Influence of $FeTiO_3$ Addition on TiO_2 Coating Formation Characteristics in Plasma Spray

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Abstract

To improve the visible light responsivity of TiO_2, $FeTiO_3$ with band gap of 2.85 eV was added into TiO_2 powder with band gap of 3.2 eV in this study. The microstructure and phase compositions of plasma sprayed TiO_2, TiO_2-30%$FeTiO_3$, TiO_2-50%$FeTiO_3$ and $FeTiO_3$ coatings were investigated. The $FeTiO_3$ coating plasma sprayed under the arc current of 400 A consisted of rutile TiO_2, $FeTiO_3$, Fe_2TiO_5, and thermally metastable $Fe_2Ti_3O_9$ and γ-Fe_2O_3, while TiO_2-30%$FeTiO_3$ coating contained anatase TiO_2, rutile TiO_2 and $FeTiO_3$ only. The relative deposition rate of TiO_2-30%$FeTiO_3$ powder under the arc current of 400 A was approximated to be 4 μm/pass.

Keywords: TiO_2, plasma spray, photocatalyst, $FeTiO_3$

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 include TiO_2, CdS, WO_3, ZnO, and $SrTiO_3$ etc[1]. 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[2].

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 light irradiation with a wavelength less than 387 nm. This limits the application of sunlight as an energy source for the photocatalysis. Recently, visible light responsive photocatalysts are studied intensively[3].

The band gap of bulk $FeTiO_3$ is 2.85 eV[4], which means it can absorb visible light. $FeTiO_3$ is an incongruent melting material with the melting point of approximately 1683K[5]. To elucidate the influence of $FeTiO_3$ on the photocatalytic activity of plasma sprayed TiO_2-$FeTiO_3$ coatings, TiO_2, $FeTiO_3$ and TiO_2-$FeTiO_3$ powders were designed in this study. The influence of $FeTiO_3$ on TiO_2 coating formation characteristics in plasma spray were discussed in detail. And the photocatalytic activity of deposited coatings will be given in oral presentation.

2. Materials and Experimental Procedure

2.1 Feedstock Powders and Substrate

$FeTiO_3$ particles with average size of 1.4 μm were agglomerated to $FeTiO_3$ feedstock powder with average size of 32.5 μm. To manufacture TiO_2-30%$FeTiO_3$ and TiO_2-50%$FeTiO_3$ feedstock powders, TiO_2 particle with average size of 0.2 μm was mechanically and uniformly mixed with 1.4 μm $FeTiO_3$ particles with corresponding weight ratio. The average size of TiO_2, TiO_2-30%$FeTiO_3$ and TiO_2-50%$FeTiO_3$ feedstock powders was 33.7 μm, 30.4 μm and 28.9 μm, respectively. The substrate was stainless steel (JIS SUS304).

2.2 Plasma Spray Equipment and Characterization

The thermal spray equipment was a plasma spray system (Plasmadyne-Mach1, Miller Thermal, USA). Argon was applied as primary gas, and helium was applied as secondary gas. The thermal spraying parameters are given in **Table 1**.

The phase compositions and microstructure were examined by XRD and SEM. To evaluate the fabrication characteristics of the feedstock powder at various plasma spraying conditions, the powder deposition rate was defined as RDRP. The definition of RDRP was given in previous report in detail[6]

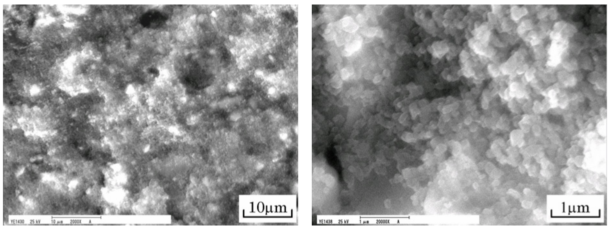
Table1 Plasma spraying parameters.

Argon gas pressure (MPa) /flow (slpm)	0.42/58
Helium gas pressure (MPa) /flow (slpm)	0.21/9
Arc current (A)	400~800
Arc voltage (V)	28~30
Spraying distance (mm)	70

3. Results and Discussion

3.1 Typical Microstructure of $FeTiO_3$ and TiO_2-$FeTiO_3$ Coatings

The coating became denser with the increasing of arc current for the higher plasma power according to the cross section of TiO_2-30%$FeTiO_3$ sprayed coatings. As clearly shown in **Fig.1**, many primary particles with average size of about 200 nm remained in the coating sprayed under the arc current of 400 A for the low energy transferred from plasma jet. The Relative Deposition Rate of TiO_2-30%$FeTiO_3$ Powder (RDRP), which was approximated to be 4 μm/pass, did not differ significantly from that of TiO_2 powder as shown in **Fig. 2**. With the increase of arc current to 600 A or 800 A, the relative deposition rate of TiO_2-30%$FeTiO_3$ powder increased obviously.



(a) (b)

Fig.1. Surface morphologies of TiO_2-30%$FeTiO_3$ coating sprayed under the arc current of 400A ((a) low magnification, (b) high magnification.).

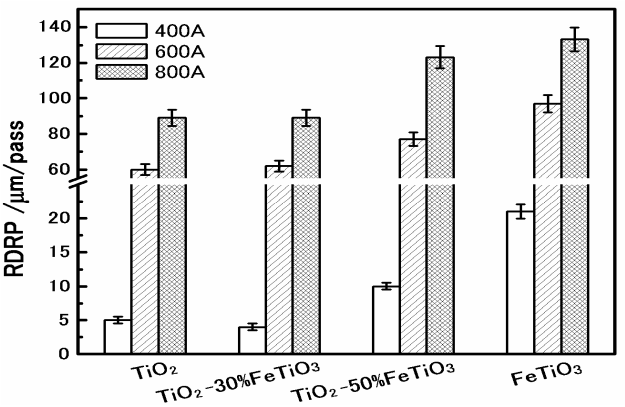


Fig.2. Relative deposition rate of TiO_2, TiO_2-30%$FeTiO_3$, TiO_2-50%$FeTiO_3$ and $FeTiO_3$ powder (RDRP) under the arc current of 400A, 600A and 800A.

3.2 Compositions of $FeTiO_3$ and TiO_2-$FeTiO_3$ Coatings

According to the x-ray diffraction patterns of plasma sprayed $FeTiO_3$ coating under the arc current of 400 A, the $FeTiO_3$ coating consisted of rutile TiO_2, $FeTiO_3$, Fe_2TiO_5, $Fe_2Ti_3O_9$ and γ-Fe_2O_3 (maghemite). Y. Chen[7] reported that the thermal oxidation process of $FeTiO_3$ by high energy ball milling in air consists reactions (1)~(3). The $Fe_2Ti_3O_9$ and γ-Fe_2O_3 are thermally metastable products which are normally difficult or impossible to be produced by conventional thermal equilibrium processes. These metastable phases were also observed in plasma sprayed $FeTiO_3$ coatings. Thus it can also be inferred that plasma spraying technique is a method to form metastable substance.

$$4FeTiO_3 + O_2 \rightarrow Fe_2Ti_3O_9 + TiO_2 + Fe_2O_3 \quad (1)$$

$$Fe_2O_3 + TiO_2 \rightarrow Fe_2TiO_5 \quad (2)$$

$$Fe_2Ti_3O_9 \rightarrow Fe_2TiO_5 + 2TiO_2 \quad (3)$$

The TiO_2-30%$FeTiO_3$ coating sprayed under the arc current of 400 A consisted of anatase TiO_2, rutile TiO_2 and $FeTiO_3$. Under the arc current of 400 A, large part of anatase TiO_2 and $FeTiO_3$ still remained in it, and Fe_2TiO_5 and $Fe_2Ti_3O_9$ phase were undetectable. With the increasing of arc current to 600 A or 800 A, Fe_2TiO_5, $Fe_2Ti_3O_9$ and Fe_2O_3 phases appeared in the sprayed TiO_2-30%$FeTiO_3$ coatings.

With the increase of the weight content of $FeTiO_3$ from 30% to 50% in the TiO_2-$FeTiO_3$ feedstock powder, $Fe_2Ti_3O_9$ and Fe_2TiO_5 phases appeared under the low arc current of 400 A for the large content of low melting point $FeTiO_3$ in the powder.

4. Conclusions

To improve the visible light responsivity of TiO_2, $FeTiO_3$ with band gap of 2.85 eV was added into TiO_2 powder to fabricate high photocatalytic coating by plasma spraying technique. The phase compositions and microstructure of plasma sprayed $FeTiO_3$, TiO_2-30%$FeTiO_3$ and TiO_2-50%$FeTiO_3$ coatings were investigated. The $FeTiO_3$ coating plasma sprayed under the arc current of 400 A consisted of rutile TiO_2, $FeTiO_3$, Fe_2TiO_5, and thermally metastable $Fe_2Ti_3O_9$ and γ-Fe_2O_3, while TiO_2-30%$FeTiO_3$ coating sprayed under the arc current of 400 A contained anatase TiO_2, rutile TiO_2 and $FeTiO_3$ only. The relative deposition rate of TiO_2-30%$FeTiO_3$ powder under the arc current of 400 A was approximated to be 4 μm/pass.

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