The Determination of Film Resistance by Means of the Frequency at the Maximum Phase Angle and the Estimation of the Degradation of the Coating Film

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Synopsis. The determination of film resistance (R_f) was investigated by means of the frequency at the maximum phase angle ($f_{\theta_{max}}$), as obtained from electrochemical impedance measurements. $f_{\theta_{max}}$ was linearly correlated with R_f. The degradation of the coating film was obviously and rapidly evaluated from $f_{\theta_{max}}$ by comparison with R_f.

Recently, the degradation of coating films and under-film corrosion have been widely investigated by means of electrochemical impedance measurements.[1-6] To evaluate the degradation of coated steels, a method utilizing the break point frequency (f_h) was proposed by Tsuru et al.[7] It is based on the theory that the break point frequency (phase shift=45°) is proportional to the area of delamination. Using this theory we have been evaluating the corrosion protective property of coating films by means of the film resistance (R_f) values.[6,8-14] When a coating system has a large film resistance, however, this evaluation method can not be used. Such a condition can be seen when the initial stage is immersed in test solution and in the case of highly insulated binders. In order to estimate the R_f values in such a case, we attempted to use a new parameter of a frequency at a maximum phase angle ($f_{\theta_{max}}$). The $f_{\theta_{max}}$ is not easily affected by radio ham noise (50 Hz), for it is observed on the high frequency side in comparison with f_h. In this paper, the R_f value was determined by the use of the $f_{\theta_{max}}$ value obtained by means of electrochemical impedance measurements in order to estimate the degradation of the coating film.

Experimental

Steel plates coated with boiled linseed oil were prepared. The specimen was a cold rolled steel plate (JIS G 3141, SPCC-SB) coated at a thickness of 40 μm and with an exposed area of 9 cm^2. It was immersed in an aqueous 3% NaCl solution.

Electrochemical impedance measurements were carried out by using a frequency response analyzer, FRA (NF Electronic Instruments, 5020) and a potentiostat (Toho Technical Research, 2000). They were conducted using a standard three-electrode configuration at the immersion potential. The applied signal amplitude was 9 mV (RMS) in the frequency range from 20 kHz to 10 mHz.

Results and Discussion

Figure 1 shows Bode plots of the electrochemical impedance spectra obtained from the coated steel. After immersion for 30 minutes, the Bode plots of the electrochemical impedance spectra were disordered below 500 Hz, because the paint film was sound and radio ham noise occurred. The film resistance (R_f) was determined by the extrapolation of the frequency-

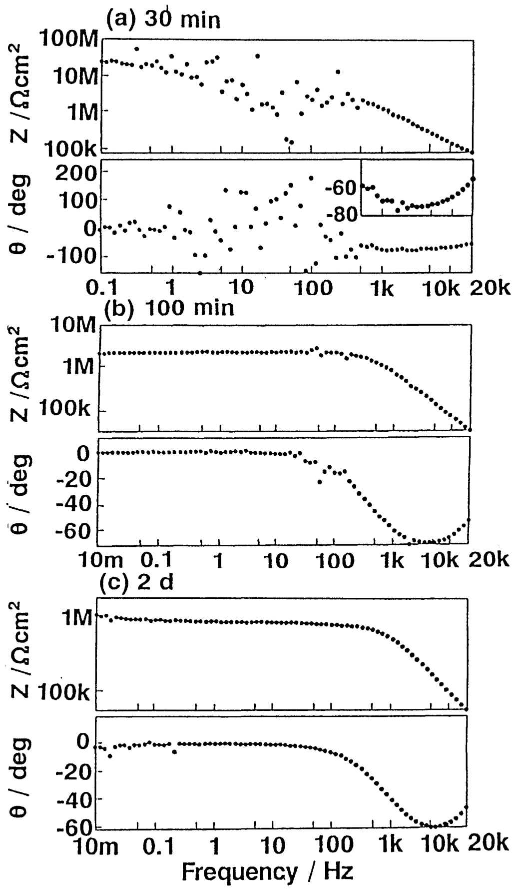

Fig. 1. Bode plots of impedance data obtained from coated steel.
(a); after 30 minutes, (b); after 100 minutes, and (c); after 2 days.

independent horizontal line to the Z axis and reading off the value of Z. It was difficult to obtain the R_f value exactly because the paint film was sound. After 100 minutes, the Z decreased and the Bode plot became comparatively stable. It can be seen from these impedance spectra that a parallel resistor/capacitor combination is present in the high frequency range. The R_f value obtained was 1.7 MΩ cm^2. After immersion for 2 days, the degradation of the film proceeded more than that after 100 minutes, judging from the decrease in the Z value and phase angle (θ)≠0° at 10 mHz. The various electrochemical parameters, R_f, the immersion potential (E), the maximum phase angle (θ_{max}), and the $f_{\theta_{max}}$ value were determined by the analysis of the Bode plot at various immersion times (Fig. 2). The R_f value after 30 minutes is represented in Fig. 2. As the Nyquist and Bode plots could not be

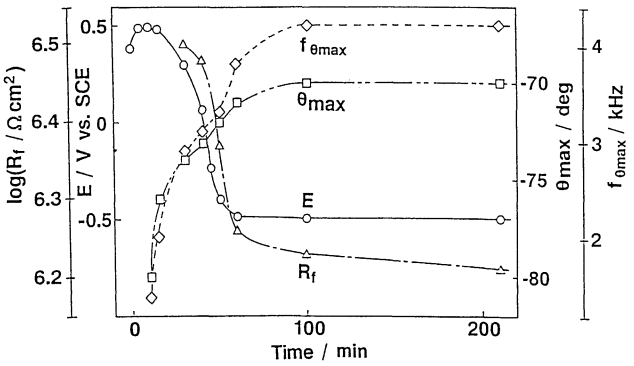

Fig. 2. Electrochemical parameters (E, R_f, θ_{max}, and $f_{\theta_{max}}$) vs. immersion time curves.
E; immersion potential, R_f; film resistance, θ_{max}; maximum phase angle, and $f_{\theta_{max}}$; frequency at θ_{max}.

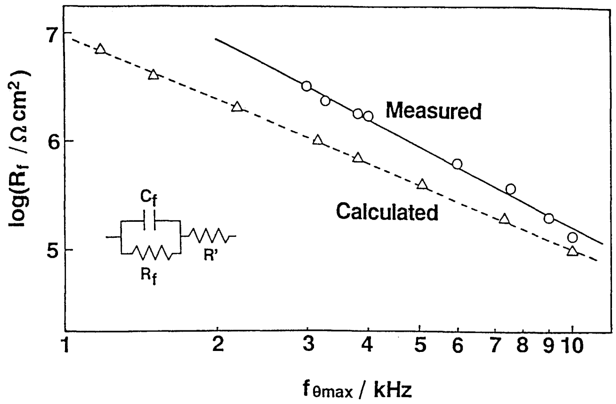

Fig. 3. Relationship between $f_{\theta_{max}}$ and R_f.

described clearly for 30 minutes after immersion, the R_f value could not be obtained. The E value was kept at ca. 0.4 to 0.5 V vs. SCE after immersion for 20 minutes after the initial immersion; thereafter it gradually shifted to a negative potential in the figure until it remained constant at ca. −0.5 V vs. SCE. In connection with the R_f value, the tendency for the E value to change is similar to that of the R_f value at an initial immersion. However, the E value is influenced by the substrate and so can not reflect the film condition directly. It is thought, therefore, that it is unsuitable to evaluate the degradation of paint film by means of the E value instead of the R_f value.

The other parameters—that is, θ_{max} and $f_{\theta_{max}}$—could be determined. The θ_{max} and $f_{\theta_{max}}$ values increased with the immersion time; this behavior corresponded to that of the R_f. The parameters of θ_{max} and $f_{\theta_{max}}$ are superior to that of E, in that these parameters enable us to understand the difference between the two time constants concerned with the paint film and the substrate; they can be determined after an initial immersion for 10 minutes. The $f_{\theta_{max}}$ is, then, related to Z (or resistance (R)) and the capacitance (C) as follows: $f_{\theta_{max}}=1/2\pi Z_{\theta_{max}}C$, where $Z_{\theta_{max}}$ is Z at θ_{max}.[15] The parameter of $f_{\theta_{max}}$ can be evaluated for the degradation of the coating film in comparison with that of θ_{max}. Figure 3 shows the relationship between R_f and $f_{\theta_{max}}$. The R_f decreased linearly in logarithms with the increase in $f_{\theta_{max}}$. The calculated data in such a relationship were also shown in the same figure; they were determined by an equivalent circuit model in this figure. The values of R' and C_f are of the pseudoresistance (apparent resistance), containing both the solution resistance (R_{sol}) and the resistance on the measuring system (R_c), and the film capacitance, respectively ($R'(=R_{sol}+R_c)=2.7\times10^4$ $\Omega\,cm^2$ and $C_f=3.0\times10^{-10}$ F cm^{-2}). The values of R' and C_f in this calculation were assumed to be constant, because they are not very variable. The impedance Z of the equivalent circuit shown in Fig. 3 is given by:

$$Z=R'+R_f/(1+j\omega C_fR_f)$$
$$=\frac{R'(1+\omega^2C_f^2R_f^2)+R_f}{1+\omega^2C_f^2R_f^2}-j\frac{\omega C_fR_f^2}{1+\omega^2C_f^2R_f^2},\qquad(1)$$

where ω is related to the frequency f by this relationship: $\omega=2\pi f$ and where $j=(-1)^{1/2}$.
Hence, the phase of the impedance θ is expressed by:

$$\theta=-\tan^{-1}\left(\frac{\omega C_fR_f^2}{R'+R_f+\omega^2C_f^2R_f^2R'}\right).\qquad(2)$$

The maximum of θ with respect to ω is given by the relationship of $d\theta/d\omega=0$ as follows:

$$\frac{d\theta}{d\omega}=-\frac{C_fR_f^2(R'+R_f+\omega^2C_f^2R_f^2R')-\omega C_fR_f^2(2\omega C_f^2R_f^2R')}{(R'+R_f+\omega^2C_f^2R_f^2R')^2+(\omega C_fR_f^2)^2}$$
$$=0.\qquad(3)$$

From Eq. 3 we obtain:

$$\omega_{max}^2=(R'+R_f)/(R_f^2R'C_f^2)=4\pi^2f_{\theta_{max}}^2,\qquad(4)$$

where ω_{max} is the maximum radial frequency. From Eq. 4 we get:

$$f_{\theta_{max}}=\frac{1}{2\pi}\left(\frac{R'+R_f}{R_f^2R'C_f^2}\right)^{1/2}.$$

By taking logarithms of both sides of this equation, we obtain:

$$\log f_{\theta_{max}}=-\log 2\pi+0.5\log(R'+R_f)$$
$$-0.5\log R_f^2-0.5\log R'C_f^2$$
$$=-\log 2\pi-0.5\log R'C_f^2$$
$$+0.5\log(R'+R_f)-\log R_f.\qquad(5)$$

If $R'\ll R_f$, the $(R'+R_f)$ term of Eq. 5 can be replaced by R_f. Substituting the values of R' ($=2.7\times10^4$ $\Omega\,cm^2$) and C_f ($=3.0\times10^{-10}$ F cm^{-2}) into Eq. 5 yields the following equation:

$$\log R_f=13-2\log f_{\theta_{max}}.\qquad(6)$$

Equation 6 indicates the calculated line in Fig. 3. The relationship between $\log R_f$ and the $f_{\theta_{max}}$ value determined by the use of the calculated data is also linear; the experimental values have the same correlation as the calculated values. The straight line of $\log R_f$ vs. $f_{\theta_{max}}$ obtained by the use of the experimental value was shifted upward in comparison with that obtained by the use of the calculated value. Such a shift may be ascribed to the fact that the center of the semicircle in the Nyquist plot was below the real axis.

That is, it seems to be caused by increased surface roughness or by geometrical effects leading to a nonuniform, repartitioning of the current density on the surface.[16,17] In this case, the relation between R_f and $f_{\theta_{max}}$ based on the measured and calculated values showed the same tendency. The R_f value can be determined by the measurement of the $f_{\theta_{max}}$ value, while the $f_{\theta_{max}}$ can be measured rapidly in the high frequency range. The precision of the electrochemical impedance measurements by means of FRA rises as the integration time increases.

At any rate, the relationship of R_f with $f_{\theta_{max}}$, as is shown in Fig. 3, can be regarded as a calibration curve. The R_f value is speedily and exactly determined by the measurement of the $f_{\theta_{max}}$ value and its relationship. The degradation of the coating film can easily be predicted by the use of the estimation method described above.

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