Protection of Carbon Steel from Atmospheric Corrosion by TiO₂ Coating

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Protection of carbon steel (C-steel) from atmospheric corrosion by TiO₂ coating was demonstrated. TiO₂ coating, as a non-sacrificial anode, absorbed solar energy and transformed it to electricity so as to provide cathodic protection to the substrate steel. A TiO₂-Fe galvanic couple was developed as an ACM (atmospheric corrosion monitor) sensor to evaluate the photoeffect and corrosion behavior of TiO₂/C-steel in atmosphere. For the TiO₂-Fe couple, type 1 sensor, an anodic output related to the anodic dissolution of the coupled Fe electrode was detected in the dark (night time), whereas in the bright (day time) the output changed from anodic to cathodic. Moreover, the cathodic output remained for a long time after stopping illumination for the multi-layer coating, TiO₂ (amorphous)/TiO₂ (anatase)/Ti-Fe oxide/a-Fe₂O₃/C-steel, type 2 sensor. Environmental conditions in terms of relative humidity, RH, and amount of deposited sea salt, Wₛ, where 1 mm wide Fe coupled to 5 mm wide TiO₂ could be protected were determined based on the following examinations:

a) visual observation for degree of rust developed on the Fe electrodes, for the type 2 sensor
b) comparison of corrosion potential of carbon steel with photo potential of TiO₂ electrode measured by Kelvin probe,
c) polarity of output current for the type 1 sensor.

It is concluded that the carbon steel could be protected from atmospheric corrosion by TiO₂ coating under conditions of lower amount of deposited sea salt and lower relative humidities.

Key words: atmospheric corrosion, cathodic protection, TiO₂, solar energy, ACM sensor, carbon steel, sol-gel.

1. Introduction

It has been shown that TiO₂ coating under illumination acts as a non-sacrificial anode and provides cathodic protection to substrate metals¹⁻⁸. For this novel approach to corrosion protection, it is a matter of primary importance to obtain a good photoeffect for the TiO₂/metal system. For TiO₂ coated carbon steel (C-steel) prepared by sol-gel method as investigated in our previous studies⁶⁻⁸, photoelectrochemical behavior was found to be significantly affected by structural and electronic properties of interfacial oxides, i.e., iron oxides and Ti-Fe oxides at the TiO₂/C-steel interface. A good photoeffect was obtained for a coating structure with an interfacial layer of a-Fe₂O₃, that is, TiO₂ (anatase) /a-Fe₂O₃ / C-steel. Moreover, photoeffect was further improved with a multi-layer coating like TiO₂ (amorphous)/TiO₂ (anatase)/Ti-Fe oxide/a-Fe₂O₃/C-steel, for which it was observed that photoeffect can remain even after stopping illumination⁹. In the multi-layer coating, TiO₂ (anatase) layer without Fe contamination exhibits a good photoeffect and behaves like the source of photo-excited electrons. The inner a-Fe₂O₃ layer acts as both a barrier to retard the diffusion of Fe into TiO₂ and a way for the transfer of photo-excited electrons from the TiO₂ (anatase) layer to the substrate. The intermediate Ti-Fe oxide layer provides deep levels for Fe(Ⅱ)/Fe(Ⅲ) redox couple, for which Fe(Ⅲ) is reduced to Fe(Ⅱ)...

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by the photo-excited electrons under illumination. The state of Fe(II) left after stopping illumination contributes to phenomenon that the electrode potential is maintained at considerably less noble value until all the Fe(II) is re-oxidized by oxygen reduction. The outer layer of amorphous TiO2 inhibits the oxygen reduction to contribute to prolonged stay of the photopotential at less noble values. So that, the multi-layer coating shows a potentiality for the corrosion protection of steel not only under illumination (day time) but also after stopping illumination (night time).

In the present work, protection of C-steel from atmospheric corrosion was demonstrated. In particular, solar energy was shown to be feasible for photoelectrochemical cathodic protection of steel since it can be absorbed and transformed to electricity by TiO2 coating. For atmospheric condition, electrolyte exists just as a thin film of water adsorbed on surface. So the photoelectrochemical behavior in atmosphere should be quite different from that in bulk solution. Moreover, conventional electrochemical measurements used in bulk solution are not suitable for the atmospheric condition. In this work, besides Kelvin probe measurement and Quartz Crystal Microbalance (QCM), a TiO2-Fe galvanic couple was developed as an ACM (atmospheric corrosion monitor) sensor to evaluate the photoeffect and corrosion behavior of the TiO2/C-steel system in atmosphere. The effects of environmental factors such as relative humidity and amount of deposited sea salt were investigated.

2. Experimental

2.1 Specimen

The C-steel sheet (mass %: C 0.111, Si 0.013, Mn 0.367, P 0.015, S 0.0056, Al 0.120, Fe bal.) was cut to a size of 50×50 mm² and polished to a mirror finish by 0.05 μm Al₂O₃ before coating. There were two kinds of coating structure prepared by sol-gel method, i.e., TiO₂ (anatase)/α-Fe₂O₃/C-steel (type 1) and TiO₂ (amorphous)/TiO₂(anatase)/Ti-Fe oxide (mole ratio Fe/Ti=1)/α-Fe₂O₃/C-steel (type 2). The preparation of sol-gel solution, dip-coating procedure and heat treatments for TiO₂ (amorphous: 200°C-10 min, 2 dip), TiO₂ (anatase: 400°C -10 min, 2 dip), Ti-Fe oxide (mole ratio Fe/Ti=1: 400°C-10 min, 1 dip) and α-Fe₂O₃ (525°C -10 min, 1 dip) were identical to our previous study.

2.2 ACM sensor

The schematic representation of the TiO₂-Fe galvanic couple used as an ACM sensor is shown in Fig.1. The grid electrode of Fe of 7×40 mm×1 mm was prepared with by vacuum deposition method on a thin layer of insulator, which had been sprayed preparatively in the same grid form on the TiO₂ coated C-steel sheet of exposed area of 7×40 mm×5 mm. The layers of Fe and insulator were 100–150 μm and ~100 μm in thickness, respectively.

With a certain amount of sea salt, Wₛ, deposited on its surface, the sensor was set in a humidity control chamber and illuminated by a 500 W high pressure Hg lamp. The chamber consisted of a quartz window on one side accompanied with filter, through which specimen was illuminated by ultraviolet light. Output of the sensor, coupled current between TiO₂ and Fe electrode, was detected by a zero resistance ammeter and recorded with a micro-computer. The amount of sea salt was controlled strictly by spraying of a certain concentration of diluted sea water.

2.3 Kelvin probe measurement

In the humidity control chamber, electrode potentials of the TiO₂ coated carbon steel and the bare carbon steel were determined independently by Kelvin probe measurement. Ag/AgCl probe was prepared with a Ag wire of φ 1 mm, which was treated with an anodic current of 3 mA/cm² in 0.1 N HCl solution. Potentials were calibrated for several kinds of metals by both the Kelvin probe and SCE under a condition of Wₛ, 10g/m² and RH 90%,
where potential measurement by SCE was possible because of enough adsorbed water on surface. And then, the potential measured by Kelvin probe \((V_{Kp})\) was converted to SCE by the derived relationship of \(V_{SC}(mV, SCE) = -110 + 1.05 V_{Kp}\).

### 2.4 Quartz Crystal Microbalance (QCM)

The amount of water adsorbed on the surface of TiO\(_2\) coating was determined by the Quartz Crystal Microbalance (QCM). First a gold (Au) electrode was prepared on each side of an AT-cut quartz by vacuum deposition method, and then the TiO\(_2\) layer was dip-coated on the gold electrodes on the both sides. The frequency change, \(\Delta f\), of 1 Hz in our experiment corresponded to the weight change, \(\Delta m\), of \(8.85 \times 10^{-9} g/cm^2\) according to the Sauerbrey equation:

\[
\Delta f = -\frac{f_0^2}{N\rho n} \Delta m,
\]

where \(f_0\) is a reference frequency of the quartz oscillator (5 MHz), \(N\) is a fixed frequency coefficient of the crystal \((1.67 \times 10^6 \text{cmHz})\), \(\rho\) is the density of the crystal \((2.65 g/cm^3)\), and \(n = 2\) is the number of exposed sides.

### 2.5 Exposure tests

Outdoor exposure tests were carried out for the TiO\(_2\)-Fe couple ACM sensors at Graduate School of Engineering, The University of Tokyo, Hongo in Tokyo. The output of ACM sensor, relative humidity and ultraviolet intensity, \(I_{UV}\), were recorded simultaneously. The intensity of ultraviolet was measured by an ultraviolet radiometer (wave length 330~490 nm).

### 3. Results and Discussion

#### 3.1 Outputs of the TiO\(_2\)-Fe couple sensors

##### 3.1.1 Type 1 sensor

Fig.2 shows the dependence of output, \(I\), on relative humidity \(RH\) for the sensor of type 1 with various amounts of deposited sea salt, \(W_s\). For the sensor in the dark (Fig.2 (a)), the output was anodic for the Fe electrode. The output increased with increasing \(RH\) and \(W_s\). With no deposited sea salt, no output greater than 0.1 nA was detected except when \(RH\) was above 90%. The output shows significant behavior at \(RH\) values near 34% and 76%, which correspond to those in equilibrium with saturated MgCl\(_2\) and NaCl solutions, respectively.

However, the situation under illumination was quite different as shown in Fig. 2(b). The output for the Fe electrode was cathodic due to anodic photo current on the coupled TiO\(_2\) electrode. The cathodic output increased with increasing \(W_s\), especially for a range of lower \(RH\). When \(W_s\) was larger than 0.03 g/m\(^2\), the cathodic output appeared to level off at \(RH\) near 80%, and an anodic one was detected at \(RH\) above 85% for the sensor with a \(W_s\) of 0.3 g/m\(^2\).

Fig.3 shows the response to illumination of the sensor output with various \(W_s\) at \(RH\) 70% (a) and 90% (b). Photoeffect appeared obviously when the light was turned on. The outputs changed from anodic (solid symbols) to cathodic (open symbols) on illumination, with
an exception when just a decreased anodic current was detected under the condition of a higher \(W_s\) of 0.3 g/m² and a RH of 90%. It was found that it took only several minutes for the outputs of this type 1 sensor to attain to a stationary anodic value after the light was turned off.

### 3.1.2 Type 2 sensor

It has been shown that less noble electrode potential given as a photo effect can be maintained for a long time even after stopping illumination for TiO₂ (amorphous)/TiO₂ (anatase)/Ti-Fe oxide/\(α\)-Fe₂O₃/C-steel (type 2) in bulk solution. In this test in atmosphere, cathodic output was also observed for the sensor of type 2 under illumination as shown in Fig. 4. The sensor with no deposited sea salt was firstly illuminated at various RH for 90 min and then kept in the dark at RH 90%. During illumination, the output was cathodic and increased gradually. Moreover, the cathodic output was still observed after stopping illumination, and it remained up to several thousand minutes even for the sensor illuminated previously at lower RHs down to 20%. The effect of deposited sea salt on the photoeffect is shown in Fig. 5. The sensor was illuminated at RH 30% for 90 min and then put in the dark at RH 90% to simulate a condition in natural atmosphere, where RH is generally lower in the day time and higher in the night time. For a higher \(W_s\) of 0.1 g/m², the output happened anodic before illumination, but it decreased and then changed to cathodic during illumination.
3.2 Electrode potentials of TiO$_2$ coating and carbon steel

In order to further understand the photoeffect and the corrosion behavior of the TiO$_2$/C-steel system, electrode potentials of both the TiO$_2$ coating and the carbon steel in atmosphere were determined by Kelvin probe measurement. Fig. 6 shows time variation of electrode potentials for the multi-layer coating (type 2). The potentials decreased gradually and became stationary after 120 min under illumination. After stopping illumination, the potential still remained at less noble values.

Fig. 6 Time variation of electrode potentials of TiO$_2$ coating, $E_{TiO_2}$, under 180 min of illumination and subsequently in the dark for 120 min at various relative humidity $RH$.

Fig. 7 Effect of relative humidity, $RH$, and amount of deposited sea salt, $W_s$, on electrode potential of TiO$_2$ coating in the dark before illumination (solid symbols) and photo-potential after 120 min of illumination (open symbols).

Fig. 8 Effect of relative humidity, $RH$, and the amount of deposited sea salt, $W_s$, on corrosion potential of C-steel, $E_{C\text{-steel}}$, in the atmosphere.

Fig. 9 Comparison of photo-potential of TiO$_2$ coating (type 2), $E_{TiO_2}$, with corrosion potential of C-steel, $E_{C\text{-steel}}$, under various conditions of $W_s$ and $RH$.

Fig. 7 shows the effect of the amount of deposited sea salt, $W_s$. Potential of the TiO$_2$ coating before illumination (solid symbols) was found to range about 0 to 200 mV vs. SCE with various $W_s$, while on illumination (open symbols) it decreased significantly. The value after 120 min of illumination decreased with increasing $RH$ and $W_s$. As shown in Fig. 8, corrosion potential of carbon steel was also measured under various $RH$ and $W_s$, and compared with photo-potentials of TiO$_2$ coating in Fig. 9. The photo-potential of TiO$_2$ coating was less noble than the corrosion potential of carbon steel except for $RH$ > 70% and $W_s$ of 0.3 g/m$^2$.
3.3 Exposure test

Fig. 10 shows an example of the sensor outputs of types 1 and 2, ultraviolet intensity $I_{uv}$ and relative humidity $RH$, in a period of 14–15th March '98. The outputs were found to be sensitive not only to $RH$ (in the night) but also to light (in the day time). For the type 1 sensor, the effect of sun light could be illustrated from the relationships among output $I$, $I_{uv}$ and $RH$ as shown in Fig. 11. Although at the same $RH$, there was difference in the output between the day and the night. The output changed from catholic to anodic on the sunset (≈16 o’clock), and the anodic one in the night decreased abruptly and became catholic in the morning when the sun shone out (≈6 o’clock).

For the type 2 sensor, an anodic output was detected only in the first night (0~6 o’clock) without any preceding illumination. As shown in Fig. 12, in the morning (6~8 o’clock), the anodic output decreased and changed to a cathodic one. The cathodic one increased gradually during the day (8~17 o’clock) and it remained through the next night (17~6 o’clock).

3.4 Protection of steel from atmospheric corrosion by TiO$_2$ coating

Photocurrent generation at TiO$_2$ corresponds to the injection of photo-generated holes (minority carriers) from the valence band into electrolyte (water). So the photoeffect of TiO$_2$ in atmosphere should relate to the adsorbed water on its surface. Recently, super-hydrophilicity of irradiated TiO$_2$ was ever reported [10, 11]. In the present work, the amount of water adsorbed on the TiO$_2$ surface with
various RH and Ws, were determined by QCM. As shown in Fig. 13, a good hydrophilicity was observed for the TiO2 coating prepared by sol-gel method. The amount of water adsorbed on the TiO2 surface was larger than that on metals, for example, on Au as shown in the figure. The adsorbed water on TiO2 increases greatly with increasing RH and Ws, while on Au it levels off at higher RH (>70%) in the case of a higher Ws (0.1 g/m2).12,13)

The type 2 coating has promised the feasibility not only in bright (day time) but also in dark (night time), which would seem generally embarrassing to the protection of TiO2 coated steel, particularly by use of solar energy. As introduced in the previous study63, the multi-layer coating rather acts as a photovoltaic system (equipped with rechargeable batteries), in which solar energy is converted to electricity and it charges batteries in addition to powering electrical devices, and then the batteries discharges and deliver power in dark. For the multi-layer coating, photoelectrons are generated in the TiO2 (anatase) layer as in the photovoltaic cell, while the Ti-Fe oxide layer is similar to the batteries and performs as an accumulator for the electrons.

Corrosion behavior of TiO2 coated C-steel varied with relative humidity, RH, and deposited sea salt, Ws, as shown in Fig.14. In the figure, the line L1 is the distinguished boundary at which the output of Fe-TiO2 sensor (type 1) changed from anodic to cathodic as shown in Fig.2(b). The line L2 presents the limit derived from Fig.9 at which the photopotential of TiO2 coating became less noble than the corrosion potential of C-steel. Both the two lines were found to move to a lower RH with increasing Ws. Rust growth tests were also carried out for Fe-TiO2 couples (type 2 sensor). In the tests, they were firstly illuminated for 120 min and then kept in dark under various conditions of RH and Ws.

For conditions of RH and Ws lower than the L2 line, no rusts was observed on the Fe electrodes when they were kept in dark for more than one day after illumination (marked by “○” in Fig.14). Slight rusty spots appeared for the conditions near the lines of L1 and L2 (marked by “●”).

4. Conclusions
Photoelectrochemical cathodic protection of carbon steel from atmospheric corrosion by TiO2 coating was demonstrated. For TiO2-Fe galvanic couple, the output was cathodic for the Fe electrode in the bright, or in the day time, and remained cathodic for a long time, or through the night time after stopping illumination for TiO2 (amorphous)/TiO2 (anatase)/Ti-Fe oxide/α-Fe2O3/C-steel. The electrode potential of TiO2 coating could be reduced to less noble value than the corrosion potential of C-steel. It was shown to be possible to protect carbon steel from atmospheric corrosion by TiO2 coating under conditions of
lower amount of deposited sea salt and lower relative humidities.

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References