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Electrochemical behavior of organic and inorganic zinc-rich coatings in 3.5% NaCl solution①

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Abstract: Performance comparisons between organic and inorganic zinc-rich paints (ZRPs) were carried out. Electrochemical impedance spectroscopy (EIS) measurements were used to assess the corrosion prevention performance of the ZRP coatings. The results show that during the cathodic protection period the potentials of the epoxy systems are less negative than those of the silicate system. For the zinc-rich ethyl silicate paints, the initial values of the resistance through the binder and the charge transfer resistance associated with zinc dissolution are several orders of magnitude lower than those of the organic zinc paints, while the initial values of the capacitance due to the binder layer between Zn dust and the double layer capacitance for zinc dissolution are several orders of magnitude higher than those of the organic zinc paints. Furthermore, the deterioration with time of capability of the zinc particles in the paint to provide cathodic protection to the steel was interpreted.

Key words: zinc-rich paints; epoxy; ethyl silicate; electrochemical impedance spectroscopy; cathodic protection
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1 INTRODUCTION

Zinc-rich coatings (ZRP) have been used for many years in order to protect steel effectively in aggressive atmospheres, mainly in marine and industrial environments, against corrosion.

It is commonly accepted that two fundamental protection mechanisms operate in ZRP[1-3]: 1) the galvanic protection stage, which requires good electrical contact among the zinc particles themselves as well as between them and the steel substrate; 2) the barrier-like behavior stage, which is reinforced by the amount and nature of zinc corrosion products leading to promotion of the stable formation of dielectric surface films. The protection mechanism of this type of paint is based on the galvanic action between the zinc particles in the paint and steel substrate[1-3]. Because of that, ZRP is able to prevent steel from corrosion even when small damages or pores occur in the film. This aspect differentiates ZRP from traditional barrier coatings. From an anticorrosive point of view, the electronic conduction between the zinc particles and the steel substrate is the principal characteristic of this paint.

EIS has been applied in the study of ZRP for some time. The two capacitive loops usually obtained from these paints in saline solutions (e.g. 3% sodium chloride (NaCl)) have been interpreted by means of simple Randles circuit consisting of resistance and parallel capacitance. Many studies concluded that the time constant at low frequency is related to the charge transfer for zinc dissolution, whereas the high-frequency range shows the dielectric properties of the polymer matrix[4-11].

The commercial ZRP currently employed includes organic and inorganic binders. It should be noted that performance comparisons between organic and inorganic primers have received scare attention.

The aim of the present work is to gain deeper insight on the corrosion protection mechanism of both organic and inorganic primers in saline solution.

2 EXPERIMENTAL

Mild steel specimens were abrasived by emery paper to white metal and degreased. ZRP (about 35 μm) was applied over mild steel. Organic zinc-rich paints and inorganic zinc-rich paints were formulated with epoxy-polyamide and ethyl silicate, respectively. The electrochemical measurements on the coated mild steel were made using a three-electrode cell in which the sample was placed horizontally. A Perspex cylinder was fixed on the sample and filled with solution.

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The exposed area was 13 cm^2. A graphite counter electrode and a saturated calomel electrode (SCE) completed the arrangement. All measurements were made in 3.5% (mass fraction) NaCl solution at ambient temperature (about 20 ℃). The impedance measurements were made using an EG&G model 273 potentiostat and a model 5210 lock-in amplifier. A sine wave of 20 mV was applied across the cell. Impedance data were collected over a frequency range from 3 mHz to 120 kHz.

3 RESULTS AND DISCUSSION

3.1 Variation of corrosion potential with immersion time

Fig. 1 presents the evolution of corrosion potential of the tested ZRP samples with immersion time. Generally, after immersion of the coated plates in the electrolyte, the corrosion potential, φ_{corr}, changes (Fig. 1) gradually from an initial potential value of -1.02~-0.95 V (vs SCE) to more positive values reaching a common level that lies intermediate between zinc and steel corrosion potentials in seawater. The stationary values of $\varphi_{corr} \cong (-0.60 \pm 0.06)$ V attained after 1 000 h to 1 300 h of immersion correspond to a situation in which the zinc galvanic action is probably suppressed due to the partial stabilization of corrosion products on the pigment surface. It should be noted that within 1 h the trend of φ_{corr} of organic ZRP is clearly different from that of inorganic ZRP. At the start of this period, φ_{corr} of organic ZRP shifts to positive value due to the activation rate of zinc is slower than the wetting rate of steel. Later, the active steel surface does not increase any more because it is completely wetted. However, new zinc particles having thicker native oxide layers continue to activate and cause the Zn/Fe area ratio to increase, hence the potential of the galvanic couple shifts to cathodic values[9-11]. While in the case of the silicate system, the initial increase of φ_{corr} does not occur.

Because inorganic ZRP have much higher porosity than organic ZRP, the wetting of steel in inorganic ZRP system is much quicker than that in organic ZRP system and it is also quicker than the activation of zinc in inorganic ZRP systems. In the inorganic ZRP systems, the nonexistence of the initial increase of φ_{corr} may be due to the higher conductivity of the ZRP and the stronger adhesive bond of inorganic zinc silicate films to the steel substrate. There is a chemical bond between silicic acid of the binder and iron on the substrate, which is analogous to that occurring on the zinc dust surface[12].

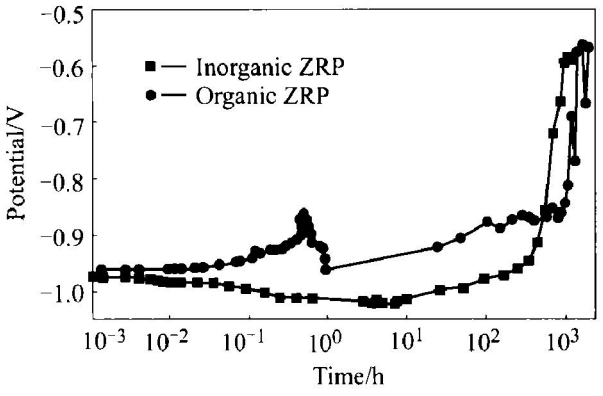

Fig. 1 Evolution of corrosion potential in ZRP coating systems

A widely applicable empirical criterion for steel cathodic protection is to ensure a minimal negative value of -0.78 V (vs SCE)[13]. It can be seen from Fig. 1 that, φ_{corr} changes fast around -0.78 V. In the present study, the time during which the painted steel exhibits more negative potentials than -0.78 V in the 3.5% NaCl immersion test is used for quantifying the ability of ZRP coatings to provide cathodic protection. Fig. 1 indicates that the potentials developed by the epoxy systems are approximately 100 mV less negative than those developed in the silicate system. This might be explained by suggesting that in the epoxy system, a compound of the binder, probably the polyamide is acting as a slight inhibitor for the zinc anodic process[14]. In the case of silicate system, this does not occur.

The gradual shift of φ_{corr} to more positive potentials with prolonging immersion time reveals the progressive loss in galvanic protection effect of ZRP. Thus, over long exposure time φ_{corr} reaches a typical value corresponding to the corrosion potential of steel in saline solution.

3.2 Electrochemical impedance spectra and evolution of ZRP coatings

During the studied life time of ZRP only one type of impedance spectra is found. The typical impedance spectrum is shown in Fig. 2, where only two time constants are observed. The equivalent circuit used for simulations is presented in Fig 3.

The plots in Fig. 4 show the dependence of R_1, C_1, R_2 and C_2 on the type of binder in the ZRP. For the zinc-rich ethyl silicate paints (Fig. 4), the initial values of R_1 and R_2 are several orders of magnitude lower than those for the organic zinc-rich paints, while the initial values of C_1 and C_2 are several orders of magnitude higher than those for the organic zinc paints. Pigment particles exhibit a higher tendency to corrode in the inorganic zinc paints than in the epoxy coatings, which is consistent with a great deal of gas evolution viewed even by visual observation (in the case of epoxy coatings, it is delicate). The gas can be H_2, which is given out by the following reactions[15]:

$$Zn + H_2O + CO_2 \rightarrow ZnCO_3 + H_2$$

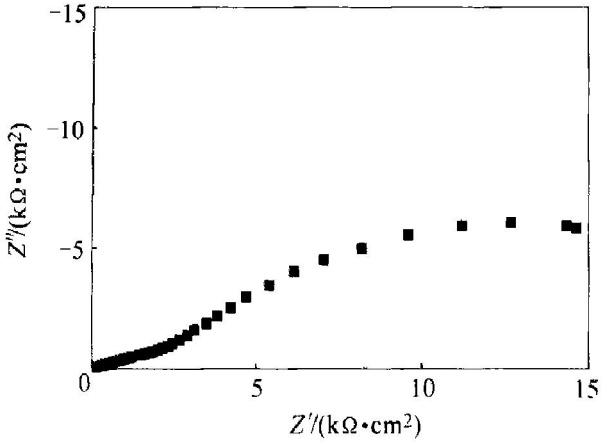

Fig. 2 Typical Nyquist plots for ZRP samples

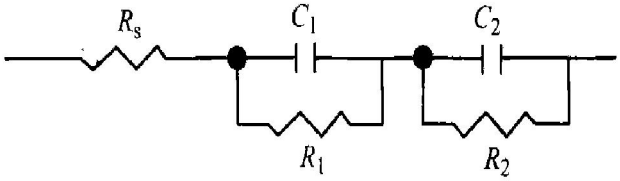

Fig. 3 Equivalent circuit for ZRP coating systems

R_s —Ohmic resistance of solution nearby ZRP sample;
R_1 —Resistance through the binder;
C_1 —Capacitance due to the binder layer between Zn dust* ;
R_2 —Charge transfer resistance associated with zinc dissolution;
C_2 —Double layer capacitance for zinc dissolution* ;
* —C_1 and C_2 are constant phase element

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2$$

$$2Zn + 2NaCl + 3H_2O \rightarrow ZnOZnCl_2 + 2NaOH + 2H_2$$

This is due to the fact that the ethyl silicate ZRP has larger porosity values and higher pigment reactivity.

For the zinc-rich ethyl silicate paints, the initial increase in R_2 values corresponds to reactivity decrease as a consequence of the loss in electrical conductivity between zinc dust and the substrate. Additionally, the accumulation of corrosion products promotes the barrier layer-like behavior. That the interfacial capacitance (C_2) decrease with time suggests the sealing effect of the corrosion products on the pores of zinc and a decrease of the real surface of the electrode.

The increase in the coating resistance (R_1) of the inorganic ZRP with immersion time may be attributed to a rise in the ohmic resistance of the coating due to the incorporation into the coating of insoluble and protective zinc corrosion products and an increase in the average thickness of the insulating layer on the zinc particles electrically connected to the base steel. At the same time, there is a drop in the value of the electric capacitance of the coating (C_1).

Taking into account of all these considerations, the evolution of the barrier effect of ZRP should appear on the impedance diagram both in the higher frequency region and in the low frequency region.

Generally, R_1 and R_2 of the inorganic ZRP tend to increase with time, but this trend may be inverted after sufficiently long periods of immersion. It is probably because the effect of progressive deterioration of the coating with the opening and widening of new channels eventually prevails over the blocking effect of base steel and zinc particles by the corrosion products.

Compared with the zinc-rich ethyl silicate coatings, zinc-rich epoxy coatings exhibit lower C_2 values and higher R_2 values (Fig. 4), which demonstrates that the activation of zinc particles of organic ZRP is more difficult than that of inorganic ZRP.

On the other hand, the better dielectric performance observed for organic ZRP, i. e. low C_1 values and higher R_1 values, indicates that the coating with organic ZRP behaves as lower water uptake. Thus, the coating composition delays water penetration, which is necessary to complete the electrical circuit for the cathodic protection action and its associated Fradaic process.

Arbeu[11] introduced the contact impedance (Z_m) among zinc particles to explain the behavior observed in the high-frequency range of the impedance spectrum. It was found that the contact capacitance (C_m) values among zinc particles was several orders of magnitude higher than the capacitance values corresponding to the dielectric properties of the epoxy binder. Hence, it was confirmed that the time constant in the high-frequency range of the impedance spectrum could be attributed to Z_m. But this experiment shows that for the organic ZRP the dielectric properties of the epoxy binder can not be ignored. The initial values of R_1 are obviously higher than the end values, while the initial Z_m values are obviously smaller than the end values. The great difference of the initial values of R_1 and C_1 between organic ZRP and inorganic ZRP can not be explained by Z_m exclusively. At the same time, considering the great difference of the initial values of R_2 and C_2 between them, the great behavior differences between organic ZRP and inorganic ZRP are attributed to the three factors: the dielectric properties of coating, the activation of zinc dust and the barrier effect of corrosion product of zinc.

At the start of immersion, because of the enwrap of epoxy binder, the activation of zinc dust in organic ZRP is much slower than that of inorganic ZRP , which causes higher values of R_1 and R_2 and

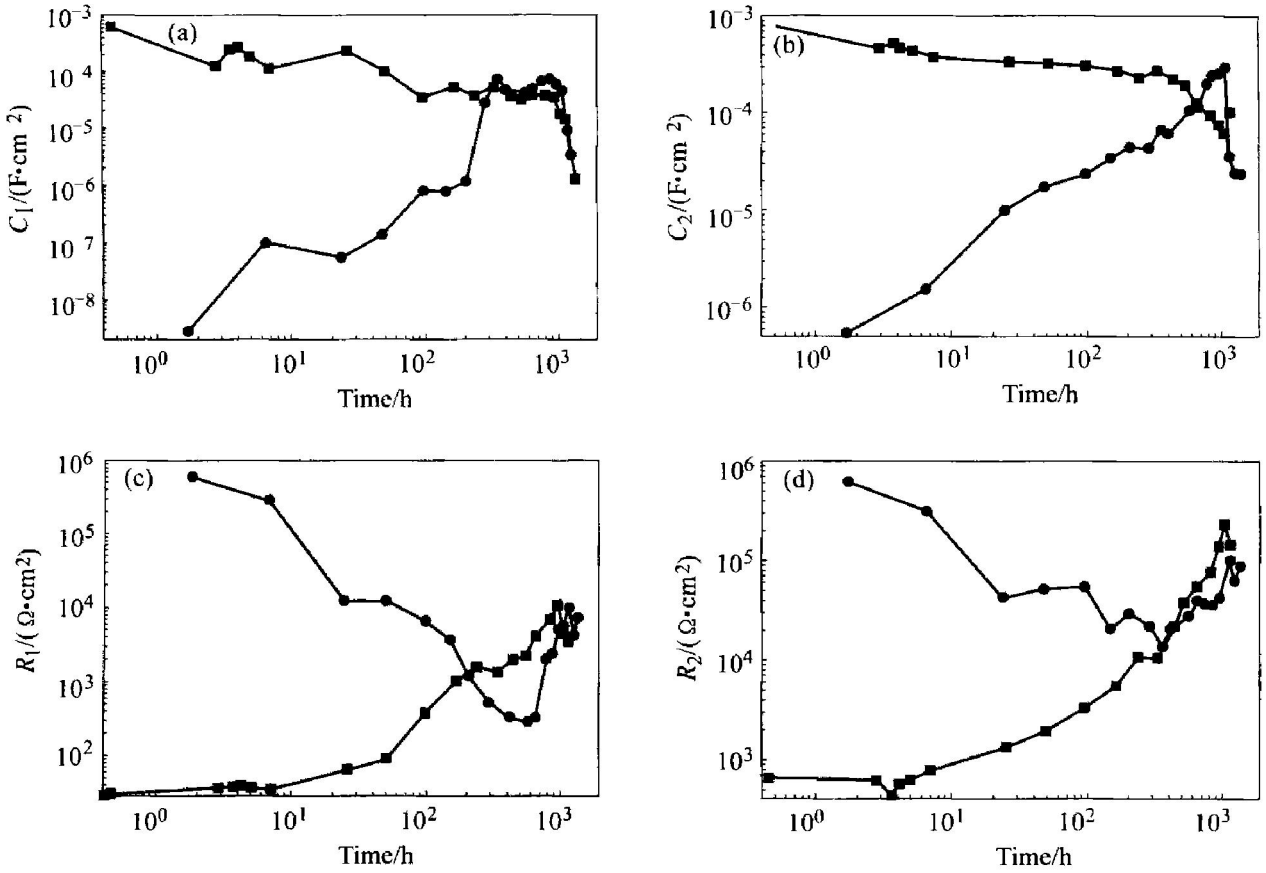

Fig. 4 Evolution of model parameters of ZRP coatings with time
■—Inorganic ZRP; ●—Organic ZRP

lower values of C_1 and C_2. Then with the gradual fading of polymer caused by the ingress of water, oxygen and other corrosive ions through the paint film and the swelling of zinc dust, C_1 increases fast while R_1 decreases dramatically. At the same time, new zinc particles having thicker native oxide layers continue to activate, and cause the Zn/Fe area ratio to increase, hence C_2 increases fast while R_2 decreases dramatically.

The above discussions on silicate-type ZRP coatings have shown that the insoluble corrosion products formed at the base of pores and perforations in the film lead to the appearance of barrier effect. Similarly, in the case of epoxy-type ZRP coatings, it is reasonable to think that the progressive formation and accumulation of insoluble zinc corrosion products within the porous coating favor the increase of R_1 and R_2 observed after about 500 h (Fig. 4).

After going into the barrier effect period, the values of the four equivalent circuit parameters of the two kinds of ZRP become close. This indicates that the epoxy binder has minor effect at this period.

3.3 Explanation for φ_{corr} evolution

For a quantitative analysis, though simplified, one can suppose that the microscopic behavior is characterized by a fully uniform distribution of potential on anodes and cathodes[16]. This is an extreme case considered by several authors in their studies of galvanic corrosion. Under the additional assumptions of a linear polarization and negligible ohmic effects, the following expression can be readily derived, which gives a rough idea of how φ_{corr} depends on the S_a/S_c area ratio and $R_{p,c}/R_{p,a}$ polarization resistance ratio:

$$\varphi_{corr}=[\varphi_c+\varphi_a\times(S_a/S_c)\times(R_{p,c}/R_{p,a})]/[1+(S_a/S_c)\times(R_{p,c}/R_{p,a})] \quad (1)$$

where φ_a and φ_c are open-circuit potentials of anode and cathode; S_a and S_c are anode and cathode areas; $R_{p,c}$ and $R_{p,a}$ are anode and cathode polarization resistance. Rearrange Eqn. (1), thus:

$$\varphi_{corr}=(\varphi_c-\varphi_a)/[1+(S_a/S_c)\times(R_{p,c}/R_{p,a})]+\varphi_a \quad (2)$$

During the cathode protect period, the $R_{p,a}$ of organic ZRP are several orders of magnitude higher than those of the inorganic zinc paints. For the epoxy ZRP system, $R_{p,a}$ and $R_{p,c}$ are influenced by the porosity of ZRP. It can be postulated that there are two diffusion layers: one outside ZRP which is estimated to be 50 μm and another through ZRP, whose thickness is about 35 μm. Because the former layers of both organic ZRP and inorganic ZRP are almost the same, the influence of porosity on $R_{p,a}$ is greater than on $R_{p,c}$. In addition, the $R_{p,a}$ of organic ZRP is also increased by the more difficult activation and the hinder of epoxy binder. As a result, the difference of $R_{p,c}$ between two types of ZRP may be smaller than

that of $R_{p,a}$. Considering the S_a/S_c values of organic ZRP may be smaller than those of inorganic ZRP, the fact that the potentials developed by the epoxy systems are approximately 100 mV less negative than the silicate system can be explained by applying these values to Eqn. (2).

Subsequently, with increasing exposure time, the shift of φ_{corr} in the noble direction will be caused by the growing role of S_c. For the later stages of coating degradation, the S_a and S_c areas may not differ too much from each other and smaller value of the expression $(S_a/S_c) \times (R_{p,c}/R_{p,a})$ is to be expected. Substituting these values in Eqn. (2), the resulting values of φ_{corr} will approach that of steel.

From the discussion above mentioned, the parameters derived from EIS data correlate well with the values of φ_{corr} while they vary coherently with time.

4 CONCLUSIONS

Because the porosity of the silicate-type ZRP coatings is quite higher than that of the epoxy-type ZRP coatings, the diffusions of water, oxygen and other corrosive ions through the paint film and the activation of zinc dust are easier for the former type of paints. Considering the polarization effect of epoxy binder, it can be explained that in the beginning of immersion: 1) the potential developed by the epoxy systems is approximately 100mV less negative than the silicate system; 2) for the zinc-rich ethyl silicate paints, the initial values of R_1 and R_2 are several orders of magnitude lower than those for the organic zinc paints, while the initial values of C_1 and C_2 are several orders of magnitude higher than those for the organic zinc paints.

For the zinc-rich ethyl silicate paints the values of diffusion coefficient of water, oxygen and other corrosive ions through the paint film decrease when the corrosion products block the coating pores. At the same time, the accumulation of corrosion products increase the contact impedance between zinc particles. These changes are responsible for the changes of equivalent circuit parameters observed with time increasing: R_1 and R_2 increase, while C_1 and C_2 decrease. In the case of organic ZRP, the dielectric properties of coating and the activation of zinc dust must be taken into account. After going into the barrier effect period, the values of the four equivalent circuit parameters of two kinds of ZRP become closer.

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