Sol-Gel Derived Ti-Fe Oxide Coating for Photoelectrochemical Cathodic Protection of Carbon Steel

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On the novel approach of corrosion protection of carbon steel by TiO_2 coating under illumination, photoeffect of TiO_2 /C-steel system is affected by the structural and electronic properties of the interfacial Ti-Fe oxide. In the present work, Ti-Fe oxide with a wide range of composition, from TiO_2 to $\alpha\text{-Fe}_2\text{O}_3$, was prepared by sol-gel method. By studying the characteristics of the Ti-Fe oxides and their influences on the photoeffect of TiO_2 /C-steel system, a multi-layer coating, expressed as from outer coating layer to substrate: TiO_2 (amorphous)/ TiO_2 (anatase)/Ti-Fe oxide/ $\alpha\text{-Fe}_2\text{O}_3$ /C-steel, was proposed for more effective photoelectrochemical cathodic protection of carbon steel. TiO_2 (anatase) layer without Fe contamination exhibits a good photoeffect and behaves like the source of photo-excited electrons. The inner $\alpha\text{-Fe}_2\text{O}_3$ layer acts as both a barrier to retard the diffusion of Fe into TiO_2 and a way for the transfer of photo-excited electrons from the TiO_2 (anatase) coating to the substrate. The outer layer of amorphous TiO_2 inhibits the oxygen reduction and reduces the photopotential to a more less noble value. The intermediate layer of amorphous Ti-Fe oxide provides deep levels for $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, for which Fe^{3+} is reduced to Fe^{2+} by the photo-excited electrons under illumination. The state of Fe^{2+} left after stopping illumination contributes to phenomenon that the electrode potential is maintained at considerably less noble value until all the Fe^{2+} is re-oxidized by oxygen reduction.

Key words: corrosion, cathodic protection, photoelectrochemistry, TiO_2 , Ti-Fe oxides, carbon steel, photoeffect, sol-gel method.

1. Introduction

Metal is expected to be protected against corrosion by a coating, which can absorb solar energy, transform it to electricity and store the electric energy up so as to protect the substrate metal functionally. The studies^{1)~7)} on corrosion protection of metal by TiO_2 coating under illumination promise such a novel approach. With high chemical stability and a moderate flat-band potential, TiO_2 coating under illumination acts as a non-sacrificial anode and protects substrate metal cathodically even with presence of coating defects. In addition, potential after stopping illumination was observed to recover slowly from photopotential to its original value before illumina-

tion. This phenomenon shows promise that photoeffect can be remained even after stopping illumination.

On corrosion protection of carbon steel by TiO_2 coating, photoeffect of TiO_2 /Carbon steel (C-steel) system had been shown to be affected by structural and electronic properties of the interfacial oxides, i.e., iron oxides and Ti-Fe oxides at the TiO_2 /C-steel interface. As shown in our previous work⁵⁾, a good photoeffect was observed for $\alpha\text{-Fe}_2\text{O}_3$ while poor for Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The photoeffect of TiO_2 /C-steel was also observed to be deteriorated by diffusion of Fe into TiO_2 . Recently, the phenomenon of slower recovery of electrode potential after stopping illumination has been found to be related to Fe doped in TiO_2 by Konishi and Tsujikawa⁷⁾. Thus it is imperative to examine the characteristics of Ti-Fe

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oxides and their influences on the photoeffect of TiO_2/C -steel system. In the present work, Ti-Fe oxide with a wide range of composition, from TiO_2 to $\alpha\text{-Fe}_2\text{O}_3$, were prepared by sol-gel method and their structural, electrochemical and photoelectrochemical behavior were examined. Based upon this, a multi-layer coating was proposed for the corrosion protection of carbon steel under illumination. The photoelectrochemical reactions and the function of each layer on the performance of photoeffects were discussed. Particular attention was focused on the phenomenon of the slower recovery of the electrode potential after stopping illumination.

2. Experimental

Two kinds of substrate specimens were used; carbon steel and tin-doped indium oxide (ITO). The carbon steel sheets (mass%: C 0.111, Si 0.013, Mn 0.367, P 0.015, S 0.0056, Al 0.120, Fe bal.) of 0.8 mm thickness were mechanically cut to a size of 25×25 mm and polished to a mirror finish by $0.05 \mu\text{m}$ Al_2O_3 . The dimension of ITO ($600 \text{ \AA}$, In_2O_3 -10 mass % SnO_2 on glass, $39 \Omega/\square$) was also 25×25 mm. Prior to coating, all steel and ITO substrates were ultrasonically cleaned in acetone and dried.

The sols for Ti-Fe oxides were obtained through mixing the two kinds of sols, given in

Table 1^{8)~10)}, according to Fe/Ti mole ratios. The sols were kept stirring at 0°C while they were dissolved and mixed. All coating films were prepared on substrates by dip-coating method. The dip-coating was dried at room temperature for 10 min, and then heated at 200°C for 10 min for each dip procedure. To increase the coating thickness, the above procedure was repeated several times, and finally heat-treated at different temperatures for 10 min.

The photoelectrochemical measurements were conducted usually under illumination of a 500 W high pressure Hg lamp. However, the photo spectra from 300 to 800 nm wave-lengths were recorded with the illumination setup of a 150 W Xenon lamp combined with a monochromator. A three electrode electrochemical cell was used, and it consisted of acryl container with a quartz window on one side and an opening on the opposite side to which the sample was fitted using a rubber O-ring. The area of the sample exposed to the electrolyte was 0.78 cm^2 . The electrolyte was 1 mol/dm³ NaHCO_3 , and pH 11 was adjusted with concentrated Na_2CO_3 solution. Polarization curves were measured by a potential sweep beginning at the spontaneous electrode potential with a scanning rate of 25 mV/min. For the measurements of cyclic voltammetry, a potential scan rate of 5 mV/s was used. The electrode potential was referred to a saturated calomel electrode (SCE).

Without specification, all the experiments were carried out in aerated condition. For deaerated condition, the solutions were thoroughly purged with 99.99% nitrogen gas. The electrochemical experiments were conducted at room temperature.

The crystallographic characteristics of Ti-Fe oxides prepared under different conditions were determined by the X-ray diffraction using a Cu $K\alpha$ beam (40 kV, 200 mA).

3. Results and Discussion

3.1 Preparation and structural characteristics

Fig. 1 shows the XRD patterns of Ti-Fe oxide powder specimens heat-treated at 400°C for 10 min. The

Table 1 The two kinds of sols for preparation of $\alpha\text{-Fe}_2\text{O}_3$, TiO_2 and Ti-Fe oxide.

Sols Composition	Sol for Fe_2O_3 (0.02 mole)	Sol for TiO_2 (0.05 mole)
Titanium Tetraisopropoxide $\text{Ti}(\text{OCH}(\text{CH}_3))_4$ (284.23)		14.2 g
Fe³⁺ Nitrate Enneahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (404.00)	8.08 g	
Nitric Acid HNO_3 (63.01)		0.3 g
2,4-Pentandione $\text{CH}_3\text{COCH}_2\text{COCH}_3$ (100.12)	1.0 g	
Ethanol $\text{C}_2\text{H}_5\text{OH}$ (46.07)	26.0 g	34.7 g
2-Methoxyethanol $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ (76.10)	15.0 g	
Water* H_2O (18)		0.8 g

* not added for Ti-Fe oxide, but only for pure TiO_2

Fig.1 The XRD patterns of Ti-Fe oxide powder specimens with different composition heat treated at 400°C for 10 min.

Fig.2 The variation of the XRD patterns with heat treatment temperature for the composition with the Fe/Ti mole ratio of 1. (h--hematite (α - Fe_2O_3); a--anatase; p--pseudobrookite; r--rutile).

powder were prepared from the sol mixtures same to the dip-coated specimen. Thick films dip-coated on quartz substrates behaved similarly. As determined from the XRD analysis, a series of solid solution compounds of Ti-Fe oxides, from pure TiO_2 (anatase) to pure α - Fe_2O_3 , were obtained. It was found from the XRD patterns that amorphous character appeared at intermediate range of composition with Fe/Ti mole ratio near 1. Fig. 2 shows the variation of the XRD patterns with heat treatment temperature for the composition with the Fe/Ti mole ratio of 1. With increasing the temperature for heat-treatment from 400°C to 600°C, the original amorphous phase were transformed to new crystalline phases. In addition to the anatase(a) and the

α - Fe_2O_3 (h), pseudobrookite (p) and rutile(r) phases were detected⁸⁾. For the specimen finally heat-treated below 300°C, there existed an almost exclusive amorphous phase for relatively high Ti content compositions while an additional weak pattern of spinel structure (γ - Fe_2O_3) was observed for relatively high Fe content compositions.

3.2 Electrochemical and photoelectrochemical properties

3.2.1 Photoeffect

The anodic polarization curves of Ti-Fe oxide under illumination are shown in Fig. 3. The photocurrent decreased significantly with increasing Fe content in TiO_2 , for example, by near one third in magnitude for Fe/Ti mole ratio of 0.01. The photocurrent for pure α - Fe_2O_3 was also detected but the beginning is the higher potential than that of TiO_2 . Photocurrent spectra were measured for different compositions from TiO_2 to α - Fe_2O_3 . The spectra are shown in Fig. 4 where they are normalized to equal maxima. From the onset of the photocurrent on the lower side of photon energy, it is found that the band gap energies are near 3.0 and 2.2 eV for the pure TiO_2 and the pure α - Fe_2O_3 , respectively. Both Fe-doped TiO_2 and Ti-doped α - Fe_2O_3 resulted in a shift of the onset energy to longer wavelength, i.e., lower photon energy. A broad absorption

Fig.3 The anodic polarization curves under illumination of Ti-Fe oxides with different compositions.

Fig.4 The photocurrent spectra of Ti-Fe oxides with different compositions. It was normalized to equal maxima.

Fig.5 The variation of the photocurrent spectra with heat treatment temperature for the composition with the Fe/Ti mole ratio of 1

extended to lower photon energy may correspond to the amorphous structure with Fe/Ti mole ratio of 1. For the specimen of Fe/Ti mole ratio of 1 the variation of the photocurrent spectra with heat treatment temperature is shown in Fig. 5. The photocurrent spectrum reveals a broad character for the specimen heat-treated at 400°C and 500°C, while two more peak spectrum with smaller peak widths were detected for the specimen at 600°C. The two peaks should be attributed to pseudo-brookite and rutile phases as identified by XRD (in Fig. 2). A similar results were reported for the samples prepared by thermal

Fig.6 The cathodic polarization curves of Ti-Fe oxides under no illumination (a) and illumination (b).

decomposition of corresponding metal salt solutions¹¹⁾.

3. 2. 2 Oxygen reduction

Fig. 6 shows the cathodic polarization curves of Ti-Fe oxides in aerated condition. The oxygen reduction currents increased with increasing Fe content in oxides, and the currents under illumination (Fig. 6 b) were larger than that without illumination (Fig. 6 a) as observed in our previous work. From the cathodic polarization curves of the pure TiO₂ heat-treated at 400°C and 200°C, it is found that the oxygen reduction was suppressed greatly for TiO₂ heat-treated at 200°C where the oxide was amorphous.

3. 2. 3 Redox reaction of Fe²⁺/Fe³⁺ in Ti-Fe oxides

The measurements of cyclic voltammetry were carried out in order to understand the reduction and re-oxidation for different compositions of Ti-Fe oxides. As shown by the

Fig. 7 The cyclic voltammograms of Ti-Fe oxides with different compositions under deaerated condition.

cyclic voltammograms in Fig. 7, the reaction current for pure TiO_2 is very low. In this deaerated condition, all the reduction and re-oxidation currents in the given potential should be of the redox reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the oxides in addition to the hydrogen evolution. It was observed that reaction currents for intermediate range of composition were larger than that for pure $\alpha\text{-Fe}_2\text{O}_3$, and there appeared a largest reduction and re-oxidation currents for the amorphous Ti-Fe oxide with Fe/Ti mole ratio of 1. This means that the redox reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ occurs easily in the intermediate range of composition.

3.3 Structure and photoeffect of a multi-layer Ti-Fe oxide coating on carbon steel

3.3.1 An inner layer of $\alpha\text{-Fe}_2\text{O}_3$

As shown in Fig. 3, TiO_2 (anatase) layer without Fe contamination exhibits a good photoeffect and even a small amounts of Fe contaminating TiO_2 coating could result in a significant decline of photoeffect. A significant diffusion of Fe into TiO_2 coating was found if TiO_2 was directly coated on carbon steel^(4),5). Thus it is imperative that we should introduce an interfacial layer between the steel substrate and TiO_2 coating, which should acts as both a barrier to retard the diffusion of Fe into TiO_2 and as a way for the

Fig. 8 The relationship of the photoeffect in terms of photopotential and photocurrent (at 0 mV vs. SCE) with heat treatment at temperature, T , for 10 min (a) and time, t , at 525°C (b) for $\alpha\text{-Fe}_2\text{O}_3/\text{C-steel}$, followed by the one at 400°C for 10 min for the $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3/\text{C-steel}$ system.

transfer of photo-excited electrons from TiO_2 coating to the substrate. Among different kinds of iron oxides which are probably formed on carbon steel in the process of coating and/or heat treatment for TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$ exhibited a good performance⁵⁾. In the present work, a layer of $\alpha\text{-Fe}_2\text{O}_3$ on steel was prepared by sol-gel method. Fig. 8 shows the relationship of the photoeffect with heat treatment condition. The optimum heat treatment condition was found to be 525°C for 10~20 min for $\alpha\text{-Fe}_2\text{O}_3/\text{C-steel}$ followed by 400°C for 10 min for the $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3/\text{C-steel}$ system. The $\alpha\text{-Fe}_2\text{O}_3$ was predominantly formed at the temperature of 525°C through the phase transformation of the sol-gel coating in addition to a little part of them from the oxidation of the substrate steel in coating defects. When

Fig. 9 The polarization curves of coatings with an outer layer of amorphous TiO_2 , TiO_2 (200°C), or/and anatase TiO_2 .

heat-treated at lower temperatures, the sol-gel film could not transform completely from the $\gamma\text{-Fe}_2\text{O}_3$ and/or amorphous to $\alpha\text{-Fe}_2\text{O}_3$. On the other hand, for a higher temperature and a longer duration there would appear an iron oxide scale, which mainly consists of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$.

3.3.2 An outer layer of amorphous TiO_2

Photopotential is determined both by the anodic photocurrent and by the cathodic current of oxygen reduction in aerated condition. As shown in Fig. 6, there is a low current of oxygen reduction for amorphous TiO_2 . Fig. 9 shows the polarization curves of TiO_2 with different coating structures under illumination. By covering the crystalline TiO_2 (anatase) coating with a layer of amorphous TiO_2 , TiO_2 (200°C), an improved photoeffect was achieved with a larger anodic photocurrent from the crystalline TiO_2 (anatase) combined with a lower cathodic current from the outer layer of amorphous TiO_2 . For TiO_2 (anatase)/ $\alpha\text{-Fe}_2\text{O}_3$ /C-steel, electrode potential after stopping illumination was found to recover to its original value before illumination relatively slowly in deaerated solution while quickly in aerated solution⁵⁾. Fig. 10 shows the recovery of the electrode potential for the TiO_2 (amorphous)/ TiO_2 (anatase)/ $\alpha\text{-Fe}_2\text{O}_3$ /C-steel in aerated solution, where the phenomenon of slower recovery of electrode potential appeared because of the oxygen reduction suppressed by the outer layer of amorphous TiO_2 , TiO_2 (200°C).

3.3.3 An intermediate layer of Ti-Fe oxide

For a multi-layer structure with an inter-

Fig. 10 The recovery of the electrode potential with and without an outer layer of amorphous TiO_2 after stopping illumination in aerated condition.

Fig. 11 The effect of Fe/Ti mole ratio for intermediate layer of Ti-Fe oxide on the recovery of the electrode potential after stopping illumination in aerated condition.

mediate layer of Ti-Fe oxide, expressed as from outer coating layer to substrate: TiO_2 (amorphous)/ TiO_2 (anatase)/Ti-Fe oxide/ $\alpha\text{-Fe}_2\text{O}_3$ /C-steel, the recovery of potential after 30 min of illumination are shown in Fig. 11. With an intermediate layer of amorphous Ti-Fe oxide with Fe/Ti mole ratio of 1, the most slow recovery rate was observed; the potential after stopping the illumination was found to remain at -450 mV after 600 min. Fig. 12 shows the effect of illumination duration on the recovery of the electrode potential. The recovery suppressed more longer with increasing illumination duration. Fig. 13 shows the effect of thickness of TiO_2 (anatase). A

Fig.12 The effect of illumination duration on the recovery of the electrode potential after stopping illumination in aerated condition.

Fig.13 The effect of thickness of TiO_2 (anatase) on the recovery of the electrode potential after stopping illumination in aerated condition.

more less noble value for the electrode potential after stopping illumination, for example, -550 mV after 600 min, was obtained with increased thickness of TiO_2 (anatase). As shown above, the phenomenon of the slower recovery of electrode potential should be related to the redox reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in intermediate Ti-Fe oxide in addition to the oxygen reduction. Under illumination Fe^{3+} can be reduced to Fe^{2+} by the photo-electrons from TiO_2 (anatase) layer, and the Fe^{2+} is re-oxidized to Fe^{3+} by oxygen reduction after stopping illumination. Increment of the amount of Fe^{2+} , such as with a more reducible amorphous Ti-Fe oxide, enhancing photocurrent by increasing the thickness of TiO_2 (anatase) coat-

ing, and increasing illumination duration, would maintain the potential after stopping illumination at less noble for more longer time until all the Fe^{2+} is re-oxidized by oxygen reduction, which is inhibited by the outer layer of amorphous TiO_2 .

4. Conclusions

By studying the characteristics of the sol-gel derived Ti-Fe oxides and their influences on the photoeffect of $\text{TiO}_2/\text{C-steel}$ system, a multi-layer coating, expressed as from outer coating layer to substrate: TiO_2 (amorphous) / TiO_2 (anatase) / Ti-Fe oxide / $\alpha\text{-Fe}_2\text{O}_3/\text{C-steel}$, was proposed for more effective photoelectrochemical cathodic protection of carbon steel. The intermediate layer of amorphous Ti-Fe oxide was shown to provide deep levels for $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, for which Fe^{3+} was reduced to Fe^{2+} under illumination. The state of Fe^{2+} left after stopping illumination maintained the electrode potential considerably less noble until all the Fe^{2+} was re-oxidized to Fe^{3+} by oxygen reduction. The outer layer of amorphous TiO_2 inhibited the oxygen reduction to contribute to prolonged stay of the photopotential at less noble values.

(Manuscript received September 25, 1997; in final form November 4, 1997)

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