JOURNAL OF MATERIALS SCIENCE **39** (2004) 353–355

Formation of *p-n* junction by plasma spraying technique to enhance the photocatalytic activity of TiO_2

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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_5, Fe_2O_3, $SrTiO_3$ etc., has attracted extensive attention after the discovery of the Fujishima and Honda phenomenon [1–3]. Among all the oxide semiconductors that have been reported, anatase titanium dioxide is an excellent photocatalyst because of its high stability against photocorrosion and favorable band-gap energy (3.2 eV) [2]. To improve the photocatalytic efficiency, it is of great importance to inhibit the recombination of the photogenerated electrons and holes. To separate the photogenerated charges spatially, one approach is to apply composite films or powders such as TiO_2/WO_3, TiO_2/Nb_2O_5 [4] etc.

Generally, the photocatalytic activity increases with increasing specific surface. Therefore, micro-powders are often applied as photocatalysts because the specific surface area is larger than that of a membrane. But in practical applications, micro-powder is very difficult to reclaim after photocatalytic reaction. In order to avoid this kind of technical problem, a number of methods have been used to form TiO_2 films, including wet chemical processing (e.g., sol-gel, screen printing), vapor processing techniques (e.g., CVD, PVD) and thermal oxidation of Ti [3].

The coating formation speed and bonding strength are very low and it is difficult to produce large surface coatings by chemical processes such as sol-gel and CVD. However, the plasma spraying technique is an economical and versatile fabrication process to produce large surface coatings with almost unlimited types of materials. The coating thickness, texture and bonding strength can be controlled easily through spraying parameters, nature of the powders and substrate state [5]. Moreover, a plasma sprayed deposit is formed by a stream of molten droplets impacting on the substrate followed by flattening, rapid solidifying and cooling process. The individual molten (or half-molten) droplets spread to form thin lamellae, the stacking of which constitutes the deposit [6]. Therefore, it is easy to deposit composite coatings by spraying technique if the feedstock powders are composite materials. The composite substances may react with each other and then produce new compounds for the heating process; and the interface between two kinds of compounds is very large because the droplets spread to form very thin lamellae (micron order). In the present research, the plasma spraying technique was used to deposit composite photocatalytic coatings using composite TiO_2-Fe_3O_4 powder. To investigate the composition of sprayed coatings in detail, thin lamella (splat) was also formed.

TiO_2 and TiO_2-Fe_3O_4 coatings and corresponding splats were formed using a Plasmadyne SG-100 torch with the conditions shown in Table I.

The microstructure, distribution of elements and compositions of the sprayed samples were analyzed by electron probe surface roughness analyzer (ERA-8800FE) (Elionix Co. Ltd., Japan) and X-ray diffraction using Cu K_α radiation ($\lambda = 1.5406$ Å) with a graphite crystal monochromator (JDX3530, Jeol, Japan).

The photocatalytic activity of the sprayed coatings was evaluated through the degradation of acetaldehyde under 1 mW/cm^2 ultraviolet light irradiation. The photoelectrochemical characteristics of plasma sprayed coatings in 0.1 N NaOH solution were studied through a three-electrode cell system under 30 mW/cm^2 xenon light irradiation. The details are described elsewhere [3, 7].

The photocatalytic degradation efficiency (defined by the inclination of the exponential degradation curve) of the TiO_2-Fe_3O_4 coating is approximately two times higher than that of the TiO_2 coating as shown in Fig. 1. According to the X-ray diffraction patterns, the TiO_2 coating consists of anatase and rutile TiO_2 phase. In the TiO_2-Fe_3O_4 coatings, the n-type TiO_2 semiconductor particle reacted with the Fe_3O_4 particle and

TABLE I Plasma spraying parameters

Ar gas pressure (MPa)/flow (slpm)	0.42/58
He gas pressure (MPa)/flow (slpm)	0.21/9
Arc current (A)	600
Arc voltage (V)	30
Spraying distance (mm)	70

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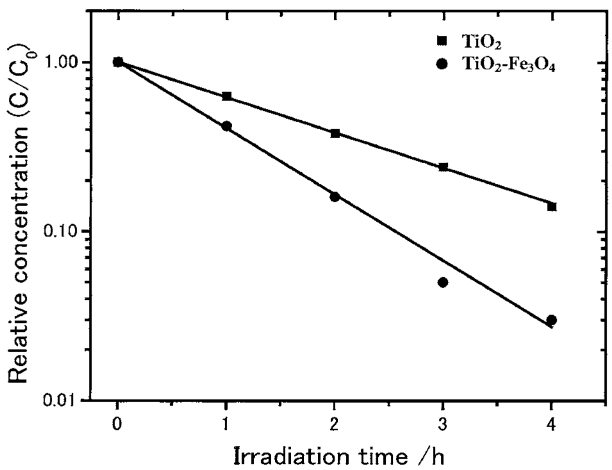

Figure 1 The photocatalytic decomposition characteristics of the acetaldehyde by plasma sprayed TiO_2 and TiO_2-Fe_3O_4 coatings.

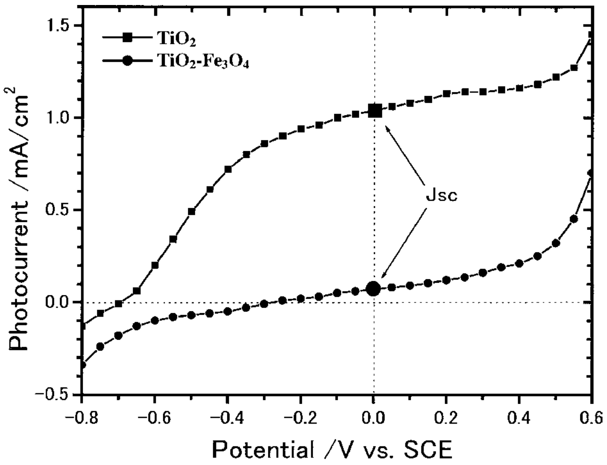

Figure 2 The photocurrent-potential curves of plasma sprayed TiO_2 and TiO_2-Fe_3O_4 electrodes.

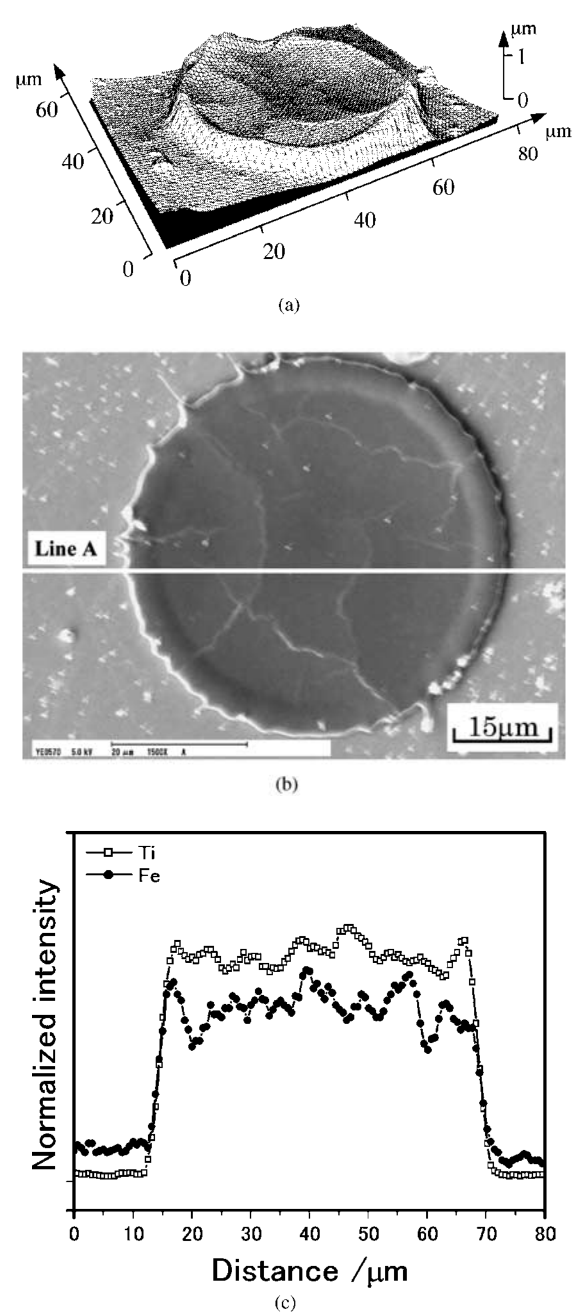

Figure 3 The 3-D view (a), plane view (b) of TiO_2-Fe_3O_4 splat, and Ti, Fe elements distribution (c) of line A illustrated in plane view.

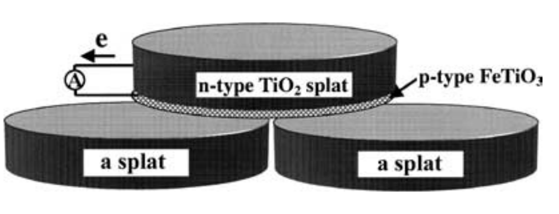

Figure 4 A proposed *p-n* junction formation model in the TiO_2-Fe_3O_4 coating.

concurrently produced *p*-type $FeTiO_3$, and consequently produced a *p-n* junction in the interface between the flattened TiO_2 lamella and $FeTiO_3$ compound. For the formation of a micro *p-n* junction, which may spatially separate the photo-generated electrons and holes as in a Si solar cell, the photocatalytic activity was improved. The existence of a *p-n* junction was clearly proved by the photocurrent-potential measurement and EDAX analysis results. The photocurrent density (photocurrent value (Jsc), with potential equal to 0 V) of sprayed TiO_2-Fe_3O_4 coating was much lower than that of TiO_2coating (Fig. 2), but the bubble (from water photolysis) formation speed from the TiO_2-Fe_3O_4 electrode is about three times quicker than that from the TiO_2. That is to say, the $FeTiO_3$/TiO_2 islands act as micro-photoelectrolysis cells in a short circuit configuration in the TiO_2-Fe_3O_4 coating, and the initiated electron cannot flow to the cathode (Pt) through the output circuit and this results in a low photocurrent. The 3-D view, plane view and line A analysis results of TiO_2-Fe_3O_4 splat are shown in Fig. 3. The thickness of the splat is not greater than 1 μm. The circumference is thicker than the central region, which may result from the high impacting speed of the particle on the substrate. The Ti and Fe elements distribute uniformly as illustrated in Fig. 3c, and it can be reasonably inferred that numerous *p-n* junctions were formed in it. The Ti/(Fe + Ti) ratio in the TiO_2-Fe_3O_4 splat approximates to 0.88, which is in good agreement with the ratio for the feedstock powder and sprayed coating. According to the above results, a *p-n* junction formation model in plasma sprayed TiO_2-Fe_3O_4 coating is illustrated in Fig. 4. The micro-TiO_2 and $FeTiO_3$

constitutes innumerable micro-cells. From these investigations, a promising approach for manufacturing high performance photocatalytic coatings by plasma spraying technique, using its special advantages, has been suggested.

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Received 29 May
and accepted 9 July 2003