

# Photo-Effects of Sol-Gel Derived $\text{TiO}_2$ Coating on Carbon Steel in Alkaline Solution

Jiangnan Yuan\* and Shigeo Tsujikawa\*\*

\* *Shanghai Institute of Metallurgy, Chinese Academy of Sciences*

\*\* *Department of Metallurgy, Faculty of Engineering, The University of Tokyo*

On the corrosion protection of carbon steel by sol-gel derived  $\text{TiO}_2$  coating under the illumination of light, the photoelectrochemical behavior of  $\text{TiO}_2$ /steel system is investigated. The diffusion of Fe ions into  $\text{TiO}_2$  in the heat treatment of the coating process greatly degrades the photo-effect of  $\text{TiO}_2$  coating. An Fe oxide layer at the  $\text{TiO}_2$ -steel interface, formed by oxidizing the steel above  $500^\circ\text{C}$  in air before coating, has been shown to retard the diffusion. The importance of  $\alpha\text{-Fe}_2\text{O}_3$  in the photo-response of  $\text{TiO}_2$ /steel and the effect of its changing properties with oxidation temperature are discussed. The results on the effect of heat treatment condition in the coating process show that the  $\text{TiO}_2$ /steel specimens exhibit remarkably less noble photopotentials when the heating temperature is increased above  $300^\circ\text{C}$ , which is related to the crystallization of  $\text{TiO}_2$  above this temperature. The ennoblement of photopotential caused by the further increase in heating temperature above  $500^\circ\text{C}$  is a result of Fe diffusion through the oxide layer at the interface. Under the optimum conditions for steel oxidation and  $\text{TiO}_2$  coating, the feasibility of localized corrosion prevention by  $\text{TiO}_2$  coating under illumination is clearly demonstrated by the fact that the photopotentials of  $\text{TiO}_2$ /steel in deaerated solution are much less noble than the repassivation potential of carbon steel.

**Key words :**  $\text{TiO}_2$  coating, sol-gel method, heat treatment, oxidation, carbon steel, illumination, photo-effect, corrosion protection.

## 1. Introduction

Semiconductor or ceramic coatings on metallic substrates by sol-gel method have attracted growing research interests during recent years<sup>1)~5)</sup>. Owing to the relative simplicity of this coating process and its ability to produce coatings with various compositions which are difficult or even impossible for other conventional coating methods, the sol-gel derived coatings endow metallic materials with some unique properties which are of profound significances in applications. Noticeable examples are demonstrated by our recent work on the stainless steel and copper coated with n-type semiconductor  $\text{TiO}_2$ <sup>1), 2)</sup>, in which the  $\text{TiO}_2$ -coated stainless steel and copper exhibited remarkable photoresponses. The importance of these studies lies in that a new area in corrosion science has been pioneered :

the corrosion protection of metals by n-type semiconductor coating under the illumination of light.

In the present work, we are concerned with the photoelectrochemical behavior of carbon steel coated with  $\text{TiO}_2$  coating by sol-gel method. In alkaline environments, the passivated carbon steel would suffer pitting and crevice corrosion<sup>6)</sup>. The feasibility of the prevention of these forms of corrosion by  $\text{TiO}_2$  coating under illumination is shown by the fact that the flatband potential,  $E_{fb}$ , of  $\text{TiO}_2$  is well less noble than the repassivation potential,  $E_R$ , of carbon steel in alkaline solution<sup>6), 7)</sup>. Unlike the cases of stainless steel and copper, it was found that the strong interaction between carbon steel and  $\text{TiO}_2$  due to the high reactivity of Fe<sup>8)</sup> as well as the oxidation of the steel during the heat treatment of the sol-gel process would greatly degrade the photo-effect of  $\text{TiO}_2$  coating. We also found that this problem can be solved by the oxidation of

\* 865 Changning Road, Shanghai, China, 200050

\*\* 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113 Japan

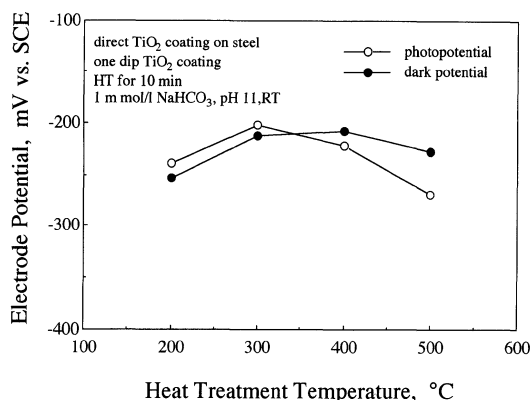


Fig. 1 Photo-effect of the carbon steel directly coated with  $\text{TiO}_2$  under different heating temperatures for 10 minutes. Test solution was aerated 1 m mol/l  $\text{NaHCO}_3$  (pH 11) at room temperature.

steel before coating. Reported in this paper are the results showing the importance of an Fe oxide layer at the  $\text{TiO}_2$ -steel interface and the effect of the change in the Fe oxide itself on the photoelectrochemical behavior of  $\text{TiO}_2$ /steel system.

## 2. Experimental

Carbon steel sheet with a thickness of 0.8 mm (mass% C: 0.111, Si: 0.013, Mn: 0.367, P: 0.015, S: 0.0056, Al: 0.120, Fe: bal.) was used as provided by Shin Nippon Steel Co.. The specimens, cut from the steel sheet with a size of  $30 \times 40$  mm, were polished to a mirror finish by  $0.05 \mu\text{m}$   $\text{Al}_2\text{O}_3$ , rinsed with acetone, and finally dried in air. Before  $\text{TiO}_2$  coating the steel specimens were oxidized in air at different temperatures.

$\text{TiO}_2$  coating was applied to the specimen by sol-gel dip coating method. Detailed  $\text{TiO}_2$  sol solution preparation can be found elsewhere<sup>9)</sup>. Coating process was the same as in our previous paper<sup>1)</sup> except that the heat treatment of the gel coating was carried out in air at different temperatures for 10 minutes.

The test solution, prepared from analytical grade reagents and de-ionized water, was 1 m mol/l  $\text{NaHCO}_3$  adjusted to pH 11 with concentrated  $\text{Na}_2\text{CO}_3$  solution. Without specification, all the experiments were carried out in the aerated solutions. Under the deaerated conditions, the solutions were thoroughly purged with 99.99% nitrogen gas for 30 minutes before

measurements. The capacitance measurements for the oxidized steels were conducted using a superimposed sinusoidal signal with a frequency of 25 Hz, since the donor density,  $N_D$ , obtained at lower frequencies would be more reliable for  $\alpha\text{-Fe}_2\text{O}_3$ <sup>10)</sup>. The measurements of photopotential,  $E_{ph}$ , and the polarization curves under illumination were carried out using a 500 watt high pressure Hg lamp as a light source. Electrode potential was referred to a saturated calomel electrode (SCE). All the experiments were performed at room temperature.

XPS examination for the surface analysis of  $\text{TiO}_2$ /steel specimens was carried out by ESCA 850 (Shimadzu Corp.) electron spectrometer using Mg  $K\alpha$  radiation (8 kV, 30 mA) as the source of excitation. Depth profiling was obtained by sputtering the surface with neon ions (2 kV, 15 mA at a neon gas pressure of  $4 \times 10^{-4}$  Pa). The relative concentrations were calculated from the areas of elements in the spectra against their respective sensitivities. The spectra were calibrated against the binding energy of Au  $4f_{7/2}$  (84.0 eV).

## 3. Results and Discussion

### 3.1 The importance of an Fe oxide layer at the $\text{TiO}_2$ -steel interface

For the carbon steel directly coated with  $\text{TiO}_2$ , the photo-effect of the  $\text{TiO}_2$  coating was insignificant, as shown by the variation of  $E_{ph}$  with heat treatment temperature in Fig. 1. Slight n-type photo-effects of  $\text{TiO}_2$  coatings were observed only when the temperature was raised up to 400 and 500°C with the shift in potential less than 30 mV. These results were quite different from those in our previous studies<sup>1), 2)</sup>, in which the less noble shifts of potentials were found to be more than 200 mV under the heating temperature of below 300°C for stainless steel and above 400°C for copper, respectively. For  $\text{TiO}_2$ /steel system, the importance of an Fe oxide layer between the coating and the substrate steel is demonstrated in Fig. 2. The steel was oxidized at 500°C for 40 min before coating. The heat treatment for  $\text{TiO}_2$  coating was conducted at 400°C for 10 min, which would give rise to a fully crystallized anatase structure with relatively high photo-efficiency<sup>11)</sup>. It is seen that typical polarization curves were obtained, as in the cases

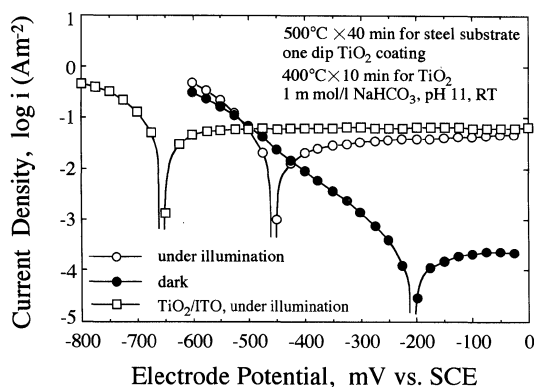


Fig. 2 Polarization curves of TiO<sub>2</sub>-coated carbon steel in aerated 1 m mol/l NaHCO<sub>3</sub> solution (pH 11) at room temperature. The steel was oxidized at 500°C for 40 minutes in air. Heat treatment condition for TiO<sub>2</sub> coating : 400°C for 10 minutes.

of TiO<sub>2</sub>/stainless steel and TiO<sub>2</sub>/Cu. The remarkable photo-effect of TiO<sub>2</sub> coating on steel substrate was indicated by a large shift of potential, about 250 mV, under illumination. Furthermore, the anodic photocurrent was the same order of magnitude as that of TiO<sub>2</sub>/ITO system. As discussed in our previous paper<sup>1)</sup>, Fig. 2 also shows an important feature of the photopotential determination for the TiO<sub>2</sub>/metal system. Due to the porous structure of the TiO<sub>2</sub> coating derived by the current sol-gel technique, the TiO<sub>2</sub>-coated steel can be seen as a galvanic couple with TiO<sub>2</sub> acting as a non-sacrificed anode under illumination. Consequently, the photopotential is determined by the combination of the cathodic process on steel surface ( $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ ) and the anodic process on the TiO<sub>2</sub> surface ( $4\text{OH}^- + 4\text{e}^+ \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$ ). Previous studies on Cu<sup>1)</sup> showed that the  $E_{\text{ph}}$  would be moved toward less noble direction by the increase of anodic photocurrent observed on thicker TiO<sub>2</sub> coating. Likewise, any change in the cathodic process would also result in a change in  $E_{\text{ph}}$ . Compared with the cathodic polarization curve of TiO<sub>2</sub>/steel, the reduction of dissolved oxygen has a much larger overpotential on ITO surface, which led to a  $E_{\text{ph}}$  less noble than that of TiO<sub>2</sub>/steel.

Fig. 3 shows the effect of the oxidation duration at 500°C on the  $E_{\text{ph}}$  of TiO<sub>2</sub>/steel with the TiO<sub>2</sub> coating being heated at 400°C for 10 min. For the steel oxidized for short period of time

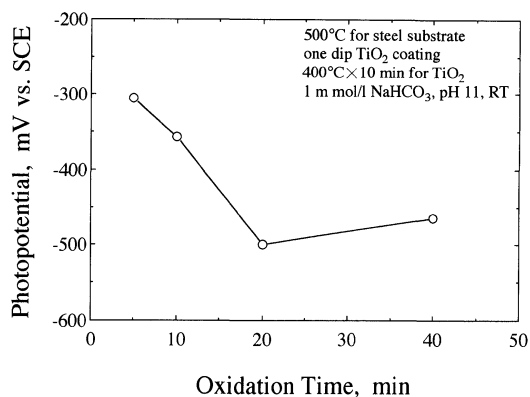


Fig. 3 Effect of oxidation time at 500°C on the photopotential of TiO<sub>2</sub>/steel in aerated 1 m mol/l NaHCO<sub>3</sub> solution (pH 11) at room temperature. Heat treatment condition for TiO<sub>2</sub> coating : 400°C for 10 minutes.

(5 min), the photo-effect was weak, nearly the same as the steel without oxidation. As the oxidation time increased,  $E_{\text{ph}}$  changed greatly toward less noble direction and leveled off when the oxidation time exceeded 20 min. With regard to the poor photo-effect shown in Fig. 1, X-ray diffraction examination of the TiO<sub>2</sub>/Fe powder, prepared by heating the dried TiO<sub>2</sub> sol mixed with Fe, FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>, respectively, ruled out the possibility of the formation of any Ti compounds with Fe at 400°C. To understand the  $E_{\text{ph}}$  change in Fig. 3, XPS technique was applied to examine the TiO<sub>2</sub>/steel under various conditions. For the steel oxidized at 500°C for less than 20 min, a significant amount of Fe was detected on the TiO<sub>2</sub> coating surface. The binding energies of Fe 2p<sub>3/2</sub> (710.4 eV) and Ti 2p<sub>3/2</sub> (458.9 eV) can be associated to Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, respectively, which were consistent with the results of X-ray diffraction studies. The depth profiles are shown in Fig. 4 with the steel being oxidized at 500°C for 10 min (Fig. 4a) and 20 min (Fig. 4b). For the specimen with shorter time of oxidation, the concentration of Fe in the coating was so high that a pure TiO<sub>2</sub> coating no longer existed. Consequently, poor photo-effect could be expected for such a specimen covered with a mixture of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. When the oxidation time increase above 20 min, the surface layer mainly consisted of TiO<sub>2</sub>, which may explain a remarkable change in  $E_{\text{ph}}$  toward less noble direction

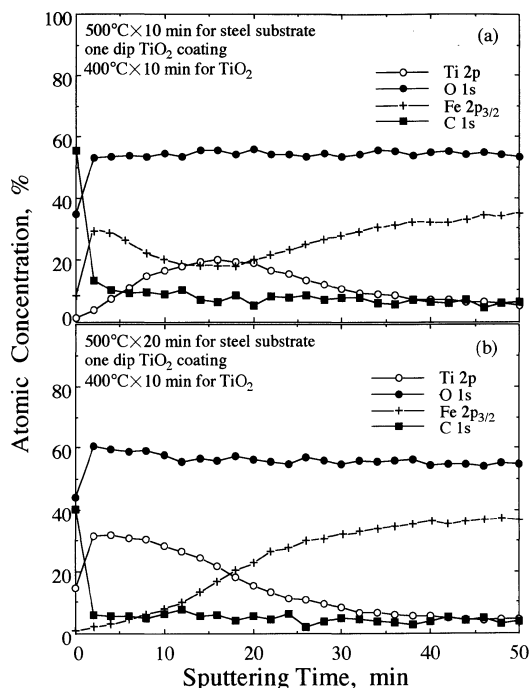


Fig.4 XPS depth profiles of  $\text{TiO}_2$ /steel. Heat treatment condition for  $\text{TiO}_2$  coating :  $400^\circ\text{C}$  for 10 minutes. The steel was oxidized in air at  $500^\circ\text{C}$  for 10 minutes (a) and  $500^\circ\text{C}$  for 20 minutes (b).

shown in Fig. 3. A further discussion on the importance of an oxide layer at the  $\text{TiO}_2$ -steel interface involves the oxidation kinetics of Fe since the heat treatment required for  $\text{TiO}_2$  coating may cause the oxidation of steel during coating process. Two possible origins of Fe in the coating are : i) corrosion of the steel when in contact with sol solution which contained  $\text{H}_2\text{O}$  and  $\text{HCl}$  ; ii) diffusion of Fe into  $\text{TiO}_2$  coating as a result of oxide growth during heat treatment. It is supposed that the latter would be more possible. As shown in Fig. 4b, oxidation of the steel at  $500^\circ\text{C}$  for 20 min led to an insignificant diffusion of Fe into coating. At this temperature, the scale formed on steel surface was reported to consist of  $\text{Fe}_3\text{O}_4$  with a thin layer of  $\text{Fe}_2\text{O}_3$  on it<sup>12</sup>. The coverage of the  $\alpha$ - $\text{Fe}_2\text{O}_3$  layer would be increased with the oxidation time near  $500^\circ\text{C}$ <sup>13</sup> or at higher oxidation temperatures. Under these circumstances, the rate of following oxidation at 400 with relative high  $P_{\text{O}_2}$  during the heat treatment in the sol-gel process would be very low<sup>14</sup>. Thus the Fe diffusion during coating

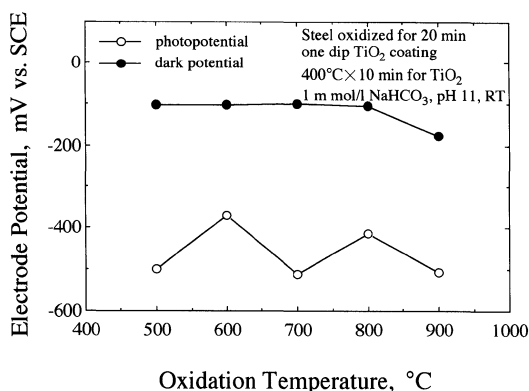


Fig.5 Effect of oxidation temperature on the photo-effect of  $\text{TiO}_2$ /steel in aerated 1 m mol/l  $\text{NaHCO}_3$  solution (pH 11) at room temperature. Heat treatment condition for  $\text{TiO}_2$  coating :  $400^\circ\text{C}$  for 10 minutes.

process was greatly suppressed.

### 3.2 Behavior of oxidized steel without $\text{TiO}_2$ coating

The effect of oxidation temperature on  $E_{\text{ph}}$  was examined up to  $900^\circ\text{C}$ . Fig. 5 shows that while all the specimens exhibited strong photo-effects under these oxidation conditions, the change of  $E_{\text{ph}}$  with oxidation temperature is significant. At the oxidation temperatures of 500, 700, and  $900^\circ\text{C}$ , the resultant  $E_{\text{ph}}$  were nearly same, about  $-500$  mV, while noble  $E_{\text{ph}}$  of  $-350$  mV and  $-400$  mV were observed at 600 and  $800^\circ\text{C}$ , respectively. XPS examination revealed that the diffusion of Fe was hindered by the Fe oxides under these conditions. It follows that the above results reflect the change of the properties for the Fe oxide formed at various temperatures, which have influences on the  $E_{\text{ph}}$  because the specimen was a heterojunction of  $\text{TiO}_2$  with Fe oxides in nature. In fact, such a heterojunction is much complicated since the Fe oxides have a structure of  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  below  $570^\circ\text{C}$  and  $\text{FeO}/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  above  $570^\circ\text{C}$ <sup>15</sup>. Both FeO and  $\text{Fe}_3\text{O}_4$  are p-type semiconductors, while  $\alpha$ - $\text{Fe}_2\text{O}_3$  is an n-type semiconductor. The beneficial effect of  $\alpha$ - $\text{Fe}_2\text{O}_3$  has been discussed in previous section, however, its high resistivity ( $10^{14} \Omega \cdot \text{cm}$  for undoped  $\alpha$ - $\text{Fe}_2\text{O}_3$ ) should not be overlooked. A detailed study on the effect of the property change of Fe oxides on the photoelectrochemical behavior of this heterojunction is beyond our concern, however, some electrochemical measurements of the steel substrates oxidized

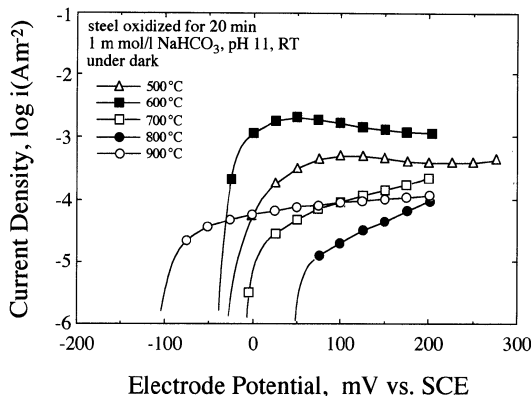


Fig. 6 Dark polarization curves of the oxidized steel in aerated 1 m mol/l  $\text{NaHCO}_3$  solution (pH 11) at room temperature. The steel specimens were oxidized in air for 20 minutes at various temperatures.

at various temperatures may provide useful information relevant to our purpose. Shown in Fig. 6 are the dark polarization curves of the oxidized steel specimens (without  $\text{TiO}_2$  coatings). It is seen that the anodic behaviors under different oxidation temperatures are quite different from each other. Firstly, the oxidation at  $600^\circ\text{C}$  resulted in a higher dissolution rate than at  $500^\circ\text{C}$ . At these two temperatures, the anodic currents exhibited a slight decrease with the increase of potential near 100 mV. Since  $\alpha\text{-Fe}_2\text{O}_3$ , on the top of the oxide layer, is very stable in alkaline solution, high dissolution rate can be considered to result from a thin, or alternatively, discontinuous  $\alpha\text{-Fe}_2\text{O}_3$  layer<sup>16</sup>. Secondly, the anodic dissolution greatly decreased when the oxidation temperature was higher than  $600^\circ\text{C}$ , and the lowest anodic current and the most noble  $E_{\text{corr}}$  were observed at  $800^\circ\text{C}$ , which was due to the increased thickness and continuousness of the  $\alpha\text{-Fe}_2\text{O}_3$  layer, as would be expected. Finally, for the steel oxidized at  $900^\circ\text{C}$ , the anodic current exhibited a much flatter increase with potential and a very less noble  $E_{\text{corr}}$ .

The Mott-Schottky plots for the capacitance data of the oxidized steel specimens are shown in Fig. 7. At  $500^\circ\text{C}$ ,  $C^{-2} \sim E$  exhibited a very good linearity while a negative slope portion was observed in the noble potential region ( $> -200$  mV), suggesting the effect of the p-type  $\text{Fe}_3\text{O}_4$ . The effect of  $\text{Fe}_3\text{O}_4$  became so strong at  $600^\circ\text{C}$  that the linearity of the  $C^{-2} \sim E$  curve was very poor, which is in good agreement

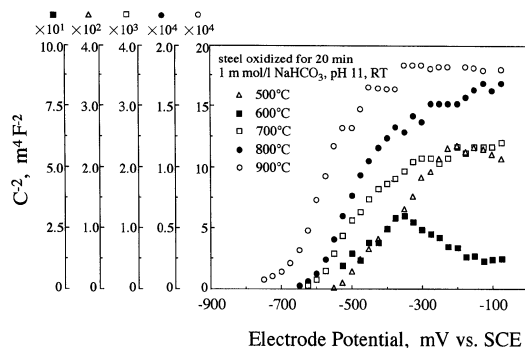


Fig. 7 Mott-Schottky plots for the oxidized steel specimens in deaerated 1 m mol/l  $\text{NaHCO}_3$  solution (pH 11) at room temperature with a frequency of 25 Hz. The steel specimens were oxidized for 20 minutes in air at various temperatures.

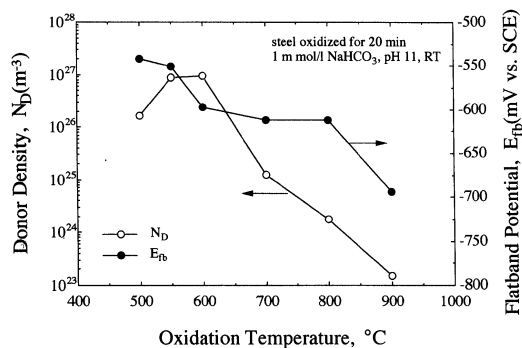


Fig. 8 Donor density,  $N_D$ , and flatband potential,  $E_{\text{fb}}$ , as a function of oxidation temperature for the steel specimens oxidized for 20 minutes in air. Test solution was deaerated 1 m mol/l  $\text{NaHCO}_3$  (pH 11) at room temperature.

with the results in Fig. 6. Above  $700^\circ\text{C}$  the negative slope portion was no longer observed and the  $C^{-2} \sim E$  curves showed two linear regions with different slopes typical of  $\alpha\text{-Fe}_2\text{O}_3$ <sup>17</sup>. The temperature dependence of both the donor density,  $N_D$ , calculated from the slopes in the less noble potential region with the dielectric constant of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\epsilon$ , taken as  $120^{10}$ , and the flatband potential,  $E_{\text{fb}}$ , extrapolated from the linear region, are shown in Fig. 8. It is seen that the  $N_D$  decreased with temperature above  $700^\circ\text{C}$ . For the  $E_{\text{fb}}$ , an obvious less noble shift was found from  $800$  to  $900^\circ\text{C}$ , while at lower temperature the change of  $E_{\text{fb}}$  with temperature appeared to be less significant. Fig. 9 shows the photocurrent at

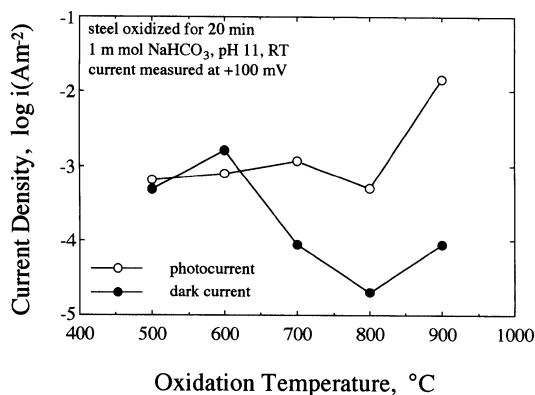


Fig.9 The effect of oxidation temperature on the photocurrent at +100 mV for the steel specimens oxidized for 20 minutes in air. Test solution was aerated 1 m mol/l  $\text{NaHCO}_3$  (pH 11) at room temperature.

100 mV of the oxidized steel as a function of oxidation temperature. The interesting features are that the photocurrent was rather smaller than the dark current at 600°C and that the photoelectrolysis process was greatly enhanced for the steel oxidized at 900°C.

Combining the results from Fig.6 to Fig.9, an explanation given to the photopotential behavior in Fig. 5 can be described as followings. The weak photo-effect at 600°C resulted from the effect of  $\text{Fe}_3\text{O}_4$ . The poor coverage of  $\alpha\text{-Fe}_2\text{O}_3$  on the steel surface may bring about the direct contact of  $\text{TiO}_2$  with  $\text{Fe}_3\text{O}_4$ . Under these circumstances, an energy barrier would be formed at this p-n junction, which would hinder the migration of the photo-excited electrons in the conduction band of  $\text{TiO}_2$  to approach the steel substrate. With the increase of oxidation temperature, the effect of  $\text{Fe}_3\text{O}_4$  would be eliminated by the improved coverage of  $\alpha\text{-Fe}_2\text{O}_3$ . The noble  $E_{\text{ph}}$  of  $\text{TiO}_2/\text{steel}$  at 800°C (Fig. 5) can be attributed to the decreased  $N_{\text{b}}$  of the  $\alpha\text{-Fe}_2\text{O}_3$  (Fig. 8), which would be expected to influence the charge transfer in  $\alpha\text{-Fe}_2\text{O}_3$ , as can be inferred from the small photocurrent of  $\alpha\text{-Fe}_2\text{O}_3$  formed at 800°C (Fig. 9). At 900°C, although the  $N_{\text{b}}$  of  $\alpha\text{-Fe}_2\text{O}_3$  was further decreased, the charge transfer process was different, as evidenced by the different slopes<sup>18)</sup> of the dark  $E \sim i$  polarization curves shown in Fig. 6 and the largest photocurrent shown in Fig. 9. Furthermore, Fig. 8 shows a significant less noble shift in  $E_{\text{fb}}$  from 800°C to

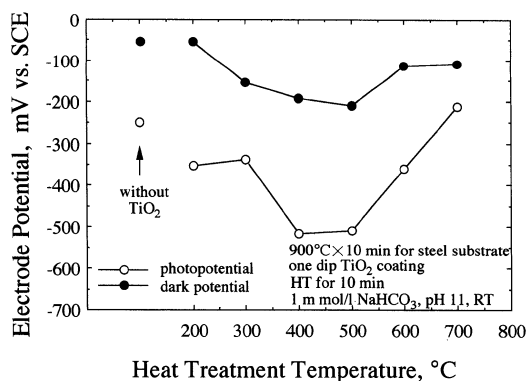


Fig.10 Effect of the heat treatment temperature on the photopotential of  $\text{TiO}_2/\text{steel}$  in aerated 1 m mol/l  $\text{NaHCO}_3$  solution (pH 11) at room temperature. The steel was oxidized at 900°C for 10 minutes in air.

900°C. Therefore the mismatch of the conduction bands of  $\text{TiO}_2$  and  $\alpha\text{-Fe}_2\text{O}_3$  would be decreased, which also favored the migration of electrons generated in  $\text{TiO}_2$  to cross the  $\text{TiO}_2\text{-Fe}_2\text{O}_3$  interface<sup>19)</sup>.

### 3.3 Effect of heat treatment temperature on the photopotential of $\text{TiO}_2/\text{steel}$

The above results show that the optimum oxidation temperatures for the least noble  $E_{\text{ph}}$  were 500, 700, and 900°C. Generally, no significant effect of oxidation time prolonged above 10 min was found at these temperatures. The oxide scale obtained at 900°C appeared to be very good, especially with high adhesiveness to the steel. Therefore, the steel oxidized at 900°C for 10 min was chosen as the substrate to investigate the effect of heat treatment temperature of  $\text{TiO}_2$  coating. The results, together with the  $E_{\text{ph}}$  of the oxidized steel without  $\text{TiO}_2$  coating, are shown in Fig.10. For the coatings heated at 200 and 300°C, the  $E_{\text{ph}}$  were nearly same. Under these heating conditions, the photo-effect from  $\text{TiO}_2$  coating is evidenced by the  $E_{\text{ph}}$  about 100 mV less noble than that of the oxidized steel without  $\text{TiO}_2$  coating. Another temperature independent region was found to be around 400 to 500°C with much less noble  $E_{\text{ph}}$  than the previous one. From 300 to 400°C, the remarkable change in  $E_{\text{ph}}$  toward less noble direction should be related to the crystallization of amorphous  $\text{TiO}_2$  to anatase in this temperature region<sup>11)</sup>, since the crystallized  $\text{TiO}_2$  coating would be more favorable for the photoelectrolysis process than the

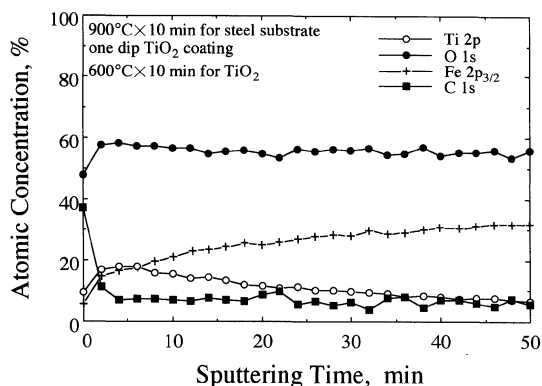


Fig. 11 XPS depth profiles of  $\text{TiO}_2$ /steel. Heat treatment condition for  $\text{TiO}_2$  coating :  $600^\circ\text{C}$  for 10 minutes. The steel was oxidized at  $900^\circ\text{C}$  for 10 minutes in air.

amorphous one, as discussed in our previous paper. Raising the temperature above  $500^\circ\text{C}$  led to an ennoblement of  $E_{\text{ph}}$ . XPS examination (Fig. 11) demonstrated that a significant amount of Fe had diffused into the coating, indicating that  $\alpha\text{-Fe}_2\text{O}_3$  could not retard the diffusion of Fe, in other words, that the oxide growth was outward in nature at higher temperature<sup>20</sup>. In fact, the diffusion of Fe ions to form new  $\alpha\text{-Fe}_2\text{O}_3$  on the original scale surface was so remarkable at  $700^\circ\text{C}$  that a recognizable  $\text{TiO}_2$  coating in the XPS depth profiles did not exist. In this case, the  $E_{\text{ph}}$  of  $\text{TiO}_2$ /steel was even more noble than that of the oxidized steel (Fig. 10), which can be explained by the fact that the photo-effect of  $\alpha\text{-Fe}_2\text{O}_3$  was deteriorated by doping with high concentration of  $\text{TiO}_2$ <sup>21</sup>.

### 3.4 The feasibility of corrosion protection of carbon steel by $\text{TiO}_2$ coating

Under present  $\text{TiO}_2$  coating technique, the least noble  $E_{\text{ph}}$  of  $\text{TiO}_2$ /steel was about  $-500$  mV within the investigated coating and steel oxidation conditions, which was more noble than the repassivation potential for the crevice corrosion,  $E_{\text{R, CREV}}$ , of carbon steel (about  $-750$  mV vs. SCE)<sup>6</sup>. As well known, the  $E_{\text{fb}}$  of  $\text{TiO}_2$  is close to the standard potential of hydrogen evolution<sup>7</sup>, which corresponds to a value of about  $-890$  mV at pH 11. Theoretically, the relative positions of the  $E_{\text{fb}}$  of  $\text{TiO}_2$ , which is the least noble limit for the  $E_{\text{ph}}$  of  $\text{TiO}_2$ , and the  $E_{\text{R, CREV}}$ , of carbon steel predict the possibility of the prevention of localized corrosion for carbon steel. The noble  $E_{\text{ph}}$  of

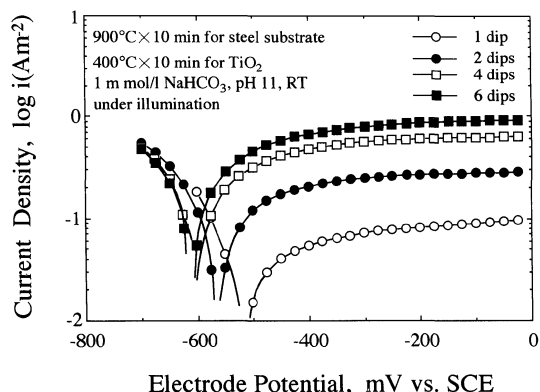


Fig. 12 Polarization curves under illumination for  $\text{TiO}_2$ /steel with different thicknesses of  $\text{TiO}_2$  coating. The steel specimens were oxidized at  $900^\circ\text{C}$  for 10 minutes in air with  $\text{TiO}_2$  coating being heated at  $400^\circ\text{C}$  for 10 minutes. Test solution was aerated 1 m mol/l  $\text{NaHCO}_3$  (pH 11) at room temperature.

$\text{TiO}_2$ /steel may result from the effect of substrate on the cathodic process of the specimens, as suggested by the results in Fig. 2. As discussed in section 3.1, a much less noble  $E_{\text{ph}}$  can be obtained by increasing the photocurrent of the  $\text{TiO}_2$  coating. Fig. 12 shows the effect of coating thickness on the polarization curves under illumination with the steel being oxidized at  $900^\circ\text{C}$  for 10 min and the  $\text{TiO}_2$  coating being heated at  $400^\circ\text{C}$  for 10 min. The thickening of  $\text{TiO}_2$  coating was in the same manner as reported previously<sup>1</sup> with every one dip coating corresponding to about  $0.1\ \mu\text{m}$ . It is apparent that the photocurrent increased significantly with the coating thickness. However, the less noble change in  $E_{\text{ph}}$  was limited, a decrease of about 100 mV from one dip to six dips of  $\text{TiO}_2$  coating, comparing to an order of magnitude increase in photocurrent. The limited decrease in  $E_{\text{ph}}$  can be attributed to the nearly unchanged cathodic behavior under different coating thicknesses, indicating the porosity of the  $\text{TiO}_2$  coating<sup>22</sup>. Fig. 13 summarized the results of the effect of coating thickness on the  $E_{\text{ph}}$  of  $\text{TiO}_2$ /steel in both aerated and deaerated solutions. The remarkable difference of  $E_{\text{ph}}$  between aerated and deaerated solutions confirmed the important role played by the dissolved oxygen in determining the  $E_{\text{ph}}$  of  $\text{TiO}_2$ /metal system<sup>1</sup>. A very important feature to be noted in Fig. 13 is that the  $E_{\text{ph}}$  in

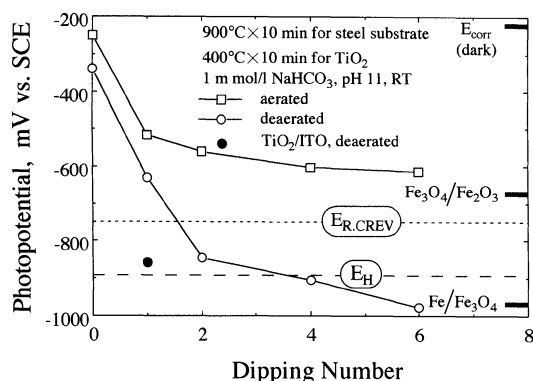


Fig. 13 Effect of coating thickness on the photopotentials of  $\text{TiO}_2$ /steel in both aerated and deaerated 1 m mol/l  $\text{NaHCO}_3$  (pH 11) at room temperature. The steel specimens were oxidized in air at  $900^\circ\text{C}$  for 10 minutes with  $\text{TiO}_2$  coating being heated at  $400^\circ\text{C}$  for 10 minutes. The dotted line represents the repassivation potential,  $E_{R, CREV}$ , of carbon steel and the dashed line is the hydrogen evolution potential,  $E_H$ , at pH 11.

deaerated solution for the specimens with more than two dips of coating reached a very less noble level corresponding to the  $E_{fb}$  of  $\text{TiO}_2$ . The significance of these results is the indication that the localized corrosion of carbon steel can be prevented by the sol-gel derived  $\text{TiO}_2$  coating under the conditions of a proper thickness of the coating and the suppressed cathodic process of  $\text{TiO}_2$ /steel system. Since the reduction of dissolved oxygen takes place mainly on the metal surface<sup>1)</sup>, the results in Fig. 13 suggested a way of further decreasing the  $E_{ph}$  of  $\text{TiO}_2$ /steel in the presence of oxygen by decreasing the porosity of  $\text{TiO}_2$  coating resulted from the sol-gel process, which will be our future work of this research series.

With the increase of coating thickness from one dip to two dips, Fig. 13 also shows that the  $E_{ph}$  in deaerated solution experienced a remarkable decrease, while the further thickening of  $\text{TiO}_2$  coating brought about limited change in  $E_{ph}$ . In deaerated solution, the  $\text{TiO}_2$ /steel specimens with more than two dips of coating exhibited  $E_{ph}$  close to the  $E_{fb}$  of  $\text{TiO}_2$  (near the standard potential of hydrogen evolution). In the case of  $\text{TiO}_2/\text{Cu}^{1)}$ , the  $E_{ph}$  was found to be very close to the  $E_{fb}$  of  $\text{TiO}_2$  and independent of the coating thickness. Referred

to the  $E_{ph}$  of  $\text{TiO}_2$ /ITO with one dip coating also shown in Fig. 13, the noble value of  $E_{ph}$  for  $\text{TiO}_2$ /steel with same thickness implies that  $\alpha\text{-Fe}_2\text{O}_3$  had some influence in the less noble potential region.

#### 4. Conclusion

As a preliminary study on the corrosion protection of carbon steel by sol-gel derived  $\text{TiO}_2$  coating under the illumination of light, the photoelectrochemical behavior of  $\text{TiO}_2$ /steel system was investigated. It was found that the noble photopotential for the steel directly coated with  $\text{TiO}_2$  resulted from the diffusion of Fe into the coating in the coating process. An Fe oxide layer at the  $\text{TiO}_2$ -steel interface can retard this diffusion and greatly improve the photo-response of  $\text{TiO}_2$ /steel. Under high temperature ( $>500^\circ\text{C}$ ) treatment for  $\text{TiO}_2$  coating, Fe diffusion was observed even in the presence of Fe oxide layer and was responsible for the noble photopotential. Amongst various forms of Fe oxides,  $\alpha\text{-Fe}_2\text{O}_3$  was considered to be important for obtaining the less noble photopotential while the property change of  $\alpha\text{-Fe}_2\text{O}_3$  with oxidation temperature was shown to influence the photo-effect of  $\text{TiO}_2$ /steel. Although the photopotentials observed under the optimum coating conditions were still more noble than the repassivation potential for crevice corrosion of carbon steel in the aerated solution, the feasibility of the prevention of localized corrosion by  $\text{TiO}_2$  coating under illumination was clearly demonstrated by the significantly less noble photopotential of  $\text{TiO}_2$ /steel in deaerated solution.

(Manuscript received February 2, 1995 ; in final form June 26, 1995)

#### References

- 1) J. Yuan, R. Fujisawa, and S. Tsujikawa : *Zairyo-to-Kankyo*, **43**, 433 (1994).
- 2) R. Fujisawa, T. Shinohara, and S. Tsujikawa : Proc. of 40th Japan Corrosion Conf., p.37 (1993).
- 3) O. D. Sanctis, L. Gomez, N. Pellegrini, C. Parodi, A. Marajofsky, and A. Duran : *J. Non-Cryst. Solids*, **121**, 338 (1990).
- 4) A. G. Williams and L. V. Interrante : "Better Ceramics Through Chemistry", ed by C. J. Brinker, D. E. Clark, and D. R. Ulrich, p.151, Elsevier (1984).



- 5) A. Kawashima, Y. Wang, E. Akiyama, H. Habazaki, K. sami, and K. Hashimoto: *Zairyo-to-Kankyo*, **43**, 654 (1994).
- 6) G. Nakayama and M. Akashi : *Mat. Res. Soc. Symp. Proc.*, **212**, 279 (1991).
- 7) H. O. Finklea: "Semiconductor Electrode", ed by H.O. Finklea, p.43, Elsevier (1988).
- 8) J. Pan and T. E. Madey : *J. Vac. Sci. Technol.*, **11A**, 1667 (1993).
- 9) T. Yoko, K. Kamiya, and S. Sakka : *Denki-Kagaku*, **54**, 284 (1986).
- 10) R. A. Fredlein and A. J. Bard : *J. Electrochem. Soc.*, **126**, 1892 (1979).
- 11) J. Yuan, R. Fujisawa, T. Shinohara, and S. Tsujikawa : *Proceedings of 40th Japan Corrosion Conference*, p. 45 (1993).
- 12) D. A. Channing and M. T. Graham : *Corros. Sci.*, **12**, 271 (1972).
- 13) J. E. Castel and M. R. Hunt : *Corros. Sci.*, **16**, 137 (1976).
- 14) W. E. Boggs, R. H. Kachik, and G. E. Pellissier : *J. Electrochem. Soc.*, **112**, 539 (1965).
- 15) K. Hauffe : "Oxidation of Metals", p. 273, Plenum Press, New York, (1965).
- 16) R. Francis and D. G. Lees : *Corros. Sci.*, **16**, 847 (1976).
- 17) J. H. Kennedy and K. W. Frese, Jr.: *J. Electrochem. Soc.*, **125**, 723 (1978).
- 18) S. M. Wilhem, K. S. Yun, L. W. Ballenger, and N. Hackerman : *J. Electrochem. Soc.*, **126**, 419 (1979).
- 19) P. A. Kohl, S. N. Frank, and A. J. Bard : *J. Electrochem. Soc.*, **124**, 225 (1977).
- 20) A. Bruckman and G. Simkovich : *Corros. Sci.*, **12**, 595 (1972).
- 21) J. H. Kennedy and K. W. Frese, Jr.: *J. Electrochem. Soc.*, **125**, 709 (1978).
- 22) T. Yoko, K. Kamiya, and S. Sakka : *Bulletin of the Japan Institute of Metals*, **28**, 176 (1989).