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ORIGINAL PAPER

Assessment of corrosion resistance of surface-coated galvanized steel by analysis of the AC impedance spectra measured on the salt-spray-tested specimen

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Abstract In the present work, corrosion resistance of surface-coated galvanized steel was quantitatively determined by an analysis of the alternating current (AC) impedance spectra measured on the salt-spray-tested specimen. To evaluate the corrosion resistance of the surface-coated galvanized steel, AC impedance spectroscopy was performed on the salt-spray-tested specimen previously exposed to salt-sprayed corrosive environment. From the analysis of the impedance spectra, the area fraction transient of white rust $\theta_2(t)$ was theoretically derived from the equivalent circuit equation by using two fitting parameters. The values of the two fitting parameters were determined by fitting the empirical transient equations to the area fraction of the resin coating layer and to the total resistance obtained from the impedance spectra measured, respectively. From the analyses of $\theta_2(t)$ for four kinds of surface-coated galvanized steels with various resin coating layers, it is indicated that as the values of the two fitting parameters decrease in the order of CP, GI, OD and OM (commercial trade names) specimens, the corrosion resistance increases in that order as well. Furthermore, from the quantitative comparison of the two fitting parameters with the polarization resistance of the upper resin coating layer R_p determined from the potentiodynamic polarization curve, it is suggested that the two fitting parameters decrease in value as well with increasing R_p.

Keywords Surface-coated galvanized steel · Salt spray test · Corrosion resistance · AC impedance spectroscopy · Area fraction transient of white rust

Introduction

Many researchers have investigated various organic or inorganic coatings to protect cold-rolled steels from corrosion [1–5]. It has been generally known that the degradation mechanisms of polymer-coated metal surfaces are mainly dominated by electron-transfer reactions and the electroreduction of oxygen at the metal/polymer interface. In this respect, new ways to improve the corrosion protection of metals aim to slow down the reaction kinetics.

Traditionally, salt spray test has been widely used to characterize the corrosion behaviour of the steels coated with organic or inorganic materials in the field of cold-rolled steel making. Salt spray test has many advantages such as standardised protocols for conducting the exposure and evaluating the results, procedural simplicity and the ability to discriminate. However, the application of salt spray test to the characterization of the corrosion behaviour of the surface-coated galvanized steels has been criticized because this test does not simulate real operation conditions, and its result shows some scattering from equipment to equipment [6–8]. Furthermore, it needs a relatively long time until reliable results are obtained, and it has some difficulties in estimating the coating resistance quantitatively.

During the progress of the salt spray test, the degradation of the surface-coated galvanized steel proceeds by the breakdown of the coating layers, resulting in the formation of white rust that is temporally dependent on the area fractions of the coating layers. Therefore, to develop a new

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method to improve the corrosion protection of metals, it is necessary to systematically investigate the degradation mechanism of the coating layers focusing on the time dependence of the area fraction of the respective coating layer. However, little attention has been paid to the theoretical study on the degradation mechanism of the surface-coated galvanized steel.

In recent years, alternating current (AC) impedance spectroscopy has been developed for studying corrosion mechanisms as well as measuring corrosion rates in the field of corrosion [9–11]. Especially, it has been recently reported that AC impedance spectroscopy can be applied to evaluate the resistance of organic [12–15] and inorganic [16–18] coating layers, and it can provide a quantitative measurement for corrosion protection in a way that salt spray test cannot.

Under these circumstances, the present work is aimed at determining the corrosion resistance of the surface-coated galvanized steel by an analysis of the AC impedance spectra measured on the salt-spray-tested specimen. For this purpose, two fitting parameters controlling the area fraction transient of the resin coating layer and the inverse total resistance transient, respectively, were first determined by fitting the empirical transient equations to the measured impedance spectra. The transient for the area fraction of white rust was then theoretically derived based upon the equivalent circuit equation by employing the two fitting parameters. The corrosion behaviour of the surface-coated galvanized steels was examined with four various compositions and kinds of resin coating layers by employing the derived area fraction transient of white rust. Finally, the two fitting parameters were qualitatively compared with the polarization resistance of the upper resin coating layer determined from the potentiodynamic polarization curve.

Experimental

The surface-coated galvanized steels used in this work were commercially produced by Pohang Iron & Steel Co. (POSCO), Pohang, Korea. Figure 1 shows the schematic diagram of the layer arrangement of the surface-coated galvanized steel. The surface-coated galvanized steel consists of three coating layers: the upper acryl-based resin coating layer with a thickness of 1.2 to 2.0 μm applied at 1.2 to 2.0 g m^{-2}, the medium phosphated conversion coating layer with a thickness of approximately 0.3 μm coating applied at 0.3 g m^{-2} and the lower Zn coating layer with a thickness of roughly 3 μm applied at 20 g m^{-2}. The substrate was used as the cold-rolled carbon steel containing 0.12 wt% C, 0.5 wt% Mn, 0.04 wt% P and 0.045 wt% S with a thickness of roughly 0.5 mm.

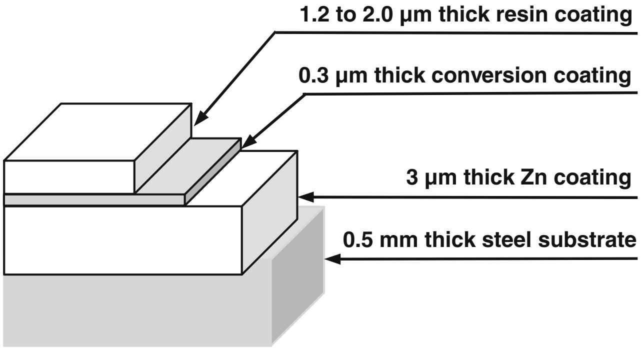

Fig. 1 The schematic diagram of the layer arrangement of the surface-coated galvanized steel that consists of three coating layers: the upper acryl-based resin coating layer with a thickness of 1.2 to 2.0 μm applied at 1.2 to 2.0 g m^{-2}, the medium phosphated conversion coating layer with a thickness of approximately 0.3 μm applied at 0.3 g m^{-2} and the lower Zn coating layer with a thickness of roughly 3 μm applied at 20 g m^{-2}. The composition of the cold-rolled carbon steel substrate: 0.12 wt% C, 0.5 wt% Mn, 0.04 wt% P and 0.045 wt% S with thickness of roughly 0.5 mm

In this work, the corrosion resistance was evaluated from four kinds of surface-coated galvanized steels that are designated as CP, GI, OD and OM (commercial trade names). They were simply distinguished by the composition and kind of acryl-based resin coating layer with nearly the same thickness, but they were almost identical with the other coating layers in their composition and thickness. The CP specimen was used as the reference specimen, and the other specimens served as the comparison specimens. Apart from the three-layered CP, GI, OD and OM specimens, the two-layered conversion-coated galvanized steel specimen and single-layered galvanized steel specimen were additionally prepared for the determination of the coating resistances of the conversion coating layer and Zn coating layer, respectively.

The salt spray test was conducted on the three-layered CP, GI, OD and OM specimens according to the American Society for Testing and Materials B 117 that specified exposure in an enclosed chamber at 35 °C to a fog, generated from 5 wt% sodium chloride (NaCl) solution [15]. The individual test specimens with an area of 105 cm^2 were exposed to this salt-spraying corrosive environment, and then they were inspected visually at regular intervals of 24 h up to 120 h.

In an attempt to find out the relationship between the results of the salt spray test and those of the AC impedance spectroscopy, the AC impedance spectra were measured on both the fresh and salt-spray-tested specimens using Zahner IM6e impedance measurement unit. A three-electrode electrochemical cell was employed for this experiment. A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Before the electrochemical measurement, the specimen with an area of 7.07 cm^2 was exposed to 0.5 M Na_2SO_4 aqueous solution for 30 min to attain an open-circuit potential.

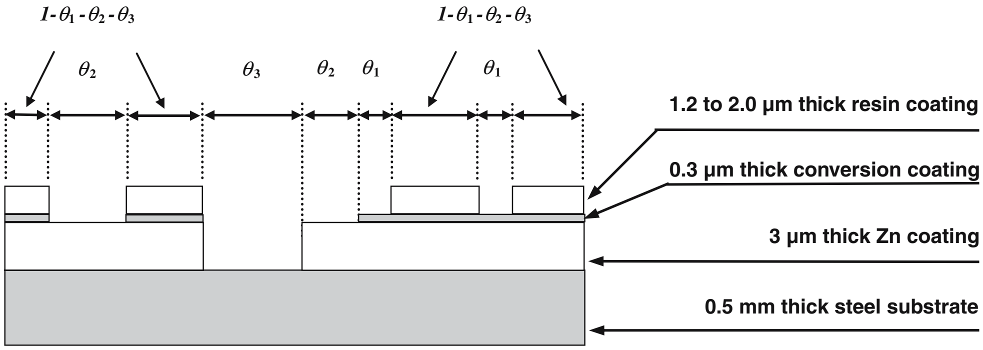

Fig. 2 Schematic representation of the cross-section of the salt spray tested specimen

After that, the AC signal of 5-mV amplitude was superimposed on an open-circuit potential at room temperature over the frequency range from 10^5 Hz down to 10^{-1} Hz during the measurement. To evaluate the corrosion resistance, the measured impedance spectra were analysed based upon the equivalent circuit fit for describing the interface property of the salt-spray-tested specimen by using the complex nonlinear least squares (CNLS) fitting method written first by Macdonald [20] and later modified in our laboratory [21]. Furthermore, to determine the specific resistances of the resin coating layer, conversion coating layer and Zn coating layer, the AC impedance spectra were measured on the fresh three-layered CP, GI, OD and OM, the fresh conversion-coated galvanized steel and the fresh galvanized steel specimens, respectively.

Incidentally, to determine the polarization resistance of the upper resin coating layer, potentiodynamic polarization experiment was performed on the fresh three-layered CP, GI, OD and OM specimens with an exposed area of 7.07 cm^2 in the applied potential range of −1.5 to 0 V (SCE) with a scan rate of 0.5 mV s^{-1} by using a Potentiostat/Galvanostat (EG&G Model 263A) interfaced with a personal computer.

Results and discussion

Theoretical derivation of the area fraction transient of white rust $\theta_2(t)$ from the AC impedance spectra

The degradation of the surface-coated galvanized steel during the progress of salt spray test may proceed as follows: First, the upper resin coating layer is damaged in the downward direction, and the medium conversion coating layer is then exposed to corrosive environment. As the exposure time goes on, the area fraction of the conversion coating layer increases in the lateral direction by reducing the area fraction of the resin coating layer. Similar to the resin coating layer, the medium conversion coating layer is also damaged in the downward direction, and the area fraction of the Zn coating layer increases in the lateral direction with increasing exposure time. Finally, white rust, i.e. Zn oxide, is formed on the surface of the Zn coating layer [16, 22].

In this respect, the schematic representation of the cross-section of the salt-spray-tested specimen is given in Fig. 2. Here, θ_1 (−), θ_2 (−) and θ_3 (−) designate the area fractions of the conversion coating layer, Zn coating layer and steel substrate, respectively. The area fraction is defined as the ratio of the exposed area occupied by each coating layer to the total area of the specimen in the lateral direction.

To quantitatively analyse the AC impedance spectra experimentally measured on the surface-coated galvanized steel specimens, the equivalent circuit in Fig. 3a was constructed based upon the schematic representation of the cross-section of the salt-spray-tested specimen in Fig. 2. Here, R_s (Ω cm^2) is the uncompensated ohmic resistance of

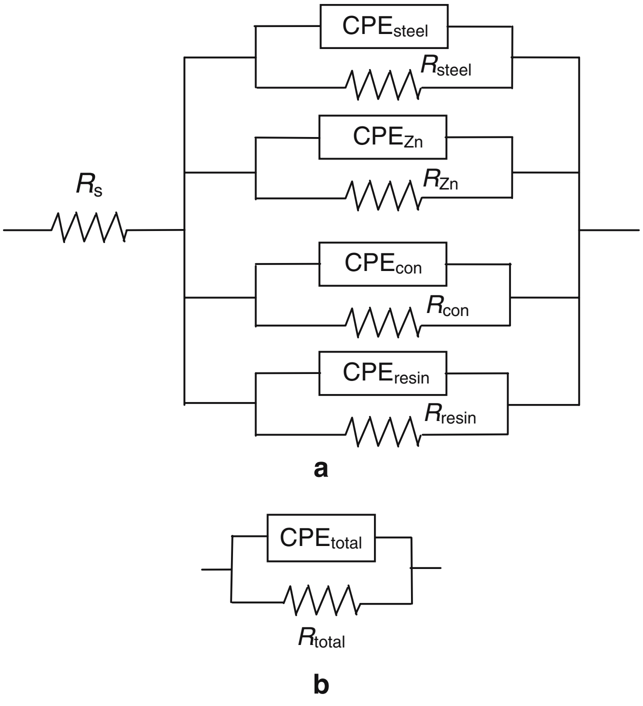

Fig. 3 **a** The equivalent circuit proposed based upon the schematic representation of the cross-section of the salt-spray-tested specimen in Fig. 2, and **b** its reduced form used for the CNLS fitting method

the electrolyte. R (Ω cm^2) and CPE (F cm^{-2}) denote the specific resistance and constant phase element of each coating layer, respectively. The specific resistance is an intrinsic property that is strongly dependent on the composition and thickness of the coating layer. The subscript resin, con, Zn and steel in Fig. 3a refers to the resin coating layer, conversion coating layer, Zn coating layer and steel substrate, respectively.

Reducing the equivalent circuit in Fig. 3a to the equivalent circuit in Fig. 3b, the total resistance $R_{\mathrm{total}}(t)$ (Ω cm^2) is expressed as:

$$R_{\mathrm{total}}(t) = R_{\mathrm{s}} + \left[\frac{\theta_3(t)}{R_{\mathrm{steel}}} + \frac{\theta_2(t)}{R_{\mathrm{Zn}}} + \frac{\theta_1(t)}{R_{\mathrm{con}}} + \frac{1-\theta_1(t)-\theta_2(t)-\theta_3(t)}{R_{\mathrm{resin}}}\right]^{-1} \tag{1}$$

Assuming that the value of R_{s} is negligibly small as compared with those values of the other resistances, the contribution of R_{s} to $R_{\mathrm{total}}(t)$ can be out of consideration. Furthermore, in the present work, since salt spray test was conducted within the exposure time of 120 h at which the steel substrate was not exposed to corrosive environment yet, the value of $\theta_3(t)$ was considered to be zero. Under these circumstances, Eq. 1 becomes the following simple equivalent circuit equation:

$$\frac{1}{R_{\mathrm{total}}(t)} = \frac{\theta_2(t)}{R_{\mathrm{Zn}}} + \frac{\theta_1(t)}{R_{\mathrm{con}}} + \frac{1-\theta_1(t)-\theta_2(t)}{R_{\mathrm{resin}}} \tag{2}$$

Here, R_{resin}, R_{con} and R_{Zn} are the time-invariant parameters, but $R_{\mathrm{total}}(t)$, $\theta_1(t)$ and $\theta_2(t)$ vary with the exposure time. Accordingly, $R_{\mathrm{total}}(t)$ is the function of only $\theta_1(t)$ and $\theta_2(t)$. Here, $\theta_1(t)$ and $\theta_2(t)$ are dependent upon each other. The specific resistance of each coating layer R_{resin}, R_{con} and R_{Zn} in Eq. 2 was experimentally estimated from the AC impedance spectra measured on the fresh CP, conversion-coated galvanized steel and galvanized steel specimens, respectively. The values of R_{resin}, R_{con} and R_{Zn} were determined to be 85, 18 and 0.57 kΩ cm^2, respectively.

We first calculated the area fraction transient of the conversion coating layer $\theta_1(t)$ and then determined the area fraction transient of white rust $\theta_2(t)$. Within the exposure time of 40 h, white rust is not formed $\{\theta_2(t)=0\}$, and hence, $\theta_1(t)$ can be easily derived from Eq. 2 as follows:

$$\theta_1(t) = \frac{R_{\mathrm{con}}}{R_{\mathrm{resin}} - R_{\mathrm{con}}}\left(\frac{R_{\mathrm{resin}}}{R_{\mathrm{total}}(t)} - 1\right) \tag{3}$$

The value of θ_1 at an instantaneous time is calculated by the value of R_{total} experimentally determined from the AC impedance spectra.

Now, we can take the following empirical transient equation for $\{1-\theta_1(t)\}$ that represents the area fraction transient of the resin coating layer within the exposure time of 40 h. Here, it was assumed that the degradation of the surface-coated galvanized steel occurs in a similar way to the pitting failure, and hence, the empirical equation was formulated based upon the Weibull distribution function [23, 24], which is generally used for the description of the probability of pit embryo formation:

$$\{1-\theta_1(t)\} = \exp\left(-At^2\right) \tag{4}$$

where A (s^{-2}) is the fitting parameter that entirely limits the area fraction transient of the resin coating layer in shape. For a given value of $(1-\theta_1)$, the parameter A is proportional to the second power of the inverse exposure time.

To investigate the effect of A on $\{1-\theta_1(t)\}$, $\{1-\theta_1(t)\}$ was theoretically calculated as a function of A, as shown in Fig. 4. Here, the instantaneous time at $(1-\theta_1)=0.95$ and $t\{(1-\theta_1)=0.95\}$ was usually regarded as time to breakdown of the upper resin coating layer. It is noted that as the value of A increased, $t\{(1-\theta_1)=0.95\}$ was shortened, and at the same time, the more the value of A was increased, the more steeply decreased the value of $(1-\theta_1)$ was with progressing exposure time. Thus, it is reasonable to think that the parameter A includes the term of time to breakdown of the upper resin coating layer $t\{(1-\theta_1)=0.95\}$; that is, as the value of A increases, the breakdown of the upper resin coating layer occurs more rapidly. Consequently, it is reasonable to say that A is closely related to the breakdown of the upper resin coating layer.

Figure 5 depicts the area fraction transients of the resin coating layer $\{1-\theta_1(t)\}$ for the CP specimen experimentally

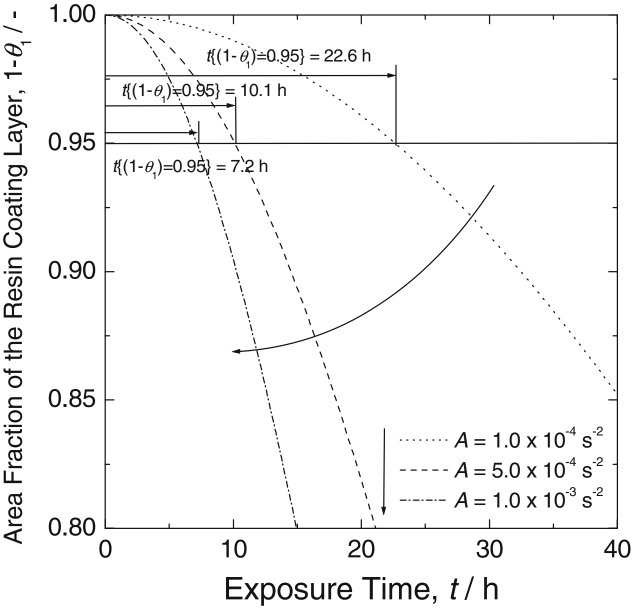

Fig. 4 Plots of the area fraction transients of the upper resin coating layer $\{1-\theta_1(t)\}$ theoretically calculated from Eq. 4 as a function of A

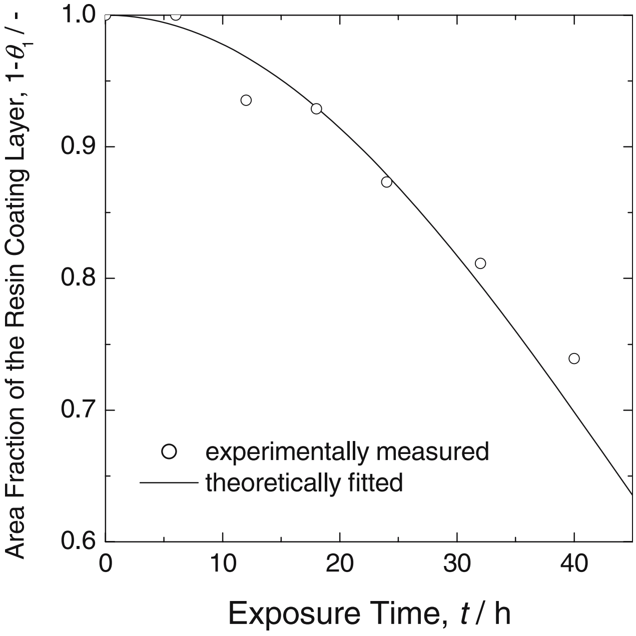

Fig. 5 Plots of the area fraction transients of the upper resin coating layer $\{1-\theta_1(t)\}$ experimentally measured from the CP specimen using Eq. 3 (*open circle*) and theoretically fitted to Eq. 4 (*solid line*)

measured from Eq. 3 with the help of the data of the AC impedance spectra (open circle) and theoretically fitted to Eq. 4 (solid line). From the comparison of the experimentally measured $\{1-\theta_1(t)\}$ with that of the theoretically calculated, it is revealed that $\{1-\theta_1(t)\}$ calculated at $A = 2.24\times10^{-4}\ \mathrm{s}^{-2}$ (Table 1) fits the best to that value experimentally measured from the CP specimen using Eq. 3.

Assuming that Eq. 4 is still valid even after the formation of white rust, Eq. 4 can be extended into the following equation which represents the area fraction transient of the resin coating layer at the exposure time longer than 40 h:

$$\{1-\theta_1(t)-\theta_2(t)\} = \exp\left(-At^2\right) \tag{5}$$

Table 1 The parameters *A* for susceptibility to the breakdown of the upper resin coating layer and *B* for susceptibility to the white rust formation determined by fitting the empirical equations to the area fraction of the resin coating layer and to the total resistance obtained from the measured impedance spectra for the CP, GI, OD and OM specimens, respectively

Specimen	A (s^{-2})	B (s^{-4})
CP	2.24×10^{-4}	1.79×10^{-8}
GI	1.84×10^{-4}	1.76×10^{-8}
OD	9.87×10^{-5}	6.71×10^{-9}
OM	2.95×10^{-6}	4.15×10^{-10}

By inserting Eq. 5 to the equivalent circuit equation of Eq. 2, the area fraction transient of white rust $\theta_2(t)$ is expressed as a function of $R_{\mathrm{total}}(t)$ as follows:

$$\theta_2(t) = \frac{R_{\mathrm{Zn}}(R_{\mathrm{resin}}-R_{\mathrm{con}})}{R_{\mathrm{resin}}(R_{\mathrm{con}}-R_{\mathrm{Zn}})}\exp\left(-At^2\right) + \frac{R_{\mathrm{con}}R_{\mathrm{Zn}}}{R_{\mathrm{con}}-R_{\mathrm{Zn}}}\left(\frac{1}{R_{\mathrm{total}}(t)}-\frac{1}{R_{\mathrm{con}}}\right) \tag{6}$$

Here, to determine the value of $R_{\mathrm{total}}(t)$, the CP specimen was previously exposed to corrosive environment for

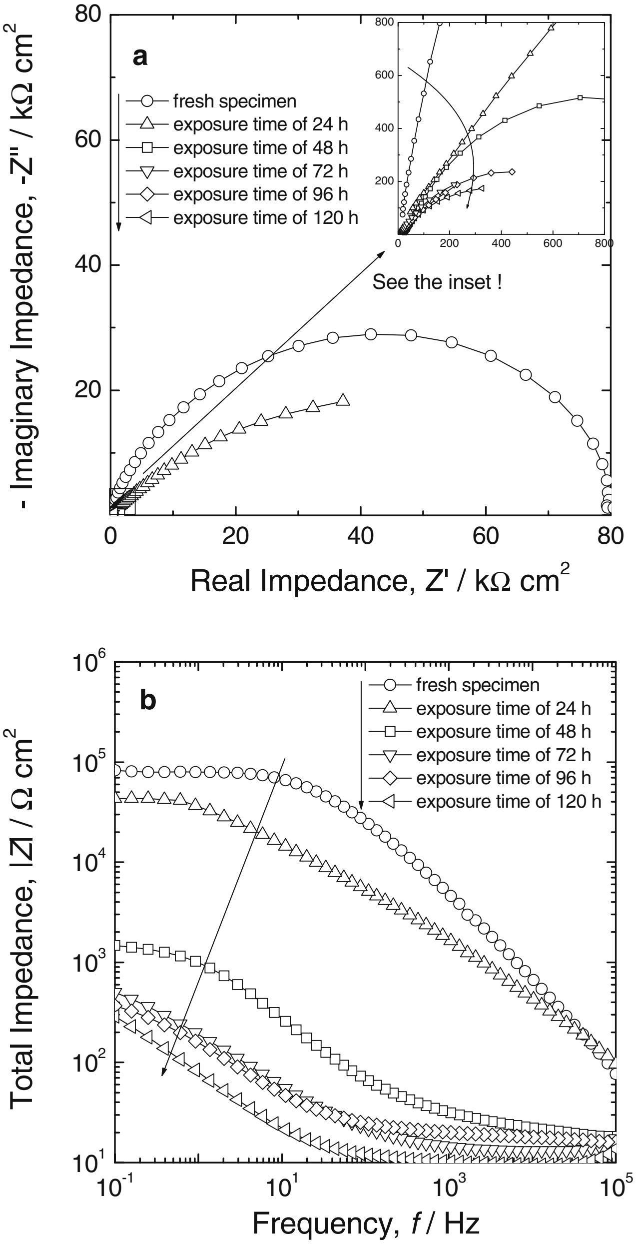

Fig. 6 **a** The Nyquist plots and **b** Bode magnitude plots of the AC impedance spectra measured on the salt-spray-tested CP specimen in 0.5 M Na_2SO_4 aqueous solution at an open-circuit potential as a function of the exposure time. The CP specimen was previously exposed to corrosive environment for various times

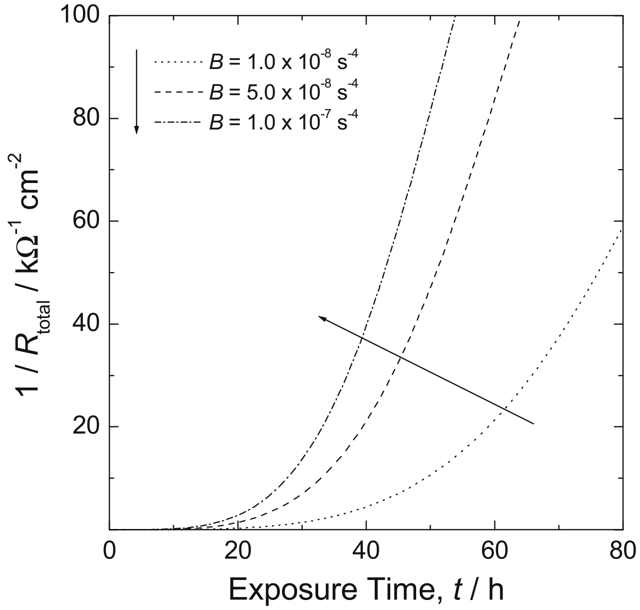

Fig. 7 Plots of the inverse of the total resistances against time (inverse total resistance transients) $1/R_{total}(t)$ theoretically calculated from Eq. 7 as a function of B

various times, and then, the AC impedance spectra were measured on the salt-spray-tested CP specimen in 0.5 M Na_2SO_4 aqueous solution at an open-circuit potential as a function of the exposure time. The resulting data are given in Fig. 6 in Bode plots as well as in Nyquist plots. The value of R_{total} was quantitatively determined by using the CNLS fitting method based upon the equivalent circuit proposed in Fig. 3b. The resulting value of R_{total} decreased with progressing exposure time.

From the fact that in the progress of the exposure time, R_{total} decreases in value, and finally, it reaches R_{Zn} at infinite time. Similar to Eq. 4, we can take another empirical transient equation for $1/R_{total}(t)$ as follows [23, 24]:

$$\frac{1}{R_{total}(t)} = \frac{1}{R_{Zn}}\left[1 - \exp\left(-Bt^4\right)\right] \tag{7}$$

where B (s^{-4}) is the fitting parameter that crucially determines the total resistance transient $R_{total}(t)$ in shape. For a given value of $1/R_{total}(t)$, the parameter B is proportional to the fourth power of the inverse exposure time.

Keeping in mind that white rust is formed by the degradation of the upper resin coating layer followed by that of the medium conversion coating layer, it is plausible that the parameter B indicates a measure about how fast the degradation of the medium conversion coating layer proceeds to be superimposed on that of the upper resin coating layer. To explore the contribution of B to $1/R_{total}(t)$, $1/R_{total}(t)$ was theoretically calculated as a function of B, as illustrated in Fig. 7. It was found that the more the value of B was increased, the more steeply increased the value of $1/R_{total}$ with progressing exposure time, implying that the parameter B includes the term of time to formation of white rust. That is, as the value of B increases, the formation of white rust occurs more quickly. From the above results, it can be said that B is closely related to the formation of white rust.

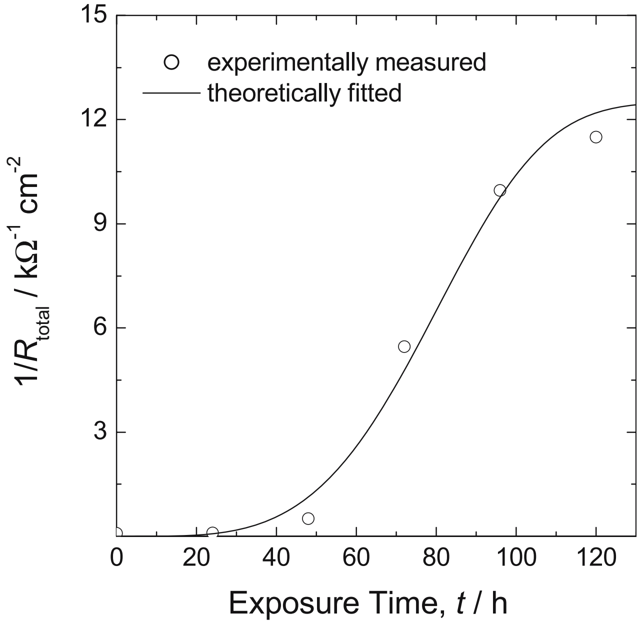

Fig. 8 Plots of the inverse of the total resistances against time (inverse total resistance transients) $1/R_{total}(t)$ experimentally measured from the CP specimen (*open circle*) and theoretically fitted to Eq. 7 (*solid line*)

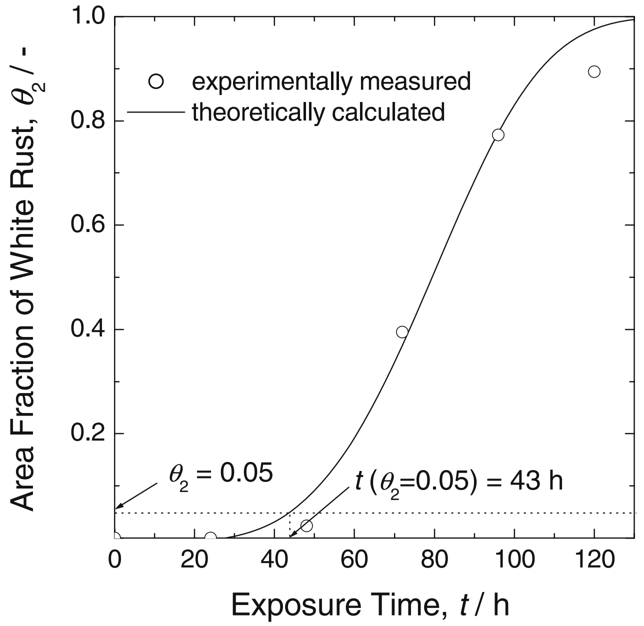

Fig. 9 Plots of the area fractions of white rust against time (area fraction transients of white rust) $\theta_2(t)$ experimentally measured from the CP specimen by the salt spray test (*open circle*) and theoretically calculated from Eq. 8 (*solid line*)

Figure 8 demonstrates the values of $1/R_{\mathrm{total}}$ with respect to the exposure time experimentally determined from the CP specimen (open circle) and theoretically fitted to Eq. 7 (solid line). It was found that the value of $1/R_{\mathrm{total}}$ experimentally measured from the AC impedance spectra was quite well fitted with that value of $1/R_{\mathrm{total}}$ theoretically calculated from Eq. 7. The data fitting yielded the value of B for the CP specimen as 1.79×10^{-8} s^{-4}, which is listed in Table 1.

By inserting Eq. 7 to Eq. 6, the area fraction transient of white rust $\theta_2(t)$ is rearranged as:

$$\theta_2(t) = \frac{R_{\mathrm{Zn}}(R_{\mathrm{resin}} - R_{\mathrm{con}})}{R_{\mathrm{resin}}(R_{\mathrm{con}} - R_{\mathrm{Zn}})}\exp\left(-At^2\right) + \left[1 - \frac{R_{\mathrm{con}}}{R_{\mathrm{con}} - R_{\mathrm{Zn}}}\exp\left(-Bt^4\right)\right] \tag{8}$$

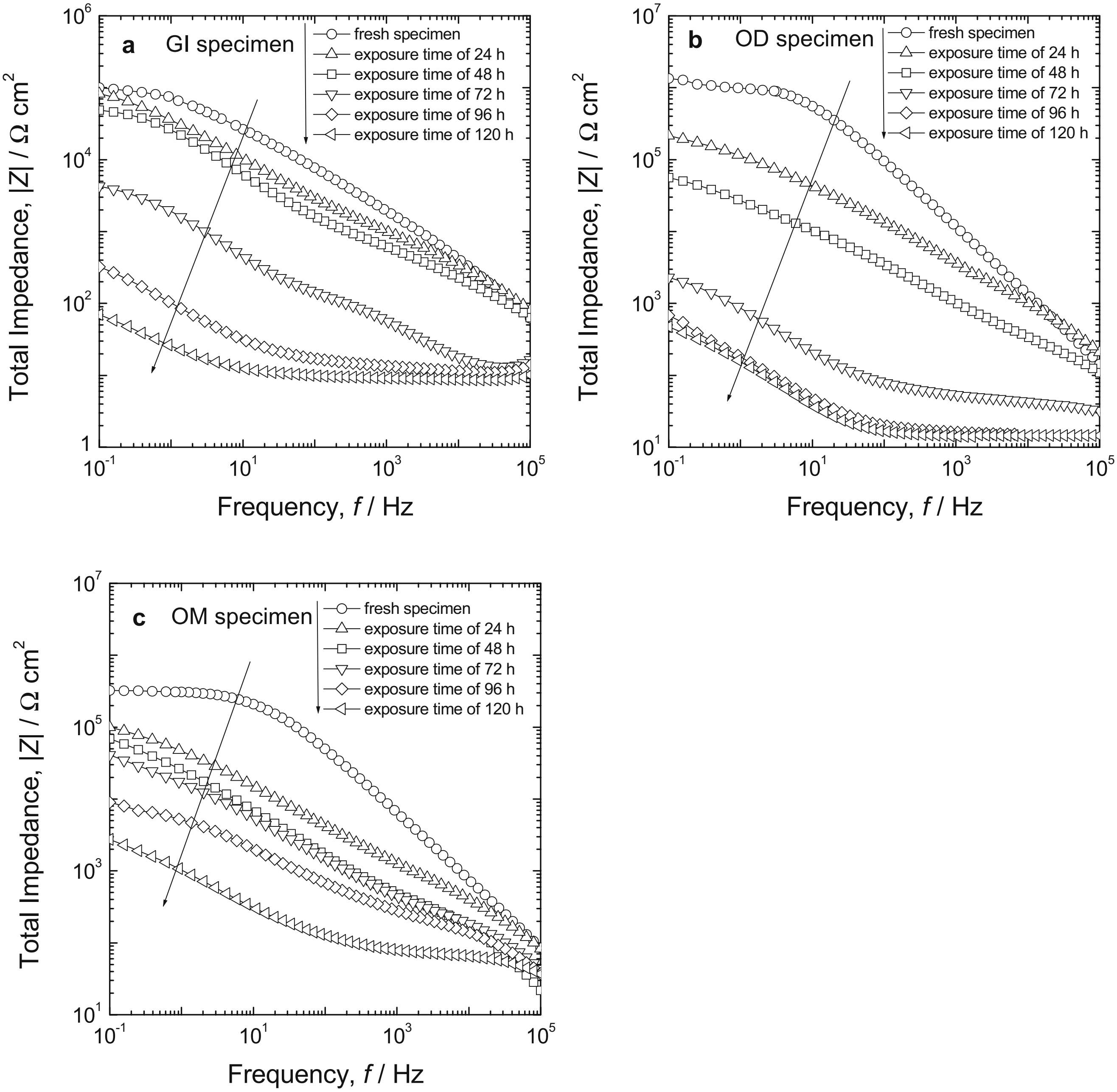

Fig. 10 Bode magnitude plots of the AC impedance spectra measured on the salt-spray-tested **a** GI, **b** OD and **c** OM specimens in 0.5 M Na_2SO_4 aqueous solution at an open-circuit potential. The specimens were previously exposed to corrosive environment for various times

It is worthwhile noting from Eq. 8 that $\theta_2(t)$ consists of two terms. The first term represents the contribution of the breakdown of the upper resin coating layer, and the second term exhibits the contribution of the formation of white rust.

Figure 9 shows the area fraction transients of white rust $\theta_2(t)$ for the CP specimen experimentally measured by salt spray test (open circle) and theoretically calculated from Eq. 8 (solid line). It was noted that the value of θ_2 calculated from Eq. 8 was in good agreement with that value of θ_2 experimentally measured on CP specimen by salt spray test. In the practice of salt spray test, time to the white rust formation at $\theta_2=0.05$ is usually regarded as a criterion for judging pass or fail. In this respect, time to failure at $\theta_2=0.05$, $t(\theta_2=0.05)$ was theoretically determined to be 43 h for the CP specimen. From the above results, it is confirmed that Eq. 8 theoretically derived in the present work is valuable for the quantitative estimation of the area fraction transient of white rust in practical application.

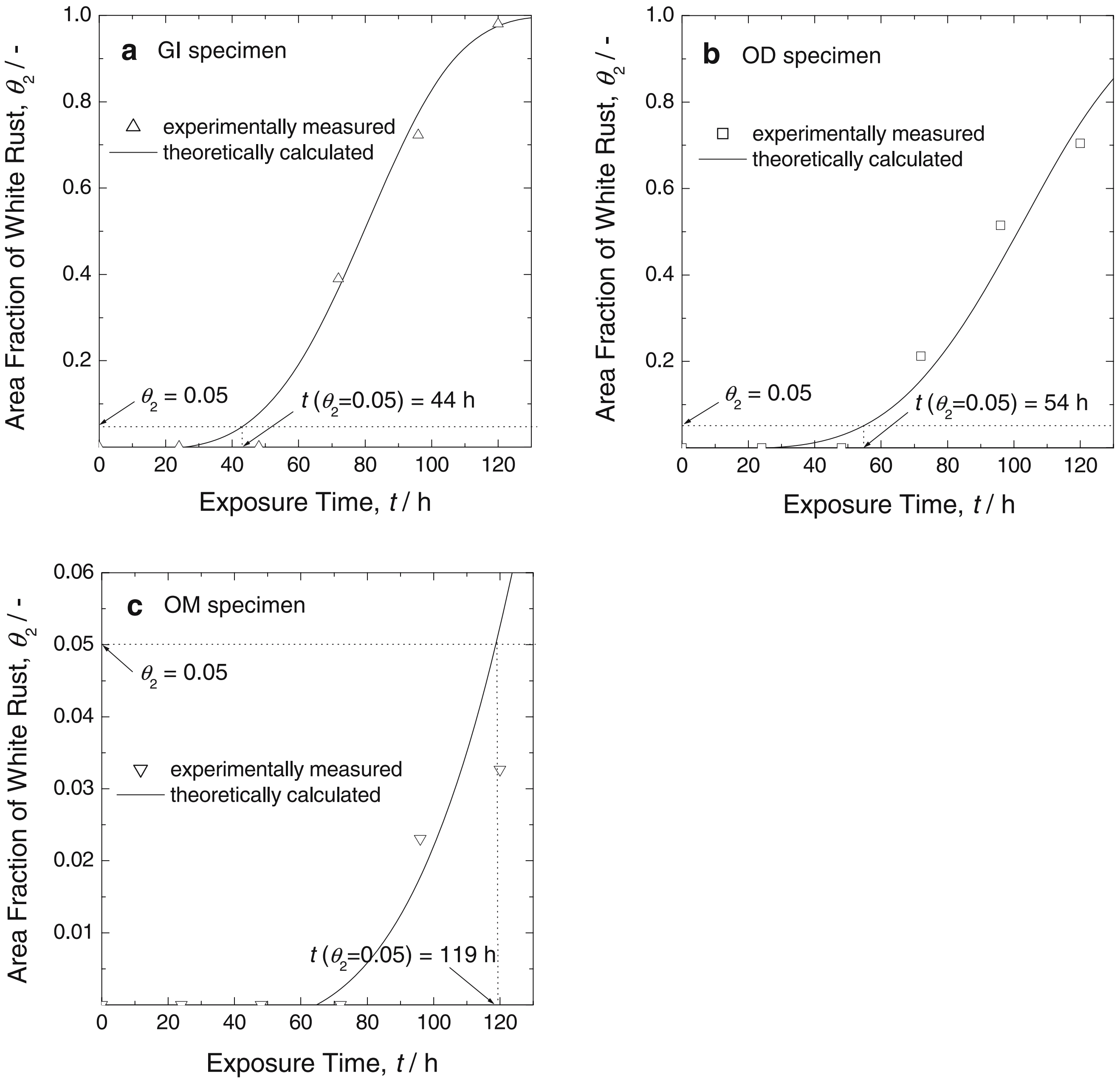

Fig. 11 Plots of the area fractions of white rust against time (area fraction transients of white rust) $\theta_2(t)$ for the **a** GI, **b** OD and **c** OM specimens experimentally measured by the salt spray test (*open triangle*, *open square*, *open inverted triangle*) and theoretically calculated from Eq. 8 (*solid line*)

Characterization of resistance to corrosion in terms of the area fraction transient of white rust $\theta_2(t)$

Now, the corrosion resistances of the surface-coated galvanized steels with the four various compositions and kinds of resin coating layers were examined based upon the derived area fraction transient of white rust $\theta_2(t)$. Figure 10a,b and c shows the Bode magnitude plots of the AC impedance spectra experimentally measured on the salt-spray-tested GI, OD and OM specimens, respectively. All the specimens were previously exposed to corrosive environment for various times. Similarly to the CP specimen, it was found that the value of the total impedance $|Z|$ decreased with progressing exposure time, implying that the value of R_{total} decreases with the progress in exposure time.

To follow the effect of the resin coating layer on the corrosion resistance of the surface-coated galvanized steel, the AC impedance spectra measured on the GI, OD and OM specimens were analysed in the same manner as those obtained from the CP specimen. The value of A for susceptibility to the breakdown of the upper resin coating layer was determined by fitting Eq. 4 to the area fraction of the resin coating layer evaluated from the experimentally measured impedance spectra, and the value of B for susceptibility to the white rust formation was estimated by fitting Eq. 7 to the total resistance obtained from the measured impedance spectra. Here, the values of R_{resin} were determined to be 119, 1,060 and 322 kΩ cm^2 from the AC impedance spectra measured on the fresh GI, OD and OM specimens, respectively.

The resulting values of A and B for the GI, OD and OM specimens are listed in Table 1. Figure 11a,b and c depicts $\theta_2(t)$ for the GI, OD and OM specimens, respectively, theoretically calculated from Eq. 8 by using the values of A and B given in Table 1. It was found that the values of θ_2 theoretically calculated from Eq. 8 accorded well with those values of θ_2 experimentally measured by using the salt spray test.

Moreover, from the area fraction transient of white rust, the values of $t(\theta_2=0.05)$ for the GI, OD and OM specimens were calculated to be 44, 54 and 119 h, respectively. This indicates that the white rust formation is retarded as both the parameters A and B decrease in value; that is, as the values of A and B decrease in the order of CP, GI, OD and OM specimens, the corrosion resistance increases in that order. Furthermore, from the fact that the values of A and B for the four kinds of surface-coated galvanized steels, i.e. CP, GI, OD and OM, are different from one another, it is proposed that the corrosion resistance of the surface-coated galvanized steel is highly dependent on the composition and kind of the resin coating layer.

Qualitative comparison of the susceptibility indices A and B with the polarization resistance of the upper resin coating layer R_{p}

The potentiodynamic polarization experiment was performed on the fresh three-layered CP, GI, OD and OM specimens, whereas the AC impedance spectroscopy was

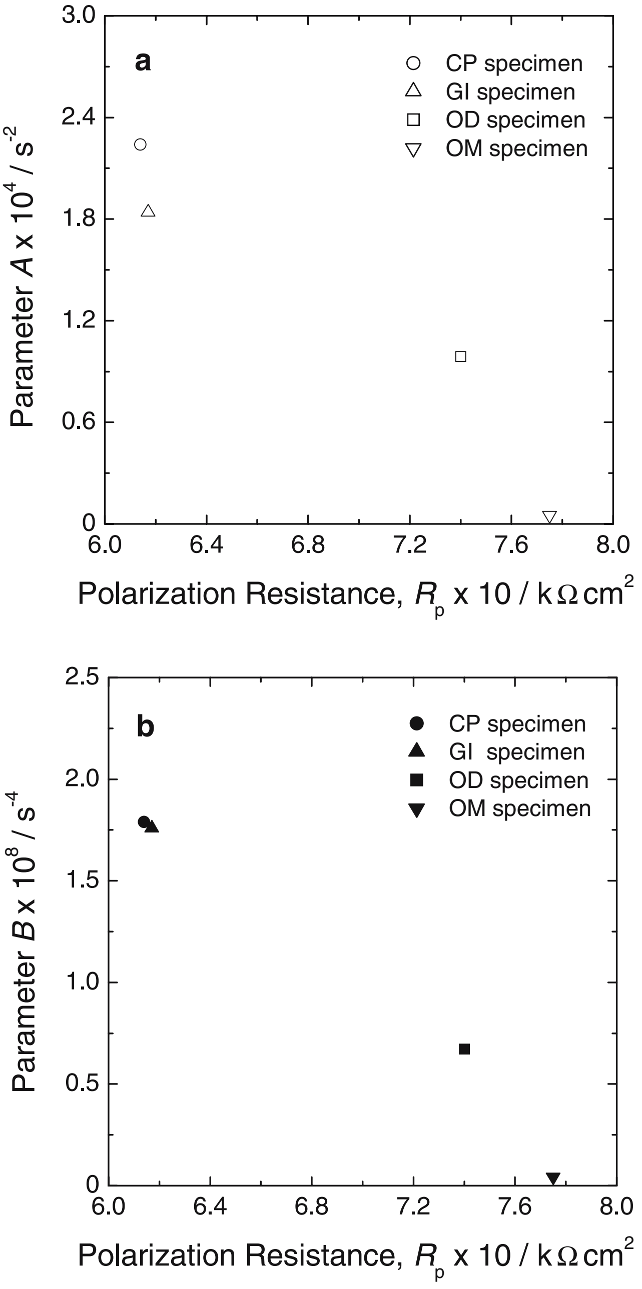

Fig. 12 Plots of **a** the parameter A (*open symbols*) and **b** the parameter B (*closed symbols*) against the polarization resistance of the upper resin coating layer R_{p} obtained from the four kinds of surface-coated galvanized steels with various compositions and kinds of resin coating layers: (*open circle*, *closed circle*) CP specimen; (*open triangle*, *closed triangle*) GI specimen; (*open square*, *closed square*) OD specimen; (*open inverted triangle*, *closed inverted triangle*) OM specimen

carried out on the salt-spray-tested CP, GI, OD and OM specimens to compare the fitting parameters A and B with the polarization resistance of the upper resin coating layer R_p. The polarization resistance R_p was determined from the slope of the polarization curve on a linear scale at the open-circuit potential. The values of R_p for the CP, GI, OD and OM specimens were experimentally measured to be 0.61, 0.62, 0.74 and 0.78 kΩ cm^2, respectively.

The corresponding corrosion rate i_{corr} was calculated to be 1.51, 1.50, 1.29 and 1.13 μA cm^{-2}, respectively, from the Stern–Geary equation by taking the value of R_p measured and the Stern–Geary constant B_{SG}. Here, B_{SG} is described by:

$$B_{SG} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \tag{9}$$

where β_a and β_c are the Tafel slopes in the anodic and cathodic branches of the polarization curve on a semi-logarithmic scale, respectively. It was revealed that B_{SG} shared a constant value 9×10^{-4} V in NaCl solution irrespective of the specimen.

Figure 12 plots the fitting parameters of A and B against R_p obtained from the CP, GI, OD and OM specimens. It was found that the parameter A as well as B decreased with increasing R_p. From the above results, it is concluded that the value of R_p is closely related to the parameter A as well as B, that is, as the parameter A for susceptibility to the breakdown of the upper resin coating layer as well as B for susceptibility to the white rust formation decreases, the corrosion protection of the surface-coated galvanized steel is more improved.

Conclusions

The present work demonstrates how to effectively evaluate the corrosion resistances of the four kinds of surface-coated galvanized steels with various resin coating layers. The values of the fitting parameters A and B were theoretically determined by fitting the empirical equations to the area fraction of the resin coating layer and to the total resistance calculated from the impedance spectra measured on the salt-spray-tested specimen, respectively. The polarization resistance of the upper resin coating layer R_p was also determined from the potentiodynamic polarization curve. The results are summarized as follows:

1. From the analysis of the AC impedance spectra measured, the area fraction transient of white rust $\theta_2(t)$ was theoretically derived from the equivalent circuit equation by using the fitting parameters A and B, limiting the area fraction transient of the resin coating layer $1-\theta_1(t)$ and the inverse total resistance transient $1/R_{total}(t)$, respectively. It is suggested that A and B represent the indices for susceptibility to the breakdown of the upper resin coating layer and for susceptibility to the formation of white rust, respectively. From the coincidence of the θ_2 value measured with that θ_2 value calculated, it is confirmed that $\theta_2(t)$ theoretically derived in the present work will be useful for the quantitative estimation of the area fraction transient of white rust in practical application.
2. From the analyses of the area fraction transients of white rust $\theta_2(t)$ for the four kinds of surface-coated galvanized steels with four various compositions and kinds of resin coating layers, it is suggested that as the value of A as well as B decrease in the order of CP, GI, OD and OM (commercial trade names) specimens, the white rust formation is retarded; that is, the corrosion resistance increases in that order.
3. From the comparison of the values of A and B with those values of R_p, it was found that both the parameters A and B decreased with increasing R_p. Consequently, it is indicated that the value of R_p is closely related to both the parameters A and B; that is, as the parameter A as well as B decreases, the corrosion protection of the surface-coated galvanized steel is more improved.

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