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Physical Aging Mechanism of Epoxy Coating by Hygrothermal Cycling Test

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The anticorrosive performance of epoxy coating was examined by using the hygrothermal cyclic test and the degradation mechanism of the coating was investigated by using the AC impedance method. The relationship between the results obtained from different tests was studied. It was revealed that the hygrothermal cyclic test can be used as an effective acceleration test for the degradation of organic coating. It was also found in hygrothermal cyclic test that the epoxy coatings have the resistance to stresses at some extent. The degradation of organic coating seems to be caused by the decrease of resistance of coating and the increase of both capacitance and free volume in the organic coating.

Keywords *: EIS, epoxy coating, hygrothermal cyclic test, DSC.*

1. Introduction

In recent years, anticorrosive organic coating is one of the most widely used methods for the corrosion control of metal, both to maintain appearance and to prevent loss of structural integrity. Thus, organic coatings should isolate the metal from the corrosive environment. However, organic coatings can be degraded under various service conditions because they comprise polymeric material, leading to redluction of its anti-corrosive effectiveness. Therefore, it is very important to evaluate coating performance more reliably in a short time for a systematic development of more effective coating systems and the prediction of their service life.

Recently, new acceleration test method, combining electrochemical impedance spectroscopy (EIS) and hygrothermal cyclic test, has been proposed to evaluate anticorrosive properties of coating systems.[1)-3)] In this method, AC impedance technique and acceleration test in the temperature range around Tg of organic coating can provide the test results of improved reproducibility and reliability, which can be used to analyze the degradation mechanism of anticorrosive organic coating.[2)-6)]

It is well known that there is close relationship between the water absorption and anticorrosive performance of organic coating and this can be monitored by using the components of measured impedance, resistance and capacitance.

In the present study, the anticorrosive performance of epoxy coating was evaluated by using the hygrothermal cyclic test and the degradation mechanism of the coating was monitored by using the AC impedance method. The relationship between the change of physical property of organic coating, such as cross-linking density measured by DSC, and the change of impedance value during the degradation was also examined.

2. Experimental

2.1 Specimen preparation

The electrochemical impedance cell for the monitoring of restoration of organic coating was prepared by embedding the carbon steel (5×15×3 mm) into epoxy resin mold, as shown in Fig. 1. The surface of specimen was blasted to have the surface roughness of 1 μm. The dry film thickness of coatings was 100±5 μm.

2.2 Measurement of AC impedance of coated specimens

The impedance was measured using the two electrodes method. The electrolyte was a 0.5 M-NaCl solution and the area of electrode was 13.9 cm^2. The AC impedance data were obtained using the electrochemical impedance spectroscopy FRA 1260 and the dielectric interface 1296 (Solartron, England) over the frequency range of 100 MHz to 1 mHz. The applied AC and DC voltages were 20 mV and 0.02 V, respectively. The capacitance was measured

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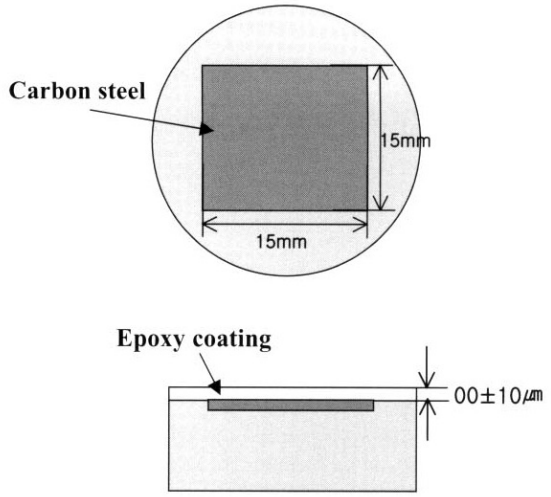

Fig. 1. Schematic diagram of electrochemical impedance cell.

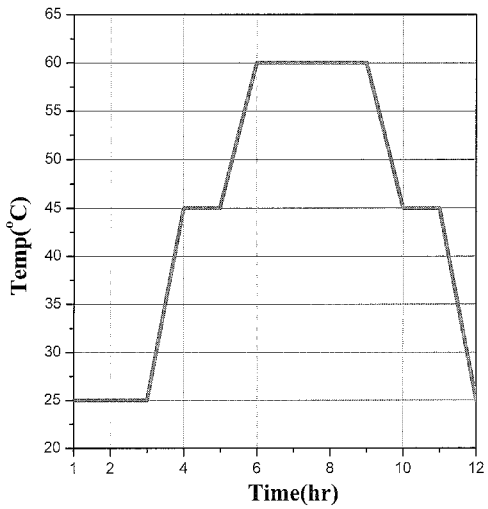

Fig. 2. Diagram of hygrothermal cyclic test process.

at the frequency of 1 kHz. The measured impedance data were fitted in both the Bode and Nyquist plots.

2.3 Hygrothermal cyclic test

The hygrothermal cyclic tests were performed by repeating the cycle (Fig. 2) in a 0.5 M-NaCl solution. In each cycle, the temperature of specimen was changed to accelerate the absorption of electrolyte into organic coating. The highest temperature was set to 60 ℃ since the Tg of organic coating was found to be 62.587 ℃ by DSC measurement.

2.4 DSC measurement

The DSC measurements were carried out to monitor the change of ΔH (cross-linking density) and glass transition temperature at the point of decrease in resistance of epoxy coating. The weight of sample was 3～5 mg and the temperature range was 0～100 ℃. All DSC measurements were performed at the heating rate of 5 ℃/min under nitrogen atmosphere.

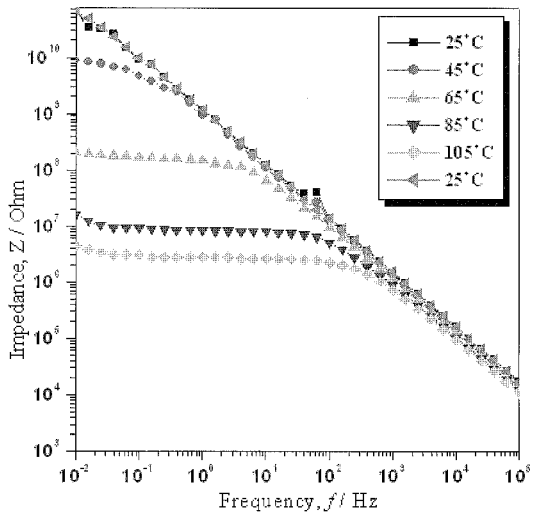

Fig. 3. EIS modulus of epoxy coating at different temperatures.

3. Results and discussion

3.1. Impedance measurement at different temperature

The organic coatings have the resistance to stresses at some extent. However, the ability of organic coating to restore is decreased by the long duration of stress.

The change of resistance of organic coating with the variation of temperatures (25 ℃→ 45 ℃→65 ℃→85 ℃ →105 ℃→25 ℃) was measured and the results are shown in Fig. 3. With increasing temperature, the impedance value, |Z|, at low frequency decreased; 10^{11}Ω at 25 ℃→ 10^{10}Ω at 45 ℃→ 10^{8}Ω at 65 ℃→ 10^{7}Ω at 85 ℃→ 10^{6}Ω at 105 ℃. When the temperature decreased to 25 ℃, the impedance value showed initial value. These results may indicate the ability of organic coating to restore.

3.2 Water absorption measurement

The water absorbed into organic coating during the hygrothermal cyclic test can be estimated from the capacitance of the coating at 1 kHz. The amount of water absorbed into the coating was calculated using the Brasher-Kingsbury equation and the results were shown in Fig. 4.

3.3 Impedance measurement during hygrothermal cyclic test

The impedance of organic coating was measured during hygrothermal cyclic test and the measured impedance data were fitted in the Bode plot (Fig. 5). It can be seen from the results in Fig. 5 that the organic coating has the

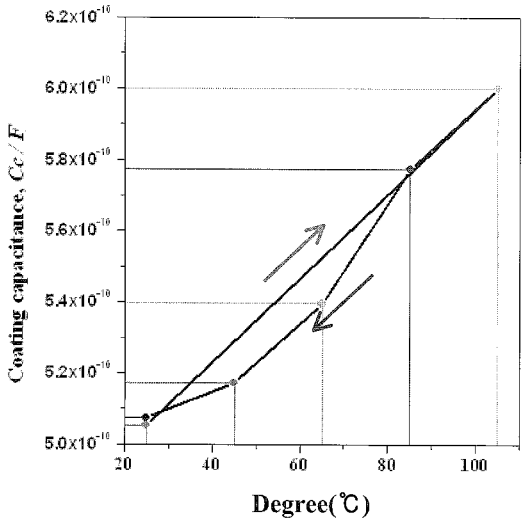

Fig. 4. Reversible change of the coating capacitance values for epoxy coating during thermal cycling.

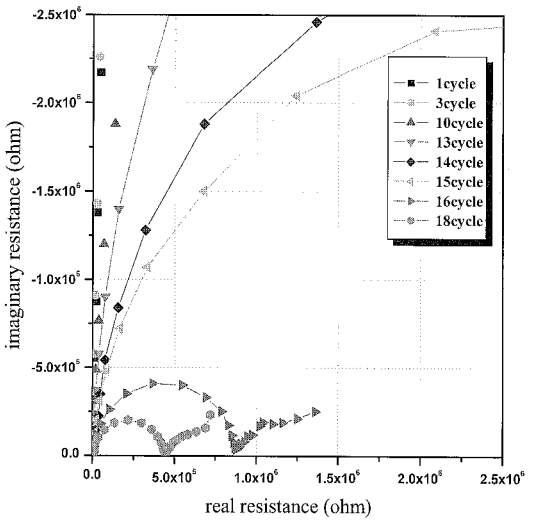

Fig. 6. Nyquist plot for epoxy coating during hygrothermal cyclic test.

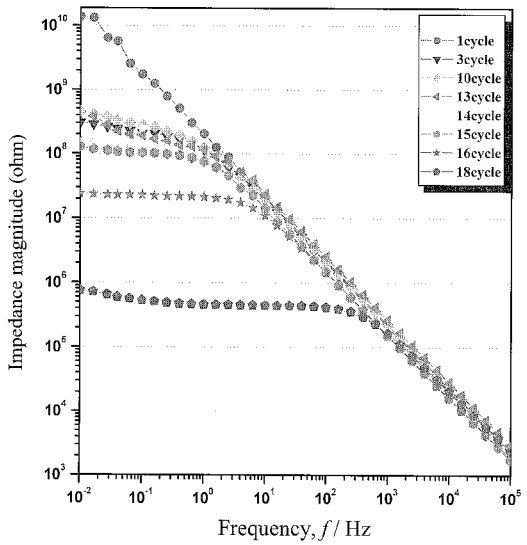

Fig. 5. Change of impedance characteristics for epoxy coating with the number of cycle.

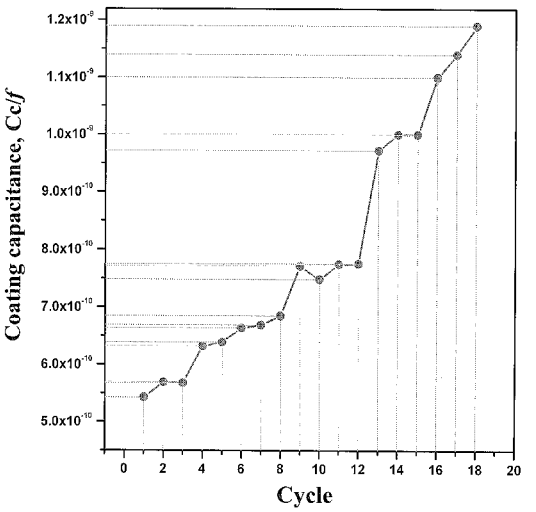

Fig. 7. Change of coating capacitance characteristics of epoxy coating with the number of cycle.

resistance to stresses at some extent until 3rd cycle and, after 4th cycle, the ability of organic coating to restore is diminished so quickly.

Fig. 6 shows the impedance data fitted in the Nyquist plot. It is found that the impedance value decreased with increasing number of cycle. After 16th cycle, Warburg impedance relating to diffusion through organic coating was observed. The change of impedance of organic coating during hygrothermal cyclic test may be due to the rapture of molecular structure and increase of free volume in organic coating.

Fig. 7 illustrates the change of capacitance of organic coating during hygrothermal cyclic test. Generally water absorbed into organic coating until saturation approaching quasi-equilibrium and then the water absorption increases again by the degradation of organic coating. However, as shown in Fig. 7, the quasi-equilibrium state was not observed in the case of hygrothermal cyclic test of organic coating and the water absorption increased continuously. From considering above results, it can be said that the hygrothermal cyclic test can be used as an effective acceleration test for the degradation of organic coating.

3.4 DSC measurement

The Tg and change of ΔH of the organic coating at the stage of large decrease in impedance were measured by using DSC, and the mechanism of degradation and the

Table 1. DSC (Tg) change, impedance and coating capacitance data.

Cycle number	1	3	4	11	15	18
Tg (℃)	62.59	62.40	59.33	57.47	56.09	41.39
Change of impedance (Ω/10mHz)	1.72×10^{10}	1.63×10^{10}	4.56×10^{8}	1.67×10^{7}	6.48×10^{6}	7.57×10^{5}
Change of coating capacitance (Cc, μF)	5.43×10^{-10}	5.68×10^{-10}	6.39×10^{-10}	7.74×10^{-10}	1×10^{-9}	1.19×10^{-9}

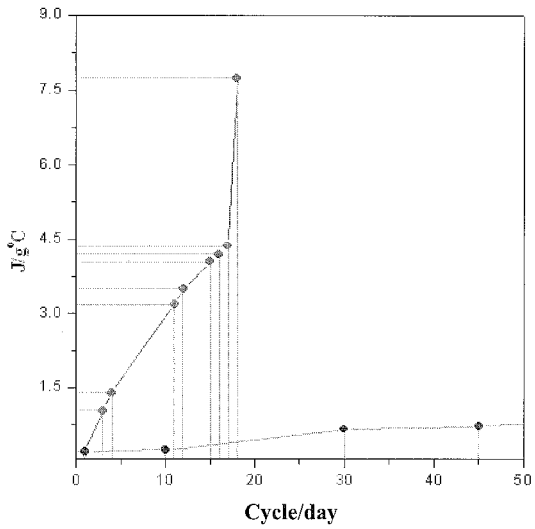

Fig. 8. Change of ΔH characteristics of epoxy coating during hygrothermal cycle test and immersion test.

change of cross-linking density in organic coating were examined.

Fig. 8 shows the change of ΔH of the organic coating during hygrothermal cyclic test and immersion test. In the case of immersion test, the ΔH of the organic coating was not changed largely. On the contrary, it was observed in hygrothermal cyclic test that the ΔH of the organic coating increased linearly up to 15th cycle and then increased so quickly. This results may be ascribed to the fact that the cross-linking density in organic coating decreased and then water absorption increased during hygrothermal cyclic test, leading to acceleration of the degradation of organic coating.

Table 1 reveals the change of Tg, impedance at 10 mHz and capacitance at 1 kHz during he hygrothermal cyclic test. The Tg, impedance and capacitance of organic coating decreased with the increasing number of cycle.

Above results indicate that the degradation of organic coating can be examined from the measurement of change of Tg, impedance and capacitance of the organic coating.

4. Conclusions

In the present study, the anticorrosive properties of epoxy coating was evaluated by using the hygrothermal cyclic test and the degradation behavior of the coating was monitored by using the AC impedance method. The change of physical property of organic coating was also measured by DSC. The relationship between the results obtained from different tests was examined.

The following conclusions were drawn from the present study:

1) The hygrothermal cyclic test can be used as an effective acceleration test for the degradation of organic coating.

2) It was found in hygrothermal cyclic test that the epoxy coatings have the resistance to stresses at some extent.

3) The degradation of organic coating may be caused by the decrease of resistance of coating and the increase of both capacitance and free volume in the organic coating.

Acknowledgment

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