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Abstract :   The epoxy coatings on A3 steel sheets containing calcite or aluminum triphosphate (AlTP) , were investigated by Electrochemical Impedance Spectroscopy (EIS). The results showed that calcite pigment is not an inhibitor , but an extender pigment , and that AlTP pigment can considerably enhance the protective performance of epoxy coating. The triphosphate ion at the interface between the steel substrate and the coating can complex with the corrosion-product , such as ferric and ferrous ions , and form a compact protective film which effectively separates the steel substrate from the aggressive media.

Key words :   Electrochemical impedance spectroscopy , Inhibitive performance , Aluminum triphosphate , Organic coating

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1   Introduction

In 1995 , the cost on corrosion of metals in the United States has reached almost   300 billions per year. In order to reduce the loss of corrosion , many protection methods have been used. Organic coating is one of the most effective , economical and popular methods as yet. It costs over 60 percent of the cost of the total methods[1]. The various pigments in anticorrosive coatings protect the metal substrates by different mechanisms , either by creation of alkaline environments , by passivation of the active centers originating from geometrical or structural defects , by decreasing the oxygen permeation from the environment or the iron ion diffusion through the coating , or by buffering the formation ions , or by sacrificial metal powers in the coating[2]. A small amount of

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inhibitors can obviously retard corrosion, so inhibitors have been considered more and more impor-
tant. Although the traditional inhibitors, such as lead- and chrome- based pigments, have good
inhibitive performances, they have high toxicity too, they are strictly limited, or prohibited to use
in many countries and regions. Thus the application and research of inhibitors are bound to focus
on the highly effective, multifunctional and environment-friendly inhibitors[3].

Analysis of impedance data is commonly carried out over a wide frequency range with the aid
of Nyquist complex plane plots or Bode plots in order to determine the individual components of an
equivalent eletrical circuit model that represents the painted metal/ solution interface. The relative
changes in the values of these components, such as paint film resistance, R_{pf}, and capacitance,
C_{pf}, substrate double layer capacitance, C_{dl}, charge-transfer resistance, R_{ct} and Warburg diffu-
sion impedance, Z_w, over the immersion time history of the sample, can supply valuable mecha-
nistic information on the stages involved in corrosion degradation of the painted metal, as well as
providing a quantitative means of comparing the performance of different samples[4]. Further-
more, with the little disturbance of alternate current, the samples can be sustained quasi-stable
state and measured during a long period without being damaged[5,6]. As a result, a very impor-
tant area for application of ac impedance is the evaluation of the corrosion behavior of polymer
coated metals. The equivalent circuit for coated steel sheet is usually regarded as Fig. 1.

2   Experimental

To prepare the coated electrode, the sur-
face of the A3 steel sheet (100×200 mm) was
abraded with $60^{\#}$, $80^{\#}$ sand cloth in succession,
cleaned, degreased with ethanol, covered with
the coating $165 \pm 20 \mu$ m in thickness and air
dried in ambient temperature for one week,
placed a plastic tube (inner diameter $= 90$mm)
on the coated sheet with 704 binder, air dried.
The pigment composition of three coated steel
sheets are listed in Table 1. A saturated calomel
electrode and a platinum plate were used as ref-
erence and counter electrodes, respectively. The
solution was made of distilled water and NaCl
(AR), and the concentration was 3 % (wt %).
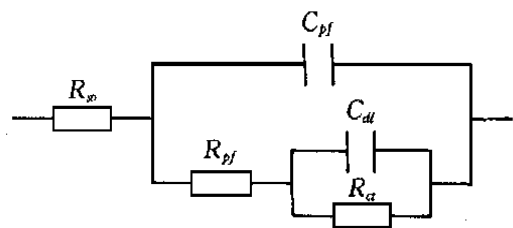

Fig. 1   Equivalent circuit for coated steel sheet
$R_s o$: solution resistance $R_p f$: resistance of
coating film $C_p f$:capacitance of coating film
$C_d l$: capacitance of double layer at electro-
chemical reaction at metal/ coating interface
$R_c t$: resistance of electrochemical reaction at
metal/ coating interface

Impedance data were obtained by CH Instruments 604 Electrochemical Analyzer at ambient
temperature and air-open system. The frequency span was 10^5 to 10^{-2} Hz with ± 20 mV ac signal.

Tab. 1   The pigment composition of three coated steel sheets

Sample	pigment Composition
Blank	Titanium dioxide
Calcite	Calcite + titanium dioxide
AlTP	Aluminum triphosphate + titanium dioxide

3   Results and Discussions

3.1   Deterioration processes of various samples

3.1.1   Deterioration process of blank sample

The EIS spectra for Blank sample are presented in Fig. 2. The coating resistance was 1.8×10^7 $\cdot cm^2$ after the sample was immersed for one week. It indicates that the amount of the aggressive media reaching the interface between the steel substrate and the organic coating through the pinholes is still small at the initial stage of immersion, and the steel substrate is protected well. The EIS spectrum shows two time constants after the sample was immersed for eleven days, namely, a semicircle and a large deviated semicircle. It is probably because the aggressive media on the interface are continuously accumulated with immersion time, and the corrosion on the steel substrate becomes more serious. Then, the coating resistances were fluctuant and slightly reduced (at the same order of magnitude) because of the " auto-repairing action"[7]. The deviated semicircle at the lower frequencies was changed into a semicircle after the sample was immersed for fifty-four days, and the coating resistance further decreased to 2.5×10^6 $\cdot cm^2$. It indicates that the swell and degradation of the organic coating are more serious, the adhesion between the steel substrate and the organic coating is obviously reduced because the volume of the corrosion-product is larger than that of the steel itself, then the coating is delaminated, and the aggressive media can easily arrive the interface, so the corrosion is accelerated.

3.1.2   Deterioration process of calcite sample

The EIS spectra for Calcite sample are presented in Fig. 3. (a) The coating resistance was 1.5×10^7 $\cdot cm^2$ after the sample was immersed for one week. Thus, the steel substrate is protected well by the coating at this stage. (b) The EIS spectrum shows two time constants after the sample was immersed for twenty-three days, and a typical semicircle at the lower frequencies after fifty-three days. It is probably because the amount of the aggressive media increases with immersion time, and the corrosion of the steel substrate is more serious. Compared Fig 2 with Fig 3, it can be seen that the EIS responses of Calcite sample and Blank sample are very similar, i.e. , (a) and (b).

3.1.3   Deterioration process of AlTP sample

The EIS spectra for AlTP sample are presented in Fig. 4. The coating resistance was $5.0 \times$

10^7 $\cdot cm^2$ after the sample was immersed for one week and subsequently decreased with time. However, it was after several immersion weeks when the coating resistance began to rise and stabilized at 4 5×10^7 $\cdot cm^2$ for a period of time. The coating resistance remained 3.5×10^7 $\cdot cm^2$ even at the 94th day. The probable reasons are as follows: active functional groups of AlTP make themselves combine well with the epoxy resin. This results in that the coating with AlTP can form more compact film. So the aggressive media are more difficult to reach the coating/steel interface through the coating of the AlTP sample than that of the Blank or Calcite sample. As the immersion time increases, the coating swells with more and more aggressive media, the coating resistance decreases, and the corrosion on the steel substrate is accelerated. The accumulation of the aluminum triphosphate arrives at a certain quantity very soon. Triphosphate ion can complex with the corrosion product, such as ferric and ferrous ions. A compact protective film forms on the surface of the steel, so the steel substrate is separated from the aggressive media. The coating resistance ascends at beginning, then, remains stable for a very long time. Subsequently, because of the degradation of the coating and the arrival of large amount of aggressive media on the surface of the protective film, the protective film is damaged. At the same time, the damaged film can be repaired by the "auto-repairing action" of aluminum triphosphate. These two processes exist simultaneously and compete with each other on the surface of the steel substrate. In the end, the corrosion process is gradually predominant. The coating resistance slowly decreases, but the descent is slower than those of the Blank and Calcite samples. It is 3.5×10^7 $\cdot cm^2$ even after ninety-four days of exposure to 3% NaCl solution.

3.2 Variations of coating resistance in deterioration process

It is well known that the coating cannot protect the steel substrate well when the coating resistance is less than 1.0×10^7 $\cdot cm^2$. The variations of coating resistance with immersion time are compared in Fig. 5. The coating resistances of the Blank sample and the Calcite sample were only a little more than 1.0×10^7 $\cdot cm^2$ at the initial stage, but became less than 1.0×10^7 $\cdot cm^2$ after twenty-three days. During the whole measurement period, the coating resistance of the Calcite sample was almost equal to that of the Blank sample, suggesting that calcite pigment has no inhibitive performance.

However, the AlTP was not the case. The coating resistance of the AlTP sample was much larger than those of the Blank and Calcite samples during the whole period of measurement. It even rose after several immersion weeks and stabilized at 4 5×10^7 $\cdot cm^2$ for a very long time, then decreased slowly, but still remained higher than 1.0×10^7 $\cdot cm^2$ at the 94th day. Therefore, AlTP is a good inhibitor.
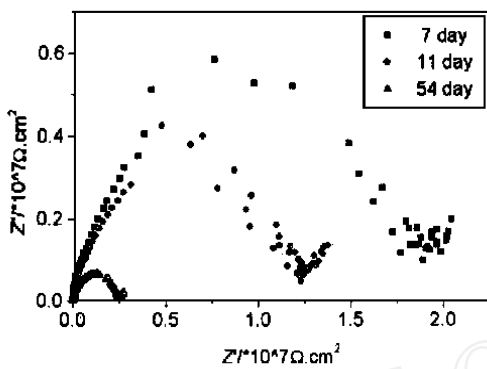
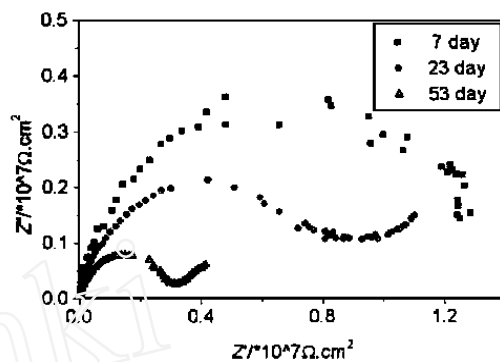Fig. 2   EIS spectra for Blank sample immersion in 3 % NaCl solution

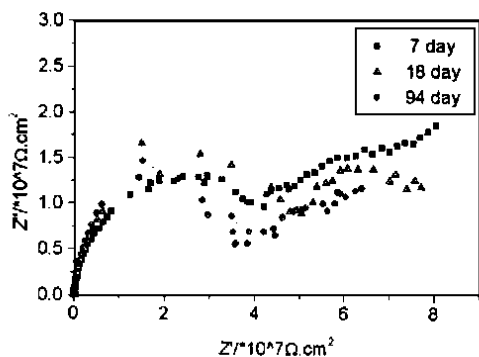Fig. 3   EIS spectra for Calcite sample immersion in 3 % NaCl solution

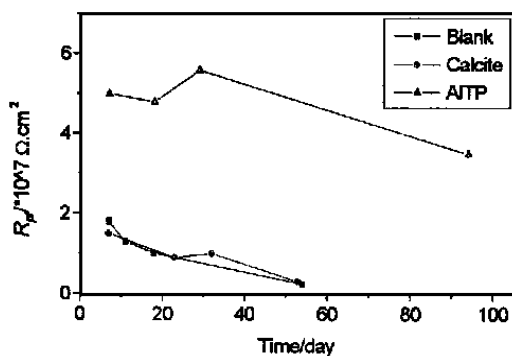Fig. 4   EIS spectra for AlTP sample immersion in 3 % NaCl solution

Fig. 5   Variations of coating resistance with immersion time

4   Conclusions

(a) Calcite is not an inhibitor , but an extender pigment in the epoxy coatings.

(b) The aluminum triphosphate that is an active pigment can considerably enhance the protective performance of the epoxy coatings. The triphosphate ion at the interface between the steel and the coating can complex with the corrosion-product , such as ferric and ferrous ions , and form a compact protective film that separates effectively the steel substrate from the aggressive media.

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