Evaluation of Iron Corrosion Rate in Solution Containing Inhibitors by Using Couloustatic Method

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In order to expand and clear the applicable range of the coulostatic method to measure the metal corrosion rate in solution, the method was tested by measuring the corrosion rate of iron in water containing three types of inhibitor, i.e., potassium chromate, polyphosphate with calcium ion and sodium nitrate, in stagnant state. Though the potential decay curve did not obey the theoretical equation at the initial stage because of the film formation by the inhibitors, the overpotential $\eta_i$ at $t=0$ was obtained by extrapolating the linear parts of the log $\eta_i$ plots to $t=0$. The corrosion rates obtained by using $\eta_i$ and other parameters gave good agreement with those obtained by the weight loss method for the same samples. So, from a practical standpoint, the coulostatic method was found to be applicable for iron corrosion rate monitoring in the solution containing above inhibitors.

Key wards: coulostatic method, corrosion rate measurement, iron corrosion, inhibitor, weight loss method

1. Introduction

The polarization resistance method to obtain metal corrosion rates in solution is a familiar electrochemical technique. Its principal advantage is in its rapidity compared to the weight loss method. However, the polarization resistance method involves several problems. The method needs ohmic drop correction if the solution is a high resistance medium. The measurements become markedly time dependent in case of very low corrosion rate. To overcome these defects, the coulostatic method was successfully applied to corrosion rate measurement. However, the applicable range of the method is not so clear. To expand its applicability to a wide range of corrosion systems, we tested the method by measuring the corrosion rate of steel in water containing various types of corrosion inhibitors in stagnant state.

2. Description of the Method

Polarization resistance $R_p$ is inversely related to corrosion rate $i_{corr}$ of the metal,

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)} \cdot R_p^{-1} \quad (1)$$

where $\beta_a$ and $\beta_c$ are Tafel slopes for anodic and cathodic processes.

The coulostatic method has been developed on the basis that the interface of the metal and solution can be represented by a simple $C_nR_p$ parallel equivalent circuit within a small voltage amplitude from the natural potential, where the $C_n$ responds to double layer capacitance. When a small amount of charge is sent to a corroding metal, the potential of the metal jumps from its corrosion potential (natural potential in the solution) to another potential. As the charge is consumed by corrosion reaction, the jumped potential decays to the initial value. Qualitatively, if the corrosion rate is high, the potential decay is fast. This decay process can be expressed by Equation 2,

$$\log \eta_t = \log \eta_0 - t/(2.303 \cdot C_n R_p) \quad (2)$$

where $\eta_t$ and $\eta_0$ are overvoltage at time $t$ and 0,
respectively. From the value of $\eta_0$ and supplied charge amount $\Delta q$, $C_d$ can be calculated using Equation 3.

$$C_d = \frac{\Delta q}{\eta_0}$$

(3)

Thus, by obtaining the value of $\eta_0$ and the relationship between overvoltage decay and time, $R_p$ value can be determined.

For the calculation of the corrosion current density $i_{corr}$ by using Eq. 1, anodic and cathodic Tafel slopes are necessary, which can be also determined by the coulometric method. In the Tafel slope measurement, the amount of charge is chosen to yield a 50 mV or larger overvoltage in order to eliminate the effect of the opposite reaction. The final formula for calculating the Tafel slope is given in Equation 4,

$$\beta = \frac{\Delta \eta}{\log \left( \frac{t_3 - t_2}{t_2 - t_1} \right)}$$

(4)

where $\Delta \eta$ is an arbitrary interval of overvoltage which divides the decay curve, $t_1$, $t_2$ and $t_3$ are read three succeeding times from these succeeding points. The value of $\Delta \eta$ is usually 5 to 10 mV. To obtain the anodic Tafel slope $\beta_a$, a test piece is polarized in the anodic direction and in the reverse direction for the cathodic Tafel slope, $\beta_c$. Both $\beta_a$ and $\beta_c$ can be calculated in the same manner using Equation 4. Thus, a corrosion current density can be obtained by using Equation 1.

3. Experimental

The overvoltage decay curves necessary for calculating the polarization resistance and Tafel slopes were measured by using a corrosion meter (Hokuto Denko HK-201) which could apply a given amount of electric charge to a test piece in solution, a transient time converter (Riken Denshi TCC-1000-11) and a $Y-t$ recorder. Commercially available steel coupons (JIS SS41) were used as test pieces, which were also used as a counter electrode. Two steel coupons immersed in the solution were measured alternately as test electrode. A saturated calomel electrode was used as reference electrode. Three types of inhibitors, i.e., potassium chromate, polyphosphate with calcium ion and sodium nitrite, were tested. The solution used in experiments were made from reagent grade chemicals with distilled water. All measurements were carried out at a room temperature (26±2°C) under atmospheric pressure.

![Fig. 1 Overvoltage decay curve for steel (SS41) in 0.1% NaCl solution containing 100 ppm K$_2$Cr$_2$O$_7$ after immersion for 506 hours at room temperature. (Reprinted by permission of the Electrochemical Society Inc.)](image)

![Fig. 2 log $\eta_0$–t relationship for steel according to Fig. 1. (Reprinted by permission of the Electrochemical Society Inc.)](image)
without expelling the dissolved oxygen in the solution.

4. Results and Discussion

An example of overpotential decay curve obtained in 0.1\% NaCl solution containing 100 ppm K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} is shown in Fig. 1. By analyzing this curve, polarization resistance can be obtained. The coulostatic method utilizes the linear polarization in the vicinity of the corrosion potential, and analyzes the overvoltage decay curve on the assumption that the electric properties of the corroding metal are expressed by a simplified C–R equivalent circuit. Consequently, if the large pseudo-capacity due to the film formation or the corrosion product layer is present on the metal surface, it is expected to have some effect on the determination of $C_a$ and $R_p$.

The relation between log $\eta$ and $t$ obtained from the curve (Fig. 1) shows that the plots after about 0.3 s indicate a fairly good linearity in agreement with the theoretical equation (Fig. 2), while, at the initial stage of the decay curve, they deviate from the linear relationship. Usually, measured log $\eta$–$t$ relation more or less deviates from a linear relationship indicated by Equation 2. This is because that an actual metal solution interface has complicated structure which would be impossible to be indicated by single equivalent C–R component.

A coulostatic decay curve is a frequency response to a current impulse having a wide frequency range, usually spreading from 0.01 Hz to 10 kHz. As a result, it implies some information besides corrosion reaction itself. For example, an frequency analysis using Fourier transformation on painted steels immersed in corroding solutions has made clear that a coulostatic decay curve has mainly two sorts of information\textsuperscript{5}. One is a response of the painted film itself, which is obtained from rather high frequency region. Another response which can be obtained from lower frequency region corresponds to the corrosion reaction occurred under the film. Further, similar polarization resistance values were obtained by a Fourier transformation for lower frequency region and a direct analysis of log $\eta$–$t$ relation using linear portion appeared in the latter part of the curve. For inhibitor containing systems, similar analysis would be effective to obtain a polarization resistance value from a log $\eta$ plot. The initial part of the curve which deviated from a linear relationship would be a duplicated response of the interface including charging process. So, analysis was made by extrapolating the linear part of the curve and obtained corrosion rate was compared with the value determined by weight loss measurements.

For the curve shown in Fig. 2, the $\eta_0$ value was obtained by extrapolating the linear parts of the log $\eta$ plots to $t=0$. The value of $\eta_0$ was found to be 3.7 mV, from which the differential capacity $C_a$ was calculated as 1.36 F/m\textsuperscript{2}. Polarization resistance $R_p$ was deduced as 0.93 $\Omega$m\textsuperscript{2} from the
slope of \( \log \eta - t \) plot with the aid of \( C_d \) value.

Next, the Tafel slopes were obtained. Figure 3 shows anodic and cathodic overvoltage time curves. By using these curves, Tafel slopes were calculated as \( \beta_a = 30 \) mV and \( \beta_a = 29 \) mV, respectively. Combining \( R_p \) value and Tafel slopes, a corrosion current was calculated to be \( \approx 10^{-12} \) A/m\(^2\), which was in agreement with the value obtained by weight loss method (Table 1). Time dependency of corrosion rate is shown in Fig. 4. This system showed almost the constant corrosion rate with immersion time. In the solution containing 0.1% NaCl and 200 ppm NaN\(_2\) as inhibitor, corrosion rate as initial state of immersion fluctuated, but showed constant and very small values after 500 hours of immersion showing this system is in inhibited condition (Fig. 5). Another example is shown in Figure 6, where polyphosphate with calcium ion is used as inhibitor. The corrosion protection effect began to appear gradually with time. It is said that calcium salt additions lead to formation of a diffusion barrier film containing both calcium and phosphorus on cathode areas\(^6\). Figure 6 shows a film formation takes time of a few hundreds hours.

In order to examine whether the corrosion rates shown in Figs. 4–6 are reliable or not, the corrosion rates of the same test pieces were calculated by measuring weight losses after about 500 hours immersion in each solution. Corrosion rates obtained by the coulostatic method for each measuring point were averaged graphically for the entire immersion periods and compared with those calculated from the weight losses (Table 1). Two kinds of corrosion rates for each system coincide with each other as listed in Table 1. Thus, although the protective film due to three types of inhibitors forms on the test piece, so such a film results in a deviation from the linearity in the logarithmic overvoltage decay curve (Eq. 2), and gives relatively large apparent \( C_d \) value, the coulostatic method is found to be applicable for iron corrosion rate monitoring in the solution containing some sorts of inhibitors, i.e., potassium chromate, polyphosphate with calcium ion, and sodium nitrite and is a useful tool from a practical stand point.

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References