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Photocatalytic Activity and Photo-absorption of Plasma Sprayed TiO_2-10%Fe_3O_4 Coatings †

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Abstract

To inhibit the rapid recombination of exited electrons and holes and improve the illumination absorption of the TiO_2 based photocatalyst during photocatalysis, one kind of novel TiO_2-10%Fe_3O_4 coating was prepared by plasma spraying. The effects of spraying parameters and the Fe_3O_4 additive to anatase TiO_2 powder on the microstructure, surface morphology and photo-absorption of plasma sprayed TiO_2 coatings were systematically studied. The photocatalytic activity of the sprayed coatings is evaluated through the photo-degradation of acetaldehyde. The UV-VIS-NIR absorption spectra of the deposited coatings were obtained by using Shimazu UV-3100PC scanning spectrophotometer. The results showed that the TiO_2-10%Fe_3O_4 coatings consist of anatase TiO_2, rutile TiO_2, Fe_3O_4 and the $FeTiO_3$, and the content of anatase TiO_2 was estimated to be about 4%, which is lower than that of TiO_2 coatings of from 8% to 15%, With an increase in plasma arc power, the content of anatase TiO_2 in the coatings decreased. It was found that TiO_2 coatings deposited on mild steel can decompose acetaldehyde under the illumination of ultraviolet rays, and the degrading activity is improved with an increase in the content of anatase TiO_2 in the coatings. Moreover, the addition of Fe_3O_4 can enhance the photocatalytic activity for the higher light absorption and the formation of $FeTiO_3$ compound in the TiO_2-10%Fe_3O_4 coatings.

KEY WORDS: (Plasma Spraying) (Photocatalytic Activity) (UV-VIS-NIR) (Fe_3O_4) (TiO_2)

1. Introduction

The mineralization of toxic organic pollutants by photoreaction, using semiconductors such as TiO_2, CdS, SnO_2, WO_3, SiO_2, ZrO_2, ZnO, Nb_2O_3, Fe_2O_3, $SrTiO_3$ etc., has attracted extensive attention after the discovery of the Fujishima and Honda phenomenon[1-10]. Among all the oxide semiconductors that have been reported, titanium dioxide is an excellent photocatalyst for its high stability against photo-corrosion and favorable band-gap energy (photo-activity), and can break down most kinds of refractory organic pollutants and inorganic waste substances, including detergents, dyes, pesticides, herbicides, Cr^{3+}, $HgCl_2$ and CH_3HgCl under ultraviolet irradiation, which is based on the strong oxidative power of photo-generated holes and $\cdot OH^-$ radicals on the photocatalyst surface[11-16]. However, it has been also realized that the band gap of TiO_2 (about 3.2ev) 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 no greater than 387nm. This limits the application of sunlight as an energy source for the photocatalysis. Recently, there have been many methods to improve photocatalytic activity of the TiO_2 by ion implantation and adding the other semiconductor such as WO_3, Al_2O_3 etc.[6-10].

Generally, micro-powders are often applied as photocatalysts because the specific surface area is larger than that of membrane. But in practical application, several problems with using micro-powders in photochemical processing are apparent, such as (a) separation of the catalyst from the suspension after the reaction is difficult, (b) the suspended particles tend to aggregate, especially when they are present at high concentrations, and (c) particulate suspensions are not easily applicable to continuous flow systems. In order to avoid these technical problems, several approaches have been taken. For example: (a) powder-type photo-catalysts have been immobilized on various supports, including glasses, silica, polymers, vesicles and micelles; and (b) catalysts have been prepared in film through sol-gel, CVD, oxidation of Ti plate and spraying method, etc.[17].

In this study, the TiO_2 and TiO_2-10%Fe_3O_4 coatings

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were deposited on mild steel (SS400) by plasma spraying, and the characters of the coatings were analyzed with SEM, X-ray diffraction, UV-3100PC scanning spectrophotometer and photocatalytic activity evaluation system.

2. Materials and experimental procedures

2.1 Materials

The variation of catalytic activity with particle size is associated with an increase in the specific area and the corresponding increase of available active sites. If the size of the feedstock powder is smaller than 10 μ m, it is difficult to deposit coatings by thermal spraying for the low speed of the particles. So to satisfy the two demands, the original diameter of the TiO_2 powder is held at 0.2 μ m, and polyvinyl alcohol is used as a binder for the thermal spraying TiO_2 powder (diameter about 30 μ m). Because the photocatalytic activity of anatase titanium dioxide is better than of rutile, anatase TiO_2 was used as feedstock powder and the average size of the TiO_2 powder is 33.7 μ m. It is reported that the additive has an effect on the photocatalytic activity or sunlight absorptive ability of the coatings[18-20]. So Fe_3O_4 particles are added into the TiO_2. The average size of TiO_2-10%wt.Fe_3O_4 powder is about 30 μ m. The substrate is a kind of mild steel (SS400).

2.2 Plasma spraying equipment

The thermal spraying equipment was a plasma spraying system, whose commercial gun name is Plasma DYNE Gun. Argon was used as a primary plasma gas and helium was used as the secondary gas. The thermal spraying parameters are illustrated in **Table 1**.

Table 1 Plasma spraying parameters

Ar pressure (MPa)	0.42
He pressure (MPa)	0.21
Arc current (A)	500, 400
Arc voltage (V)	32,34
Spraying distance (mm)	70,100

2.3 Analysis of the feedstock powders and sprayed coatings

An optical microscope and scanning electron microscope (SEM) were used to examine the structure characteristics of the feedstock powders and the sprayed coatings. The phase composition of the feedstock powders and the sprayed coatings were investigated by X-ray diffraction using Cu-K$_\alpha$ radiation (λ =1.5405 Å) in the range 2θ=20～65 degrees. From the X-ray diffraction results, the content of anatase TiO_2 in the coatings was calculated by the following equation[21].

$$A = \frac{1}{1 + 1.265\frac{I_R}{I_A}} \qquad (1)$$

where I_A is the highest peak intensity of anatase phase, I_R is the highest peak intensity of rutile phase, A is the content of anatase TiO_2 in the coatings.

2.4 Evaluation set-up of photocatalytic activity

In this experiment, the photocatalytic activity of the sprayed coatings was evaluated by the home-made set-up, which is shown in **Fig.1**. The foul gas is acetaldehyde and the ultraviolet light (λ =360nm) intensity on the sample surface was set in 1.0mW/cm^2. In the experimental procedure, the decomposition of the concentration (ppm) of the foul gas with time (h) was measured with a Kitakawa type gas detector at a certain time interval. The results for photocatalytic activity of titanium dioxide indicate that the destruction rates of various contaminants by photocatalyst fit the Langmuir-Hinshelwood kinetic equation[20,22,23]. The Langmuir-Hinshelwood rate form is

$$\ln(\frac{C_0}{C}) = t / \tau \qquad (2)$$

where C is the concentration of the reactant (ppm), C_0 is the initial concentration of the reactant (ppm), t is the irradiation time (hour), τ is the constant of photocatalytic activity.

According to equation (2), the smaller the value of τ the better of the photocatalytic activity of the coatings. Therefore, the τ can be used as the characteristic decomposition time to evaluate the effectiveness of the sprayed coatings to decompose the foul gas.

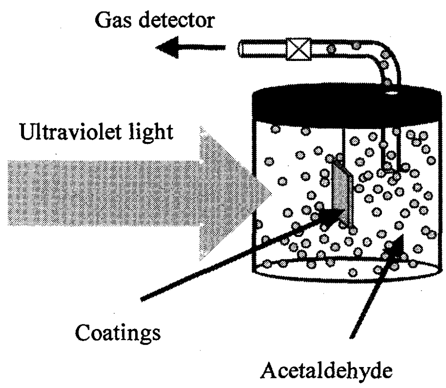


Fig.1 The evaluation set-up for photocatalytic activity of the sprayed coatings.

2.5 Diffuse reflectance spectroscopy

The UV-VIS-NIR spectra of the plasma sprayed coatings were recorded using a Shimazu UV-3100PC scanning spectrophotometer equipped with a diffuse reflectance accessory. The absorption intensity were 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 coating. The f(R) is proportional to the absorption coefficient[24)].

3. Results and Discussion

3.1 The structure of the sprayed TiO_2 coatings

Fig.2 shows the typical microstructure of TiO_2 coatings by plasma spraying. It indicates that the coatings are not very dense, contain many holes, and the TiO_2 powders are not melted fully. It seems that a part of 0.2 μ m original particles still exist in the coatings. This kind of phenomenon will be a benefit to increase the specific surface and then improve the photocatalytic activity of the sprayed coatings.

According to X-ray diffraction pattern (**Fig.3**) and equation (1), the content of anatase phase in the sprayed coating was evaluated about 8.8% under the arc current of 500A and the spraying distance of 70mm, and about 11% under the arc current of 500A and the spraying distance of 100mm. While at 400A, contents were 15.4% and 15.6% for 70mm and 100mm, respectively.

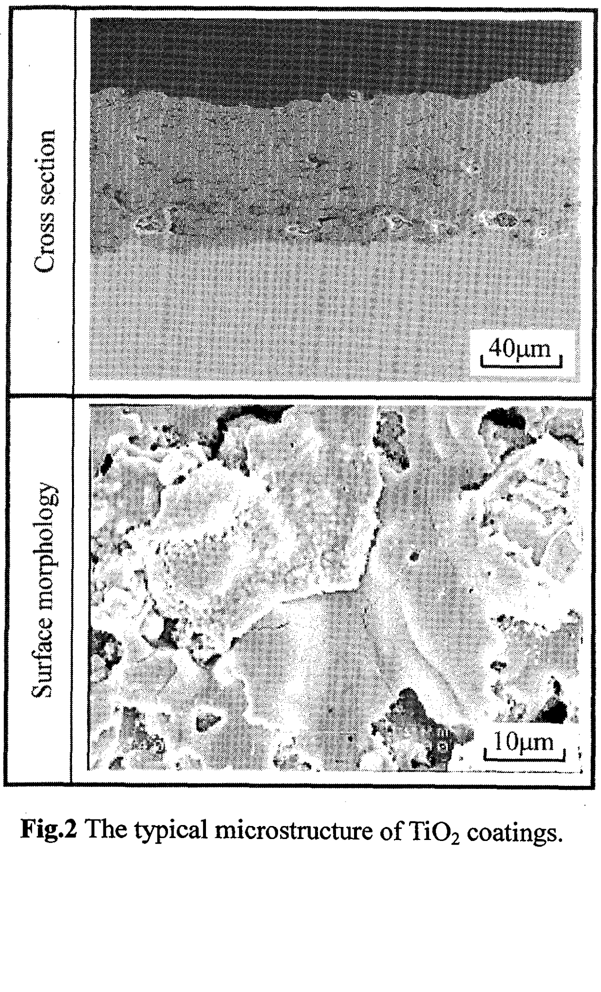


Fig.2 The typical microstructure of TiO_2 coatings.

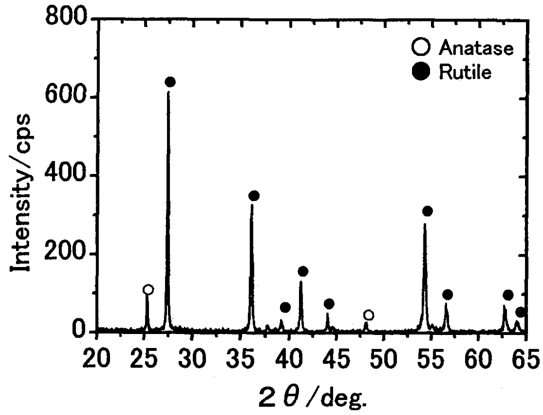


Fig.3 The typical X-ray diffraction pattern of TiO_2 coatings.

3.2 The structure of the sprayed TiO_2-10%Fe_3O_4 coatings

Unmelted or partially melted TiO_2-10%Fe_3O_4 powders in the coatings are fewer than for TiO_2 powders under the same spraying conditions as shown in **Fig.4.** This possibly results from the low melting point (about 1873K) of the added Fe_3O_4. **Fig.5** presents the typical X-ray diffraction pattern of the sprayed TiO_2-10%Fe_3O_4 coatings. It is noticed that these consist of rutile phase, anatase phase, Fe_3O_4 additive and iron titanium oxide. Moreover, the X-ray diffraction intensity of the anatase

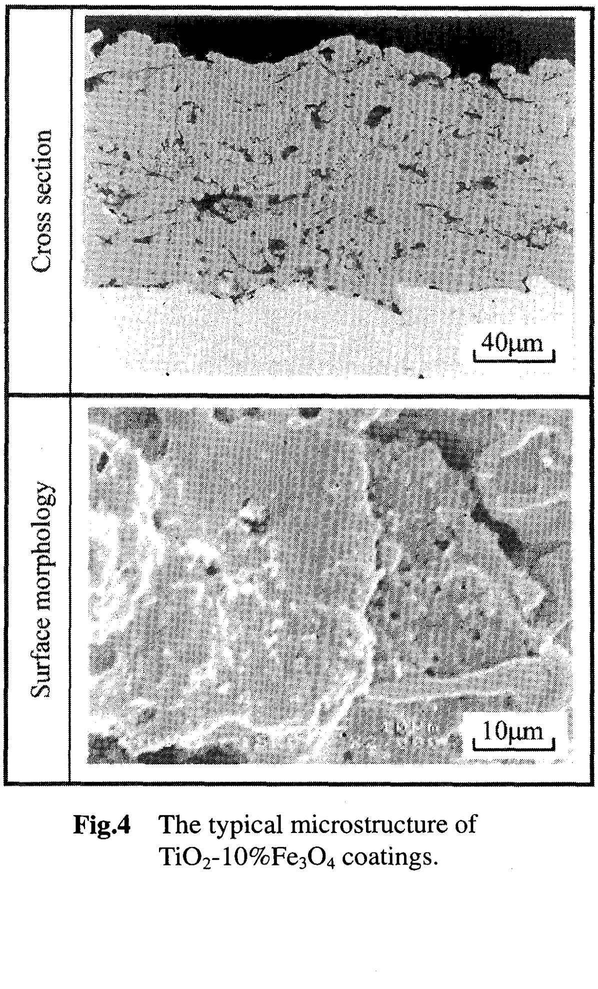


Fig.4 The typical microstructure of TiO_2-10%Fe_3O_4 coatings.

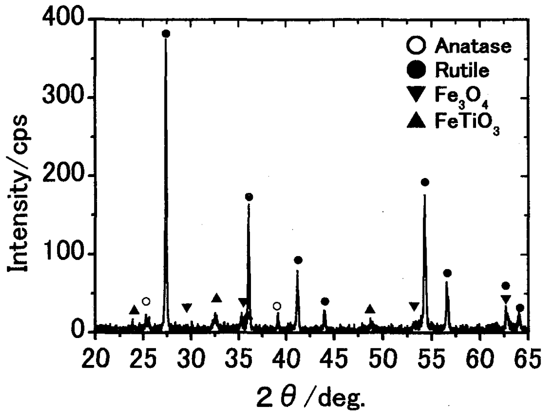


Fig.5 The typical X-ray diffraction pattern of TiO_2-10%Fe_3O_4 coatings.

TiO_2 is very low, this evidences the melting state of the powders too. The content of anatase TiO_2 in the sprayed TiO_2-10%Fe_3O_4 coatings is only about 4% under these experimental spraying conditions (**Table1**).

3.3 The photocatalytic activity of the sprayed TiO_2 and TiO_2-10%Fe_3O_4 coatings

Fig.6 illustrates the decomposition characteristic of the acetaldehyde by the sprayed TiO_2 coatings under different parameters. It indicates that the TiO_2 coatings can decompose acetaldehyde under illumination by ultraviolet rays and the photocatalytic activity of TiO_2 coatings at 400A and 100mm is better than that under the other conditions, perhaps for the highest anatase content in the coatings. According to the equation (2), the τ values of the sprayed TiO_2 coatings under different spraying parameters were calculated as shown in **Fig.7**. The TiO_2-10%Fe_3O_4 coatings have also photocatalytic activity like the TiO_2 coatings and the τ values were summarized in **Fig.7** to compare with the TiO_2 coatings. The results clearly show that the photocatalytic activity of the TiO_2-10%Fe_3O_4 coatings is better than that of the TiO_2 coatings despite the lower content of anatase TiO_2 in the coatings, which reveals Fe_3O_4 can improve the photocatalytic activity of the TiO_2 coatings to some degree.

3.4 Search for the original reason of photocatalytic activity

Because the light absorptive ability of the photocatalyst is a main factor to affect the photocatalytic activity, the diffuse reflectance of sprayed TiO_2 coatings and the TiO_2-10%Fe_3O_4 coatings was investigated using the Shimazu UV-3100PC scanning spectrophotometer. As shown in **Fig.8**, the Kubelka-Munk values (calculated by Kubelka-Munk function f(R)) of TiO_2-10%Fe_3O_4 coatings, which are about 2.6 at the experimental light wavelength of 360nm, are higher than that of the TiO_2 coatings of about 1.5. The spectra do not sharply drop in the wavelength range of 340nm to 400nm and shift to longer wavelengths, which means that more irradiation light energy can be utilized. Moreover, in the procedure of plasma spraying, a few Fe_3O_4 powders reacted with TiO_2 powders and produce iron titanium oxide compounds, such as $FeTiO_3$ (**Fig.5**), The band gap of anatase TiO_2 is about 3.2ev, but the band gap of iron titanium oxide compounds is general lower than 2.8ev. Therefore, as shown in **Fig.9**, when the semiconductor is irradiated, the electron-hole pairs possibly form in two steps. First step: the electron is raised from the valence band to the conduction band of $FeTiO_3$, and second step: the electron in the conduction band of $FeTiO_3$ is raised to the conduction band of TiO_2, and the benefit is to extend the light absorption range and inhibit recombination of the excited holes and electrons. Then improved efficiency of the photon, results in the higher photocatalytic activity of the TiO_2-10%Fe_3O_4 coatings.

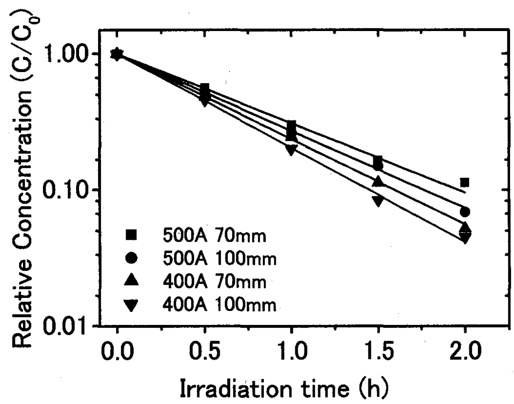


Fig.6 The photocatalytic decomposition characteristics of TiO_2 coatings.

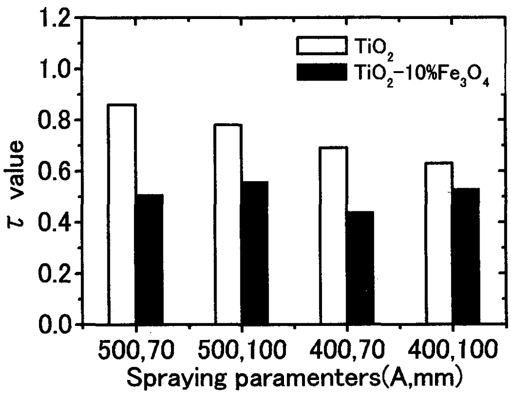
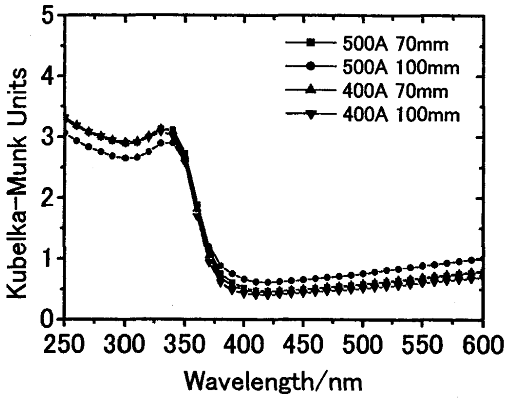
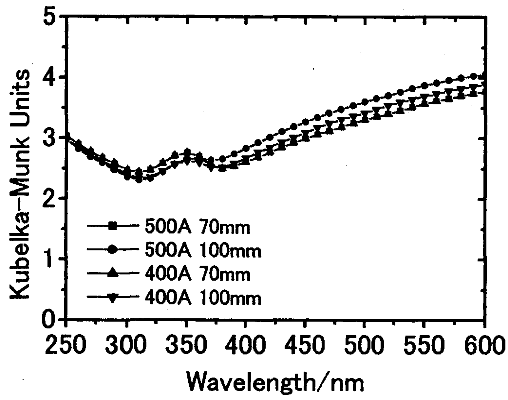


Fig.7 The τ values of plasma sprayed TiO_2 and TiO_2-10%Fe_3O_4 coatings.



(a)



(b)

Fig.8 Diffuse reflectance spectra of plasma sprayed TiO_2 (a) and TiO_2-10%Fe_3O_4 coatings (b).

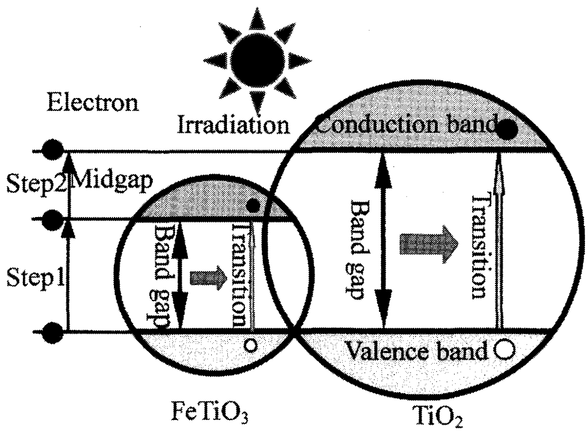


Fig.9 The proposed photocatalytic activity improvement model of TiO_2-10%Fe_3O_4 coatings.

4. Conclusions

TiO_2 coatings and TiO_2-10%Fe_3O_4 coatings were deposited on mild steel substrates by plasma spraying. The experimental results clearly show that the content of anatase TiO_2 in the coatings was about 4-15%, which was influenced by the melting state of spray particles during the thermal spraying process. With an increase in the heat input to spray droplets, the content of anatase TiO_2 in the coatings was decreased. For the low melting point of Fe_3O_4, the addition of Fe_3O_4 leads to a decrease in the content of anatase TiO_2 in the coatings. It was observed that TiO_2 coatings deposited on mild steel have photocatalytic activity, and the degrading activity of acetaldehyde is improved with an increase in the content of anatase TiO_2 in the coatings. Moreover, Fe_3O_4 particles can improve the photocatalytic activity for the higher photo-absorptive ability of the TiO_2-10%Fe_3O_4 coatings and the formation of low band gap iron titanium oxide compounds.

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