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Photocatalytic performance of plasma sprayed $TiO_2-ZnFe_2O_4$ coatings

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Abstract

A novel $TiO_2-ZnFe_2O_4$ coating has been prepared by plasma spraying. The effects of spraying parameters and the composition of powders on the microstructure, surface morphology and photo-absorption of plasma sprayed coatings were studied. The photocatalytic efficiency of the as-sprayed coatings was evaluated through the photo mineralization of methylene blue. It was found that TiO_2 coatings can decompose methylene blue under the illumination of ultraviolet rays, and the degrading efficiency is improved with an increase in the content of $FeTiO_3$ in the coatings. However, the presence of large amount of $ZnFe_2O_4$ compound would substantially lower the photocatalytic efficiency of the $TiO_2-ZnFe_2O_4$ coatings for the unfavorable photo-excited electron–hole transfer process.

Keywords: Plasma spraying; Photocatalytic activity; TiO_2; $ZnFe_2O_4$

1. Introduction

Heterogeneous photocatalysis, a new wastewater treatment and water purification technique, has been a fast growing research area in the past decade [1,2]. Among all oxide semiconductors that have been applied, titanium dioxide is the most promising one for its high stability against photo-corrosion, favorable band-gap energy (photoactivity) and low cost. However, for such applications titania exhibit at least two disadvantages: poor efficiency in the conversion of solar energy and difficulty in reclaiming when used as powder.

There are generally two main crystal phases in TiO_2 photocatalyst, anatase and rutile. It is commonly believed that anatase is the active phase in photocatalytic reactions [3,4]. Pure rutile normally shows weak activity in contrast with anatase [5]. However, it has been also realized that the band-gap of anatase (approximately 3.2 eV) means that the electron can only be excited from the valence band (VB) to the conduction band (CB) by the high energy UV light irradiation with a wavelength no longer than 385 nm. This limits the application of sunlight as an energy source for the photocatalysis. Recently, many studies have been devoted to the extension of the photoresponse and improvement of the photoactivity by ion implantation and adding the other semiconductor such as WO_3, ZnO, Al_2O_3, Fe_3O_4, etc. [6–13]. Particularly, narrow band-gap semiconductor has been paid more consideration. Because the overlap of different band could promote the excitation of the valence band electrons, $ZnFe_2O_4$, with a relatively narrow band-gap [14] (ca. 1.9 eV), has been used as a novel photocatalyst. Valenzuela et al. [15] have reported that $ZnFe_2O_4$ has some photocatalytic activity. Yuan and Zhang [16] have synthesized $TiO_2-ZnFe_2O_4$ nanocomposite, which exhibits better photoactivity than pure TiO_2 nanomaterials.

Generally, the photocatalytic performance increases with the increase of specific surface. Therefore, micro-powders are often applied as photocatalysts because the specific surface area is larger than that of the membrane. But in practical application, micro-powder is very difficult to reclaim after photocatalytic reaction. In order to avoid this technical problem, a number of methods have been used to form TiO_2 films, including wet chemical processing (such as sol–gel, screen printing) and vapour deposition techniques (e.g. CVD, PVD), etc. But the coating formation speed and bonding strength are very low and it is difficult to produce

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Table 1
Plasma spraying parameters

Coating	(a)	(b)	(c)	(d)	(e)
Component	TiO_2+3 wt.% $ZnFe_2O_4$	TiO_2+3 wt.% $ZnFe_2O_4$	TiO_2+15 wt.% $ZnFe_2O_4$	TiO_2+30 wt.% $ZnFe_2O_4$	Pure P25
Plasma gas [SLPM]	50	50	50	50	50
Arc current [A]	600	400	400	400	400
Arc voltage [V]	36	35	35	35	35
Power [kW]	21.6	14	14	14	14
Spraying distance [mm]	80	80	80	80	80

large surface coatings by chemical process such as sol–gel and CVD. In contrast with these methods, plasma spraying technique is an economical and versatile fabrication process to produce large surface coatings. The coatings' thickness, texture and bonding strength can be controlled though spraying parameters, powders and substrate state [17], etc. So, to investigate the effects of $ZnFe_2O_4$ additive to TiO_2 when they formed coatings, a series of TiO_2–$ZnFe_2O_4$ composite coatings were deposited on stainless steel by plasma spraying technique in our experiment, and the characters of the coatings were analyzed with SEM, X-ray diffraction, UV–Vis–NIR spectrophotometer and photocatalytic activity evaluation system.

2. Experimental

2.1. Materials

In our experiment, TiO_2 (Degussa , P25) and $ZnFe_2O_4$ powders were used as raw materials. The TiO_2 powder (P25), which is a commercial benchmarking photocatalyst, has a relatively large surface area (49 m^2g^{-1}) and consists of anatase and rutile phases in a ratio of about 3 : 1. The average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively. And the average size of $ZnFe_2O_4$ is about 30 nm. In order to investigate the effect of $ZnFe_2O_4$ additive, the $ZnFe_2O_4$ and TiO_2 nanoparticles were mixed with ratio of $ZnFe_2O_4$: TiO_2 = 0.03, 0.15, 0.3. Polyvinyl alcohol was used as a binder for the plasma spraying TiO_2–$ZnFe_2O_4$ powder. The mixed powders were agglomerated into micro-size powders by spray-dried technology. The substrate is a 50 × 20 mm stainless steel plate.

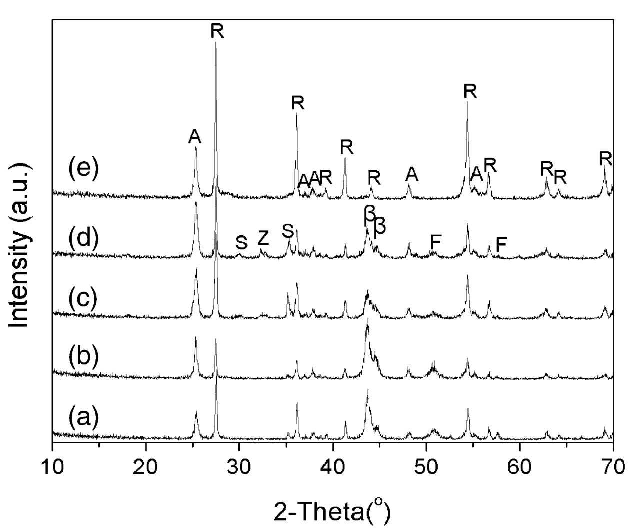

Fig. 1. XRD patterns of as-sprayed coatings (A=anatase, R=rutile, S=spinel, β=β-TiO_2, F=$FeTiO_3$, Z=$ZnTiO_3$).

2.2. Plasma spraying equipment

An A-2000 atmospheric plasma spraying system (Sulzer-Metco, Switzerland) was used to deposit coatings. Argon was used as the only plasma gas. The definite spraying parameters are illustrated in Table 1.

2.3. Characterization techniques

The crystallite phases of the coatings were examined by D/max 2550V X-ray Diffraction Analysis using Cu-K_α radiation. The average crystallite sizes of the spinel phase of $ZnFe_2O_4$, and anatase as well as rutile phases of TiO_2, were estimated from the full width at half-maximum of their most intense diffraction peaks using Scherrer's formula. The surface morphologies of the coatings were examined using a JSM-6700F Field Emission Scanning Electron Microscope. UV–Vis absorbance spectra of the coatings were recorded on a Cary 500 Scan UV–Vis–NIR spectrophotometer, and $BaSO_4$ was used as reference.

The photocatalytic efficiency of the as-sprayed coatings was evaluated through the photo mineralization of methylene blue (MB) solution (10 mg/L). The methylene blue concentration in the solution was determined by a Shimadzu

Table 2
The average crystallite size of the as-sprayed coatings

Coating	Average crystallite size [nm]		
	Anatase	Rutile	Spinel
(a)	37	122	42
(b)	45	134	39
(c)	31	80	54
(d)	34	160	39
(e)	41	215	α

[α]No phase present within the sample.