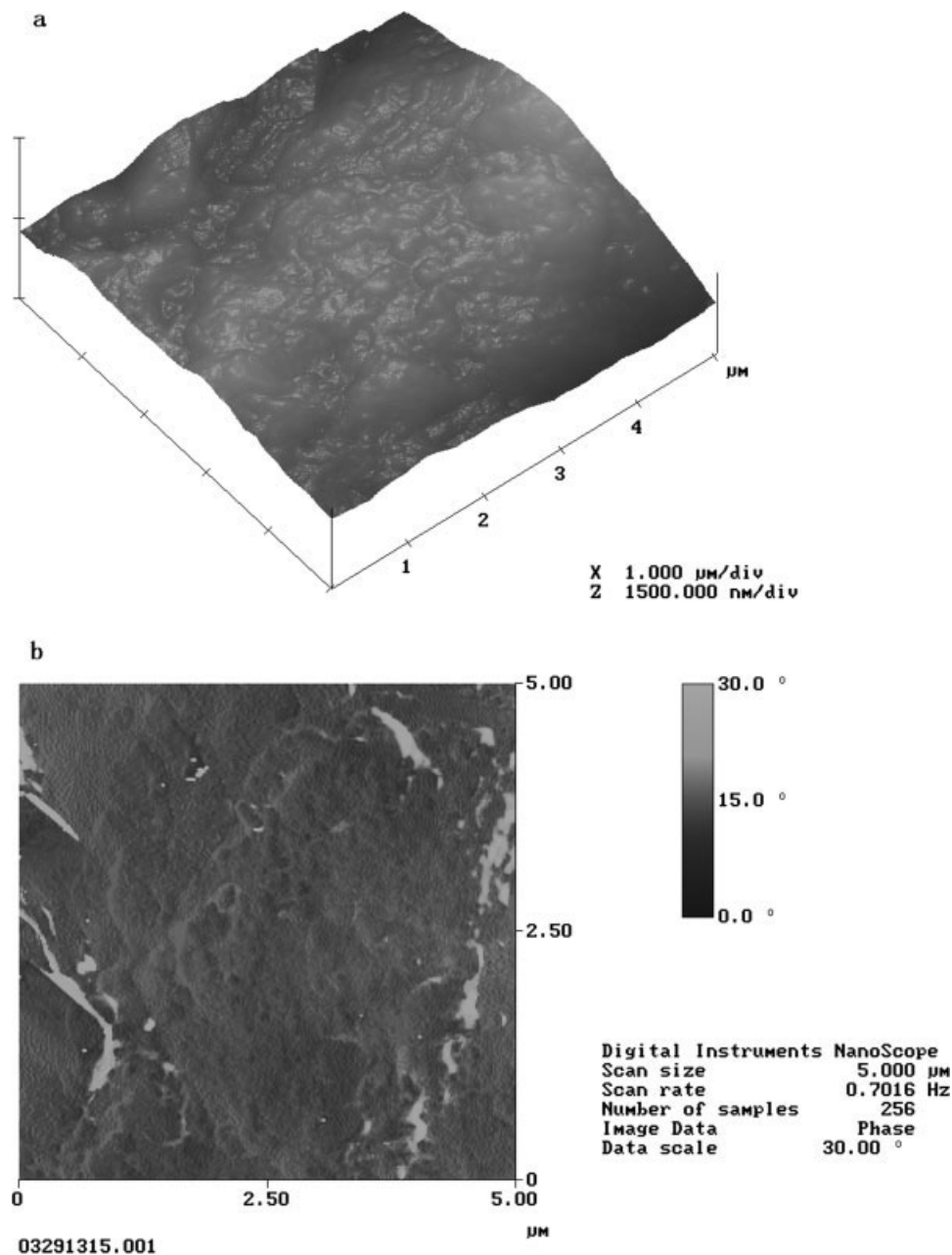
The film of Polyurethane paint coated on metal is continuous and more compact than other layers, and there are no visible voids on the background [Fig. 3(a)]; In the image of epoxy layer, its surface layer is relative rough and not flat [Fig. 3(b)], because it contains a lot of pigments exposed at the coating surface. The pigments are slice-like ferric oxide which uniformly dispersed at the surface of epoxy film. Some ferric oxide pigment is uncovered, at which points the pigment is overturned, enveloped, and visually noticeable. At this condition, however, the coating containing such a pigment, still displays very good protection against corrosion. For alkyd coating film imaged, the surface of the layer is more flat and compact, but there are many visible pits on the background, and some porosity is still big [Fig. 3(c)]. Chlorinated rubber film also has some voids at its surface [Fig. 3(d)], although its pit numbers are less than that of alkyd coating, one or two pits are the biggest for all tested coatings, which would result in degradation of the coating. This is in agreement with results obtained from electrochemical measurements earlier. When this coated coating became permeable to water, water could reach the metal substrate though the primer coating without difficulty.

#### AFM Images of Coating Surface

AFM has also been used to further detail surface topography of organic coatings and characterization of metal-coating interface, which is crucial to the understanding and prediction of the performance of corrosion protective coating.<sup>6</sup> This technique allows us to clearly examine the topography of samples and provide microscale information not available by other methods. In this work, AFM method was used to examine the surface morphology of different organic coating in parallel with optical microscopic observation and to image the surface features of these tested coating. The AFM images of these samples, such as polyurethane, alkyd, chlorinated rubber, and epoxy coating, are captured. Figures 4–7 show 3D projections of AFM images of these coatings, and the resolution is noted on each figure.



**Figure 3** Optical photos of four types of coating with electrochemical measurements ( $\times 640$ ). (a) polyurethane; (b) epoxy; (c) alkyd; (d) chlorinated rubber.



**Figure 4** AFM image of polyurethane, (a) in height (5  $\mu\text{m}$ ); (b) in phase (5  $\mu\text{m}$ ).

The roughness and porous nature of these coatings is shown in both type of images. At the view of height images obtained in these experiments, it can be seen that surface morphology of different coatings differs from each other. Film of alkyd coating is rougher and rougher, porous, and there is much relative height changes of coating with respect to background, but the absolute changes are so small that they are not observed by the above optical microscopy tests. The porosity of alkyd coating represents reactive points where the degradation of the film immersed in seawater began firstly. While other coating systems, such as polyurethane, epoxy, and chlorinated rubber coating, which are also pigmented, show no such roughness, without any signifi-

cant blister formation observed. Therefore, they are a good barrier to the permeation of liquids even though the AFM tip cannot detect nanoscopic pathways in these films that might exist.

In phase images recorded by AFM, the dispersion of two phases of soft and hard in polyurethane layer is not uniform. The hard phase, namely light segments in this image, may be pigments or fillers used in polyurethane coating. Although the pigments and fillers assemble together rather than isolated covering, the film formation is still continuous, without intrinsic defects which are not accessible to microscopy and can lead to electrolytic pathway in the film. This shows that the layer of polyurethane coating has

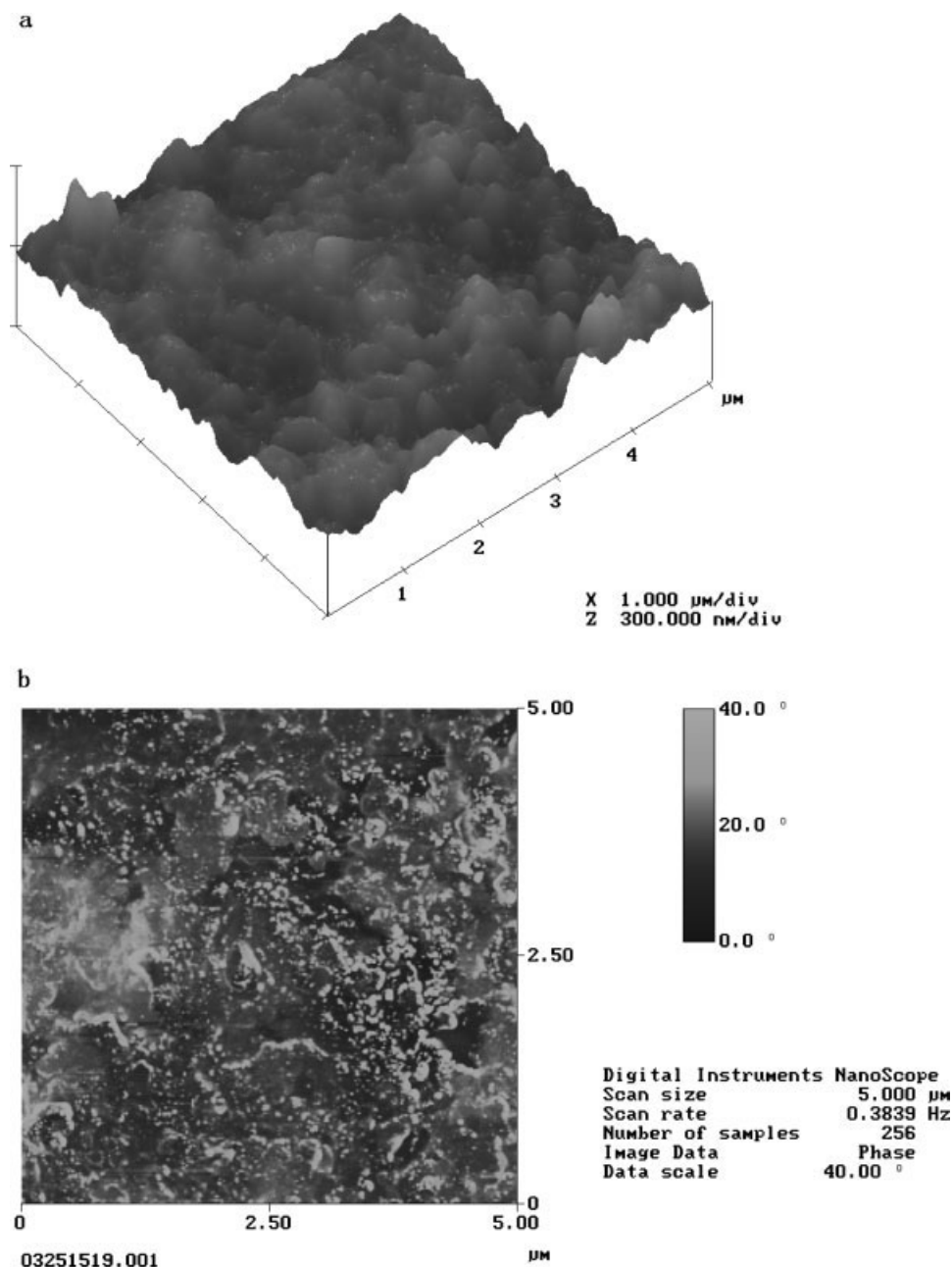


Figure 5 AFM image of alkyd, (a) in height (5  $\mu\text{m}$ ); (b) in phase (5  $\mu\text{m}$ ).

chemical stability. Compared with polyurethane coating, the ration of these two phases of alkyd and chlorinated rubber is almost equal each other. The dispersion of two phases is also uniform for these coatings. Moreover, the two phases of epoxy coating are very clear and noticeable visually, at the point which the separated hard phase surrounding epoxy looked somewhat better than other coatings. The hard sections all present the slice-shaped, which shows that pigment in epoxy layer is very uniform and fine.

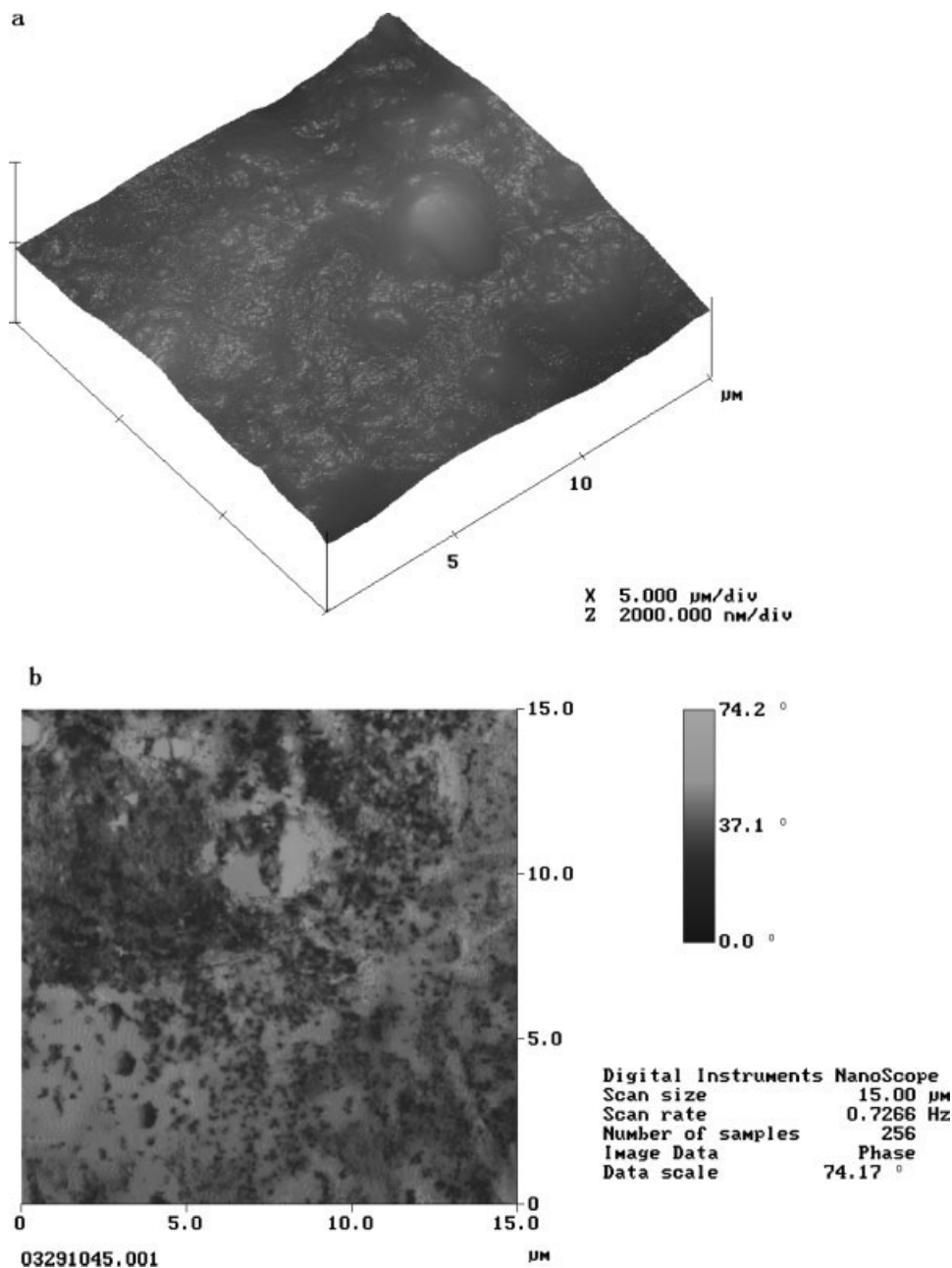
It is obvious that the flat and smooth degree of coating surface, in parallel with dispersion of soft and hard phase, is one of the most important factors which affect the performance of heavy duty anticorrosive coatings

against corrosion. Polyurethane coating is a better barrier of water and other ions than other tested coatings, because the polyurethane coating is continuous but it has somewhat visible voids. As proved, the polyurethane coating has the maximum coating resistance in the above electrochemical measurements.

## DISCUSSION

### Establish of reaction models for tested EIS of Coatings

In Figure 2(a,b,d), it is noted that the feature of EIS for polyurethane, epoxy, and chlorinated rubber coatings used in seawater represent single capacitive



**Figure 6** AFM image of chlorinated rubber, (a) in height (5 μm); (b) in phase (5 μm).

semicircle. To further study the failure of these organic coatings and dynamic processes of under film corrosion of metal, the type of EIS, which have such shape of EIS, can be explained by using the equivalent circuit model<sup>18</sup> shown in Figure 8(a), where,  $R_s$  is the solution resistance;  $C_c$  is coating capacitance;  $R_c$  is coating resistance. Fitting results of experimental data employed the model are shown in Figure 9(a,b,d). In this case, capacitive value being very small and coating resistance value being large, the coating acts as a pure capacitance. The reason for that interest lies on the fact that the capacitance of the coating is sensitive to the penetration of water. This shows that these coatings, during this period,

have good barrier ability, and seawater has not reached the interface of coating/metal. Following water uptake in the painted film with increase of immersion time, the impedance spectrum starts to deviate from the fully capacitive behavior and a resistive behavior is visible at low frequencies, which means that the coating resistance regularly decreases and the coating capacitance increases as a consequence of water uptake in the painted film, after a short time of exposure. These results indicate that the electrochemical reaction of coated metal in seawater is mainly controlled by diffusion process of water through the coating layer. The ability of anti-corrosion performance of marine coatings can be



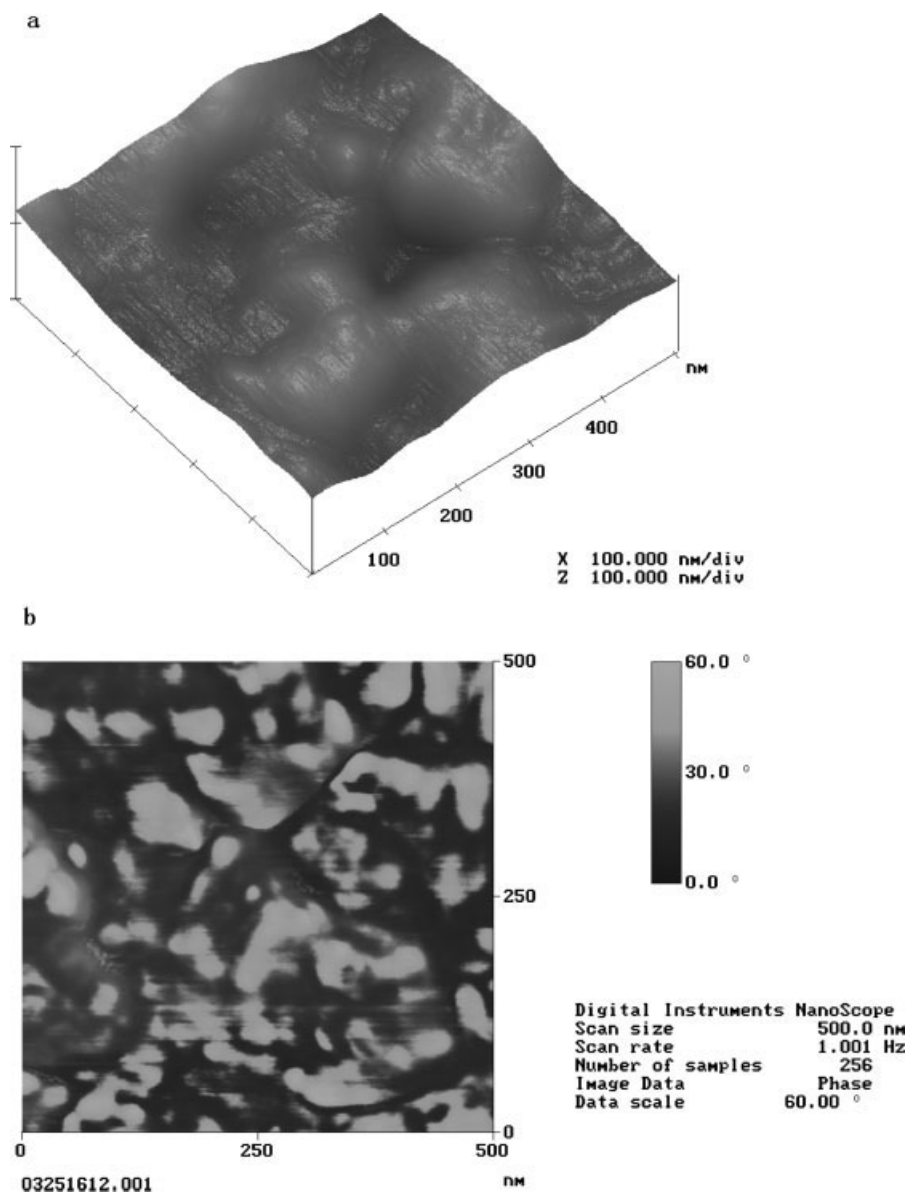


Figure 7 AFM image of epoxy, (a) in height (0.5  $\mu\text{m}$ ); (b) in of phase (0.5  $\mu\text{m}$ ).

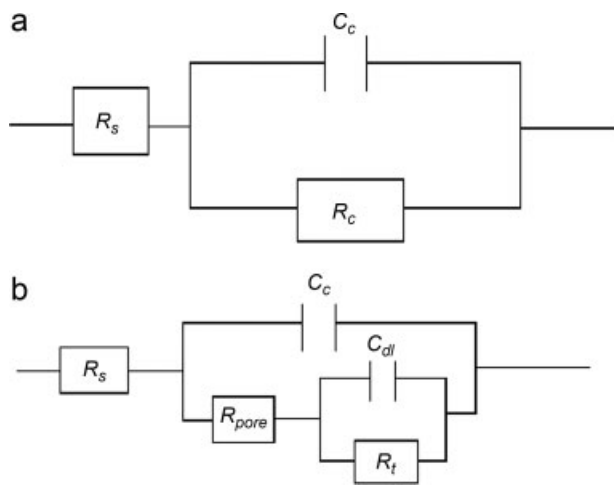
represented by coating resistance, namely the diameter of measured the capacitive loop, in EIS, and it is true that the bigger coating resistance is, the better protection property of coatings are.

From these tested results, we can conclude that polyurethane, epoxy, and chlorinated rubber coatings used in seawater have good protection effects for substrate metal. Meanwhile, the barrier performance against seawater of the polyurethane is best, and epoxy is better; chlorinated rubber coating is worst.

The EIS feature of alkyd coating in seawater is double capacitive loops, whose equivalent circuit model 2<sup>9</sup> is shown in Figure 8(b) where  $R_s$ , Solution resistance;  $C_c$ , Coating capacitance;  $R_{\text{pore}}$ , Coating film resistance;  $C_{dl}$ , double electrical layer capacitance of metal/coating interface;  $R_{ct}$ , double electri-

cal layer resistance of metal/coating interface. Fitting results are shown in Figure 9(c). For this type of EIS, the capacitive impedance in the high frequency range represents for coating performance; and the capacitive impedance for corrosion processes of the under film metal. In Figure 2(c), it is can be seen that the capacitive loop in the low frequency range representing electrochemical reaction is found, and this coating impedance is associated with the electrochemical reaction impedance. This measured results show that, in this case, the electrochemical reaction process has may become a control procedure for corrosion of metal covered with alkyd, and alkyd coating already lose its barrier effects against seawater for very shortly immersion time. Considering water and oxygen molecules can easily reach the substrate surface of coated metal through micropores in the



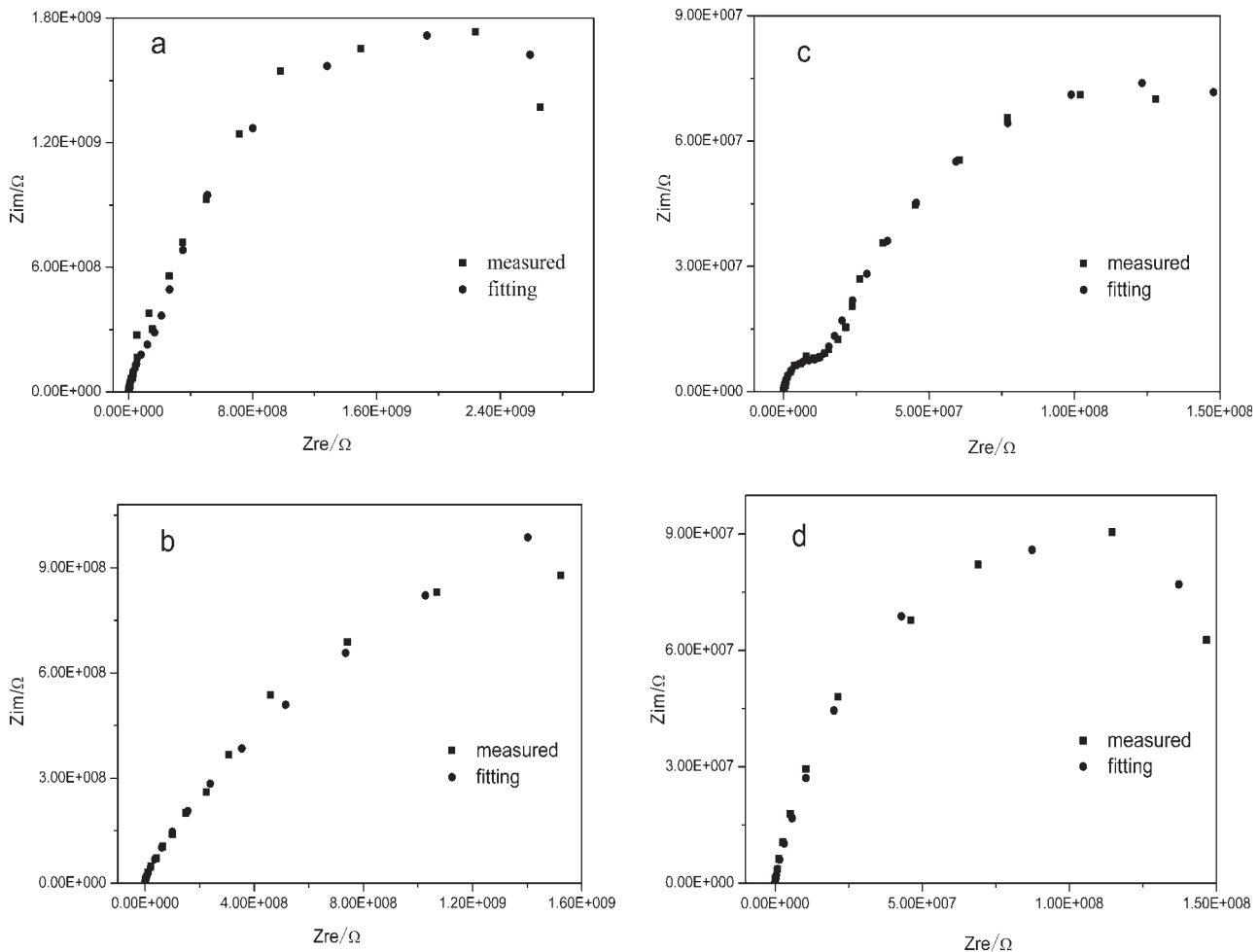


**Figure 8** EIS equivalent circuits of coated carbon steel in seawater (a) model 1; (b) model 2.

coating film found in Figures 3(c) and 5, alkyd coating performance in seawater is weak when compared with other tested coatings in this work.

### Effect of Coating Composition and Structure on Performance

To coating materials, the microdefects are unavoidable for many reasons.<sup>10</sup> These coating defects may be from the volatilization of solvents, or voids in film structure as well as porosity induced by various pigments and fillers, as found in Figures 3–7. Because of formation of these defects occurred in coating film, water, oxygen, and salts can enter into film of coatings to cause heavy degradation of coatings in seawater. When those corrosive medium penetrate to the interface of coating/metal through coatings, electrochemical corrosion of under film metal occur and it causes the coating delaminating. Two effects of these would induce performance of coatings to drop largely. This may explain why the alkyd coating has not good protection property in seawater. Nemeth et al.<sup>11</sup> studied transfer of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  through various organic layers using radioactive isotope method, and he proved that two types of these ions can reach the interface of coating/metal by diffusion.



**Figure 9** Comparison between measured impedance data and fitting data according two equivalent circuit models, (a) polyurethane; (b) epoxy; (c) alkyd; (d) chlorinated rubber.

Pigments and fillers which are enriched in organic film surface and benefit to drop permeability can block the permeability of coatings film, as found in Figure 7(b). Funke<sup>12</sup> investigated effects of pigment sizes on permeability of coated film, and thought that pigment sizes have strong influence on performance of coatings, with slice-like pigment causing diffusion pathway in the film to prolong for water, which induces the permeability of layers rapidly low. However, Christophe et al.,<sup>13</sup> in their work studied the effect of a variety of pigments on degradation for coatings by electrochemical impedance method, found that the additional pigment increase in some degree porosity in the organic layers, but only passivation pigments can promote the antipermeable performance.

Some authors thought that epoxy layer coated on metal comes into being a bodily form structure in the film, after the line type epoxy resin reacts with various curing agents. Moreover, the symmetry of epoxy molecule chains in the film causes good chains assemble and resin crystal, which greatly block water to penetrate, although epoxy is high polar film formation and its barrier effect against water lower than other coatings tested.<sup>14</sup>

It can be concluded from these tests above that physical and chemical structures, as well as pigments and fillers, have great effects on property of heavy duty anticorrosive paints. It is possible to further investigate degradation processes of organic coatings in brine and under film corrosion of substrate metals, by studying the effects of a variety of film formation, pigments, and fillers on anticorrosion behaviors with the above methods of electrochemical impedance and examination of topography.

### CONCLUSIONS

1. Polyurethane, epoxy, and chlorinated rubber coatings all present one capacitive loop in their EIS which contains phenomenally only one time constant, and alkyd coating presents two capacitive semicircle arcs. With two capacitive loops, the capacitive semicircle in the high frequency range represents barrier layer property, but the semicircle in the low frequency range represents under film corrosion reaction of metals.
2. It is clearly known from the tested result that the coating resistance of polyurethane is the maximum and alkyd coating is the minimum for these four tested coatings. From these tested results, we can conclude that polyurethane, epoxy, and chlorinated rubber coatings used in seawater have well anticorrosion property in seawater immersion test. Meanwhile, the barrier performance against seawater of the polyurethane is the best; epoxy is second; chlorinated rubber coating is third; and alkyd coating is the weakest.
3. The topography features of different layers are visible different between different layers of tested coatings at their surface topography. The film quality of polyurethane paint coated on metal is better than other layers, and imaged film of alkyd coating has many pits at its surface. AFM photos imaged have also been used to further detail surface topography for four organic coatings, and to approve effects of topography of these coatings on its electrochemical behaviors, from two views of both height and phase modes.

### References

1. Chang, T. C.; Chiu, Y. S.; Chen, H. B.; Ho, S. Y. *Polym Degrad Stab* 1995, 47, 375.
2. Wieczorrek, W. *J Elastomers Plast* 1986, 18, 9.
3. Zhang, S.; Xiao, Y. *Mater Dev Appl* 1993, 8, 15.
4. Bonora, P. L.; Deflorian, F.; Fedrizzi, L. *Electrochim Acta* 1996, 41, 1073.
5. Marchebois, H.; Savall, C.; Bernard, J.; Touzain, S. *Electrochimica Acta* 2004, 49, 2945.
6. Bierwagen, G. P.; Rebecca, T.; Chen, G.; Tallman, D. E. *Prog Org Coat* 1997, 32, 25.
7. Scantlebury, J. D.; Galic, K. *Prog Org Coat* 1997, 31, 201.
8. Deflorian, F.; Fedrizzi, L.; Rossi, S.; Bonora, P. L. *Electrochim Acta* 1999, 44, 4243.
9. Liu, H.; Xu, G.; Song, G.; Lin, H.; Chao, C. *J Chin Soc Corros Protect* 1998, 18, 52.
10. Xu, Y.; Yan, C.; Gao, Y.; Cao, C. *J Chin Soc Corros Protect* 2002, 22, 249.
11. Nemeth, Z.; Erdei, L.; Kolics, A. *Corros Sci* 1995, 37, 1163.
12. Funke, W. *J Coat Technol* 1983, 55, 31.
13. Christophe, L. P.; Colette, L.; Nadine, P. *Prog Org Coat* 2000, 39, 167.
14. Liu, Z.; Wu, F. *Paints Appl* 1996, 27, 27.