Dependence of photocatalytic activity on the compositions and photo-absorption of functional TiO$_2$–Fe$_3$O$_4$ coatings deposited by plasma spray

F.X. Ye$^a$, T. Tsumura$^b$, K. Nakata$^b$, A. Ohmori$^c$

$^a$ School of Materials Science & Engineering, Tianjin University, Weijin Road No. 92, Tianjin 300072, PR China
$^b$ Joining and Welding Research Institute, Osaka University, Osaka, Japan
$^c$ Tocalo Co. Ltd., Minamifutami, Futami-Cho, Akashi, Japan

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Abstract

Owing to the much concern with global environmental issues, Fe$_3$O$_4$ added photocatalytic TiO$_2$ coatings were deposited using plasma spray for environmental depollution. The influence of the content of Fe$_3$O$_4$ additive to the TiO$_2$ powder on the phase composition, microstructure and photo-absorption of plasma-sprayed TiO$_2$ coatings was systematically studied. The results showed that the TiO$_2$–Fe$_3$O$_4$ coatings consisted of anatase TiO$_2$, rutile TiO$_2$ and Fe$_2$TiO$_5$ pseudobrookite phase which appeared when the content of Fe$_3$O$_4$ additive was equal to or over 10%. The content of FeTiO$_3$ was highest in the sprayed TiO$_2$–10%Fe$_3$O$_4$ coatings. The addition of Fe$_3$O$_4$ improved the anatase–rutile transformation of TiO$_2$–Fe$_3$O$_4$ powders. Furthermore, it was found that TiO$_2$ coatings can decompose acetaldehyde under the illumination of ultraviolet rays, and the degrading efficiency was improved with an increase of FeTiO$_3$ content in the coatings. A two-step electron transfer model was proposed to explain the good photocatalytic activity of the sprayed coating with high content of FeTiO$_3$. However, presence of large amount of Fe$_2$TiO$_5$ compound substantially reduced the photocatalytic efficiency of the sprayed TiO$_2$–Fe$_3$O$_4$ coatings for its unfavorable photo-excited electron–hole transfer process.

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1. Introduction

To solve the environmental problems related to the hazardous wastes, contaminated groundwater and toxic air contaminants, extensive research is underway to develop commercial photocatalysts, which involve in TiO$_2$, CdS, SnO$_2$, WO$_3$, SiO$_2$, ZrO$_2$, ZnO, Nb$_2$O$_5$, Fe$_2$O$_3$, SrTiO$_3$, etc. [1–11]. Among all the oxide semiconductors that have been reported, titanium dioxide is an excellent photocatalyst due to its optical and electronic properties, chemical stability, non-toxicity and low cost [12–17].

However, it has been also realized that the band gap of anatase TiO$_2$ (about 3.2 eV) means that the electron can only be excited from the valence to the conduction band by the high power UV light irradiation with a wavelength shorter than 387 nm. This limits the application of sunlight as an energy source for the photocatalysis. Recently, visible light responsive photocatalysts are studied intensively. Domen have concentrated on the visible sensitized photocatalyst to splitting water by loading Pt, NiO, dyes on TiO$_2$ and by the other kind of photocatalyst such as NaTaO$_3$, RuO$_2$–loaded Ge$_3$N$_4$, etc [18–20]. Kudo reported the chromium and either tantalum or niobium–codoped SrTiO$_3$ photocatalyst with visible light response [21]. Asahi et al. reported the visible light photocatalysis in nitrogen-doped TiO$_2$ [22]. Anpo have synthesized iron ion-doped anatase TiO$_2$ by the hydrothermal method from titanium (IV) tetra-tert-butoxide and FeCl$_3$ or FeCl$_2$ solution [23]. The amount of doped iron ion plays a significant role in affecting its photocatalytic activity, and iron doped with optimum content can enhance photocatalytic activity, especially under visible light irradiation. Anpo also reported that the Fe ion-implanted TiO$_2$ catalysts enable the absorption of visible light up to a wavelength of 400–600 nm [24]. Some researcher also added the other semiconductors such as WO$_3$, Al$_2$O$_3$ into TiO$_2$ and fabricated composites to improve the photocatalytic activity of TiO$_2$ [6–11].
Recently, plasma-spraying technique is widely applied to fabricate coating using feedstock powders such as ZrO2, Al2O3 and TiO2 to improve surface wear resistance. The coating formation speed is very high and it is easy to form composite coatings. A plasma-sprayed coating is formed by a stream of molten or half molten droplets impacting on the substrate followed by flattening, rapid solidification and cooling processes. The individual molten droplets spread to thin lamellae, the stacking of which constitutes the coating [25].

In this study, the TiO2 and TiO2–Fe3O4 coatings were deposited on stainless steel (JIS SUS304) by plasma-spraying technique, and effects of Fe3O4 content in the TiO2–Fe3O4 feedstock powders on the phase composition and photocatalytic activity of the TiO2 coatings were analyzed with scanning electron microscopy (SEM), energy dispersive analysis of X-ray (EDAX), X-ray diffraction (XRD), UV-3100PC scanning spectrophotometer and photocatalytic efficiency evaluation system in detail.

2. Materials and experimental procedures

2.1. Feedstock powders and substrate

To study the effects of Fe3O4 particles on the photocatalytic activity of TiO2–Fe3O4 coatings in detail, five kinds of composite powders were designed, these were TiO2–5 wt. %Fe3O4, TiO2–10 wt. %Fe3O4, TiO2–12.7 wt. %Fe3O4, TiO2–22.5 wt. %Fe3O4 and TiO2–32.6 wt. %Fe3O4 powders. The average sizes of TiO2 and TiO2–Fe3O4 powders were about 32 μm. The morphology of TiO2 powder was spherical shape, which was very similar with that of TiO2–Fe3O4 powders. It is very clear that the Fe3O4 additive was distributed uniformly in the agglomerated powder according to the EDAX maps. The substrate was stainless steel (JIS SUS304).

2.2. Coatings preparation and heat treatment of feedstock powders

The thermal spraying equipment was a plasma-spraying system (Plasmadyne-Mach1 manufactured by Plasmadyne Company). Argon was used as a primary plasma gas and helium was used as the secondary gas. The argon gas pressure and flow were 0.42 MPa and 58 slpm, respectively. The helium gas pressure and flow were 0.21 MPa and 9 slpm, respectively. The spraying distance was 70 mm. The arc voltage was 28–30 V. Except the specimen preparation to study the phase changes of TiO2–32.6%Fe3O4 coating after heat treatment, which arc current of 600 A was chosen, arc current of 400 A was applied.

The anatase–rutile transformation temperature of pure anatase TiO2 powder was approximate to 1173 K. To investigate the influence of the additive on the anatase–rutile phase transformation temperature and compare the composition variations of feedstock powders in heat treatment process and in thermal spray process, they were kept in electric furnace for 2 h after reaching at treated temperature (973 K, 1123 K, 1273 K or 1423 K) with a heating rate of 0.167 K/s, and then were cooled with the furnace.

2.3. Analysis of the feedstock powders and sprayed coatings

Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) were used to examine the structure characteristics of the feedstock powders and the sprayed coatings. The phase composition of the heat-treated powders and the sprayed coatings was investigated by X-ray diffraction using Cu Kα radiation (λ = 1.5406 Å) and graphite crystal monochromator (JDX3530, JEOL, Japan). The 2θ range was 23–38° including the main diffraction line of the possible phase compositions.

2.4. Diffuse reflectance spectroscopy and calculation of energy absorbance

The UV–VIS–NIR spectra of the feedstock powders and plasma-sprayed coatings were recorded using a Shimadzu UV-3100PC scanning spectrophotometer equipped with a diffuse reflectance accessory. The absorption intensity was calculated from the Kubelka–Munk equation as \( f(R) = (1 - R)^2 / 2R \), where \( f(R) \) is Kubelka–Munk value and \( R \) is diffuse reflection of the powder or coating. The integrated energy absorbance from the light source of the sprayed coatings was estimated according to the following equation:

\[
E_{\text{total}} = \int E(\lambda) f(R_{\lambda}) \, d\lambda
\]

where \( E(\lambda) \) is the spectral irradiance of the light source, \( f(R_{\lambda}) \) the Kubelka–Munk value and \( E_{\text{total}} \) is the relative integrated energy absorbance. Generally, the increasing of \( E_{\text{total}} \) benefits to increase the photocatalytic activity [26].

The study of the tail of the absorption curve of semiconductor shows that it has a simple exponential increase. The onset of this increase (point A in Fig. 1) has been suggested as a universal method of deducing the position of the absorption edge [27,28]. In this study, the wavelength coordinate of the point on

![Fig. 1. Definition of absorption edge in absorption spectrum of semiconductor.](image)
the low wavelength side of the curve at which the liner increase in absorbance starts was marked to investigate the absorption shift of feedstock powders and sprayed coatings.

2.5. Evaluation method of photocatalytic activity

In this experiment, the photocatalytic activity of the sprayed coatings was evaluated through the photo-decomposition of acetaldehyde. Fujishima reported the acetaldehyde is finally decomposed to CO₂ and H₂O by TiO₂ photocatalyst [29]. The ultraviolet light (peak wavelength was 352 nm) intensity on the sample surface was set in 1.0 mW/cm². In the experimental procedure, the concentration (ppm) of the foul gas with time (s) was measured with a Kitakawa type gas detector at a certain time interval.

The results for photocatalytic efficiency of titanium dioxide indicated that the destruction rates of various contaminants by photocatalyst fit the Langmuir–Hinshelwood kinetic equation [30,31]. Langmuir–Hinshelwood explains the kinetics of heterogeneous catalytic processes and Langmuir adsorption isotherm is valid for the surface reaction. It is a first order kinetic equation. The Langmuir–Hinshelwood rate form is

\[ \ln \left( \frac{C_0}{C} \right) = \frac{t}{\tau} \]  

where \( C \) is the concentration of the reactant (ppm), \( C_0 \) the initial concentration of the reactant (ppm), \( t \) the irradiation time (s) and \( \tau \) is the constant of photocatalytic activity. According to Eq. (2), the smaller of the \( \tau \) value the better of the photocatalytic activity of the coatings.

3. Results and discussion

3.1. Heat-treated TiO₂ and composite TiO₂–Fe₃O₄ powders

Fig. 2 shows the X-ray diffraction results of TiO₂ and TiO₂–Fe₃O₄ feedstock powders heat treated at various temperatures. At 973 K, anatase TiO₂ kept its crystal structure, but magnetite (Fe₃O₄) additive disappeared and Fe₂O₃ formed consequently (Eq. (3)). At 1123 K, one part of anatase TiO₂ transformed into rutile in composite TiO₂–Fe₃O₄ powders, which did not take place for pure anatase TiO₂ powder (Fig. 2(B) a). This implies that the addition of Fe₂O₃ improved the anatase–rutile transformation of TiO₂–Fe₃O₄ powders and the transformation temperature, which was in the range of 973–1123 K, decreased at least 50 K comparing with pure TiO₂ powder of 1173 K.

At the heat-treated temperature of 1273 K, anatase phase transformed completely to rutile in composite TiO₂–Fe₃O₄ powders, which did not take place for pure anatase TiO₂ powder (Fig. 2(B) a). This implies that the addition of Fe₂O₃ improved the anatase–rutile transformation of TiO₂–Fe₃O₄ powders and the transformation temperature, which was in the range of 973–1123 K, decreased at least 50 K comparing with pure TiO₂ powder of 1173 K.

At the heat-treated temperature of 1273 K, anatase phase transformed completely to rutile in composite TiO₂–Fe₃O₄ powders. But anatase TiO₂ phase was still detectable in pure TiO₂ powder. At the higher temperature of 1423 K, all Fe₂O₃ reacted with TiO₂ and produced stable Fe₂TiO₅ (Eq. (4)).

\[ 4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \]  

\[ \text{Fe}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Fe}_2\text{TiO}_5 \]  

Fig. 2. X-ray diffraction patterns of heat-treated TiO₂ and TiO₂–Fe₃O₄ feedstock powders at 973 K (A) and 1123 K (B) (Notes: (a) TiO₂ powder, (b) TiO₂–5%Fe₃O₄ powder, (c) TiO₂–10%Fe₃O₄ powder, (d) TiO₂–12.7%Fe₃O₄ powder, (e) TiO₂–22.5%Fe₃O₄ powder and (f) TiO₂–32.6%Fe₃O₄ powder.)

3.2. Compositions of plasma-sprayed TiO₂ and TiO₂–Fe₃O₄ coatings

The X-ray diffraction patterns of plasma-sprayed TiO₂ and TiO₂–Fe₃O₄ coatings are illustrated in Fig. 3. The relative intensity of anatase phase decreased with the increasing of Fe₃O₄ amount, which indicates that the feedstock powders were more melted with the addition of Fe₃O₄. This was in good agreement with the results of heat-treated feedstock powders discussed in Section 3.1. Fe₃TiO₃ phase appeared with the addition of Fe₃O₄ till 22.5% (Eq. (5)), and became undetectable with the additive amount to 32.6%. The relative intensity of Fe₃TiO₃ was highest in TiO₂–10%Fe₃O₄ coating comparing with the other coatings, which indicates that this coating had the highest content of Fe₃TiO₃ compound. However, Fe₃TiO₃ phase, which is thermally metastable compound, did not appear in heat-treated
Fig. 3. X-ray diffraction patterns of TiO<sub>2</sub> and TiO<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> coatings plasma sprayed under the arc current of 400 A and spraying distance of 70 mm: (a) TiO<sub>2</sub> coating, (b) TiO<sub>2</sub>–5%Fe<sub>3</sub>O<sub>4</sub> coating, (c) TiO<sub>2</sub>–10%Fe<sub>3</sub>O<sub>4</sub> coating, (d) TiO<sub>2</sub>–12.7%Fe<sub>3</sub>O<sub>4</sub> coating, (e) TiO<sub>2</sub>–22.5%Fe<sub>3</sub>O<sub>4</sub> coating and (f) TiO<sub>2</sub>–32.6%Fe<sub>3</sub>O<sub>4</sub> coating.
TiO$_2$–Fe$_3$O$_4$ powders. Thus, it can be inferred plasma-spraying technique is a method to form metastable substance:

$$\text{Fe}_3\text{O}_4 + 2\text{TiO}_2 \rightarrow \text{FeTiO}_3 + \text{Fe}_2\text{TiO}_5$$ (5)

The peak intensity of Fe$_2$TiO$_5$ phase increased continuously and obviously with the increasing of Fe$_3$O$_4$ amount, and finally became the main phase with the almost complete disappearance of ilmenite FeTiO$_3$ in the sprayed coating. For the high content of Fe$_3$O$_4$ in the TiO$_2$–32.6%Fe$_3$O$_4$ powder and high coating formation speed, a few Fe$_3$O$_4$ remained in the coating.

The formation of Fe$_2$TiO$_5$ is reported by the fact that certain percentage of Fe$^{3+}$ ion diffuses into TiO$_2$ producing a substitutional solid solution where Fe$^{3+}$ is dispersed in the lattice of TiO$_2$ due to the ion radius similarity of Fe$^{3+}$(0.67 Å) and Ti$^{4+}$(0.64 Å). The substitution of Fe$^{3+}$ in the matrix of TiO$_2$ is a favorable process [32]. This reason resulted in the high amount of Fe$_2$TiO$_5$ in the sprayed coatings when more anatase TiO$_2$ particles transformed into rutile.

During the short residence time in the plasma jet, the feed particles are completely/partially melted. The droplets impact on a substrate and experience a cooling rate of $10^4$ to $10^6$ K/s, therefore, solid solution, amorphous phase and phase segregation exists widely in composite coating [33,34]. The existence of these kinds of phenomena in sprayed TiO$_2$–32.6%Fe$_3$O$_4$ coatings was investigated. As clearly shown in Fig. 4, the relative intensity of the main diffraction of rutile phase (1 1 0) increased obviously when the coating was heat treated at 1273 K, and became higher than that of Fe$_2$TiO$_5$ phase (1 0 1). The ratio of main diffraction intensity of rutile phase (1 1 0) and Fe$_2$TiO$_5$ phase (1 0 1) of heat-treated TiO$_2$–32.6%Fe$_3$O$_4$ coating was comparable to that of heat-treated TiO$_2$–32.6%Fe$_3$O$_4$ powder. The XRD peaks of sprayed TiO$_2$–32.6%Fe$_3$O$_4$ coatings were not broad, which implies amorphous phase did not exist in it. According to the EDAX analysis results, Ti and Fe elements distributed uniformly along the perpendicular line to the coating surface, which indicates that TiO$_2$ and Fe$_2$TiO$_5$ phase segregations did not happen. It was confirmed again that Fe/(Ti + Fe) in the sprayed coating was comparable to that in TiO$_2$–32.6%Fe$_3$O$_4$ feedstock powder. As shown in Fig. 4(b), large amount of Ti segregated from TiO$_2$ and/or Fe$_2$TiO$_5$ phase after heat treatment of coating, and then the weight fraction of TiO$_2$ increased obviously. Therefore, it is considered that solid solution existed in the sprayed TiO$_2$–32.6%Fe$_3$O$_4$ coating.

### 3.3. Energy absorbance of feedstock powders and sprayed coatings

The photocatalytic performance is affected by catalyst substance, light absorptive ability, morphology, surface active site and so on. Because the light absorptive ability of the photocatalyst is a main factor to affect the photocatalytic activity, the diffuse reflectance of feedstock powders, sprayed TiO$_2$ and TiO$_2$–Fe$_3$O$_4$ coatings was investigated using the Shimadzu UV-3100PC scanning spectrophotometer. Generally, the photocatalytic activity increases with the increase of light absorptive capacity [26].

![Fig. 4. Phase changes after heat treatment of TiO$_2$–32.6%Fe$_3$O$_4$ coating prepared under the arc current of 600 A: (a) original coating and (b) heat treated at 1273 K of (a).](image)

According to the diffuse reflectance spectra of the feedstock powders (Fig. 5), the Fe$_3$O$_4$ additive did not change the absorption edge (wavelength coordinate of black circle in Fig. 5) and the light absorbance drops suddenly in the wavelength range of 340–400 nm. These imply that Fe$_3$O$_4$ particle cannot shift the photo-absorptive ability of TiO$_2$ to the visible spectral range. The diffuse reflectance spectra of the sprayed coatings are shown in Fig. 6, and to investigate the absorptive relation between light source used in this study and the sprayed coating, the spectral power distribution for UV–lamp is also illustrated in it. The light absorbance of the TiO$_2$ coating dropped suddenly in the wavelength range of 340–400 nm. However, the line slope decreased continuously and the optical absorption edge (black circle) shifted to longer wavelength with the content increase of Fe$_3$O$_4$ additive. To compare the light absorptive capacity, the integrated energy absorbance of the sprayed TiO$_2$ and TiO$_2$–Fe$_3$O$_4$ coat-
ings from the ultraviolet lamp used in this study was estimated according to Eq. (1). As shown in Fig. 7, the relative integrated energy absorbance increased with the content increase of the Fe$_3$O$_4$ additive, which means that more irradiation light energy can be utilized. It partly ascribed to FeTiO$_3$ and Fe$_2$TiO$_5$ compound as reported by Pal et al. [32], Smirnova et al. [35] and Ye [11].

3.4. Photocatalytic activity of plasma-sprayed TiO$_2$ and TiO$_2$–Fe$_3$O$_4$ coatings

Fig. 8(a) illustrates the decomposition characteristic of the acetaldehyde by the sprayed TiO$_2$ and TiO$_2$–Fe$_3$O$_4$ coatings. It indicates that the plasma-sprayed coatings can decompose acetaldehyde under illumination by ultraviolet rays and the photocatalytic activity of TiO$_2$–10%Fe$_3$O$_4$ coating was better than that of the other coatings. According to the Eq. (2), the $\tau$ values
of the sprayed TiO₂ and TiO₂–Fe₃O₄ coatings were calculated as shown in Fig. 8(b). The photocatalytic activity increased with the increasing of Fe₃O₄ weight to 10% first, but then decreased.

As discussed in coating composition section, the amount of FeTiO₃ phase in the sprayed TiO₂–10%Fe₃O₄ coating was highest, and the content of Fe₂TiO₅ phase increased substantially when the amount of Fe₃O₄ additive was over 12.7%. The good photocatalytic efficiency of TiO₂–10%Fe₃O₄ coating possibly resulted from the high content of ilmenite FeTiO₃ phase in the coating, because FeTiO₃ has good light absorbance and favorable photo-excited electron–hole separation characters [11]. Furthermore, the band gap of bulk FeTiO₃, which is 2.85 eV [36], is lower than that of TiO₂. Scaife [37] summarized the findings of some oxide semiconductors including FeTiO₃ on the flat band potential, band gaps and stabilities, and the findings indicate the valence band edge of FeTiO₃ is about in the same level with that of TiO₂. As a possible phenomenon shown in Fig. 9, when the semiconductor is irradiated, the electron possibly transfers (moves) to conduction band in two steps: first step: the electron is initiated from the valence band to the conduction band of TiO₂ and second step: the electron in the conduction band of TiO₂ injects to the conduction band of FeTiO₃. For this two-step mechanism, the lifetime of excited hole and electron pair was prolonged. Perhaps the improved efficiency of the photon is another reason for the good photocatalytic activity of the TiO₂–10%Fe₃O₄ coatings.

The band gap of pure Fe₂TiO₅ is 2.18 eV [38], which is much lower than that of TiO₂ and Fe₃O₄. Although the light absorbance increased with the amount increasing of Fe₂TiO₅ compound, the photocatalytic activity was reduced dramatically when the content of Fe₂TiO₅ was high. As it is known [32], this kind of phenomenon may result from the unfavorable charge transfer process to adsorbed substance during light illumination where excess accumulation of electron and hole undergoes recombination immediately without taking part in the photocatalytic reaction. Therefore, the electron–hole pair formation and separation process is a key factor in photocatalytic reaction.

As a result, the photocatalytic efficiency of sprayed TiO₂–Fe₂O₃ coating was improved with an increase of FeTiO₃ content in the sprayed coatings. However, when the content of Fe₃O₄ additive was over 10%, photocatalytic activity was reduced to large extent due to the presence of large amount of inactive Fe₂TiO₅ compound in the TiO₂–Fe₃O₄ coatings.

4. Conclusions

TiO₂ and TiO₂–Fe₂O₃ coatings were prepared on stainless steel substrate by plasma spraying. The results showed that the anatase–rutile transformation temperature of TiO₂–Fe₂O₃ powders was in the range of 973–1123 K, which was at least 50 K lower than that of pure anatase TiO₂ powder. The TiO₂–Fe₂O₃ coatings consisted of anatase TiO₂, rutile TiO₂ and pseudo-brookite Fe₂TiO₅ phase which appeared when the content of Fe₂O₃ additive was equal to or over 10%. With relative low amount addition of Fe₃O₄, ilmenite FeTiO₃ phase existed in the sprayed coatings. The content of anatase TiO₂ in the sprayed coatings decreased with the increasing of Fe₃O₄ content. The photocatalytic activity was improved with an increase of FeTiO₃ content in the coating, which was explained by the good photo-absorbance capacity and by the two-step electron transfer model. However, the presence of large amount of Fe₂TiO₅ compound substantially reduced the photocatalytic efficiency of the sprayed TiO₂–Fe₃O₄ coatings for the unfavorable electron–hole transfer process.

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