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Fuxing YE

December, 2003



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CHAPTER 1

General Introduction

1.1. Background

In the 1980's, the UN set up the World Commission on Environment and Development, also called the Brundtland Commission [1~4]. They produced "*Our Common Future*", otherwise known as the Brundtland Report. It defined sustainable development as development which;

“meets the needs of present generations without compromising the ability of future generations to meet their own needs”

To purify the polluted environment and avoid further pollution, heterogeneous photocatalysis has attracted great attention in recent years. Photocatalytic phenomenon was discovered by A. Fujishima and K. Honda in 1972 in Japan when they succeeded in splitting water using illuminated TiO₂ electrode [5]. From the first energy crisis of the 1970s, tremendous amount of research has been carried out in the two closely fields of semiconductor photo-electrochemistry and photocatalysis to provide fundamental insights and practical applications [6~10].

Heterogeneous photocatalysis is a discipline that includes a large variety of reactions, such as mild or total oxidations, dehydrogenation, hydrogen transfer, metal deposition, water detoxification, gaseous pollutant removal, etc. The latter two points can be considered as one of the new “advanced oxidation technologies” (AOT) for air and water purification treatment [11]. Various commercialized facilities have been developed especially in Europe, where renewable energy source is strongly emphasized. The solar photocatalytic degradation of pollutants in the compound parabolic concentrator photoreactor has been successfully applied at Plataforma Solar de Almeria Spain on the degradation of hazardous toxic compounds in water, such as phenol, atrazine, chlorinated solvents, imidacloprid, pirimicarb, acrinathrin, lindane and so on. **Fig.1.1** shows partial views of solar photochemistry compound parabolic concentrators facilities for photocatalysis installed at Hidrocen factory (Spain) and of photoelectrochemical reactors in operation [12~14]. In the reactors, powder photocatalysts are mainly applied.

The basic principles of heterogeneous photocatalysis can be summarized shortly as follows [15]. A semiconductor is characterized by an electronic band structure in

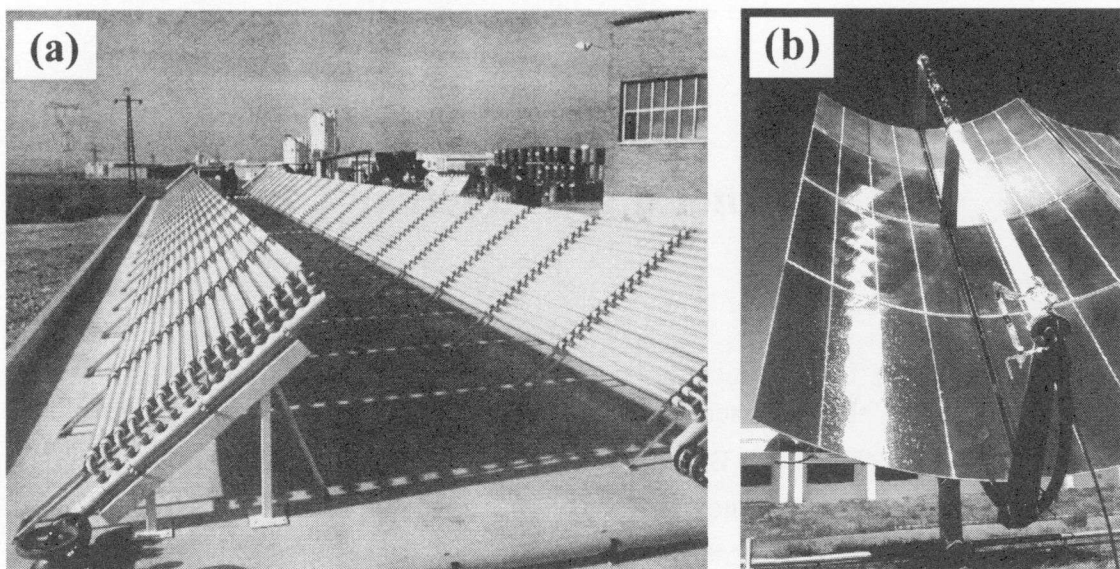


Fig.1.1. Partial views of solar photochemistry compound parabolic concentrators facilities for photocatalysis installed at Hidrocen factory (Arganda del Rey, Madrid, Spain) (a) and of photoelectrochemical reactors in operation (b). (Powder photocatalysts are mainly applied, Courtesy of S. Malato).

which the highest occupied energy band, call valence band (vb), and the lowest empty band, call conduction band (cb), are separated by a band gap, i.e. a region forbidden energies in a perfect crystal. When a semiconductor catalyst is illuminated with photons, whose energy is equal to or greater than the band-gap energy (E_{BG}), an electron from the valence band is initiated to the conduction band with simultaneous generation of a hole (h^+) in the valence band as illustrated in **Fig.1.2** [16]. The e^- and h^+ can recombine on the surface or in the bulk of the photocatalyst (particle or membrane) in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of photocatalyst. Moreover, the e^- reacts with O_2 and h^+ reacts with H_2O , and consequently produce super-oxygen ($\cdot O_2^-$) and OH radicals ($\cdot OH$) (Equations (1.1) and (1.2)), respectively. Thereby, subsequent anodic and cathodic redox reactions can be promoted. The difference with conventional catalysis is the mode of activation of the catalyst in which the thermal activation is replaced by a photonic activation.



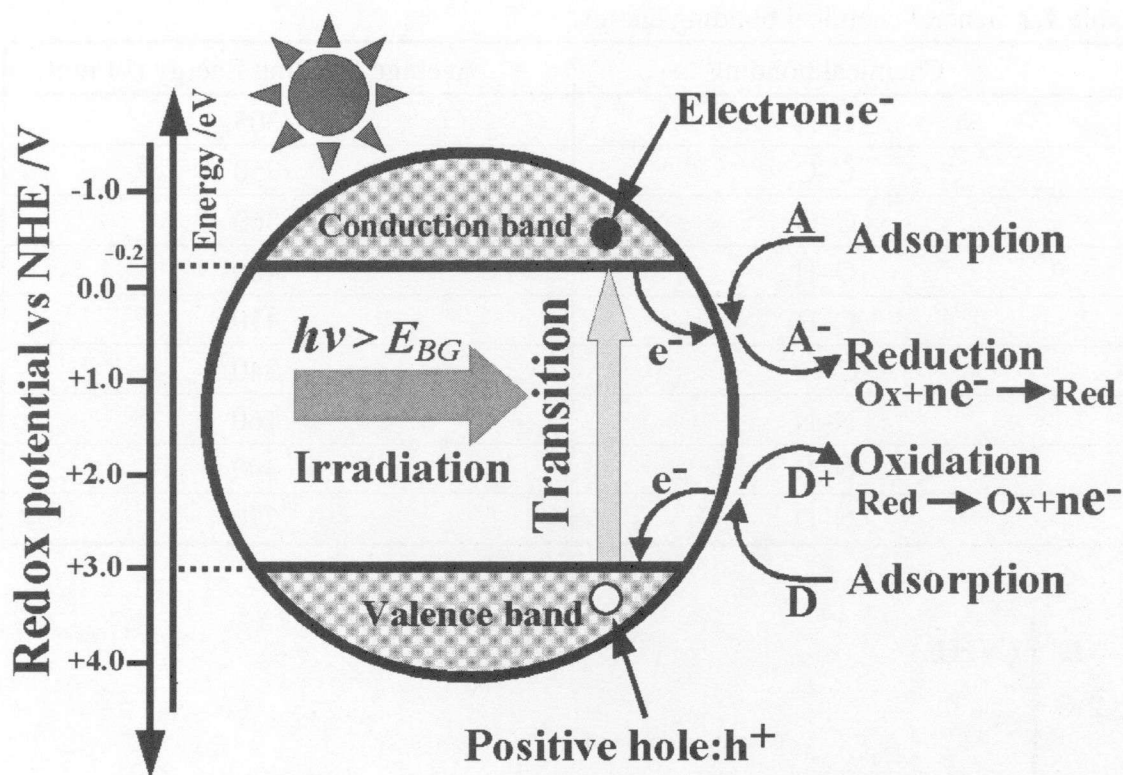


Fig.1.2. Energy band diagram of a spherical titanium dioxide particle and the basic principles of heterogeneous photocatalysis.

The oxidation potential of hydroxyl radical is 2.80V [16], which is higher than that of the general oxidizers as given in **Table 1.1**. The hydroxyl radical energy is 501kJ/mol, which is higher than the general bonding energy, such as C-C, N-H, C-O etc. as summarized in **Table 1.2**. Therefore, almost all kinds of organic substances can be oxidized by photocatalyst to simple species (H_2O , CO_2 , etc).

Table 1.1 Oxidation potential of hydroxyl radical and general oxidizers.

Oxidizer	Oxidation potential (V)	Relative oxidation potential (V)
$\cdot\text{OH}$	2.80	2.05
O	2.42	1.78
O_3	2.07	1.52
H_2O_2	1.77	1.30
HClO	1.49	1.10
Cl	1.36	1.00

Table 1.2 General chemical bonding energy.

Chemical bonding	Average Bonding Energy (kJ/mol)
C–N	305
C–C	350
C–O	360
O–H	460
C–H	410
C–Cl	340
N–N	160
N–H	390
N–O	220

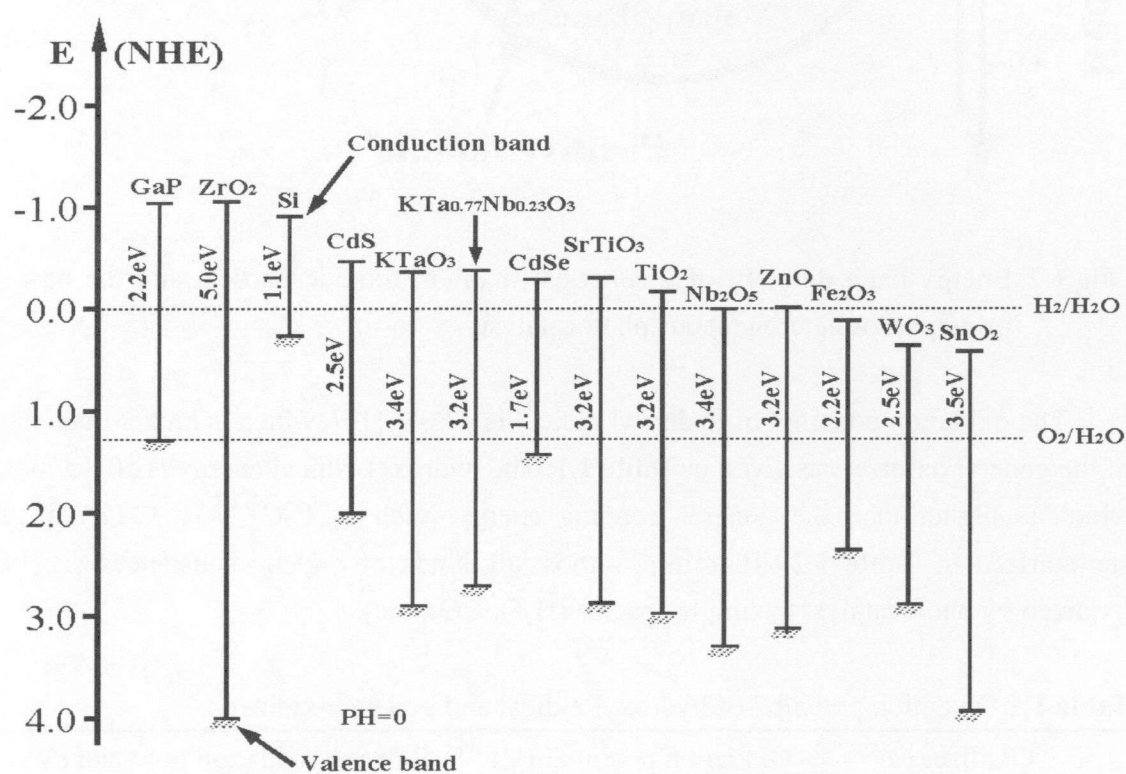


Fig.1.3. Band edge positions of various semiconductors in contact with aqueous electrolyte at pH 0.

Figure 1.3 illustrates the energy diagram of some general semiconductors [17, 18]. Among all the oxide semiconductors that have been reported, TiO_2 is an excellent photocatalyst due to its optical and electronic properties, chemical stability, non-toxicity and low cost, 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 [19–22].

Titanium dioxide crystallized in three major different structures [23–26]: rutile (tetragonal), anatase (tetragonal) and brookite (rhombohedral). Other structures exist as well, for example, cotunnite TiO_2 has been synthesized at high pressure and is one of the hardest polycrystalline materials known. However, only rutile and anatase play any role in the applications of TiO_2 and are of any interest as they have been studied with surface science techniques. Their unit cells [27] are shown in **Fig.1.4**. In both structures, each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are greater (3.79 and 3.04 Å vs. 3.57 and 2.96 Å in rutile) whereas the Ti-O distances are shorter than in rutile (1.934 and 1.980 Å in anatase vs. 1.949 and 1.980 Å in rutile). In the rutile structure each octahedron is in contact with ten neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while in the anatase structure each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass density and electronic band structure between the two crystal forms of TiO_2 as given in **Table 1.3**.

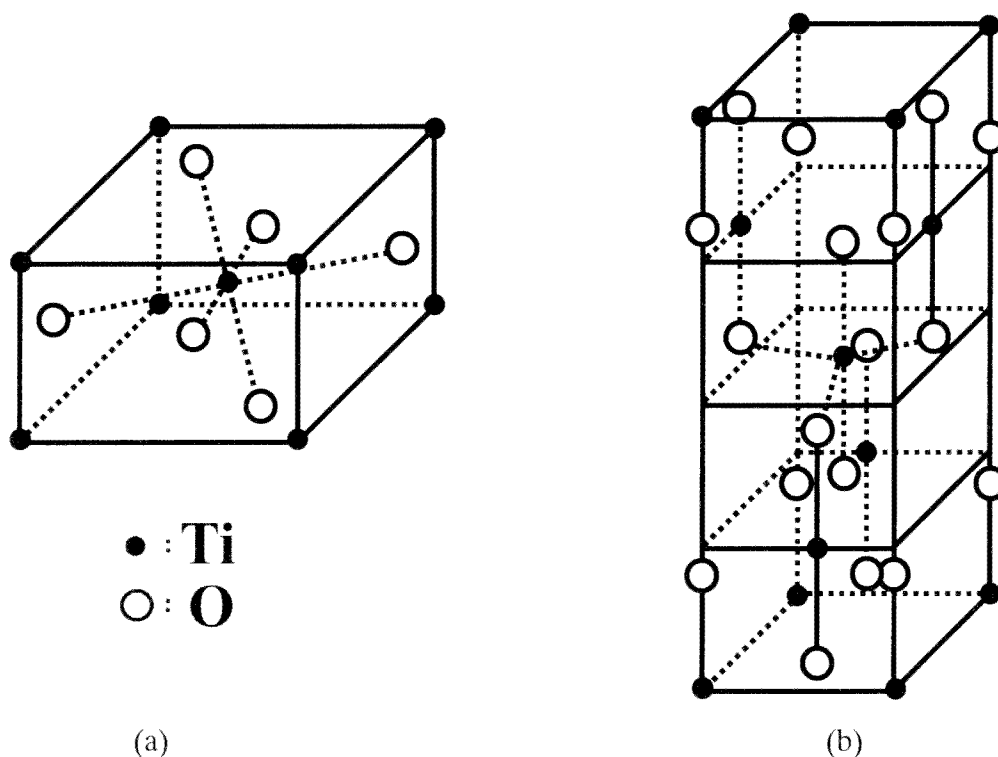


Fig.1.4. Crystal structures of rutile TiO_2 (a) and anatase TiO_2 (b).

Table 1.3 Properties of rutile and anatase TiO₂.

	Rutile TiO ₂	Anatase TiO ₂
Crystal system	Tetragonal	Tetragonal
Space group data	D _{4h} ¹⁴ – P4 ₂ /mnm	D _{4h} ¹⁹ – I4 ₁ /amd
Lattice constant a	4.593 Å	3.784 Å
Lattice constant b	2.959 Å	9.515 Å
Density	4.250 g/cm ³	3.894 g/cm ³
Melting point	2131 K	Meta-stable
Thermal expansion (×10 ⁻⁶)	7.14	10.2

The melting point of rutile TiO₂ is 2131K, and the anatase TiO₂ is metal-stable, which will transform to rutile TiO₂ at elevated temperature. As a photocatalyst, anatase TiO₂ shows higher photocatalytic activity.

The photo efficiency can be reduced by the electron-hole recombination, which corresponds to the degradation of the photoelectric energy into heat.



where N is the neutral center and E is the energy released in the form of light or of heat. To improve the photocatalytic efficiency of TiO₂, it is of great importance to inhibit the recombination of the photo-generated electrons and holes. To separate the photo-generated charges spatially, one approach is to apply composite films or powders such as TiO₂/WO₃, TiO₂/Nb₂O₅ [28–30], etc.

Moreover, it has been also realized that the forbidden energy gap of anatase TiO₂ (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 less than 387nm. As shown in **Fig.1.5**, only the ultraviolet fraction (3-5%) of the solar irradiation is active in the photo-excitation processes using pure anatase TiO₂. This limits the application of sunlight as an energy source for the photocatalysis. Recently, there have many methods to extend the spectral response of semiconductor into visible region, such as ion implantation [31], doping with N [32], and using binary metal oxides [28–30].

Generally, the photocatalytic performance increases with the increasing of specific surface. Therefore, micro-powders are often applied as photocatalysts because the specific surface area is larger than that of membrane. But in practical application, 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 TiO₂ films, including wet chemical processing (e.g.: sol-gel, screen printing), vapor processing techniques (e.g.: CVD, PVD) and thermal oxidation of Ti [33].

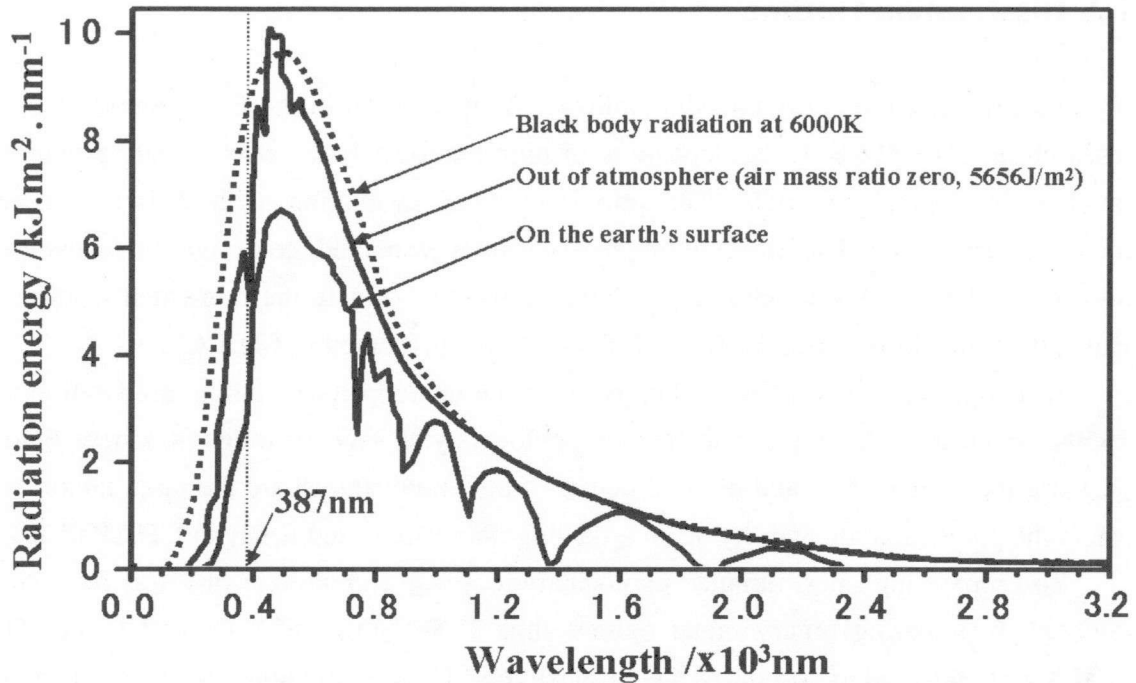


Fig.1.5. Solar energy density distribution at each wavelength.

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, plasma spraying technique is an economical and versatile fabrication process to produce large surface coatings with almost unlimited types of materials. The coatings thickness, texture and bonding strength can be controlled easily through spraying parameters, powders and substrate state, etc [34]. A plasma sprayed deposit is formed by a stream of molten (or half-molten) droplets impacting on the substrate followed by flattening, rapid solidifying and cooling process. The individual molten (or half-molten) droplets spread to thin lamellae, the stacking of which constitutes the deposit. Therefore, it is easy to deposit composite coatings by plasma spraying technique if the feedstock powders are composite materials. The composite substances may also react with each other and then produce new compounds in plasma spraying processes.

Therefore, the present work was originally motivated to deposit high performance photocatalytic activity coatings based on the TiO₂ material on stainless steel (JIS SUS304) by plasma spraying technique, and to understand the influence of Al₂O₃, Y₂O₃ and Fe₃O₄ particles on the microstructure, phase composition and photocatalytic activity of TiO₂ coatings. To investigate the FeTiO₃ substance on the photocatalytic activity of TiO₂ coatings, composite TiO₂-FeTiO₃ coatings were prepared and analyzed. Finally, the photoelectrochemical characteristics of TiO₂ and TiO₂-Fe₃O₄ electrodes were examined.

1.2. Dissertation Outline

This dissertation is organized as follows. As mentioned in the Background of this research in **CHAPTER 1**, the deposition of high photocatalytic activity coating, which involves in original materials, fabrication technique, evaluation method, is becoming increasing important. Therefore, in this thesis, efforts were made to design the feedstock powders, to apply plasma spraying technique, and to evaluate the fabricated coatings. Block diagrams illustrating the flow of this study are presented in **Fig.1.6**.

Although plasma spraying technique has been developed for coating preparation in 1950s, application for the fabrication of photocatalytic TiO₂ coatings is a new field. Because the composition and microstructure of the photocatalyst are the main factors to affect the photocatalytic activity of TiO₂ coating, there are stated firstly in **CHAPTER 2**.

To prepare high performance photocatalytic TiO₂, a great deal of effort has been devoted in preparing binary metal oxides, thus 10%Al₂O₃, 10%Y₂O₃ and 10%Fe₃O₄ oxides were selected to add into TiO₂, respectively. Their evaluation results are given in **CHAPTER 3**.

Base on the research results in **CHAPTER 3**, the Fe₃O₄ content influence on the photocatalytic activity of TiO₂ coating was discussed in **CHAPTER 4** to clarify the original reasons of the good photocatalytic activity of TiO₂-10%Fe₃O₄ coating. Because the photo absorbance character of photocatalyst is a key parameter to influence the photocatalytic activity, it was also given in it. Two-steps electron transfer model was proposed.

Next, in **CHAPTER 5**, to clarify the influence of FeTiO₃ substance on the photocatalytic activity of TiO₂ coatings, the TiO₂-FeTiO₃ powders were designed, and the composition and photocatalytic activity of TiO₂-FeTiO₃ coatings were investigated and discussed.

Because the fundamental principle of photocatalysis is the same as that of photoelectrochemistry, which originates from electron-hole pair generation and efficient separation, the photoelectrochemical characteristics of TiO₂ and TiO₂-10%Fe₃O₄ electrodes were studied. A plasma sprayed deposit is formed by the stacking of lamellae (splats). The typical TiO₂-Fe₃O₄ splat was examined to explain the different photoelectrochemical phenomena between TiO₂ and TiO₂-10%Fe₃O₄ electrode. Based on the above research results, a p-n junction formation model was proposed and confirmed. These research results are summarized in **CHAPTER 6**.

Finally, principle conclusions of this thesis are summarized in **CHAPTER 7**.

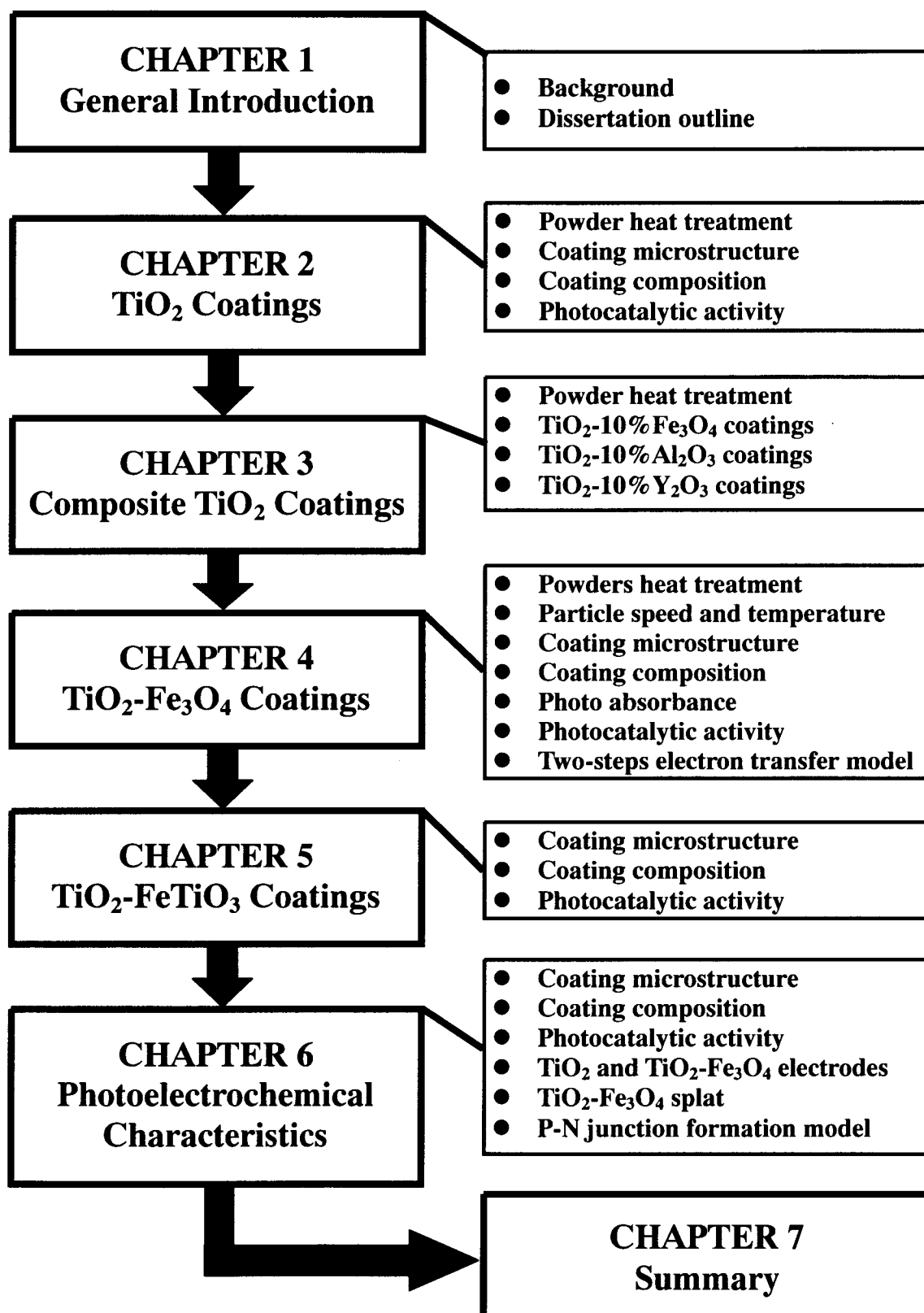


Fig.1.6. Block diagrams illustrating the flow of this study.

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CHAPTER 2

Evaluation of Plasma Sprayed TiO₂ Coatings

2.1. Introduction

Although thermal spray was invented by Swiss scientist Max Ulrich Schoop in 1910's, it was not extended until the 1950's when the expansion of the aerospace industry started to take a lead in industry technology and the development of plasma spray [1].

A plasma sprayed deposit is formed by a stream of molten (or half-molten) droplets impacting on the substrate followed by flattening, rapid solidifying and cooling process. The individual molten (or half-molten) droplets spread to thin lamellae, the stacking of which constitutes the deposit [2].

Nowadays, thermal spraying techniques have been widely applied for the production of metal and ceramic coatings on metals or the other kinds of surfaces. The applications of titanium dioxide coatings can be divided into two broad categories: as protection coatings using the rutile phase TiO₂ [3, 4] and as functional layers generally using the anatase phase TiO₂ [5, 6].

With regard to the functional layers of TiO₂, ever since the early work on photoelectrochemical reactions at TiO₂ semiconductor electrodes was reported in 1972[7], applications to environmental cleanup have been one of the most active areas in heterogeneous photocatalysis. This is inspired by the application of TiO₂-based photocatalysts for the total destruction of organic compounds in polluted air and wastewaters. Among the several semiconductor materials tested for photocatalysis, TiO₂ has proved to be the promising one due to its strong oxidizing power under UV illumination and its chemical stability [8–12].

Although extensive researches were focused on the preparation of high performance photocatalytic TiO₂ materials by chemical technique, there have not promising method to fix the photocatalytic TiO₂ powder on a kind of substrate to recycle it with high commercial interest. Furthermore, most of the supported TiO₂ is commonly reported to be less photoactive than the corresponding TiO₂ particle [13–15]. Moreover, the fabrication of photocatalytic TiO₂ coatings by thermal spraying technique can not be found except in our research group and related researchers with us until now. Therefore, the general features of plasma sprayed TiO₂ coating using anatase TiO₂

feedstock powder were studied and presented here firstly as fundamental knowledge.

In this chapter, the phase composition, microstructure and photocatalytic activity of plasma sprayed TiO₂ coatings were characterized and discussed in detail. The anatase-rutile phase transformation temperature of TiO₂ feedstock powder was investigated by electric furnace heat treatment method.

2.2. Materials and Experimental Procedures

2.2.1 Feedstock Powder and Substrate

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 these two demands, polyvinyl alcohol was used as a binder to agglomerate TiO₂ particles with average diameter of 0.2 μ m to powders with average diameter of about 30 μ m, which can be applied for thermal spraying. Because the photocatalytic activity of anatase titanium dioxide is better than of rutile, anatase TiO₂ was used as feedstock powder and the average size of the TiO₂ powder was 33.7 μ m. The size distribution of TiO₂ powder is given in **Table 2.1**. The x-ray diffraction result, morphologies of the TiO₂ powder are shown in **Fig.2.1** and **Fig.2.2**, respectively. The anatase-rutile transformation of primary anatase TiO₂ particles did not occur in the agglomeration process. Primary particle kept its original state. The substrate was stainless steel (JIS SUS304), which was washed by acetone and sandblasted before thermal spray.

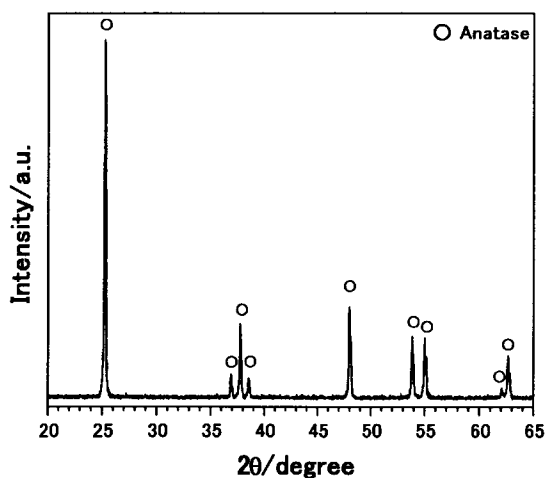
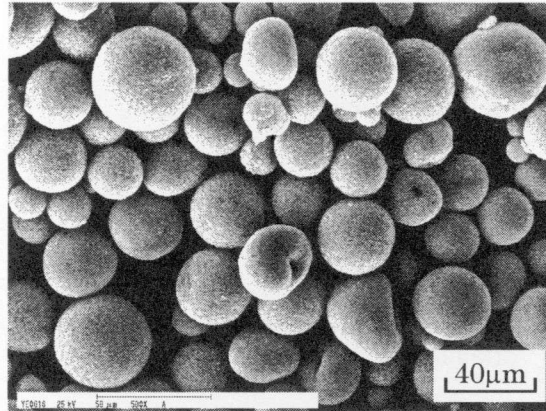


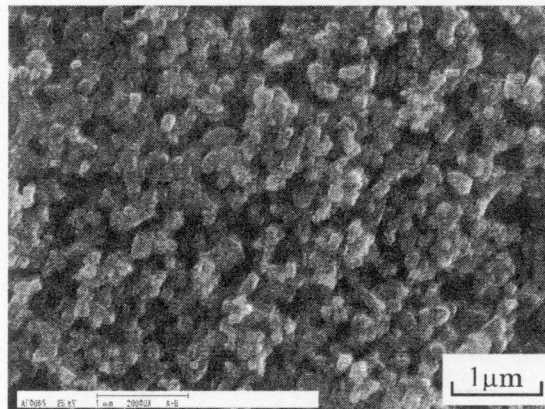
Fig.2.1. X-ray diffraction pattern of TiO₂ feedstock powder.

Table 2.1 Size distribution of TiO₂ feedstock powder.

Size (μm)	53	45	38	32	30	20	10	-10
Mass(%)	0.0	6.2	30.2	19.4	4.9	24.6	9.8	4.9



(a)



(b)

Fig.2.2. Morphologies of TiO₂ feedstock powder. (a) Low magnification, (b) High magnification.

2.2.2. Plasma Spraying Equipment

The plasma spraying system was commercial spraying equipment, which was Plasmadyne-Mach1 manufactured by Plasmadyne Company. The gun is schematically illustrated in **Fig.2.3**. The gun's unique design accepts internal or external powder injection. Because internal injection provides optimum energy transfer and particle velocity, internal injection with a powder port angle of 30° was chosen in this research. Argon was used as a primary plasma gas and helium was used as the secondary gas. Because the photocatalytic activity of anatase TiO₂ is better than that of rutile TiO₂ as

mentioned in Chapter 1, it is very important to inhibit the phase transformation of anatase TiO₂ in the heating process of plasma spraying. According to the research results of spray distance on the overall properties of TiO₂ coating, the spray distance was set as 70mm. The thermal spraying parameters are given in **Table 2.2**.

Table 2.2 Plasma spraying parameters.

Argon gas pressure (MPa)	0.42
Argon gas flow (slpm)	58
Helium gas pressure (MPa)	0.21
Helium gas flow (slpm)	9
Arc current (A)	400, 600, 800
Arc voltage (V)	28~30
Spraying distance (mm)	70

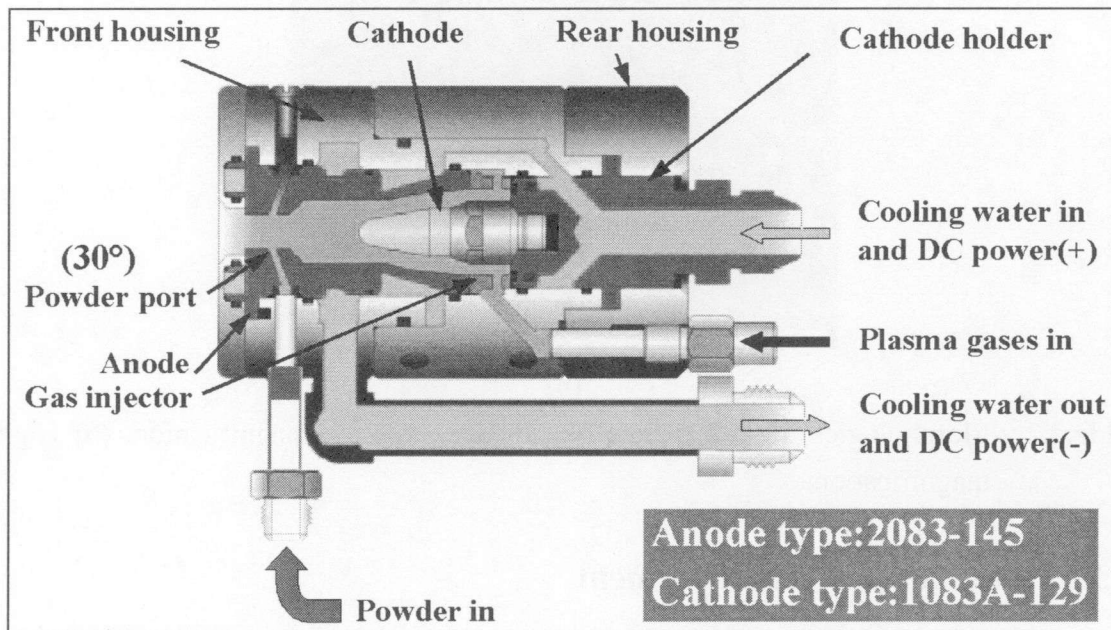


Fig.2.3. Schematic diagram of plasma spray torch applied in this study.

2.2.3. Heat Treatment Procedure of Agglomerated TiO₂ Powder

To investigate the anatase-rutile phase transformation temperature, the TiO₂ feedstock powder was kept in electric furnace for 7200s after reaching at treated

temperature (1123K, 1173K, 1223K or 1273K) with a heating rate of 1.67K/s, and then was cooled with the furnace.

2.2.4. Characterization of Powder and Sprayed Coatings

Electron probe surface roughness analyzer (ERA-8800FE, Elionix Co. Ltd., Japan) and energy dispersive analysis of x-ray (EDAX) were used to examine the structure characteristics of the powders and the sprayed coatings. The phase composition of the powders and the sprayed coatings were investigated by x-ray diffraction using Cu-K α radiation ($\lambda=1.5406\text{\AA}$) and graphite crystal monochromator (M03XHF, MAC Science Co. Ltd.). The 2θ range was $23^{\circ}\sim 38^{\circ}$. Quantitative analysis of the phase composition of the sprayed coatings was attempted by comparing the net x-ray diffraction peaks intensities of anatase (101) and rutile (110). The content of anatase phase in the sprayed coatings was calculated using the most common equation given by R. A. Spurr and H. Myers [16].

$$A = \frac{I_A}{1 + 1.265 \frac{I_R}{I_A}} \times 100\% \quad (2.1)$$

where I_A is the highest peak intensity of anatase phase (101 peak), I_R the highest peak intensity of rutile phase (110 peak) and A the content of anatase phase in the sprayed coatings.

The surface roughness of the coating was investigated by a surface roughness analyzer (DEKTAK, ULVAC, Japan).

2.2.5. Definition of Relative Deposition Speed of Feedstock Powder

In thermal spray technology, there have many parameters to evaluate the properties of sprayed coatings, such as cohesion strength, hardness, wear resistance, powder deposition efficiency and so on. The mechanical properties of sprayed coatings are very important in mechanical applications. However, great attention should be paid on not only the functional performance but also the powder deposition speed in the developments of functional coatings.

Therefore, to evaluate the fabrication characteristics of the feedstock powder at various plasma spraying conditions, the powder deposition speed was defined as Equation (2.2). The calculated result was applied to compare the powder deposition efficiency in this study.

$$RDSP = \frac{T_{Thickness} V_{Traverse} W_{Step}}{n V_{Rotation}} \quad (2.2)$$

where $RDSP$ is Relative Deposition Speed of Powder, $V_{Rotation}$ relative rotation speed of powder feeder, $V_{Traverse}$ relative traverse speed of plasma gun, W_{Step} relative step width of up-down moving equipment, $T_{Thickness}$ thickness of sprayed coating, n spray pass of the coating.

2.2.6. Photocatalytic Activity Evaluation Method

Generally, the kinetic of photocatalytic reaction follows a Langmuir-Hinshelwood mechanism [17–21] confirming the heterogeneous catalytic character of the system with the rate v varying proportionally with the surface coverage θ as:

$$v = k\theta = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (2.3)$$

where C is the reactant concentration, v the degradation rate of reactant, k the reaction rate constant, θ surface coverage, t reaction time and K surface adsorption equilibrium constant.

Equation (2.3) can be changed to

$$-\left(1 + \frac{1}{KC}\right)dC = kdt \quad (2.4)$$

The integration form of Equation (2.4) is

$$\ln\left(\frac{C_0}{C}\right) + K(C_0 - C) = kKt \quad (2.5)$$

where C_0 is the initial concentration of reactant. For dilute gas, $K(C_0 - C)$ is nearly equivalent to 0, consequently Equation (2.5) becomes Equation (2.6) letting $\tau = kK$.

$$\ln\left(\frac{C}{C_0}\right) = -kKt = -t/\tau \quad (2.6)$$

In this research, the photocatalytic activity of the feedstock powders and sprayed coatings was evaluated through the photo mineralization of acetaldehyde applying ultraviolet light. The evaluation set-up is shown in **Fig.2.4**. The irradiation profile of ultraviolet lamp is illustrated in **Fig.2.5**, and the light intensity on the sample surface was set in 1.0mW/cm². In the experimental procedure, the decomposition of the concentration (ppm) of acetaldehyde and CO₂ product concentration with time (s) were measured with two kinds of Kitakawa type gas detectors at a certain time interval.

The coatings surface area was standardized as 50×60mm. On the other hand, to

evaluate the photocatalytic activity of powder, the powder was uniformly laid on a silica glass with dimension of 50×60mm, and the weight of powder was 0.5g.

According to Equation (2.6), the smaller the value of τ the better of the photocatalytic activity of the coating/powder. Therefore, the τ can be used as the characteristic decomposition time to evaluate the catalytic effectiveness of the sprayed coating and powder.

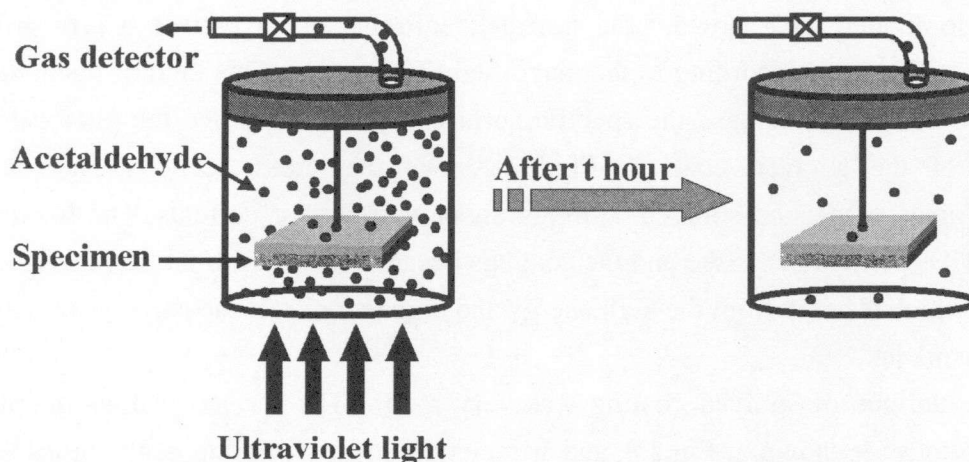


Fig.2.4. Evaluation set-up for photocatalytic activity of feedstock powder and spayed coating.

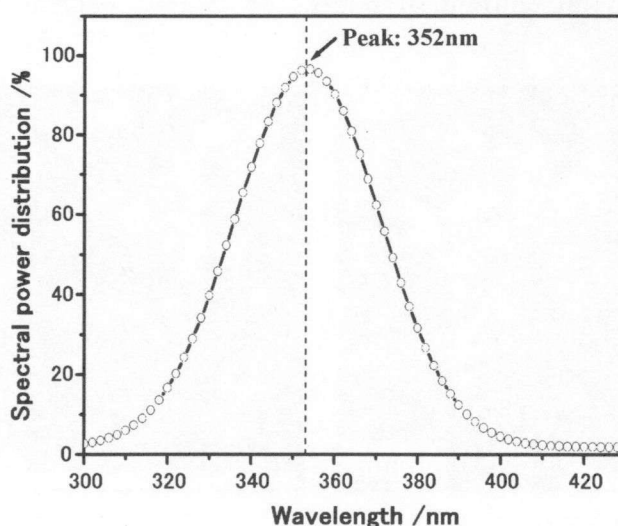


Fig.2.5. Spectral power distribution of ultraviolet lamp used for photocatalytic experiment in this study.

2.3. Results and Discussion

2.3.1. General Features of Plasma Sprayed TiO₂ Coatings

Although the rutile TiO₂, which is generally applied for improving wear resistance or as constructional material, etc, is a kind of well-known material, a few researchers are studying on anatase TiO₂ as functional material in thermal spray field. **Fig.2.6** shows the surface morphologies of TiO₂ coating plasma sprayed under the arc current of 400A. The agglomerated TiO₂ powder did not melt entirely, and a part of 0.2 μ m primary particles still existed according to the magnified SEM image. This kind of phenomenon will be a benefit to increase the specific surface and then improve the photocatalytic activity of the sprayed coating. **Fig.2.7** shows the cross sections and surface morphologies of plasma sprayed coatings under various arc currents. The fraction of melted TiO₂ particle increased and the coatings became denser with the increasing of arc current, which resulted from the high energy and high velocity of the particles transferred from plasma jet.

The surface of sprayed coating was very rough. The surface profiles of sprayed TiO₂ coatings are shown in **Fig.2.8**, and arithmetical mean deviation of the profiles (Ra) were approximate to 8.8 μ m, 6.3 μ m and 5.7 μ m under the arc current of 400A, 600A and 800A, respectively. Under lower arc current, the surface of the coating became rougher.

The relative deposition speed of anatase TiO₂ powder is shown in **Fig.2.9**. Under the arc current of 400A, the relative deposition speed was approximate to 5 μ m/pass. With more increased arc current of 600A, the relative deposition speed increased significantly.

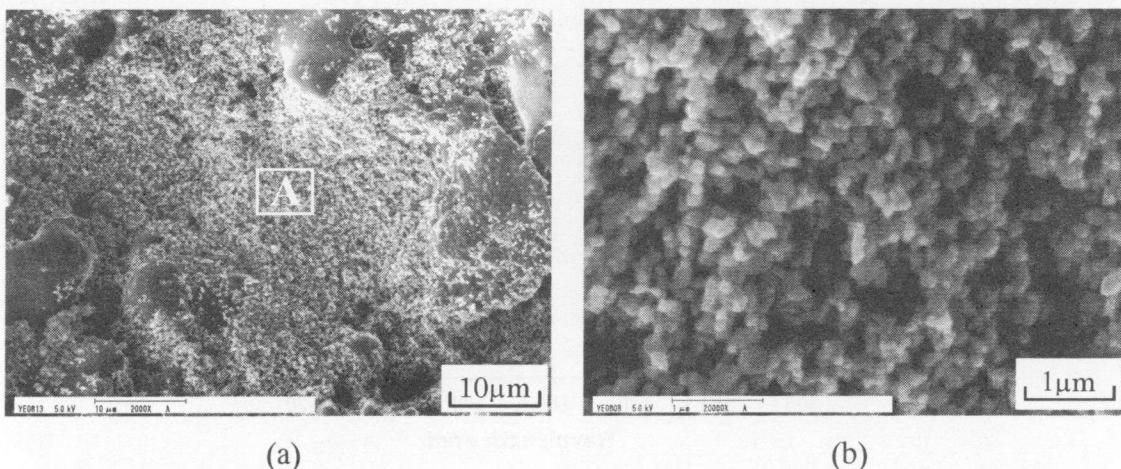


Fig.2.6. Surface morphologies of plasma sprayed TiO₂ coating under the arc current of 400A. (a) General view, (b) Magnified view of position A in (a)

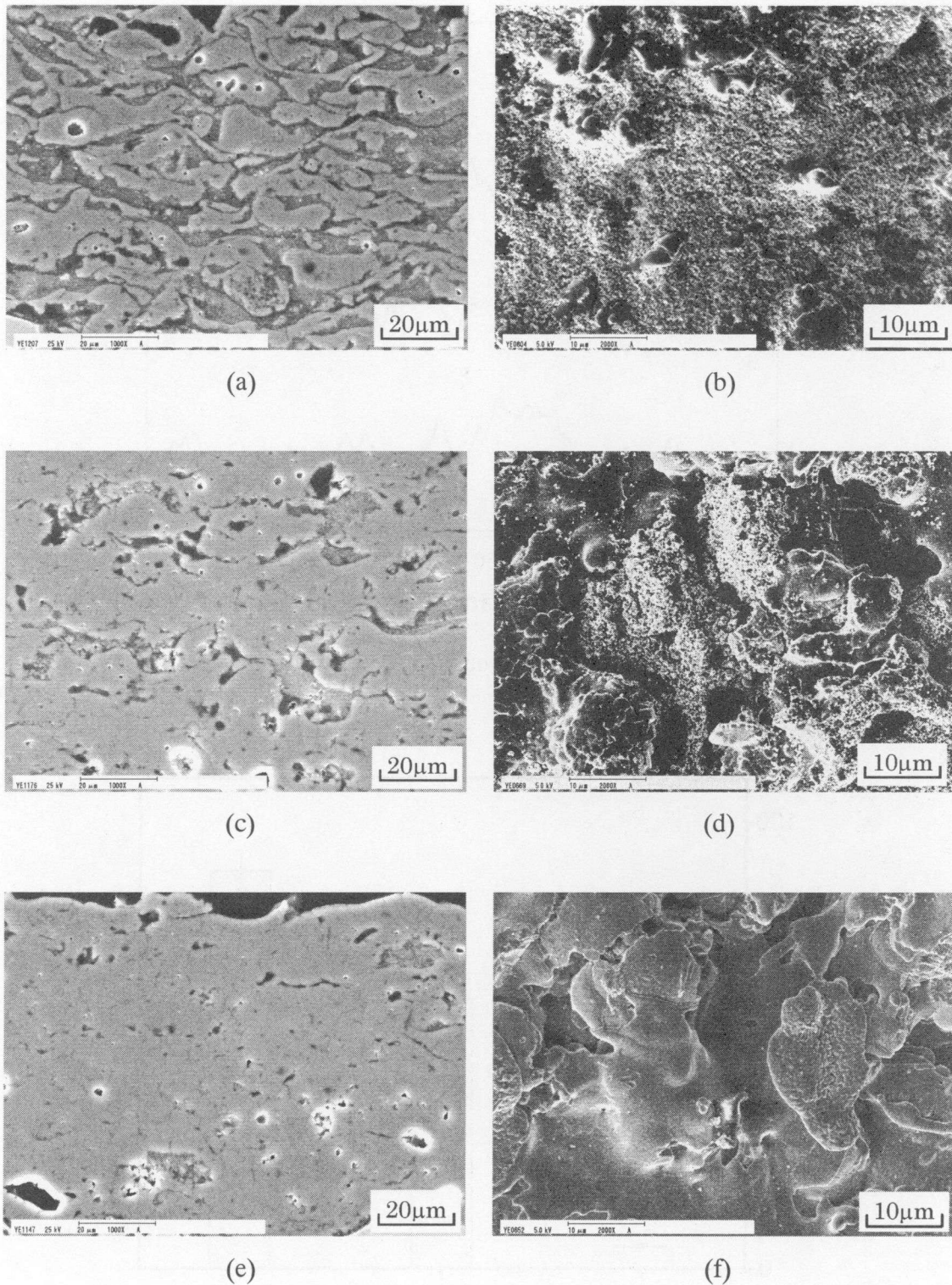


Fig.2.7. SEM micrographs of plasma sprayed TiO₂ coatings. (a), (c) and (e) Cross sections under the arc current of 400A, 600A and 800A, respectively; (b), (d) and (f) Surface morphologies, respectively.

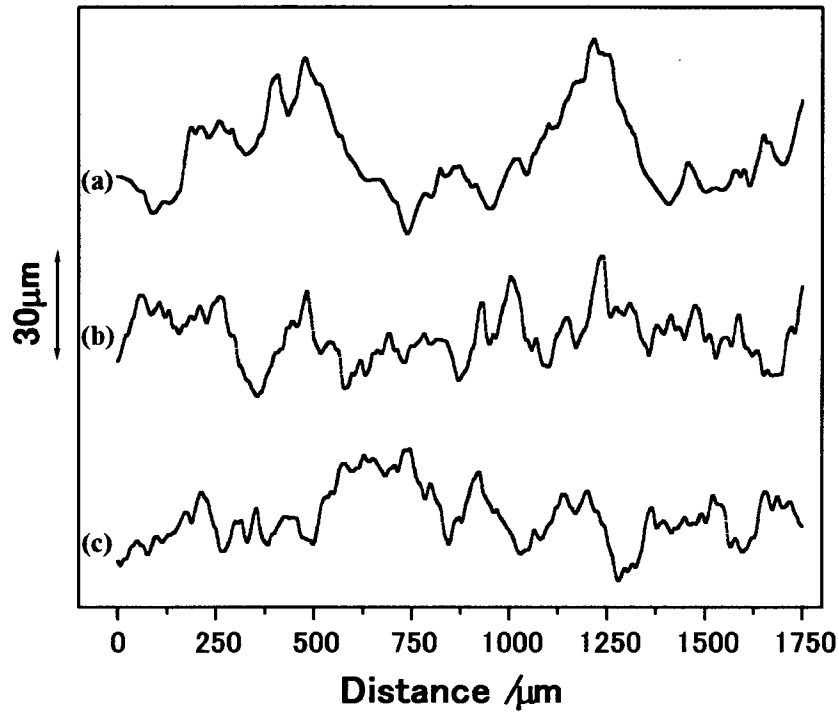


Fig.2.8. Surface profiles of plasma sprayed TiO₂ coatings under various arc currents. (a) 400A, (b) 600A, (c) 800A.

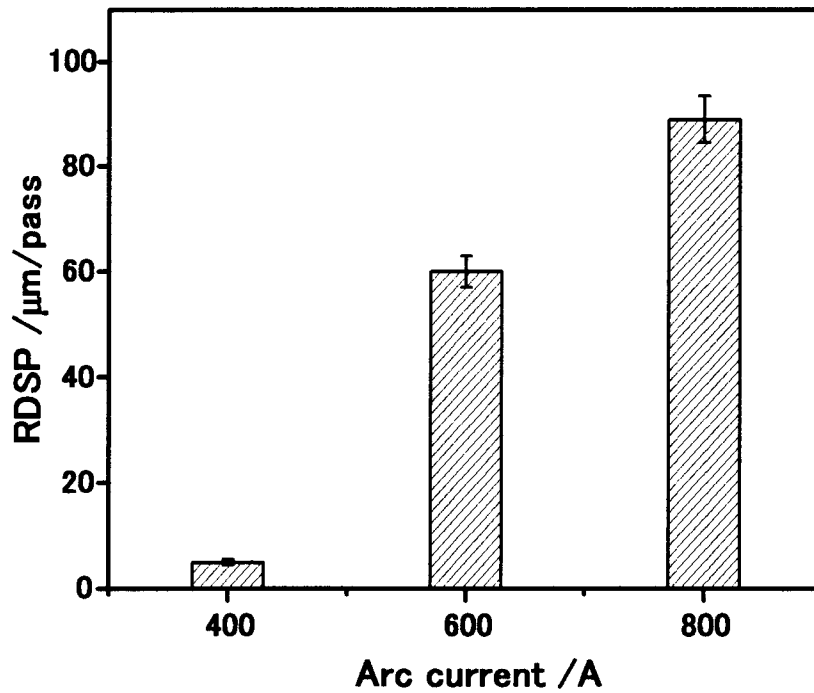


Fig.2.9. Relative deposition speed of anatase TiO₂ powder under the arc current of 400A, 600A and 800A.

2.3.2. Composition of Plasma Sprayed TiO₂ Coatings

The plasma spraying process is characterized by a high temperature, ranging from 10000K and 20000K, by the presence of a plasma reducing gas, mainly a mixture of reducing gas such as Ar, He. As a consequence of these severe conditions, chemical modification such as reduction or composition variations can take place during the plasma spraying process [22, 23].

The x-ray diffraction patterns of TiO₂ coatings plasma sprayed under arc current of 400, 600 and 800A is illustrated in Fig.2.10. To compare with the feedstock powder, the x-ray diffraction pattern of anatase TiO₂ powder is also illustrated in it. The peak height of anatase TiO₂ (101 peak) decreased with the increasing of arc current for the phase transformation of anatase to rutile TiO₂, whereas that for rutile TiO₂ (110 peak) increased continuously. Because the photocatalytic activity of anatase phase is better than that of rutile phase [24], the contents of anatase TiO₂ in the sprayed coatings were calculated and summarized in Fig.2.11 according to the x-ray diffraction patterns and Equations (2.1). The content of anatase TiO₂ in the sprayed coatings was not over 15% and decreased with the increasing of the arc current.

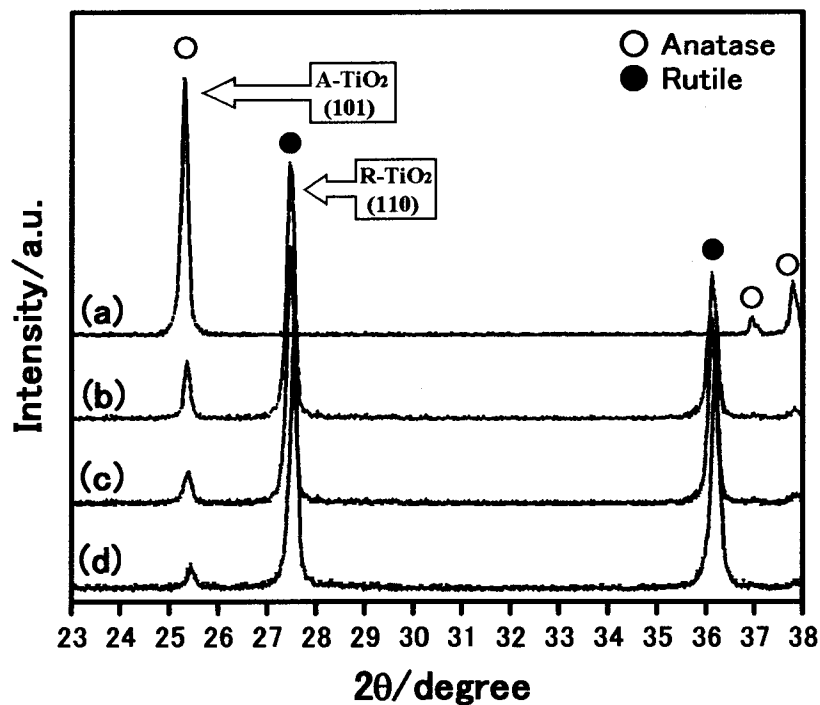


Fig.2.10. X-ray diffraction patterns of TiO₂ powder (a) and plasma sprayed TiO₂ coatings under the arc current of 400A (b), 600A (c) and 800A (d).

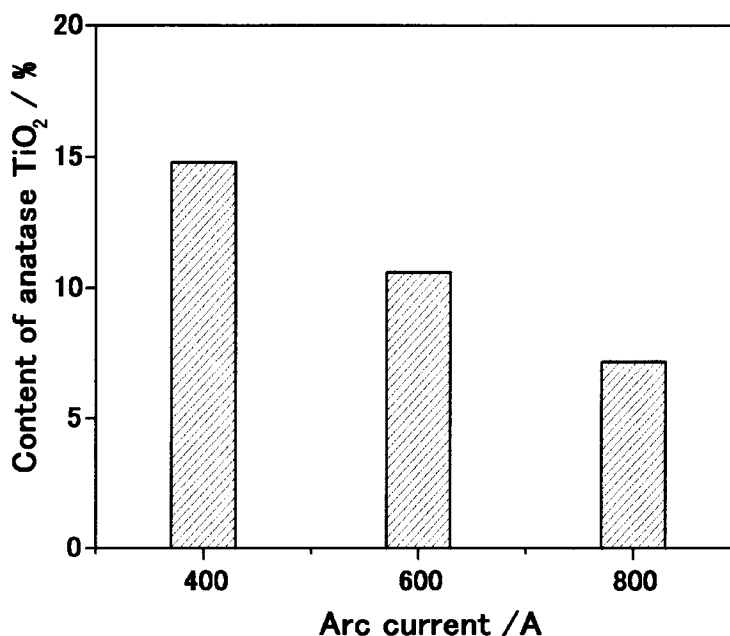


Fig.2.11. Contents of anatase TiO₂ in plasma sprayed TiO₂ coatings under the arc current of 400A, 600A and 800A.

2.3.3. Composition of Heat Treated TiO₂ Powders

Crystal structure variations of TiO₂ are well known, anatase is meta-stable and transform exothermally and irreversibly to rutile over a range of temperatures but usually at 923K to 1273K [25–27], which is governed by particle size, particle morphology, synthetic conditions and purity, etc. Because the photocatalytic activity of anatase phase is better than that of rutile phase, it is very important to know the anatase-rutile transformation temperature of anatase TiO₂ feedstock powder used in this study.

The thermal behaviors of TiO₂ have been observed by differential thermal analysis and furnace heat treatment method and so on. In this study, electric furnace heat treatment at 1123K, 1173K, 1223K and 1273K for 7200s in air with a heating rate of 1.67K/s was selected to investigate the transformation temperature of anatase TiO₂ powder. The x-ray diffraction patterns of heat treated TiO₂ feedstock powders are illustrated in **Fig.2.12**. The anatase phase kept the original phase state at the 1123K. When treated at 1173K, rutile phase appeared. And the anatase phase transformation nearly finished at 1273K. These facts implied that the anatase phase transformation

temperature was approximate to 1173K. For the low anatase-rutile phase transformation temperature, it is not easy to fabricate high performance photocatalytic coatings by plasma spraying technique with the pure anatase TiO₂ powder for the high temperature (over 10000k) of plasma jet using the method inhibiting anatase phase transformation.

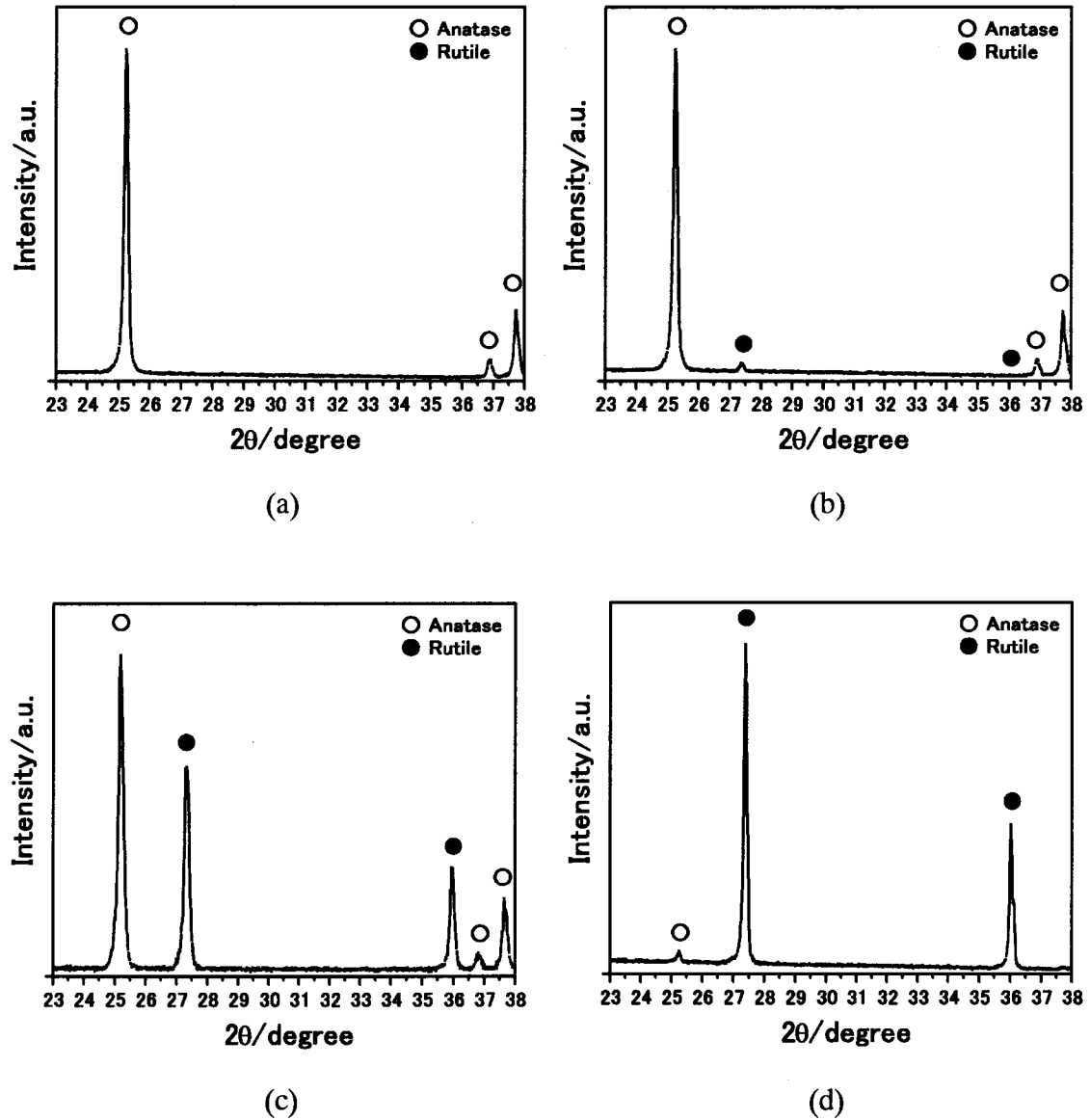


Fig.2.12. X-ray diffraction patterns of heat treated TiO₂ powders for 7200s at various temperatures. (a) 1123K, (b) 1173K, (c) 1223K, (d) 1273K.

2.3.4. Photocatalytic Activity of Plasma Sprayed TiO₂ Coatings

Figure 2.13 illustrates the decomposition characteristics of the acetaldehyde by plasma sprayed TiO₂ coatings under the arc current of 400A, 600A and 800A. In the case of sprayed TiO₂ coatings prepared under the arc current of 400A and 600A, the concentration of acetaldehyde decreased with the irradiation time. Therefore, these two kinds of TiO₂ coatings had photocatalytic activity. The degradation speed by TiO₂ coating sprayed under the arc current of 400A was higher than that by the other one. In the case of TiO₂ coating sprayed under the arc current of 800A, the concentration of acetaldehyde had not considerable change with the irradiation time, which means that this coating had not photocatalytic activity. To compare the photocatalytic activity digitally, the τ values of the plasma sprayed TiO₂ coatings were calculated by Equation (2.6) and the results are shown in Fig.2.14. For the highest anatase TiO₂ content and rough surface of the coating sprayed under the arc current of 400A, it had lowest τ value. On the contrary, with the increasing of arc current to 800A, its τ value was very high.

As a result, it is very important to inhibit the phase transformation of anatase TiO₂ in thermal spray process because rutile TiO₂ has not considerable photocatalytic activity. Therefore, it is not easy to form high photocatalytic performance TiO₂ coatings for the high temperature of plasma jet.

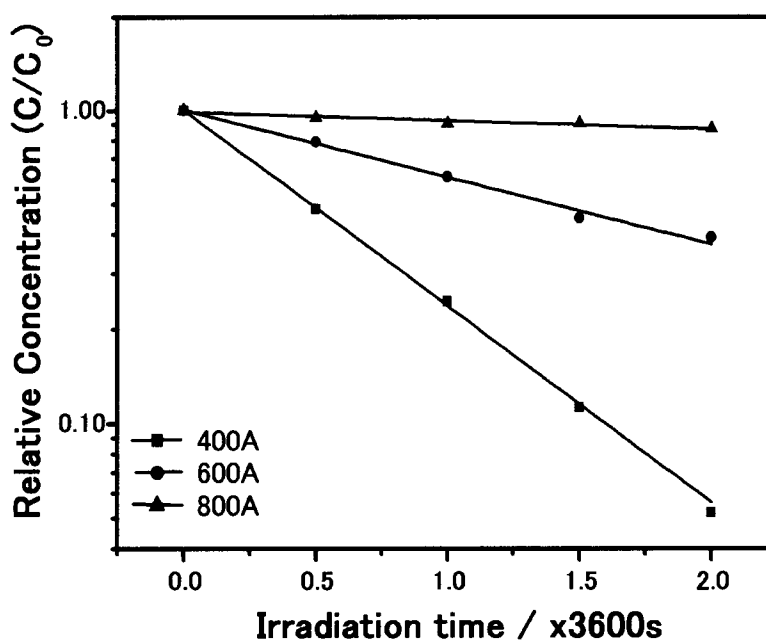


Fig.2.13. Decomposition characteristics of the acetaldehyde by plasma sprayed TiO₂ coatings under the arc current of 400A, 600A and 800A.

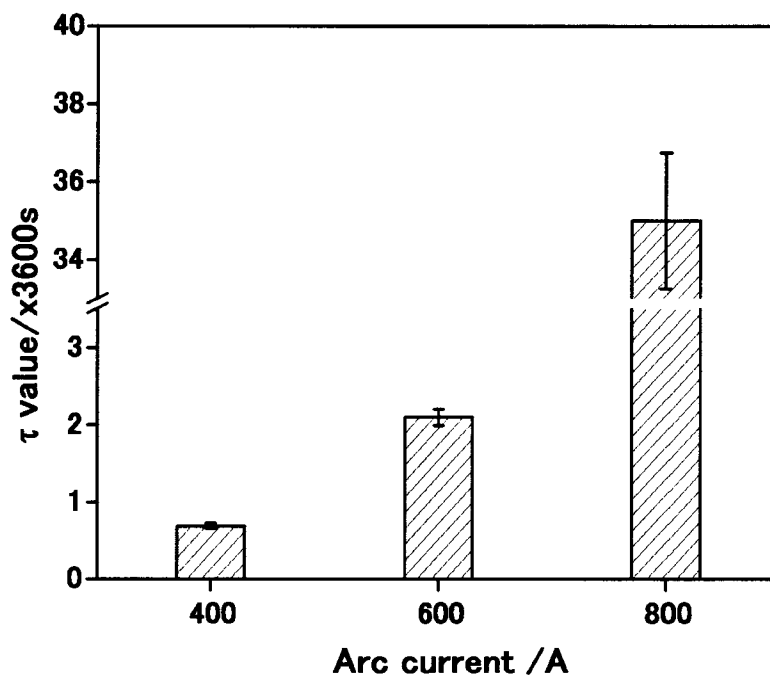


Fig.2.14. τ values of TiO₂ coatings prepared under the arc current of 400A, 600A and 800A.

2.4. Conclusions

TiO₂ coatings were prepared by plasma spraying technique using agglomerated anatase TiO₂ powder. The composition and photocatalytic activity of plasma sprayed TiO₂ coatings were investigated. The content of anatase TiO₂ in the sprayed coatings was approximate to 7-15%, which was influenced by the melting state of TiO₂ powder in plasma spraying process. The anatase to rutile phase transformation temperature of agglomerated anatase TiO₂ powder was approximate to 1173K. The TiO₂ coating sprayed under the arc current of 400A had good photocatalytic activity for the relative high content of anatase phase in it. However, the relative deposition speed, which was approximate to 5 μ m/pass, was very low. For the high temperature of plasma jet, it is not easy to fabricate high performance photocatalytic coatings by plasma spray using the pure anatase TiO₂ powder applying the technique of inhibiting anatase phase transformation.

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CHAPTER 3

Evaluation of Plasma Sprayed Composite TiO₂ Coatings

3.1. Introduction

As mentioned in Chapter 1, titanium dioxide represents one of the most efficient photocatalyst. To prepare high performance photocatalytic TiO₂, the researches can be divided into two broad fields: (1) Improving photocatalytic efficiency of TiO₂ to use UV light. (2) Extending the spectral response into visible region.

The effective photo-excitation of TiO₂ semiconductor particle requires the application of light with energy higher than the band gap energy (E_{BG}) of titanium dioxide. Therefore, the absorption thresholds correspond to 387nm and 413nm for anatase and rutile, respectively. Consequently, only the ultraviolet fraction (3-5%) of the solar irradiation is active in the photo-excitation processes using pure TiO₂ semiconductor as mentioned in Chapter 1. Because of the potential application to the conversion of solar energy to chemical energy, the development of semiconductor photocatalysts that have high reactivity under visible light has received great attention. To extend the spectral response of semiconductor into visible region as like dye-sensitized solar cell and/or to improve the photocatalytic activity, a great deal of effort has been devoted in recent years, such as Cr, V, Fe ion implantation [1-4], plasma surface modification [5,6], doping with N [7], and using binary metal oxides [8-10].

With respect to binary metal oxides, I. Bayer et al. [9] reported that Al₂O₃ acts as an electron acceptor of TiO₂, thus the presence of Al₂O₃ impurity may improve the separation of initiated electrons and holes, and then improves the photocatalytic activity of TiO₂. J. Lin et al. [10] suggested that the mean lifetime of electron-holes photo-generated by UV illumination was longer in the mixture of TiO₂/Y₂O₃ than that in pure TiO₂ according to the transient absorption decay spectra. J. Moser et al. [11] also observed the same phenomenon while study the photocatalytic property of Fe doped TiO₂ semiconductor. On the country, additive into TiO₂ has also negative influence on the photocatalytic activity in spite of the same substance, the reason is still not very clear [12, 13]. To elucidate the effects of Al₂O₃ and Y₂O₃ on the photocatalytic activity of TiO₂, investigations of TiO₂/Al₂O₃ and TiO₂/Y₂O₃ composite coatings prepared by plasma spraying technique were performed in this study.

As discussed in Chapter 2, the relative deposition speed of anatase TiO₂ powder (RDSP) for the preparation of good photocatalytic TiO₂ coating was very low. To improve RDSP and study the effect of Fe elements on the photocatalytic activity of TiO₂, Fe₃O₄ particle with relative low melting point was added into TiO₂.

In this chapter, the phase composition, microstructure and photocatalytic activity of plasma sprayed TiO₂-10%Fe₃O₄, TiO₂-10%Al₂O₃, TiO₂-10%Y₂O₃ coatings were characterized and discussed in detail. Moreover, the composition of heat treated composite TiO₂ powders was investigated.

3.2. Materials and Experimental Procedures

3.2.1 Feedstock Powders and Substrate

TiO₂ particles with average size of 0.2μm were mechanically and uniformly mixed with Fe₃O₄, Al₂O₃ and Y₂O₃ particles with 10% weight content, respectively, and then were agglomerated to TiO₂-10%Fe₃O₄, TiO₂-10%Al₂O₃ and TiO₂-10%Y₂O₃ powders with average size of about 30μm. The substrate was stainless steel (JIS SUS304). The x-ray diffraction result of the TiO₂-10%Fe₃O₄ powder is illustrated in **Fig.3.1**, and powder morphology is also given in it, which was very similar to TiO₂-10%Al₂O₃ and TiO₂-10%Y₂O₃ powders. The additives distributed uniformly in the powders according to EDAX analysis results of powder cross sections. The x-ray diffraction results of the TiO₂-10%Al₂O₃ and TiO₂-10%Y₂O₃ feedstock powders are shown in **Fig.3.2**.

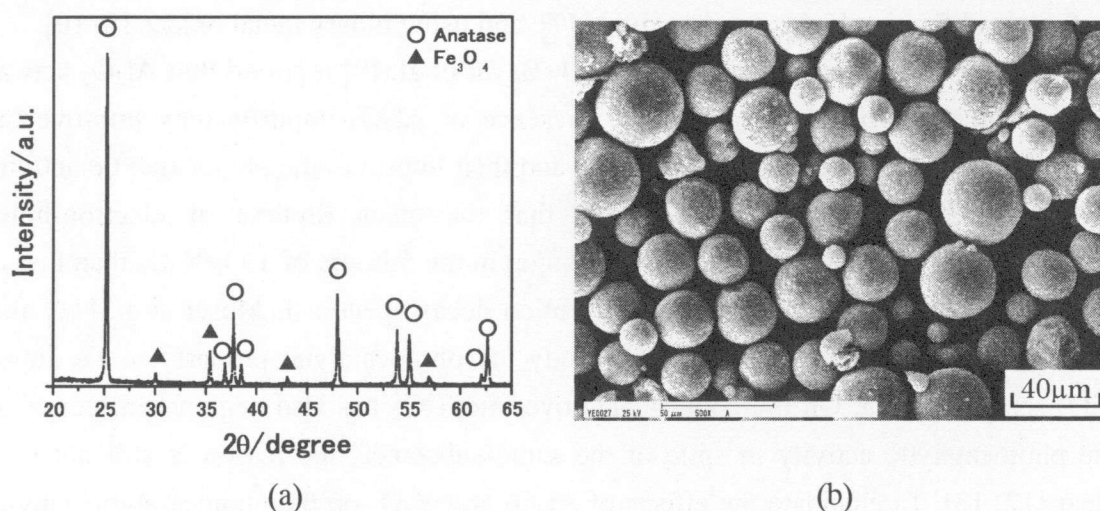


Fig.3.1. X-ray diffraction pattern (a) and morphology (b) of TiO₂-10%Fe₃O₄ feedstock powder.

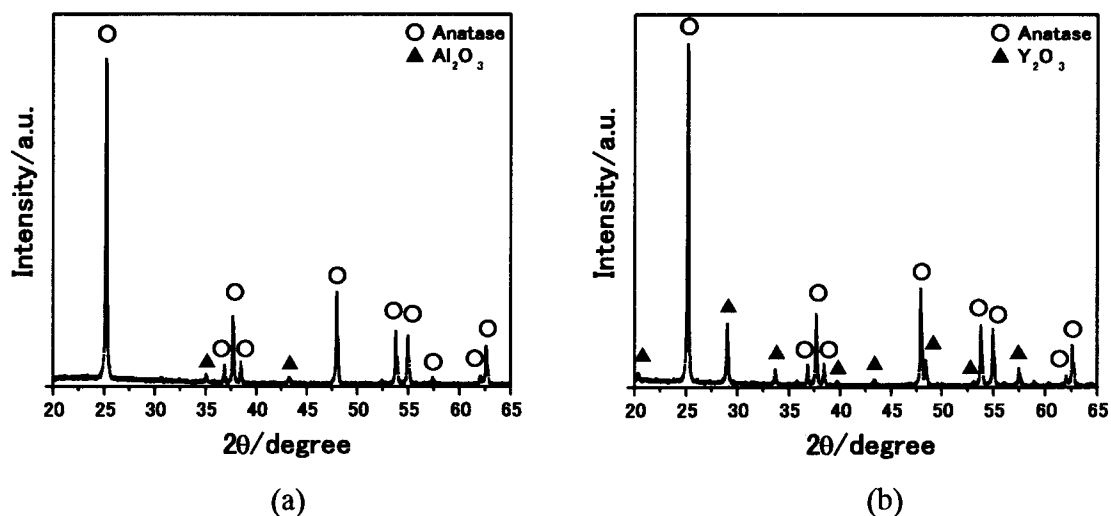


Fig.3.2. X-ray diffraction patterns of composite TiO₂ feedstock powder. (a) TiO₂-10%Al₂O₃, (b) TiO₂-10%Y₂O₃.

3.2.2. Composite Coatings Preparation and Heat Treatment of Powders

Three kinds of composite powders of TiO₂-10%Fe₃O₄, TiO₂-10%Al₂O₃ and TiO₂-10%Y₂O₃ were plasma sprayed on sandblasted JIS SUS304 steel using the equipment described in Chapter 2. According to the research results of plasma sprayed TiO₂ coatings presented in Chapter 2, the low arc current is preferable to forming high photocatalytic activity coatings. Therefore, to examine the delicate influence of additives, the arc current applied for the composite TiO₂ coating was set as 400A or 500A. The detailed conditions are given in **Table 3.1**.

The anatase-rutile transformation temperature of pure anatase TiO₂ powder was approximate to 1173K (See Chapter 2). To investigate the influence of the additive on the anatase-rutile phase transformation temperature and clarify the composition variations of feedstock powders in thermal spray process, they were kept in the furnace for 7200s after reaching at treated temperature (973K, 1123K, 1273K or 1423K) with a heating rate of 1.67K/s, and then were cooled with the furnace.

Table 3.1 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, 500
Arc voltage (V)	28~30
Spraying distance (mm)	70, 100

3.2.3. Characterization of Powders and Sprayed Coatings

The microstructure and phase characterization of powders and sprayed coatings were performed by electron probe surface roughness analyzer (ERA-8800FE, Elionix Co. Ltd., Japan) and x-ray diffraction (M03XHF, MAC Science Co. Ltd.).

The relative deposition speed of feedstock powder (RDSP) was calculated using the Equation (2.2). The photocatalytic activity of sprayed coating was evaluated by the set-up described in Chapter 2 and the τ value was calculated by Equation (2.6).

3.3. Results and Discussion

3.3.1. Heat Treated Composite TiO₂ Powders

Figure 3.3 shows the x-ray diffraction results of TiO₂-10%Fe₃O₄ feedstock powders heat treated at various temperatures. Magnetite (Fe₃O₄) additive reacted with oxygen under 973K and produced Fe₂O₃ (Reaction (3.1) and Fig.3.3(a)), which is in good agreement with the reported data measured by differential scanning calorimetry analysis (DSC) equipment [14]. One part of anatase TiO₂ transformed into rutile at 1123K, which did not observed for pure anatase TiO₂ powder (See Fig.2.12 in Chapter 2). Therefore, conclusion can be drawn that the addition of Fe₃O₄ to TiO₂ would accelerate the anatase-rutile phase transformation. The reaction of Fe₂O₃ with TiO₂ happened below 1123K, and consequently formed stable phase of pseudobrookite Fe₂TiO₅ (Reaction (3.2)).



Figure 3.4 shows the x-ray diffraction results of TiO₂-10%Al₂O₃ feedstock powders heat treated at various temperatures. Comparing the phenomena shown in Fig.3.4 and Fig.2.12, it can see that the addition of Al₂O₃ into TiO₂ seems had not any effect on the thermal behaviors of anatase TiO₂ powder below 1423K. As reported by V. Buscaglia et al. [15, 16], formation of Al₂TiO₅ occurs in an oxidizing atmosphere according to Reaction (3.3) above 1553K. Below 1553K, Al₂TiO₅ decomposes, as it is unstable in comparison to Al₂O₃ and TiO₂. That is why there had not Al₂TiO₅

compound in the heat treated TiO₂-10%Al₂O₃ powders.



Figure 3.5 shows the x-ray diffraction results of TiO₂-10%Y₂O₃ feedstock powders heat treated at various temperatures. Over 1273K, TiO₂ reacted with Y₂O₃ and produced Y₂Ti₂O₇ (Reaction (3.4) [17, 18]).

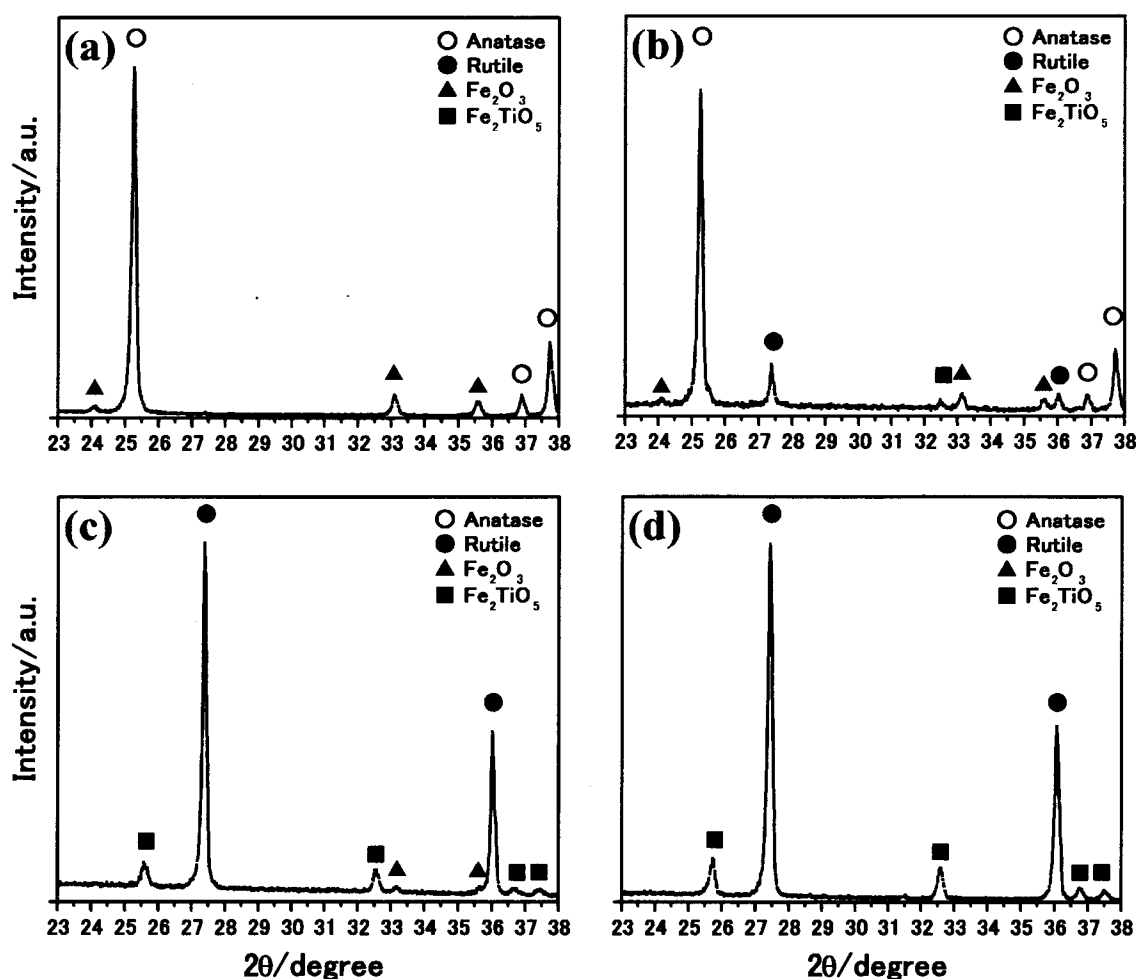


Fig.3.3. X-ray diffraction patterns of heat treated TiO₂-10%Fe₃O₄ feedstock powders at various temperatures. (a) 973K, (b) 1123K, (c) 1273K, (d) 1423K.

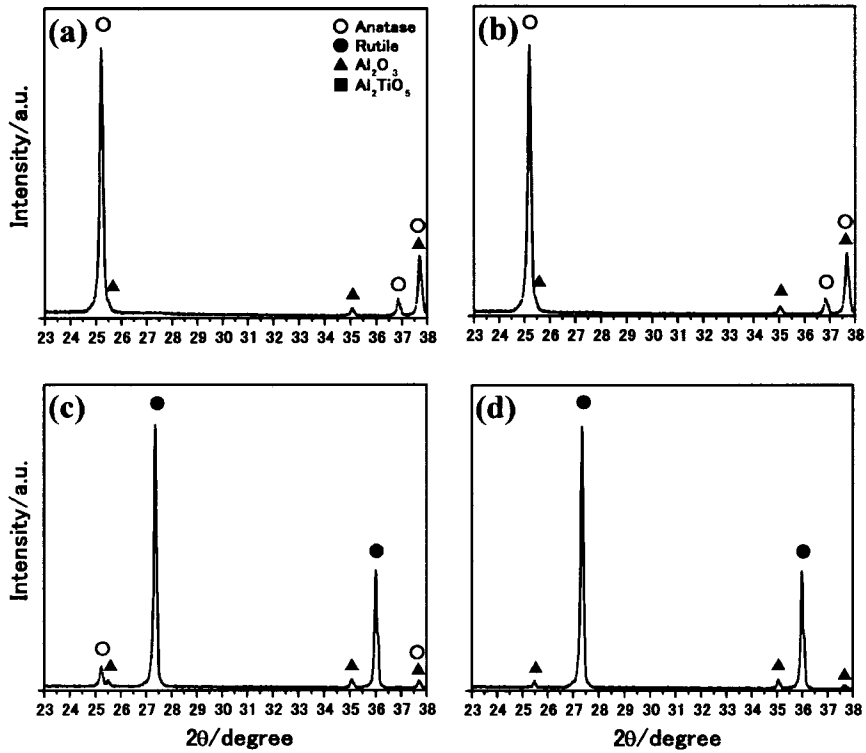


Fig.3.4. X-ray diffraction patterns of heat treated TiO₂-10%Al₂O₃ feedstock powders at various temperatures. (a) 973K, (b) 1123K, (c) 1273K, (d) 1423K.

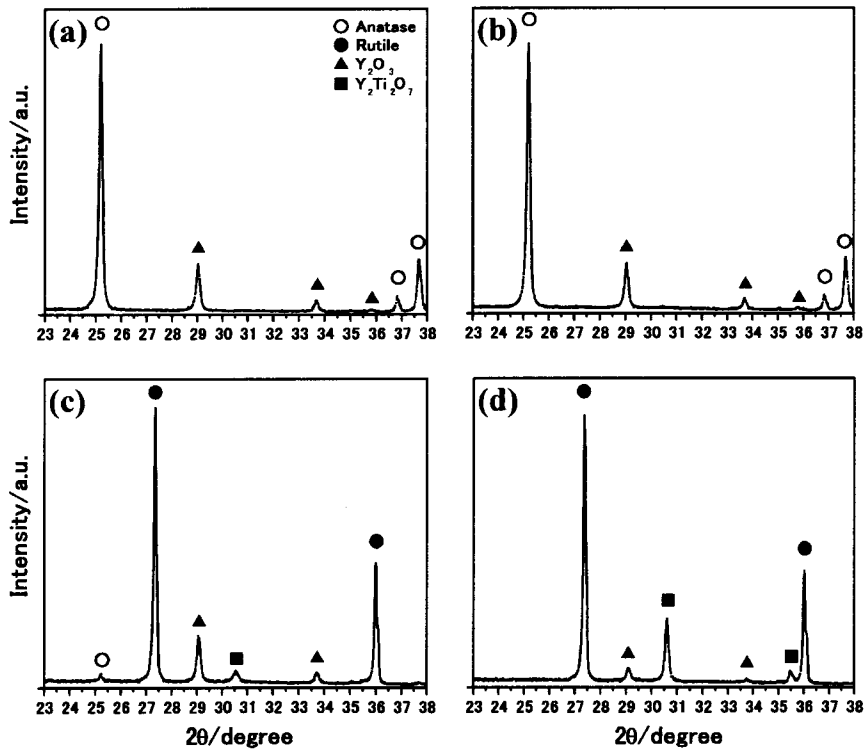


Fig.3.5. X-ray diffraction patterns of heat treated TiO₂-10%Y₂O₃ feedstock powders at various temperatures. (a) 973K, (b) 1123K, (c) 1273K, (d) 1423K.

3.3.2. Characterization of Plasma Sprayed TiO₂-10%Fe₃O₄ Coatings

Figure 3.6 shows the cross sections of plasma sprayed TiO₂-10%Fe₃O₄ coatings. Under the arc current of 400A and spraying distance of 70mm, the coating had porous structure (Fig.3.6(c)). As shown in Fig.3.7, partially melted 0.2μm particle still existed in it. This kind of phenomenon will be a benefit to increase the specific surface and then improve the photocatalytic activity of the sprayed coatings. With more increased arc current, the coating became denser, and the content of the partially melted particle decreased.

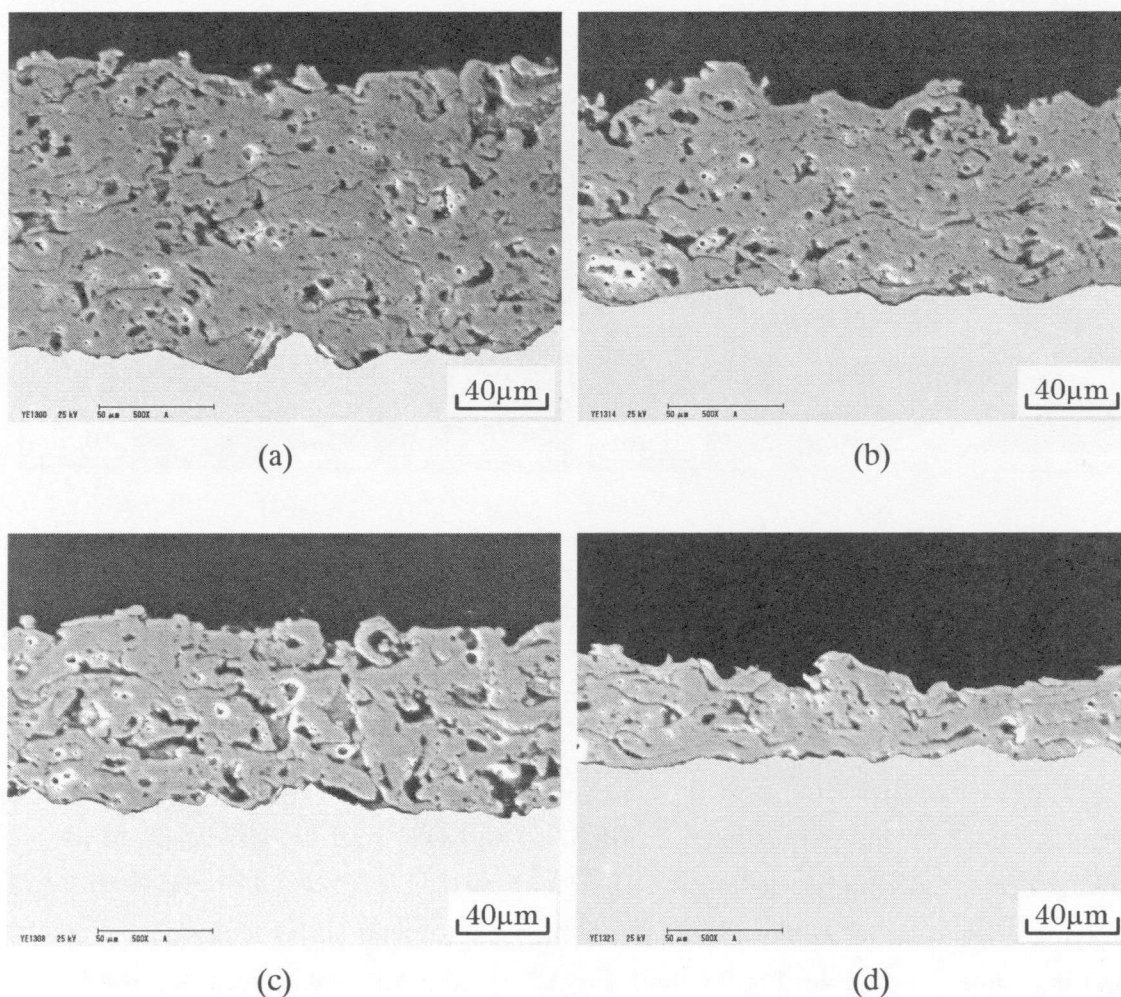


Fig.3.6. Cross sections of plasma sprayed TiO₂-10%Fe₃O₄ coatings. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d)I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

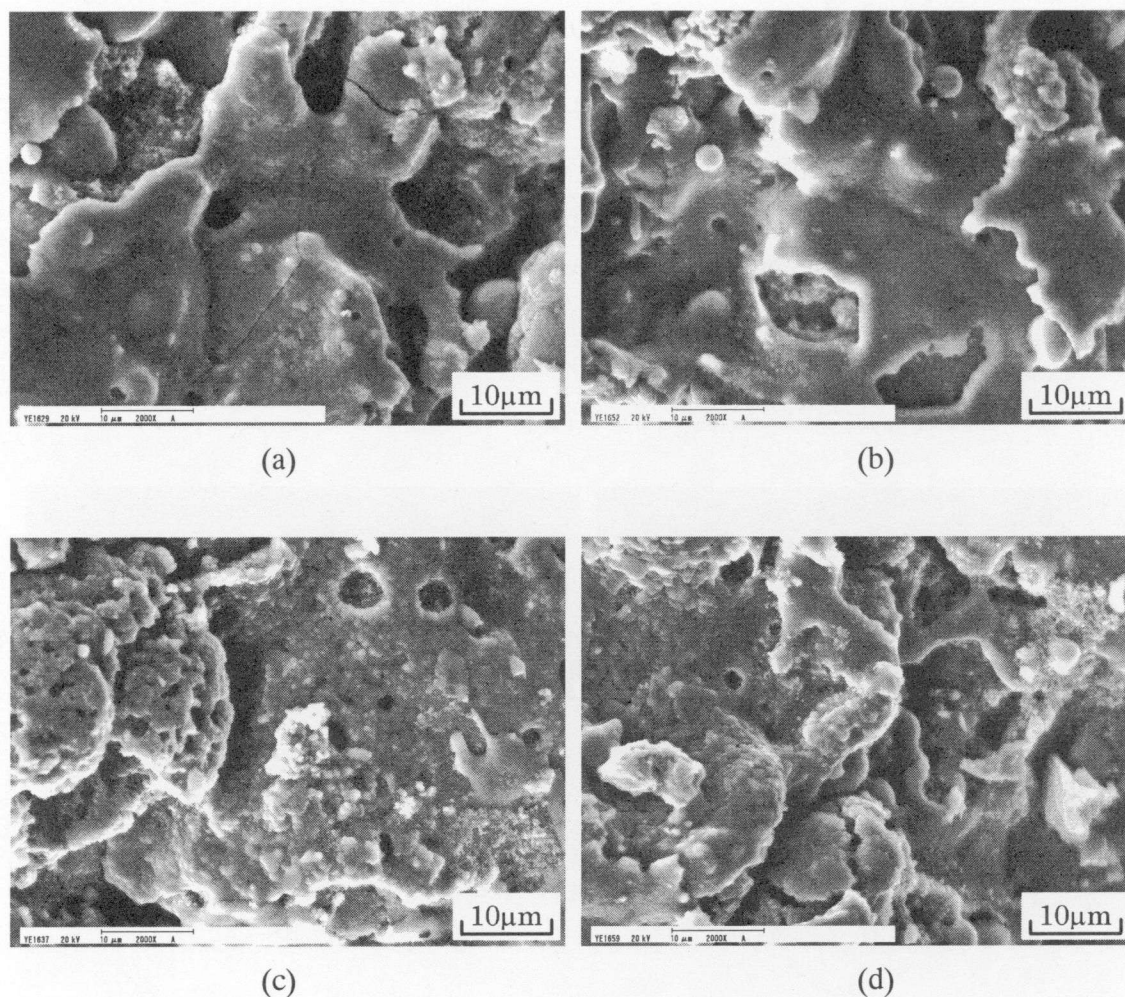


Fig.3.7. Surface views of plasma sprayed TiO₂-10%Fe₃O₄ coatings. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

The relative deposition speed of TiO₂-10%Fe₃O₄ powder (RDSP) was calculated by Equation (2.2), and is illustrated in **Fig.3.8**. The RDSP of TiO₂-10%Fe₃O₄ feedstock powder decreased with the decreasing of arc current, but increased with the decrease of spraying distance from 100mm to 70mm, which are in good agreement with the results (melting state) shown in Fig.3.6 and Fig.3.7. Under the arc current of 400A and spraying distance of 70mm, the RDSP of TiO₂-10%Fe₃O₄ powder was about 2.6 times high than that of pure TiO₂ powder (See Fig.3.8 and Fig.2.9), which means that the powder deposition efficiency was greatly enhanced for the addition of Fe₃O₄.

The x-ray diffraction patterns of plasma sprayed TiO₂-10%Fe₃O₄ coatings under various conditions are illustrated in **Fig.3.9**. The peak height of anatase TiO₂ (101 peak)

was very low. The content of anatase phase, calculated by Equation (2.1), was below 5%. These implied that large part of anatase phase in the powder transformed into rutile phase in thermal spraying process. Therefore, the addition of Fe₃O₄ to TiO₂ would accelerate the anatase-rutile phase transformation, which is in good agreement with the conclusion described in Section 3.3.1. In the sprayed coatings, a compound called FeTiO₃ appeared which did not appear in heat treated powder.

Figure 3.10 illustrates the decomposition characteristics of the acetaldehyde by plasma sprayed TiO₂-10%Fe₃O₄ coatings. The concentration of acetaldehyde decreased with the irradiation time. Therefore, prepared TiO₂-10%Fe₃O₄ coatings had photocatalytic activity. The degradation speed by the coating prepared under the arc current of 400A and spraying distance of 70mm was highest. To compare the photocatalytic activity digitally, the τ values were calculated by Equation (2.6) and are shown in Fig.3.11. Under the arc current of 400A and spraying distance of 70mm, the sprayed coating has lowest τ value, which means that it had the best photocatalytic activity. Generally, the photocatalytic activity of TiO₂ increase with the increasing of anatase content in it. However, the TiO₂-10%Fe₃O₄ coatings had good photocatalytic activity despite the very low anatase contents comparing with TiO₂ coatings described in Chapter 2. This implied that other factors also control the photocatalytic activity except the content of anatase phase in the sprayed coating. These will be discussed in detail in Chapter 4.

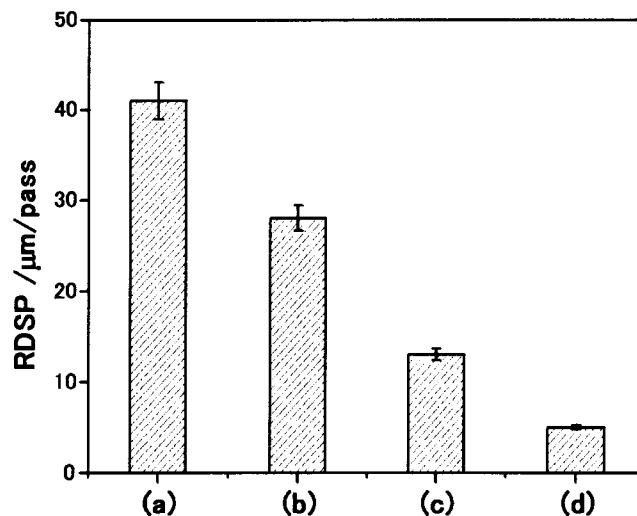


Fig.3.8. Relative deposition speed of TiO₂-10%Fe₃O₄ feedstock powder (RDSP) under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

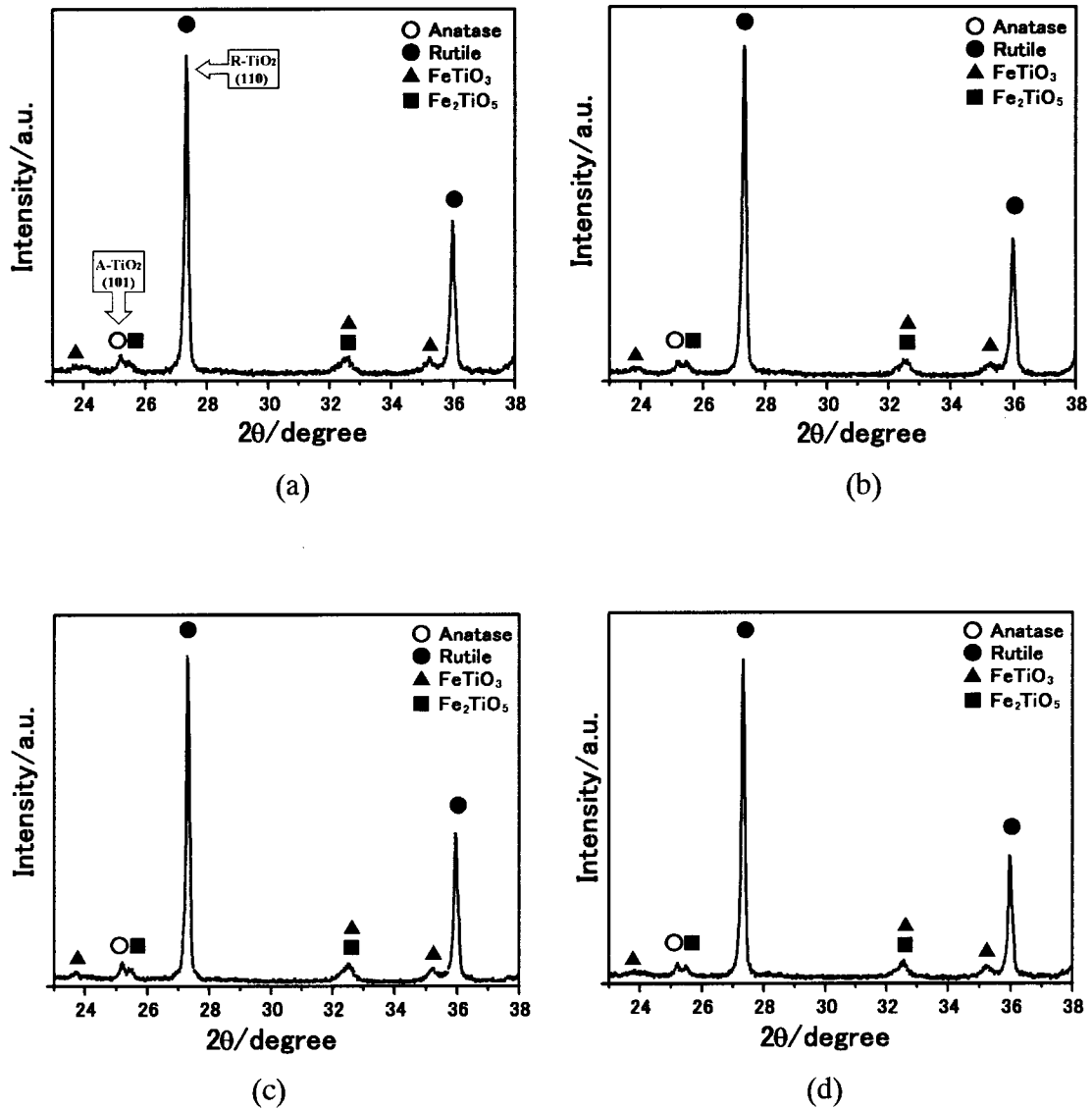


Fig.3.9. X-ray diffraction patterns of plasma sprayed TiO₂-10%Fe₃O₄ coatings under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

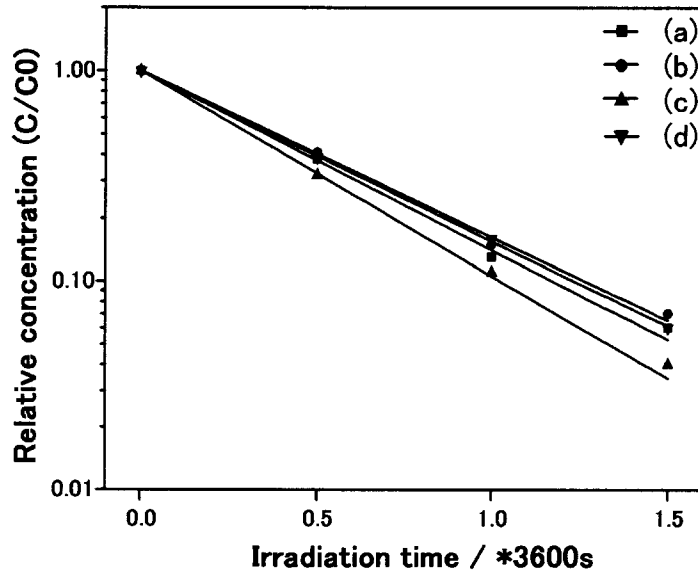


Fig.3.10. Decomposition characteristics of the acetaldehyde by TiO₂-10%Fe₃O₄ coatings prepared under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

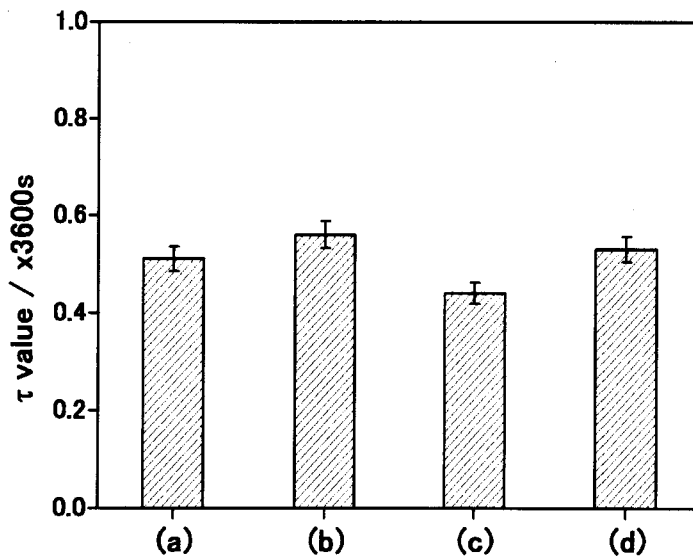


Fig.3.11. τ values of TiO₂-10%Fe₃O₄ coatings prepared under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm. (Notes: “I” denotes arc current, “SD” denotes spraying distance.)

3.3.3. Characterization of Plasma Sprayed TiO₂-10%Al₂O₃ Coatings

Figure 3.12 shows the typical cross section and surface morphology of plasma sprayed TiO₂-10%Al₂O₃ coating. The melting point of Al₂O₃ (2323K) is about 190K higher than that of rutile TiO₂, thus the TiO₂-10%Al₂O₃ powder was more unmelted than pure TiO₂ powder under the same spraying conditions. As illustrated in Fig.3.13, the relative deposition speed of TiO₂-10%Al₂O₃ feedstock powder (RDSP) was nearly the same with that of TiO₂ powder, but was lower than that of TiO₂-10%Fe₃O₄ powder.

The typical x-ray diffraction patterns of plasma sprayed TiO₂-10%Al₂O₃ coatings are illustrated in Fig.3.14. Al₂O₃ additive reacted with TiO₂, and produced Al₂TiO₅ compound. For the high solidification speed of impacted particle, Al₂TiO₅ compound did not decompose into TiO₂ and Al₂O₃. The contents of anatase phase in TiO₂-10%Al₂O₃ coatings are shown in Fig.3.15. The additive of Al₂O₃ prevented anatase-rutile transformation.

The τ values of TiO₂-10%Al₂O₃ coatings, which were calculated by Equation (2.6) according to the decomposition characteristics of acetaldehyde, are shown in Fig.3.16. The coating prepared under the arc current of 400A and spraying distance of 70mm had the highest photocatalytic activity comparing with the other sprayed TiO₂-10%Al₂O₃ coatings, which resulted from the high content of anatase phase in it. Although it increased a few percent comparing with that of TiO₂ coating prepared under the same conditions, the addition of Al₂O₃ had not great influence on the photocatalytic activity of TiO₂.

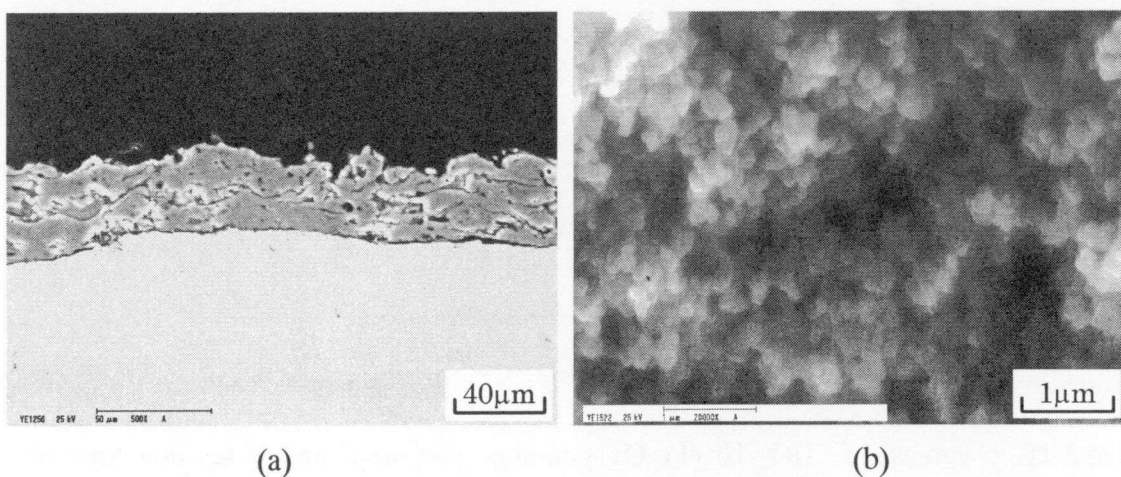


Fig.3.12. Cross section (a) and surface morphology (b) of plasma sprayed TiO₂-10%Al₂O₃ coating under the arc current of 400A and spraying distance of 70mm.

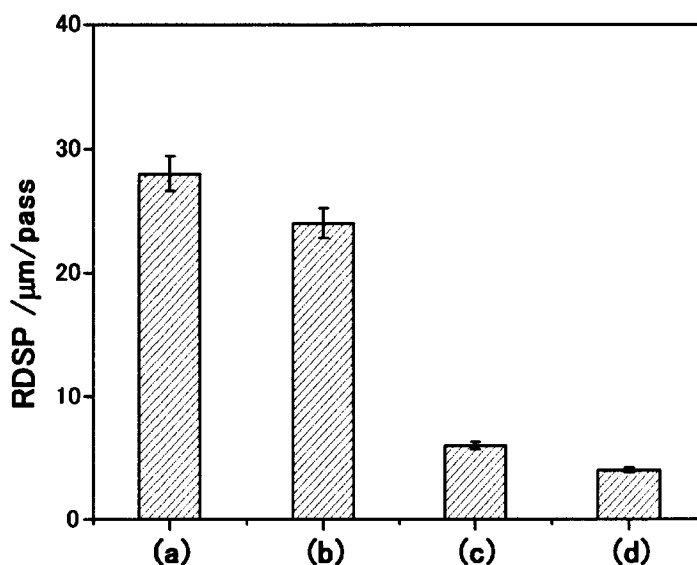


Fig.3.13. Relative deposition speed of TiO₂-10%Al₂O₃ feedstock powder (RDSP) under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm.

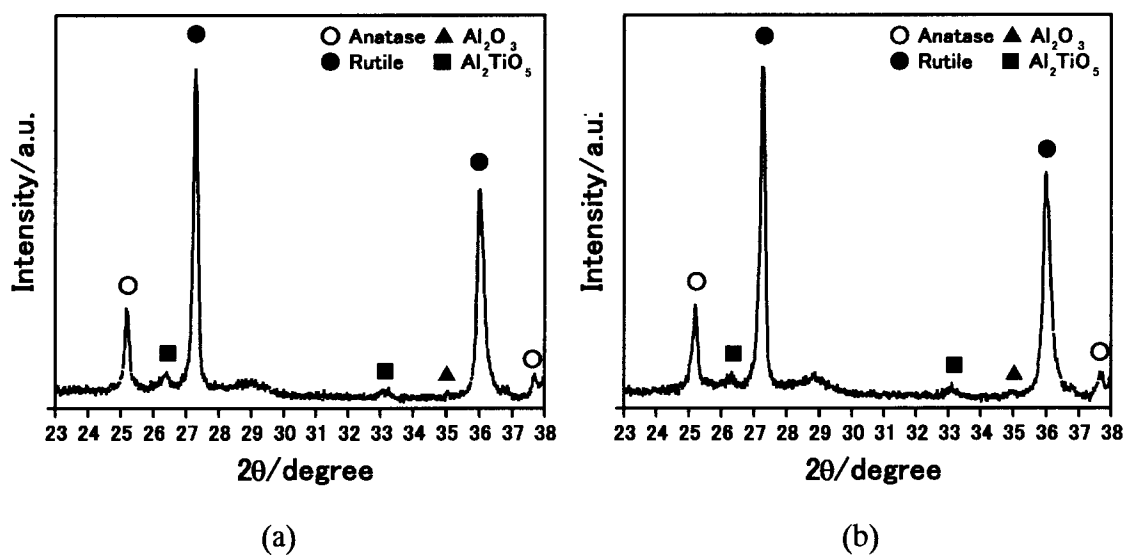


Fig.3.14. X-ray diffraction patterns of plasma sprayed TiO₂-10%Al₂O₃ coatings under various spraying conditions. (a) I=500A SD=70mm, (b) I=400A SD=70mm.

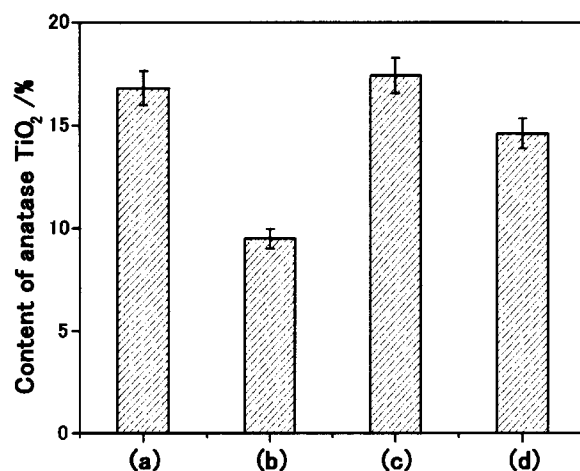


Fig.3.15. Contents of anatase TiO₂ in plasma sprayed TiO₂-10%Al₂O₃ coatings under various conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm.

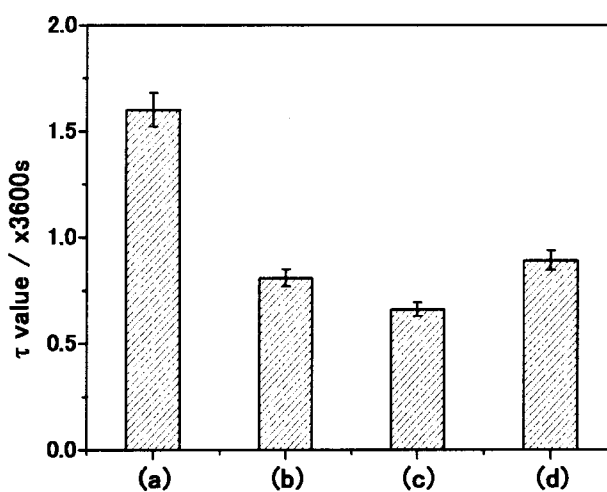


Fig.3.16. τ values of TiO₂-10%Al₂O₃ coatings prepared under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm.

3.3.4. Characterization of Plasma Sprayed TiO₂-10%Y₂O₃ Coatings

Figure 3.17 shows the cross section and surface morphology of plasma sprayed TiO₂-10%Y₂O₃ coating. Although the melting point of Y₂O₃, which is 2713K, is 580K higher than that of rutile TiO₂, TiO₂-10%Y₂O₃ powder was more melted than pure TiO₂

powder under the same spraying conditions. This also can be inferred from the relative deposition speed of TiO₂-10%Y₂O₃ powder as shown clearly in Fig.3.18. Because Y₂Ti₂O₇ compound formed (Fig.3.19) in thermal spraying process according to the reaction mentioned in Section 3.2.1, a lot of heat gave off, which improved the melting of powder and increased the RDSP. The contents of anatase phase in TiO₂-10%Y₂O₃ coatings are shown in Fig.3.20.

According to the τ values of TiO₂-10%Y₂O₃ coatings calculated by Equation (2.6), the photocatalytic activity of TiO₂-10%Y₂O₃ coating was inferior to that of TiO₂ coating under the arc current of 400A and spraying distance of 70mm. It implied that the addition of Y₂O₃ had unfavorable influence on the photocatalytic activity of TiO₂.

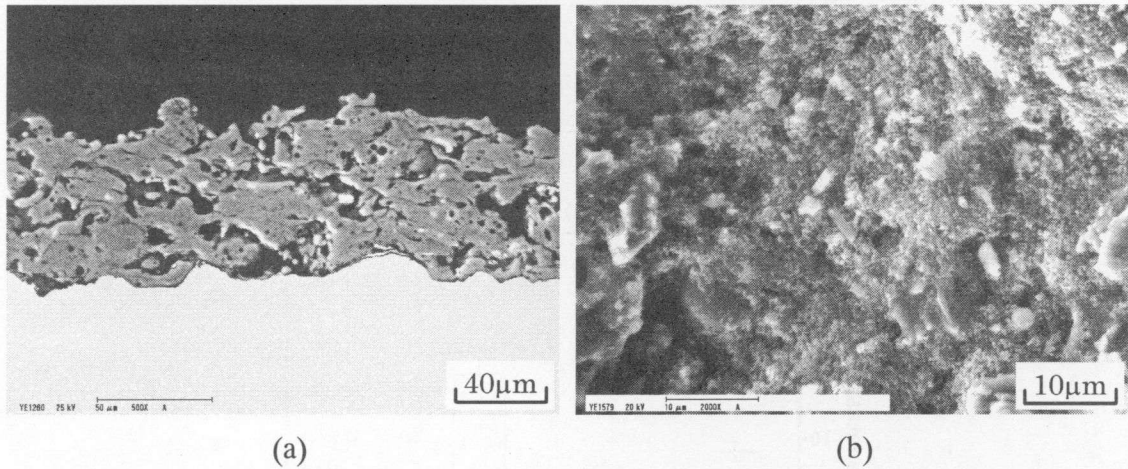


Fig.3.17. Cross section (a) and surface morphology (b) of TiO₂-10%Y₂O₃ coating plasma sprayed under arc current of 400A and spraying distance of 70mm.

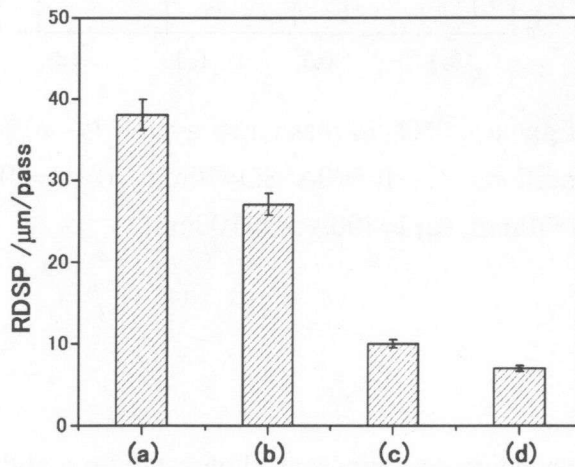


Fig.3.18. Relative deposition speed of TiO₂-10%Y₂O₃ feedstock powder (RDSP) under various spraying conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm.

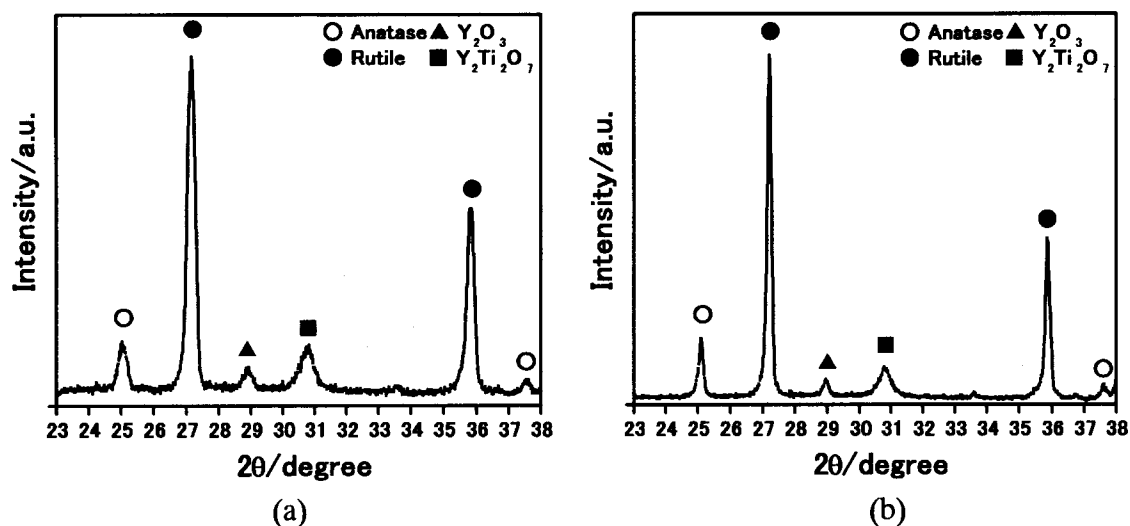


Fig.3.19. X-ray diffraction patterns of plasma sprayed TiO₂-10%Y₂O₃ coatings under various spraying conditions. (a) I=500A SD=70mm, (b) I=400A SD=70mm.

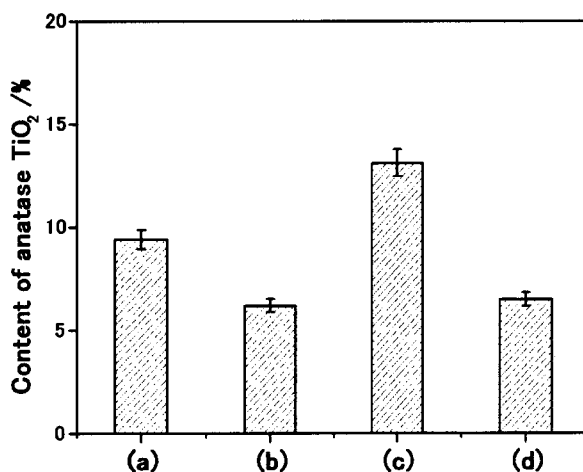


Fig.3.20. Contents of anatase TiO₂ in plasma sprayed TiO₂-10%Y₂O₃ coatings under various conditions. (a) I=500A SD=70mm, (b) I=500A SD=100mm, (c) I=400A SD=70mm, (d) I=400A SD=100mm.

3.4. Conclusions

Phase composition, microstructure and photocatalytic activity of plasma sprayed TiO₂-10%Fe₃O₄, TiO₂-10%Al₂O₃, and TiO₂-10%Y₂O₃ coatings were characterized and discussed in detail. The addition of Fe₃O₄ to TiO₂ improved the anatase-rutile transformation. The anatase content of TiO₂ in the sprayed coating was affected by the

melting degree of TiO₂ particle in thermal spraying process. Although the content of anatase TiO₂ was very low in the sprayed TiO₂-10%Fe₃O₄ coating, the photocatalytic activity was better than that of TiO₂ coating under the same spraying conditions, which implied the photocatalytic activity was not only controlled by anatase content of TiO₂. The original reasons are presented in Chapter 4. The relative deposition speed of TiO₂-10%Fe₃O₄ powder was 2.6 times than that of TiO₂ powder under the arc current of 400A and spraying distance of 70mm. However, the addition of Al₂O₃ and Y₂O₃ particle to TiO₂ particle had not favorable effect on the photocatalytic activity of TiO₂ coating. Therefore, the influence of additive on the photocatalytic activity of TiO₂ is greatly controlled by not only the kind of additive, but also by the synthetic process.

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CHAPTER 4

Influence of Fe₃O₄ Content on the Properties of Plasma Sprayed TiO₂-Fe₃O₄ Coatings

4.1. Introduction

As discussed in Chapter 3, 10wt.% addition of Fe₃O₄ into TiO₂ powder improved the photocatalytic activity of TiO₂ coating in spite of the low content of anatase phase in it, and increased obviously the relative deposition speed of TiO₂ powder. Insomuch that Fe₃O₄ may be regarded as a kind of promising material applying in photocatalytic field. However, the influence of Fe₃O₄ amount on the properties of plasma sprayed TiO₂-Fe₃O₄ coating is still unclear. To study the effects of Fe₃O₄ particles on the photocatalytic activity of TiO₂-Fe₃O₄ coatings in detail, four kinds of composite powders were further designed, these were TiO₂-5%Fe₃O₄, TiO₂-12.7%Fe₃O₄, TiO₂-22.5%Fe₃O₄ and TiO₂-32.6%Fe₃O₄ powders.

Although the plasma spray process has been developed in 1950's, photocatalytic coating preparation applying plasma spray is a new filed. Currently, most application researches in plasma spraying are focused onto the relationship between plasma deposition parameters and coating properties. Indeed, properties and microstructure of plasma sprayed coatings depend on the in-flight treatment of the particles in plasma jet. In fact, particle velocity and temperature at impact play an important role. So in order to produce desired coatings, it is essential to measure and understand in-flight particles behavior [1~3].

The photocatalytic performance is affected by catalyst substance, light absorptive ability, morphology, and 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 TiO₂ and TiO₂-Fe₃O₄ coatings was investigated. Generally, the photocatalytic activity increases with the increasing of light absorptive capacity [4].

In this chapter, the influence of Fe₃O₄ on anatase-rutile phase transformation temperature was investigated, and the phase composition of heat treated powder was quantitatively analyzed. Furthermore, the speed and temperature of in-flight particles

were measured. The phase composition, microstructure, photo absorbance and photocatalytic activity of plasma sprayed TiO₂-Fe₃O₄ coatings were characterized and discussed in detail. Moreover, the existence of solid solution, amorphous phase and phase segregation in the sprayed coatings was examined. To discuss the influence of Fe₃O₄ amount on the performance of plasma sprayed TiO₂-Fe₃O₄ coatings systematically, TiO₂ and TiO₂-10%Fe₃O₄ coatings discussed in Chapter 2 and 3 were also mentioned in this chapter.

4.2. Materials and Experimental Procedures

4.2.1 Feedstock Powders and Substrate

The feedstock powders were pure TiO₂ and five kinds of composite TiO₂-Fe₃O₄ powders. These were TiO₂, TiO₂-5%Fe₃O₄, TiO₂-10%Fe₃O₄, TiO₂-12.7%Fe₃O₄, TiO₂-22.5%Fe₃O₄ and TiO₂-32.6%Fe₃O₄ powders. The average sizes of TiO₂-Fe₃O₄ powders were about 32 μ m. The x-ray diffraction results of the powders are shown in **Fig.4.1**. It is very clear that Fe₃O₄ particles distributed uniformly in the agglomerated TiO₂-Fe₃O₄ powders according to their EDAX maps. The substrate was stainless steel (JIS SUS304).

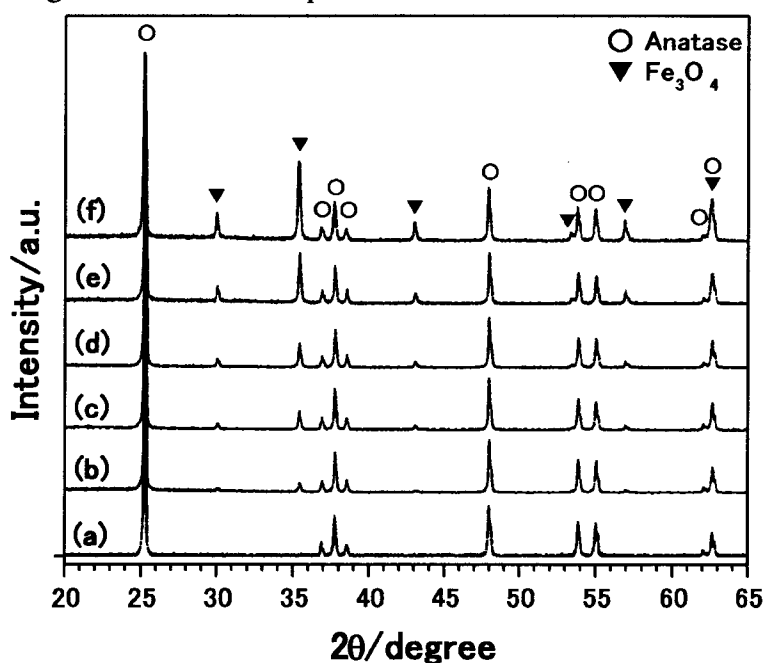


Fig.4.1. X-ray diffraction patterns of TiO₂ and TiO₂-Fe₃O₄ feedstock powders. (a) TiO₂ powder, (b) TiO₂-5%Fe₃O₄ powder, (c) TiO₂-10%Fe₃O₄ powder, (d) TiO₂-12.7%Fe₃O₄ powder, (e) TiO₂-22.5%Fe₃O₄ powder, (f) TiO₂-32.6%Fe₃O₄ powder.

4.2.2. Coatings Preparation

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. As discussed in Chapter 2 and Chapter 3, low arc current is preferable to high arc current for photocatalytic coating preparation, thus arc current of 400A was applied to study the properties with relation to photocatalyst. For the high melting and solidification speed of powder in plasma spray process, solid solution, amorphous phase and phase segregation exist widely in the coating despite the content is very different. To study the phase changes of TiO₂-32.6%Fe₃O₄ coatings after heat treatment, arc currents of 400A, 600A and 800A were chosen. The detailed plasma spraying parameters are given in **Table 4.1**.

Table 4.1 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, 600, 800
Arc voltage (V)	28~30
Spraying distance (mm)	70

4.2.3. Heat Treatment of Feedstock Powders and Sprayed Coatings

The anatase-rutile transformation temperature of agglomerated pure anatase TiO₂ powder was approximate to 1173K as reported in Chapter 2. 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, TiO₂ and TiO₂-Fe₃O₄ composite powders were kept in electric furnace for 7200s after reaching at treated temperature (973K, 1123K, 1273K or 1423K) with a heating rate of 1.67K/s, and then were cooled with the furnace.

However, to investigate abundance of solid solution in sprayed coating, specimen was kept a long time in furnace for 21600s at 1273K with a low heating rate of 0.84K/s.

4.2.4. General Characterization

Oxygen concentration in as-received and heat treated TiO₂-Fe₃O₄ coating was studied by electron probe microanalyzer (EPMA) (JXA-8600, JEOL, Japan) in attempt

to investigate the existence of solid solution in it.

Scanning electron microscope (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 were investigated by x-ray diffraction using Cu-K α radiation ($\lambda=1.5406\text{\AA}$) and graphite crystal monochromator (M03XHF, MAC Science Co. Ltd.). The 2θ range was $23^\circ\sim 38^\circ$ including the main diffraction line of the possible phase compositions. Quantitative analysis of the phase composition of the heat treated powders was attempted by comparing the integrated x-ray diffraction peaks for anatase (101), rutile (110), α -Fe₂O₃ (104), FeTiO₃ (104) and Fe₂TiO₅ (101) phase. The weight contents of anatase TiO₂, rutile TiO₂, α -Fe₂O₃, FeTiO₃ and Fe₂TiO₅ compound were calculated by Equations (4.1)~(4.6), respectively. The peak intensity relations have been established experimentally from powders mixture, of which composition was known, and the validity of this method was confirmed.

However, it is extremely complex to consider the plasma sprayed coatings applying Equations (4.1)~(4.6) because amorphous phase, phase segregation or solid solution can not be generally neglected for thermal sprayed composite coating [5~7].

$$\frac{W_{Anatase}}{W_{Rutile}} = C_1 \frac{I_{Anatase(101)}}{I_{Rutile(110)}} \quad (4.1)$$

$$\frac{W_{Fe_2O_3}}{W_{Rutile}} = C_2 \frac{I_{Fe_2O_3(104)}}{I_{Rutile(110)}} \quad (4.2)$$

$$\frac{W_{FeTiO_3}}{W_{Rutile}} = C_3 \frac{I_{FeTiO_3(104)}}{I_{Rutile(110)}} \quad (4.3)$$

$$\frac{W_{Fe_2TiO_5}}{W_{Rutile}} = C_4 \frac{I_{Fe_2TiO_5(101)}}{I_{Rutile(110)}} \quad (4.4)$$

$$W_{Anatase} + W_{Rutile} + W_{Fe_2O_3} + W_{FeTiO_3} + W_{Fe_2TiO_5} = 1 \quad (4.5)$$

$$W_{AnataseToRutile} = \frac{W_{Rutile}}{W_{Anatase} + W_{Rutile}} \times 100\% \quad (4.6)$$

where $I_{Anatase(101)}$ is the integrated intensity of the (101) reflection of anatase phase, $I_{Rutile(110)}$ the integrated intensity of (110) reflection of rutile phase, $I_{Fe_2O_3(104)}$ the integrated intensity of (104) reflection of α -Fe₂O₃, $I_{FeTiO_3(104)}$ the integrated intensity of (104) reflection of FeTiO₃ phase, $I_{Fe_2TiO_5(101)}$ the integrated intensity of (101) reflection of Fe₂TiO₅ phase, $W_{Anatase}$, W_{Rutile} , $W_{Fe_2O_3}$, W_{FeTiO_3} and $W_{Fe_2TiO_5}$ the weight fractions of anatase TiO₂, rutile TiO₂, α -Fe₂O₃, FeTiO₃ and Fe₂TiO₅, respectively, and C_1 , C_2 , C_3 and C_4 the constants which are dependent on the crystal structures and lattice parameters of the upper mentioned substances. $W_{AnataseToRutile}$ the weight fraction of anatase transformed into rutile.

The relative deposition speed of feedstock powder (RDSP) was calculated using the Equation (2.2). The photocatalytic activity of sprayed coating was evaluated by the set-up described in Chapter 2.

4.2.5. Particle Speed and Temperature Measurement

The speed and temperature of in-flight particle were measured by DPV-2000 equipment (Tecnar Automation Ltd., Canada) [8]. DPV-2000 applies infrared pyrometry along with a two-slit photo-mask in order to perform in-flight diagnostics on individual particles. A particle passing in front of the photo-mask will generate a two-peaks signal as illustrated in Fig.4.2.

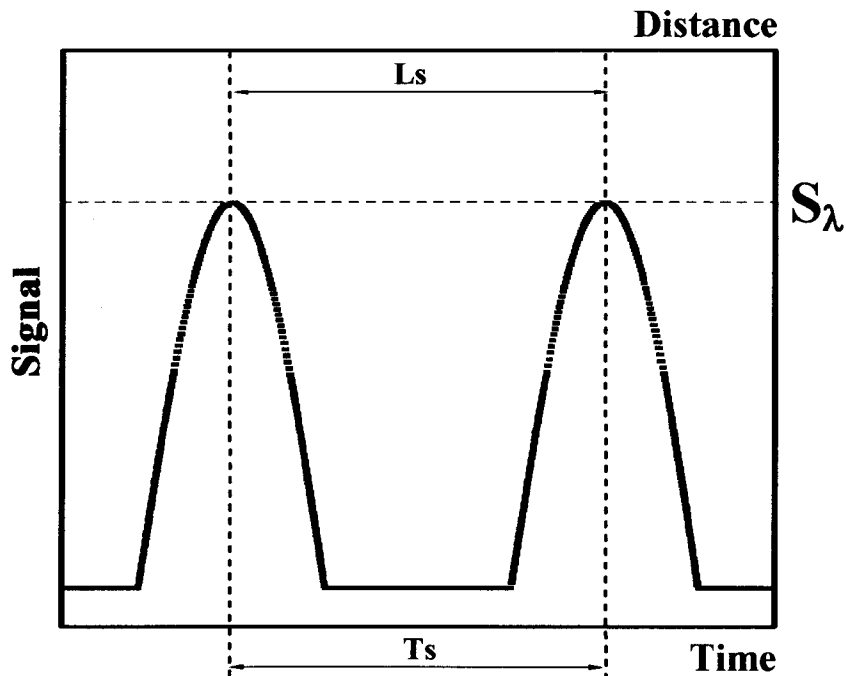


Fig.4.2. Particle velocity and temperature measurement principle of DPV-2000.

According to the signals, the velocity and temperature of particle were calculated by Equations (4.7) and (4.8).

$$Velocity_{particle} = Ls / Ts \quad (4.7)$$

$$Temperature_{particle} = f(S_{\lambda_1} / S_{\lambda_2}) \quad (4.8)$$

Where $Velocity_{particle}$ is the velocity of particle, $Temperature_{particle}$ the temperature of particle, Ls the distance of two signals from two slits, Ts the time between two signals from two slits, S_{λ_1} the intensity of the signal at wavelength of λ_1 , S_{λ_2} the intensity of the signal at wavelength of λ_2 .

4.2.6. Diffuse Reflectance Measurement

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 (Eq. (4.9)). The integrated energy absorbance from the light source of the sprayed coatings is estimated according to Equation (4.10).

$$f(R_{\lambda}) = \frac{(1-R_{\lambda})^2}{2R_{\lambda}} \quad (4.9)$$

$$E_{total} = \int E(\lambda) f(R_{\lambda}) d\lambda \quad (4.10)$$

where λ is the wavelength of light, $f(R_{\lambda})$ Kubelka-Munk value, R_{λ} diffuse reflection of the powder/coating. $E(\lambda)$ spectral irradiance of the light source, and E_{total} relative integrated energy absorbance.

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.4.3**) has been suggested as a universal method of deducing the position of the absorption edge [9, 10]. In this study, the wavelength coordinate of the point on the low wavelength side of the curve at which the linear increase in absorbance starts was marked to investigate the absorption shift of feedstock powders and sprayed coatings.

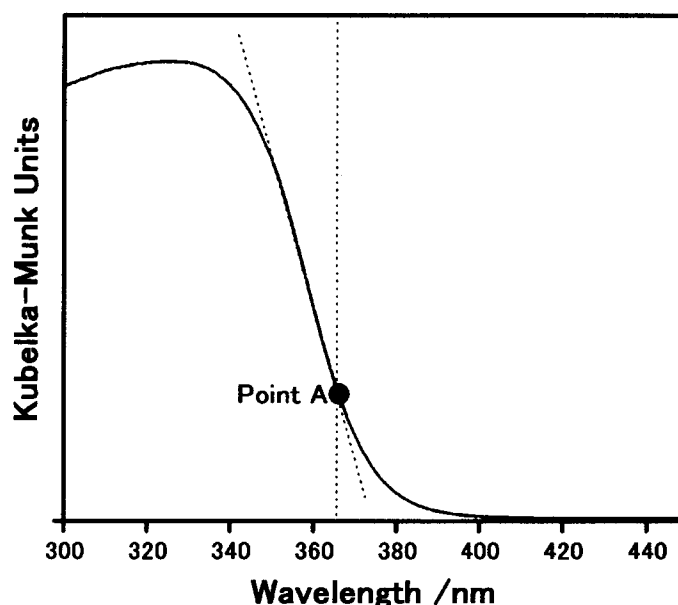


Fig.4.3. Definition of absorption edge in absorption spectrum of semiconductor.

4.3. Results and Discussion

4.3.1. Heat Treated TiO_2 and Composite $\text{TiO}_2\text{-Fe}_3\text{O}_4$ Powders

Although the $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ powder was heat treated and the results were given in Chapter 3, the details of Fe_3O_4 behavior was still unclear. Fig.4.4 shows the x-ray diffraction results of TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ feedstock powders heat treated at various temperatures. At 973K, anatase TiO_2 kept its crystal structure, but magnetite (Fe_3O_4) additive disappeared and Fe_2O_3 formed consequently (Fig.4.4(A)). One part of anatase TiO_2 transformed into rutile at 1123K in composite powders, which did not occur for pure anatase TiO_2 powder. The content of anatase TiO_2 in the heat treated powders at 1123K, which was calculated according to equations (4.1)–(4.6), decreased with the increasing of Fe_3O_4 amount as shown in Fig.4.5. The weight fractions of anatase transformed to rutile increased gradually (Fig.4.5(b)). These implied that the addition of Fe_3O_4 improved the anatase-rutile transformation of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ powders, and the transformation temperature, which was in the range of 973K to 1123K, decreased at least 50K comparing with pure TiO_2 powder.

At the heat treated temperature of 1273K, anatase phase transformed completely to rutile in composite $\text{TiO}_2\text{-Fe}_3\text{O}_4$ powders. But anatase TiO_2 phase was still detectable in pure TiO_2 powder. At the higher temperature of 1423K, all Fe_2O_3 reacted with TiO_2 and

produced stable Fe_2TiO_5 .

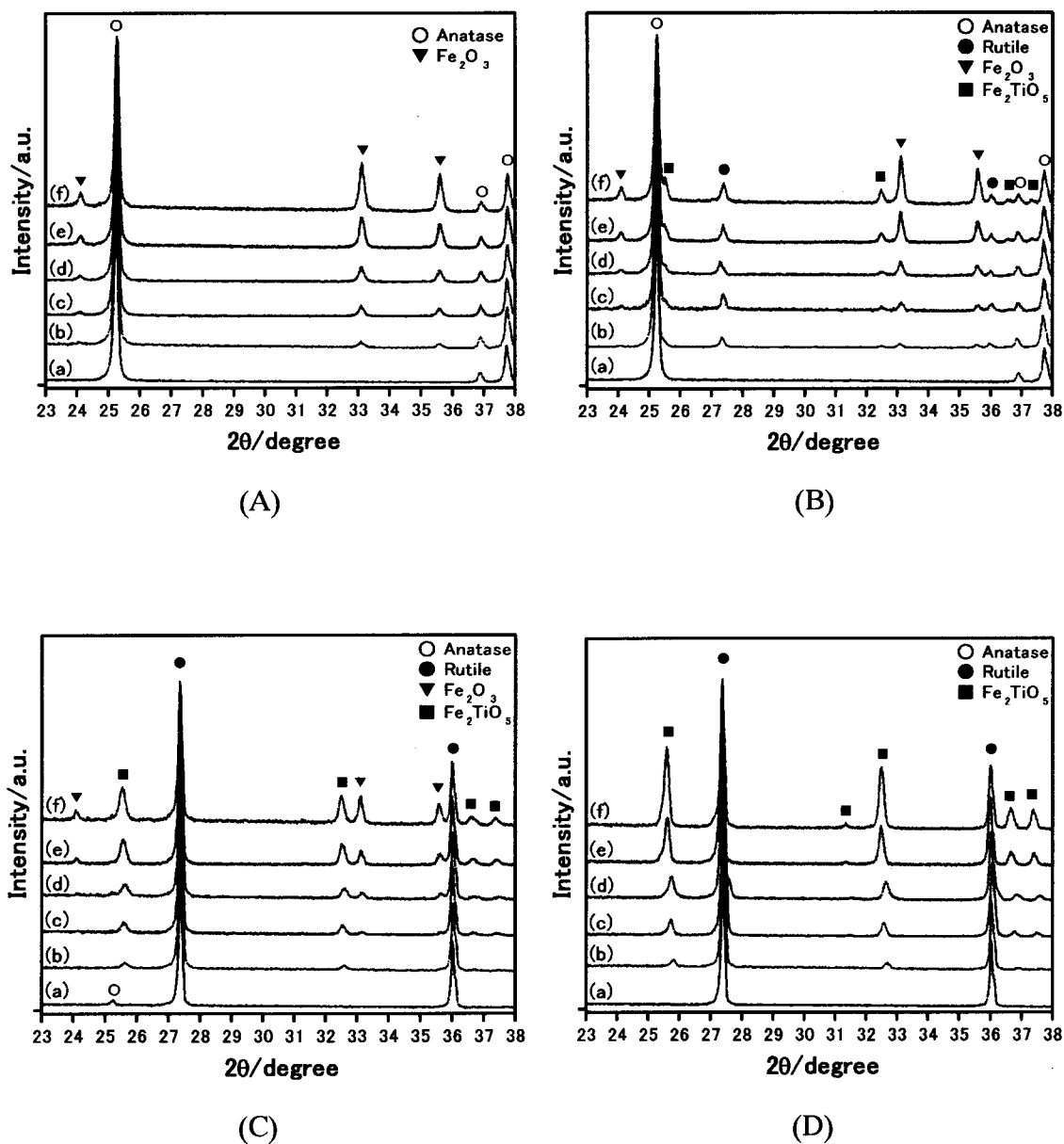


Fig.4.4. X-ray diffraction patterns of heat treated TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ feedstock powders at various temperatures. (A) 973K, (B) 1123K, (C) 1273K, (D) 1423K. (Notes: (a) TiO_2 powder, (b) $\text{TiO}_2\text{-5}\%\text{Fe}_3\text{O}_4$ powder, (c) $\text{TiO}_2\text{-10}\%\text{Fe}_3\text{O}_4$ powder, (d) $\text{TiO}_2\text{-12.7}\%\text{Fe}_3\text{O}_4$ powder, (e) $\text{TiO}_2\text{-22.5}\%\text{Fe}_3\text{O}_4$ powder, (f) $\text{TiO}_2\text{-32.6}\%\text{Fe}_3\text{O}_4$ powder.)

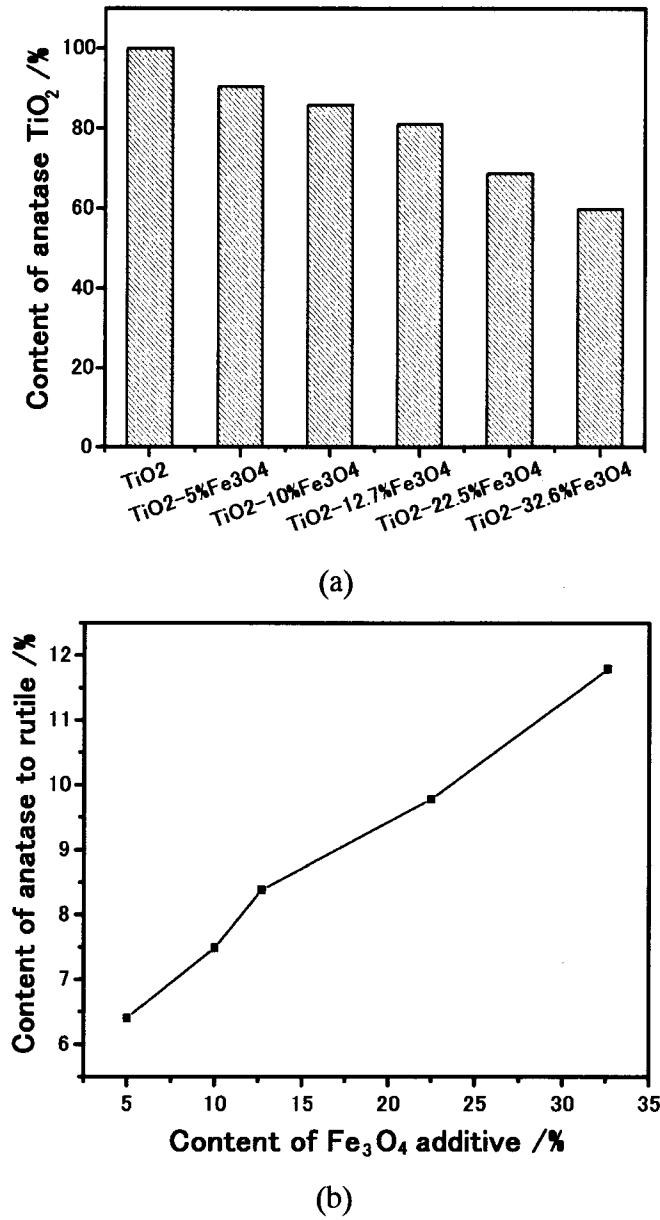


Fig.4.5. Content of anatase TiO_2 (a) and content of anatase TiO_2 transformed to rutile (b) in TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ feedstock powders heat treated at 1123K.

4.3.2. Speed and Temperature of In-flight Particles

The addition of Fe_3O_4 to TiO_2 powder had no considerable influence on the speed and temperature of in-flight TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ particles as shown in **Fig.4.6**. The average temperature of TiO_2 particles under the arc current of 400A was approximate to 2100K. The melting point of rutile TiO_2 is 2131K, thus large part of TiO_2 particles did

not melted at low arc current of 400A, which resulted in the low RDSP as shown in Fig.2.9 in Chapter 2.

On the other hand, the melting point of Fe₂TiO₅ is 1823K [11], and it is 1623K for Fe₂O₃ [12]. Moreover, reactions (4.11) and (4.12) give off heat, which may serve as the melting latent heat. Therefore, the melted proportion of TiO₂-Fe₃O₄ particle was higher than that of TiO₂ particle in spite of the same average temperature of particle, and the TiO₂-Fe₃O₄ particle was more melted with the higher content of Fe₃O₄.



Because the speed and temperature of plasma jet is higher with higher arc current, the speed and temperature of in-flight particles increased with the increasing of arc current as clearly shown in Fig.4.7.

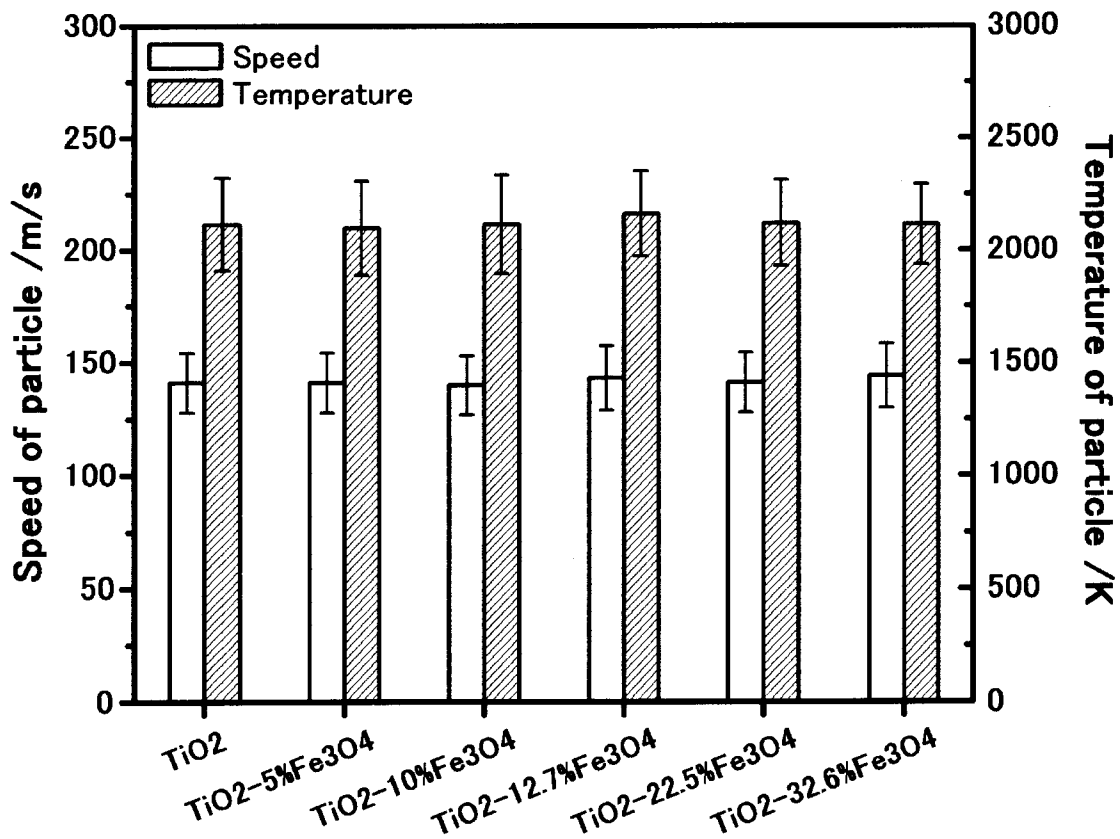


Fig.4.6. Speed and temperature of in-flight TiO₂ and TiO₂-Fe₃O₄ particles under the arc current of 400A.

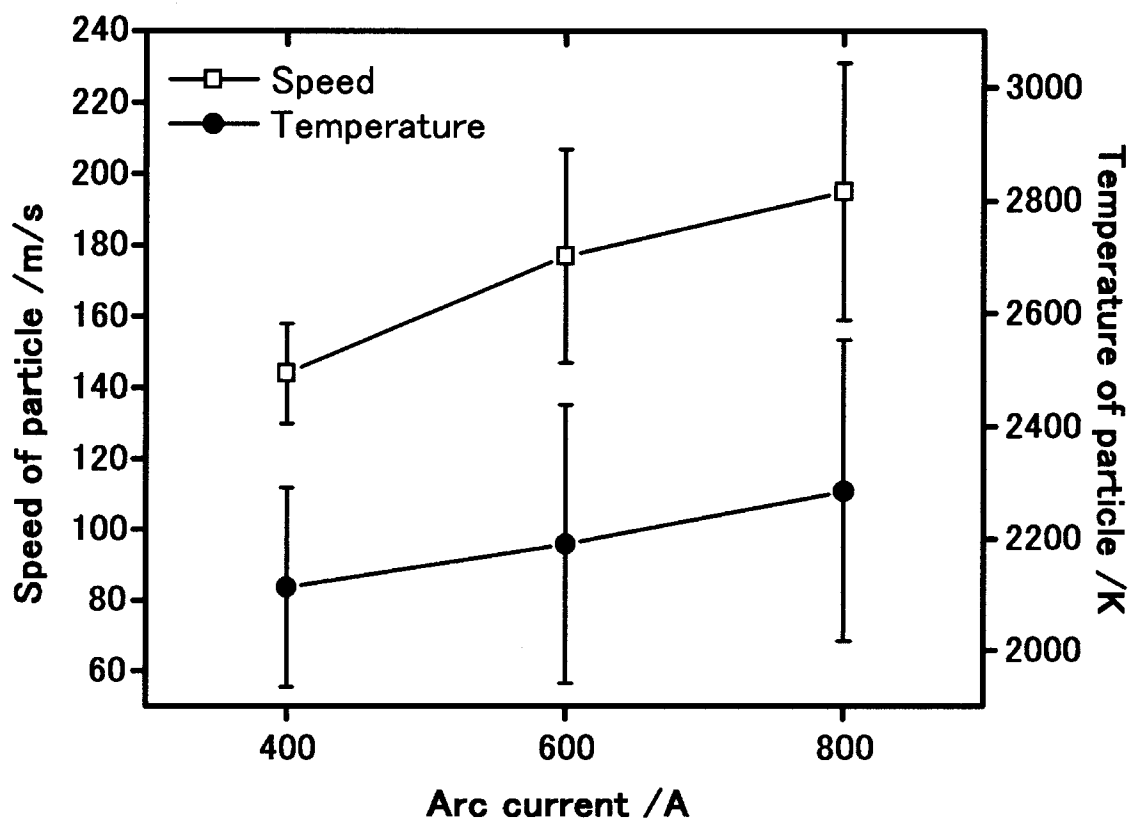


Fig.4.7. Speed and temperature of in-flight $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ particles under the arc current of 400A, 600A and 800A.

4.3.3. Composition of Plasma Sprayed $\text{TiO}_2\text{-Fe}_3\text{O}_4$ Coatings

Although the phase characterization results of $\text{TiO}_2\text{-}10\%\text{Fe}_3\text{O}_4$ coatings were presented in Chapter 3, the influence of Fe_3O_4 content on the properties of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coating was not clear. In this section, detailed information about the compositions of TiO_2 , $\text{TiO}_2\text{-}5\%\text{Fe}_3\text{O}_4$, $\text{TiO}_2\text{-}10\%\text{Fe}_3\text{O}_4$, $\text{TiO}_2\text{-}12.7\%\text{Fe}_3\text{O}_4$, $\text{TiO}_2\text{-}22.5\%\text{Fe}_3\text{O}_4$ and $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ coatings is given in order to obtain composition-property relations.

The x-ray diffraction patterns of plasma sprayed TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings under the arc current of 400A are illustrated in Fig.4.8. The relative intensity of anatase phase decreased with the increasing of Fe_3O_4 amount. This implied that the $\text{TiO}_2\text{-Fe}_3\text{O}_4$ feedstock powders were more melted with the increasing of Fe_3O_4 content, which is in good agreement with the results of the measured temperature of in-flight particles by

DPV-2000 and with the heat treatment results of feedstock powders. FeTiO₃ phase appeared with the addition of Fe₃O₄ till 22.5%, and became undetectable with the additive amount to 32.6%. The relative intensity of FeTiO₃ was highest in TiO₂-10%Fe₃O₄ coating comparing with other coating, which indicates that this coating had the highest content of FeTiO₃ compound. However, FeTiO₃ phase, which is thermally metastable compound, did not appear in heat treated TiO₂-Fe₃O₄ powders (See Fig.4.4). Thus it can be inferred plasma spraying technique is a method to form metastable substance.

The peak intensity of Fe₂TiO₅ phase increased continuously and obviously with the increasing of Fe₃O₄ amount, and finally became the main phase with the almost complete disappearance of ilmenite FeTiO₃ in the sprayed coating. For the high content of Fe₃O₄ in the TiO₂-32.6%Fe₃O₄ powder and high coating formation speed, a little Fe₃O₄ remained in the coating.

The crystal system of TiO₂ belongs to tetragonal ($a=b \neq c$). It has been reported that because TiO₂ contains interstitial channels in the c direction, certain transition metals diffuse through these channels into lattices. The diffusing ions have been found to locate preferentially on either the substitutional or interstitial sites. Moreover, FeTiO₃ is derived from α -Fe₂O₃ by replacing every other layer of the Fe atoms in (0001) planes by a layer of Ti atoms. Therefore, the formation of FeTiO₃ is possible in spite of the large ion radius of Fe²⁺(0.83Å) [13] especially in plasma spraying processes for the instantaneous melting and solidification of the feedstock particles.

Furthermore, the formation of Fe₂TiO₅ is reported by the fact that certain percentage of Fe³⁺ ion diffuses into TiO₂ producing a substitutional solid solution where Fe³⁺ is dispersed in the lattice of TiO₂ due to the ion radius similarity of Fe³⁺(0.67Å) and Ti⁴⁺(0.64Å). The substitution of Fe³⁺ in the matrix of TiO₂ is a favorable process and is easier in rutile TiO₂ for the open channel [14]. This reason may result in the high amount of Fe₂TiO₅ in the sprayed coatings when more anatase TiO₂ transformed into rutile.

For the high temperature of plasma jet, elements evaporation (particle mass loss) is a common phenomenon in plasma spraying processes [15, 16], Fe and Ti elements analysis of sprayed TiO₂-Fe₃O₄ coatings were carried out in this study. **Fig.4.9(a)** illustrates typical EDAX analysis pattern of plasma sprayed TiO₂-Fe₃O₄ coating. The weight ratios of Fe/(Ti+Fe) in TiO₂-Fe₃O₄ coatings were obtained and are shown in **Fig.4.9(b)**. The weight fractions of Fe/(Ti+Fe) in the feedstock powders were calculated according to the powder nominal composition. The results indicates that the measured weight ratio of Fe/(Ti+Fe) in the sprayed coating was comparable to that of the corresponding powder. Therefore, it can be considered that the Fe and Ti elements did

not disappear in plasma spraying processes.

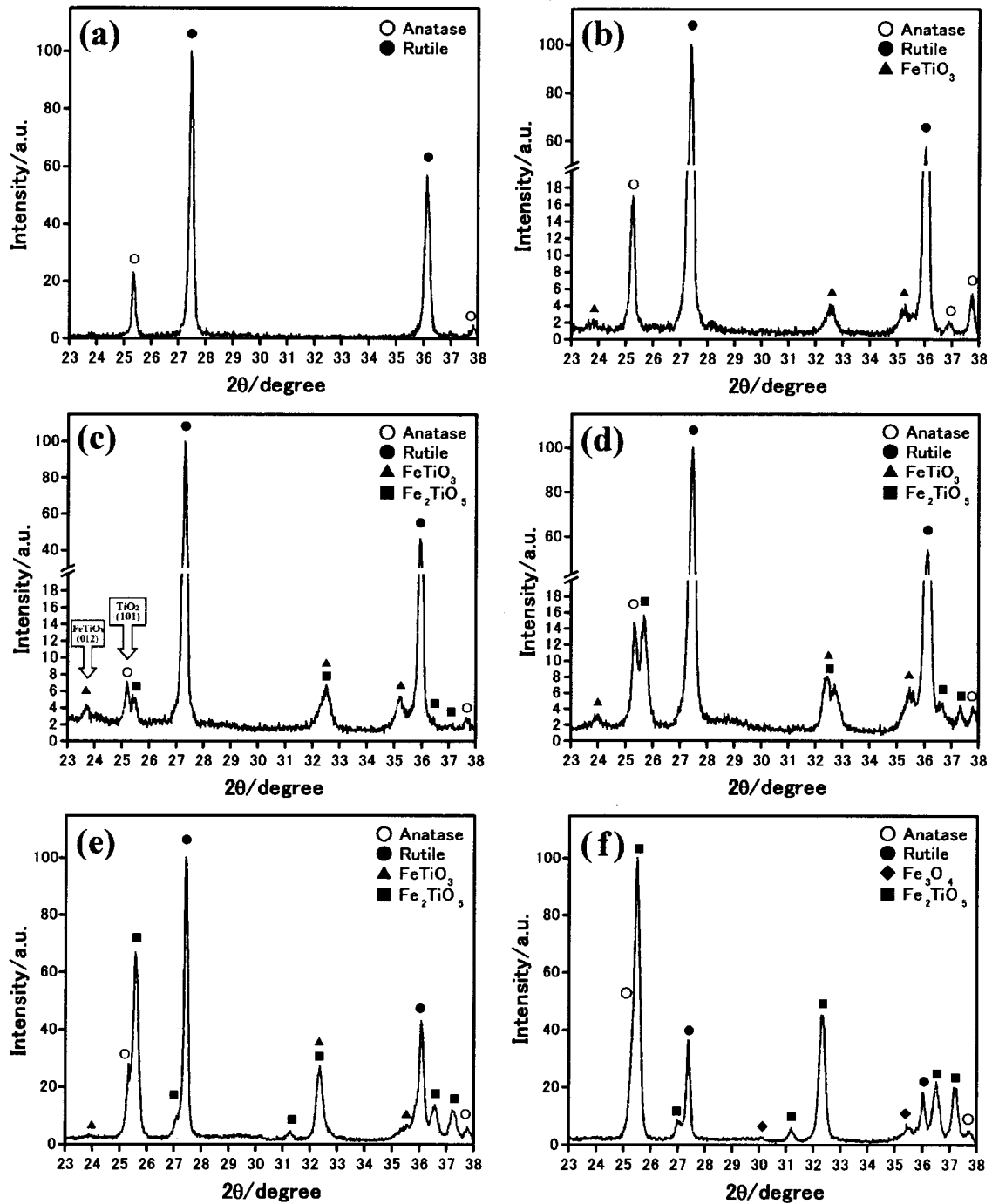


Fig.4.8. X-ray diffraction patterns of TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings plasma sprayed under the arc current of 400A and spraying distance of 70mm. (a) TiO_2 coating, (b) $\text{TiO}_2\text{-5\%Fe}_3\text{O}_4$ coating, (c) $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ coating, (d) $\text{TiO}_2\text{-12.7\%Fe}_3\text{O}_4$ coating, (e) $\text{TiO}_2\text{-22.5\%Fe}_3\text{O}_4$ coating, (f) $\text{TiO}_2\text{-32.6\%Fe}_3\text{O}_4$ coating.)

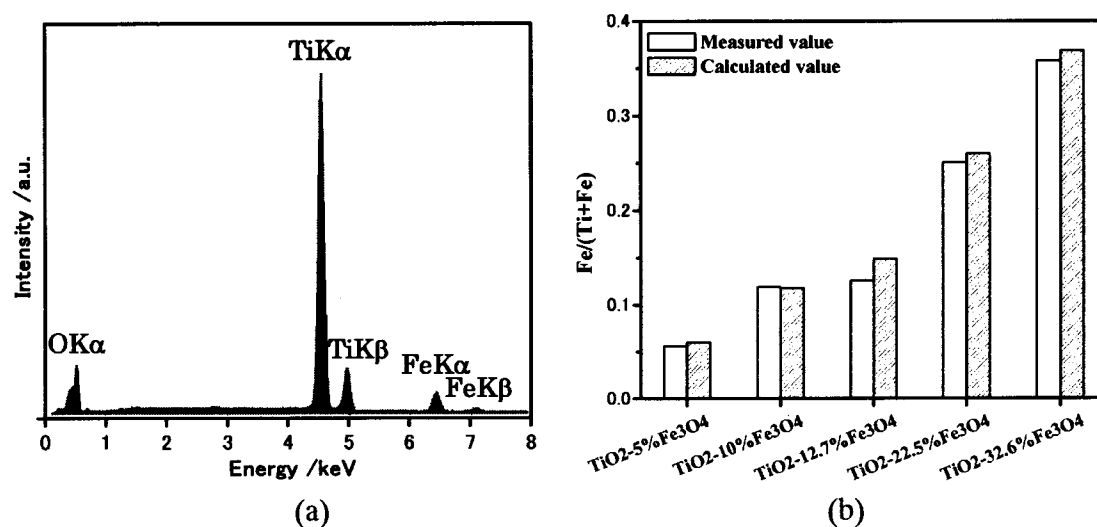


Fig.4.9. Typical EDAX analysis pattern of TiO₂-Fe₃O₄ coating (a), and the weight fractions of Fe/(Ti+Fe) in the TiO₂-Fe₃O₄ powders (Calculated value) and in the sprayed coatings (Measured value) (b).

4.3.4. Heat Treatment of Plasma Sprayed TiO₂-Fe₃O₄ Coatings

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 – 10^6 K/s, therefore, solid solution, amorphous phase and phase segregation exists widely in composite coating [6, 7]. The existence of these kinds of phenomena in sprayed TiO₂-32.6%Fe₃O₄ coatings was investigated. As clearly shown in **Fig.4.10**, the relative intensity of the main diffraction of rutile phase (110) increased obviously when the coating was heat treated at 1273K, and became higher than that of Fe₂TiO₅ phase (101). The ratio of main diffraction intensity of rutile phase (110) and Fe₂TiO₅ phase (101) of heat treated TiO₂-32.6%Fe₃O₄ coating was comparable to that of heat treated TiO₂-32.6%Fe₃O₄ powder.

The XRD peaks of sprayed TiO₂-32.6%Fe₃O₄ coatings were not broad, which implied amorphous phase did not exist in it. According to the EDAX analysis results (**Fig.4.11**), Ti and Fe elements distributed uniformly along the perpendicular line to the coating surface, which indicated that TiO₂ and Fe₂TiO₅ phase segregations did not happen. It was confirmed again that Fe/(Ti+Fe) in the sprayed coating was comparable to that in TiO₂-32.6%Fe₃O₄ feedstock powder. As shown in **Fig.4.12**, large amount of Ti segregated from TiO₂ and/or Fe₂TiO₅ phase after heat treatment of coating, and then the weight fraction of TiO₂ increased obviously. Therefore, it was considered that solid

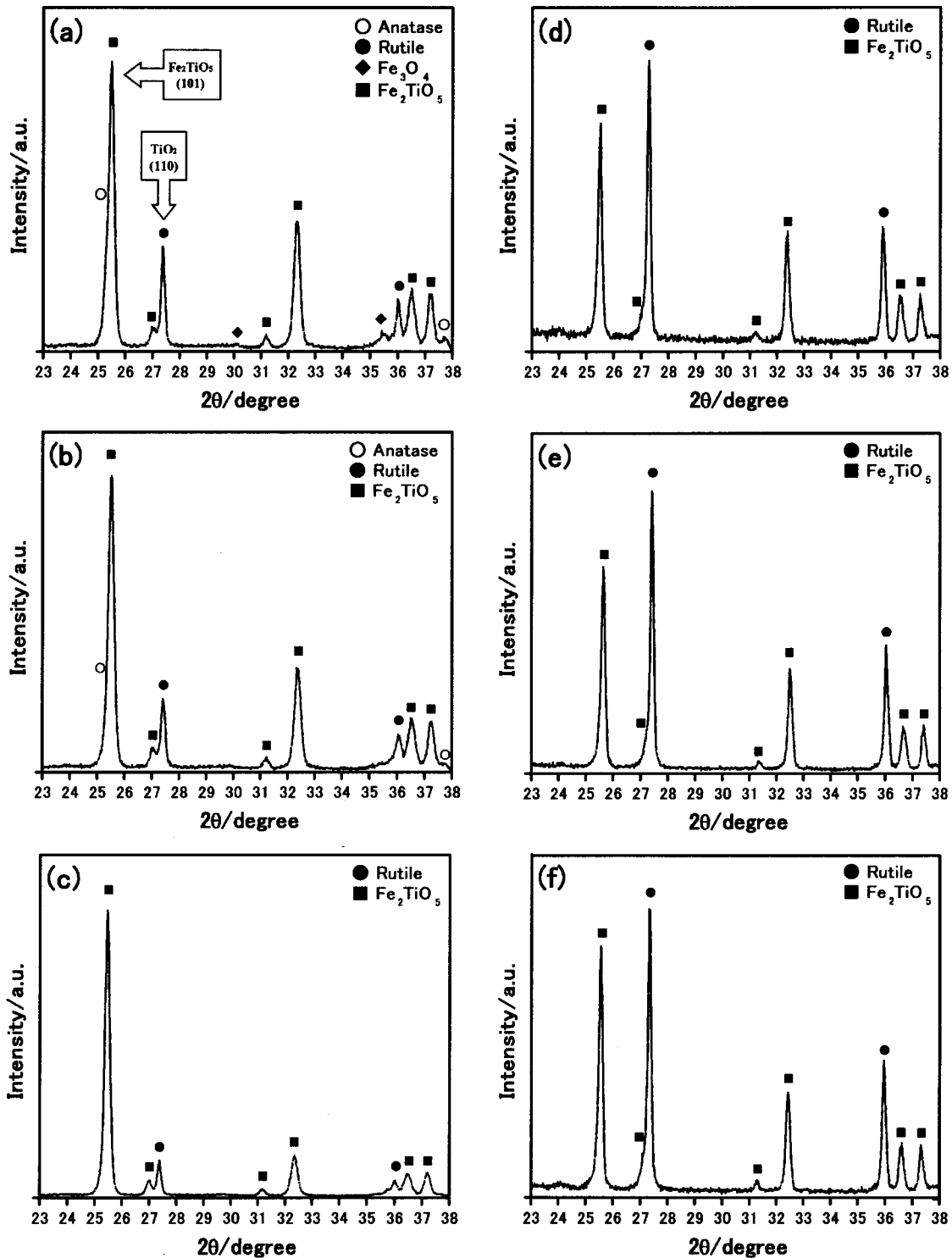


Fig.4.10. Phases changes of $\text{TiO}_2\text{-32.6\%Fe}_3\text{O}_4$ coatings. (a) Coating sprayed at 400A, (b) Coating sprayed at 600A, (c) Coating sprayed at 800A, (d) Heat treated at 1273K of (a), (e) Heat treated at 1273K of (b), (f) Heat treated at 1273K of (c).

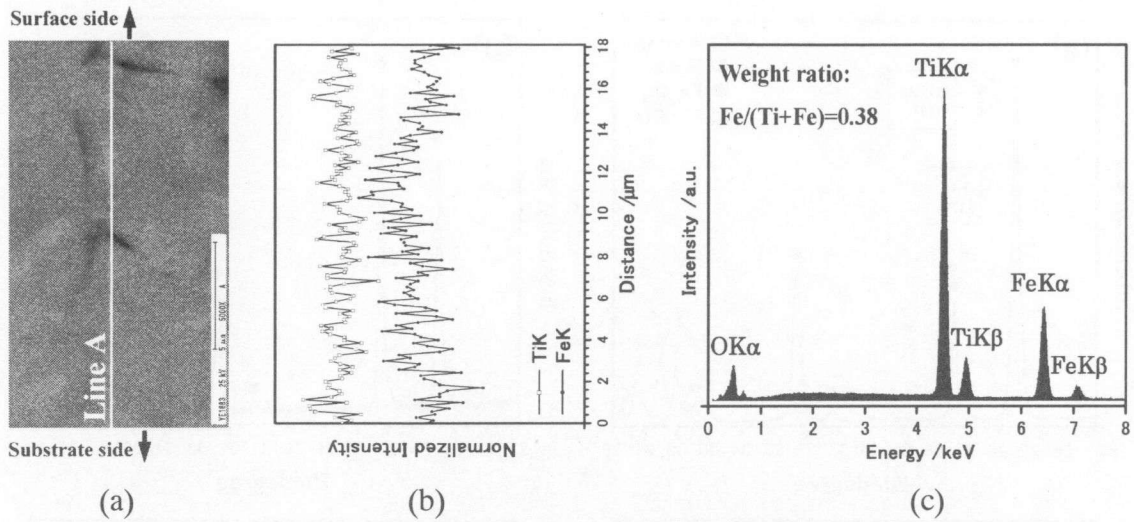


Fig.4.11. Cross section (a), Ti and Fe elements distribution (b) of *line A* in (a) and EDAX spectrum (c) of $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ coating plasma sprayed under the arc current of 600A.

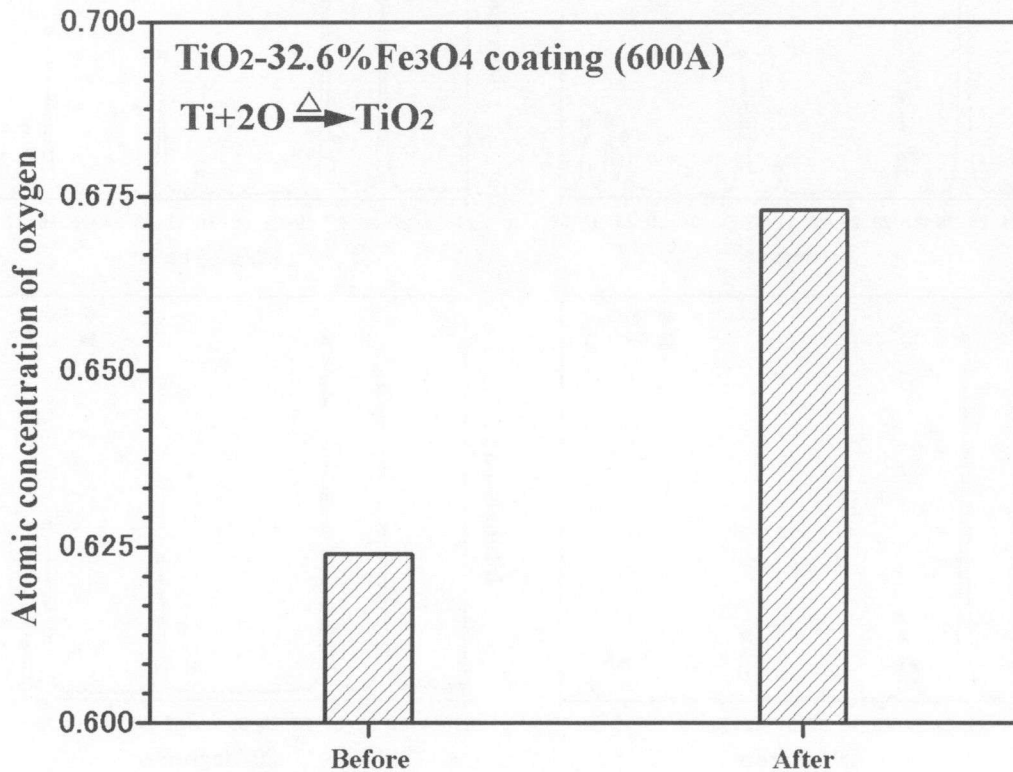


Fig.4.12. Atomic concentration change of oxygen before and after heat treatment at $1273\text{K} \times 21600\text{s}$ of $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ coating plasma sprayed under the arc current of 600A.

solution existed in the sprayed TiO₂-32.6%Fe₃O₄ coating. As shown in Fig. 4.10 (a), (b) and (c), the relative intensity of the main diffraction of rutile phase (110) decreased with the increasing of arc current. This implied the abundance of solid solution in the sprayed coatings increased with the increase of arc current, which results from the higher speed and temperature of particle transferred from plasma jet at high arc current (See Fig.4.7). The existence of solid solution may make the quantitative analysis of the coatings using the abnormal intensities absolutely meaningless.

As a result, special attentions should be paid on the quantitative measurement using the XRD method for thermal sprayed composite coating.

4.3.5. General Features of Plasma Sprayed TiO₂-Fe₃O₄ Coatings

Figure 4.13 illustrates the relative deposition speed of TiO₂ and TiO₂-Fe₃O₄ powders (RDSP). The RDSP increased with the amount increase of Fe₃O₄ additive. The RDSP of TiO₂-10%Fe₃O₄ powder, which was 13μm/pass, was over two times than that of TiO₂ powder. With the content of Fe₃O₄ to 32.6%, the RDSP was improved eight times. Conclusion has been drawn that the addition of Fe₃O₄ to TiO₂ improved obviously the TiO₂ powder deposition efficiency.

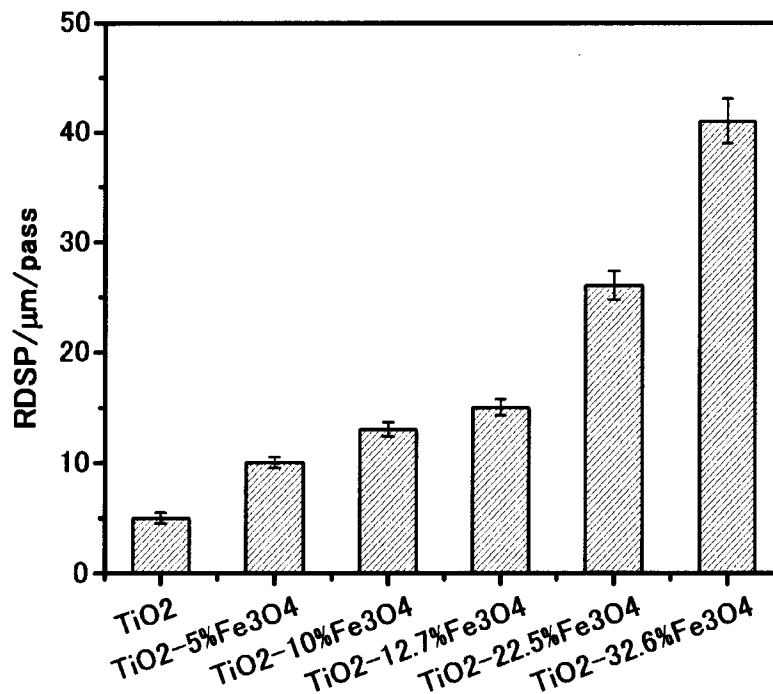


Fig.4.13. Relative deposition speed of TiO₂ and TiO₂-Fe₃O₄ powders (RDSP) under the arc current of 400A and spraying distance of 70mm.

Figure 4.14 shows the surface morphologies and cross sections of TiO₂, TiO₂-12.7%Fe₃O₄ and TiO₂-32.6%Fe₃O₄ coatings prepared by plasma spraying. The “U” denotes unmelted zone, “M” denotes melted zone in Fig.4.14 (b). TiO₂ coating is not very dense, and TiO₂ powders were not melted fully. In the TiO₂-Fe₃O₄ coatings, unmelted or partially melted TiO₂-Fe₃O₄ powders were fewer than that of TiO₂ powders under the same spraying conditions. These facts are in good agreement with the results presented in Section 4.3.2 and illustrated in Fig.4.13.

The solidification processes involve extraction of heat from the melt in a manner. The major growth morphologies are dendrites and eutectic [17, 18]. **Fig.4.15** displays a well-defined dendritic crystal in plasma sprayed TiO₂-Fe₃O₄ coating. As discussed in Section 4.3.2, one part of TiO₂ did not melt. Thus the unmelted TiO₂ may become nuclei, and then the nuclei grow into spherical crystals which rapidly become unstable and dendritic in form. These dendrites grow freely in the melt and finally impinge on one another.

4.3.6. Energy Absorbance of Plasma Sprayed TiO₂-Fe₃O₄ Coatings

According to the diffuse reflectance spectra of the feedstock powders (**Fig.4.16**), the Fe₃O₄ additive did not change the absorption edge (wavelength coordinate of black circle in Fig.4.16) and the light absorbance dropped suddenly in the wavelength range of 340nm to 400nm. These implied that Fe₃O₄ particle cannot shift the photo-absorptive ability of TiO₂ to the visible spectral range. The diffuse reflectance spectra of the sprayed coatings are shown in **Fig.4.17**, 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 Fig.4.17. In the case of TiO₂ coating, the light absorbance dropped suddenly in the wavelength range of 340nm to 400nm. However, the dropping speed decreased continuously and the optical absorption edge (black circle) shifted to longer wavelength with the content increase of Fe₃O₄ additive. To compare the light absorptive capacity, the integrated energy absorbance of the sprayed TiO₂ and TiO₂-Fe₃O₄ coatings from the ultraviolet lamp used in this study is estimated according to Equations (4.9) and (4.10). As shown in **Fig.4.18**, the relative integrated energy absorbance increased with the content increase of the Fe₃O₄ additive, which means that more irradiation light energy can be utilized. It partly ascribed to FeTiO₃ and Fe₂TiO₅ compound as reported by N. Smirnova et al. [19], F. X. Ye et al. [20] and B. Pal et al. [14].

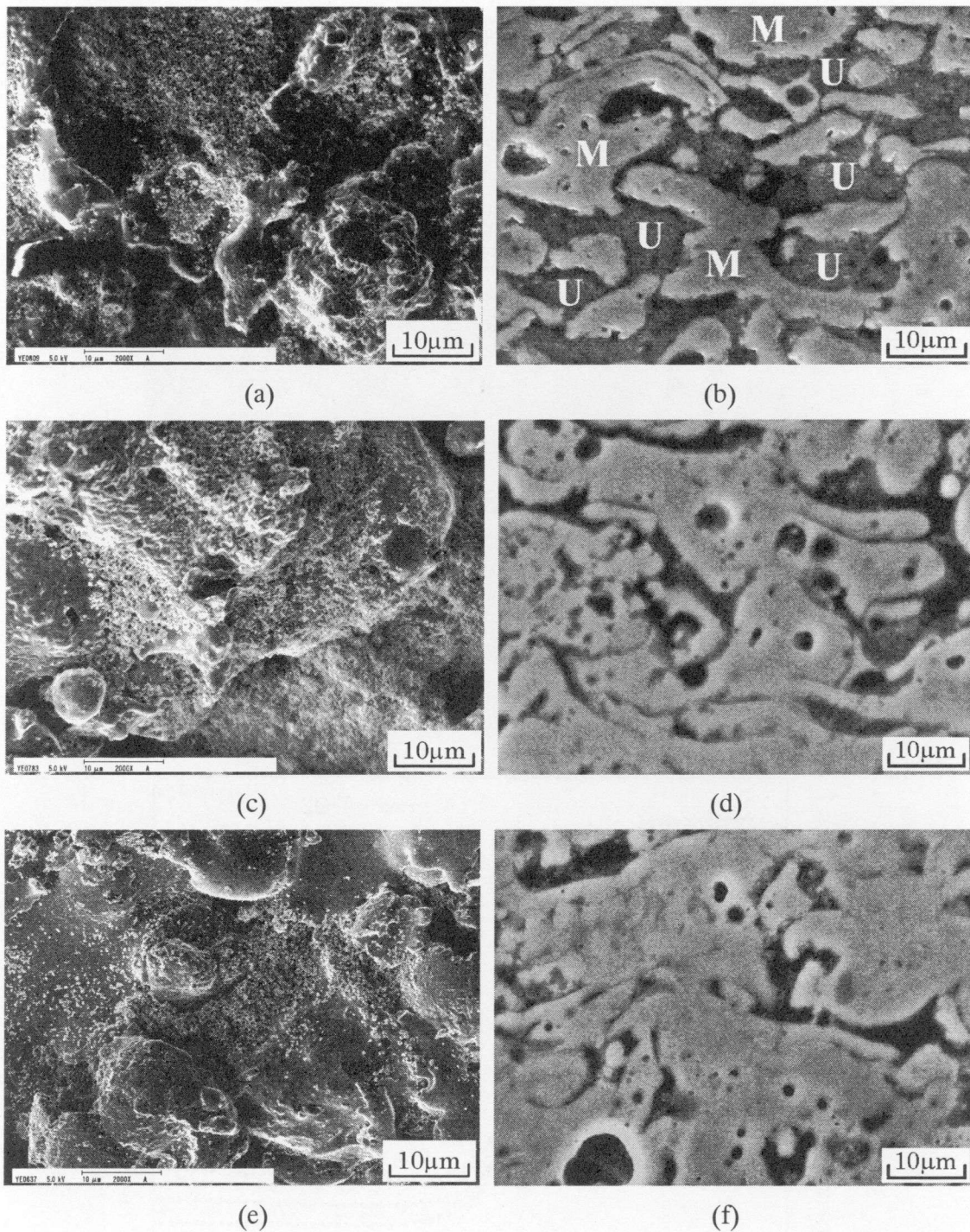


Fig.4.14. Surface morphologies and cross sections of plasma sprayed coatings under the arc current of 400A and spraying distance of 70mm. (a), (c), (e) Surface morphologies of TiO_2 , $\text{TiO}_2\text{-}12.7\%\text{Fe}_3\text{O}_4$, and $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ coatings, respectively. (b), (d), (f) Cross sections of TiO_2 , $\text{TiO}_2\text{-}12.7\%\text{Fe}_3\text{O}_4$, and $\text{TiO}_2\text{-}32.6\%\text{Fe}_3\text{O}_4$ coatings, respectively. (Notes: “U” denotes unmelted zone, “M” denotes melted zone in (b)).

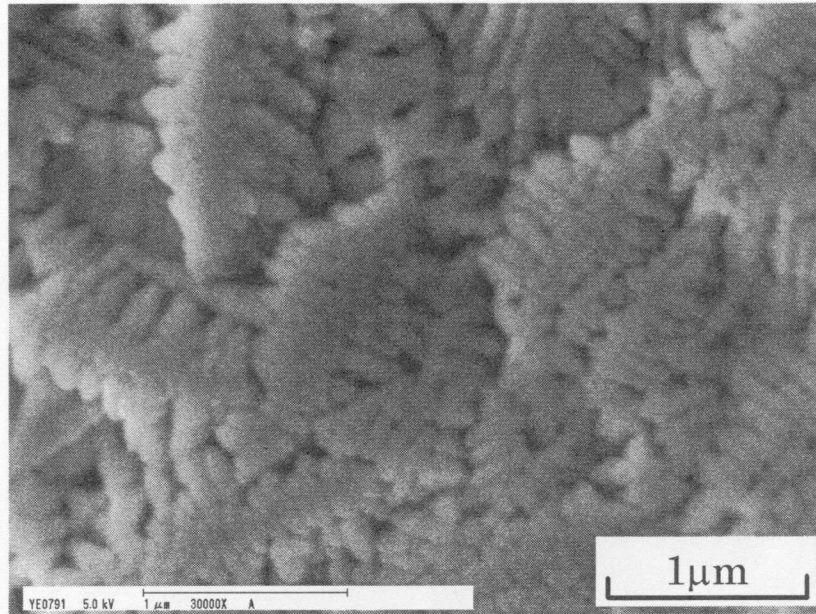


Fig.4.15. Dendritic crystal appeared in $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coating sprayed under the arc current of 400A.

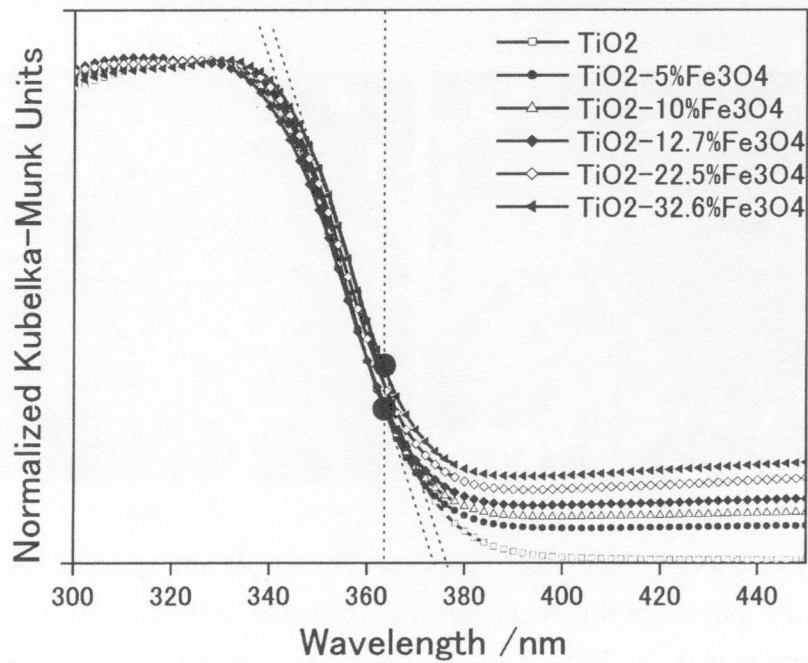


Fig.4.16. Diffuse reflectance spectra of the feedstock TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ powders.

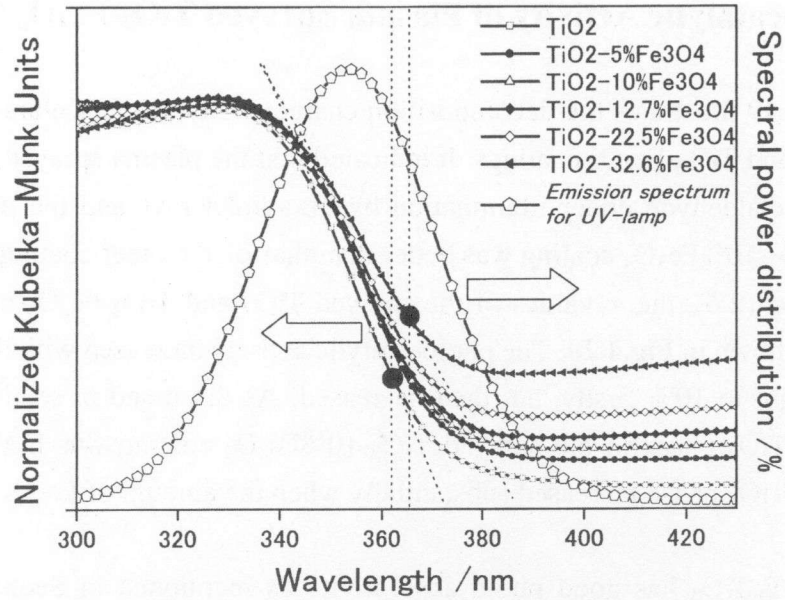


Fig.4.17. Diffuse reflectance spectra of TiO_2 , $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings sprayed under the arc current of 400A and spraying distance of 70mm, and the spectral power distribution for the ultraviolet lamp used in this study.

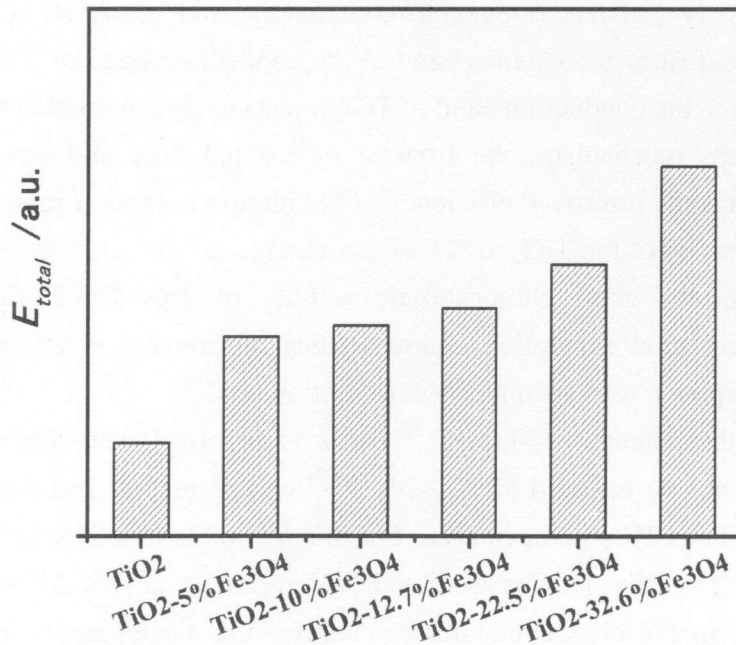


Fig.4.18. Integrated energy absorbance of TiO_2 and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings sprayed under the arc current of 400A and spraying distance of 70mm from the ultraviolet lamp used in this study.

4.3.7. Photocatalytic Activity of Plasma Sprayed TiO₂-Fe₃O₄ Coatings

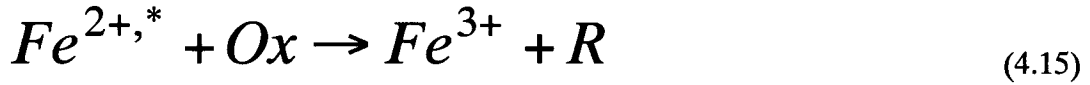
Figure 4.19 illustrates the decomposition characteristic of the acetaldehyde by the sprayed TiO₂ and TiO₂-Fe₃O₄ coatings. It indicated that the plasma sprayed coatings can decompose acetaldehyde under illumination by ultraviolet rays and the photocatalytic activity of TiO₂-10%Fe₃O₄ coating was better than that of the other coatings. According to the Equation (2.6), the τ values of the sprayed TiO₂ and TiO₂-Fe₃O₄ coatings were calculated as shown in **Fig.4.20**. The photocatalytic activity increased with the increasing of Fe₃O₄ weight to 10% firstly, but then decreased. As discussed in section 4.3.3, 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%.

Because FeTiO₃ has good photo absorptivity as mentioned in Section 4.3.6, the good photocatalytic efficiency of TiO₂-10%Fe₃O₄ coating possibly resulted from the high content of ilmenite FeTiO₃ phase in the coating, but not directly from the Fe₃O₄ particles. Furthermore, the band gap of bulk FeTiO₃, which is 2.85eV [21], is lower than that of TiO₂. As a possible phenomenon shown in **Fig.4.21**, 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-steps 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.

Furthermore, the good photocatalytic activity of TiO₂-10%Fe₃O₄ coating also resulted from the good separation characteristics of initiated electron-hole pairs as discussed in **Chapter 6** using p-n junction formation model.

Moreover, the potential of Fe²⁺/Fe³⁺ redox is slightly lower than the conduction band of TiO₂ as shown in **Fig.4.22** [22~24], Fe²⁺ can be regarded as a trap of initiated electrons like Pt in Pt/TiO₂ photocatalyst. For this favorable function, initiated electrons separate with holes easily. D. Cordischi and K. Sayama et. al [25, 26] suggested ferric ions play a role in the charge transfer mechanism via a cooperative effect with the Ti⁴⁺/Ti³⁺ couple, according to the Reaction (4.13)~(4.16). Fe²⁺/Fe³⁺ attended the oxidation-reduction reaction and then increased the photocatalytic activity of TiO₂-10%Fe₃O₄ coating.





where *Ox* and *R* are oxidized and reduced adsorbed species, respectively.

The band gap of pure Fe₂TiO₅ is 2.18eV, which is lower than that of TiO₂ and FeTiO₃. Although the light absorbance increases with the amount increasing of Fe₂TiO₅ compound, the photocatalytic activity was reduced dramatically when the content of Fe₂TiO₅ is high. As is known [14], 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-Fe₃O₄ coating is improved with an increase in the 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.

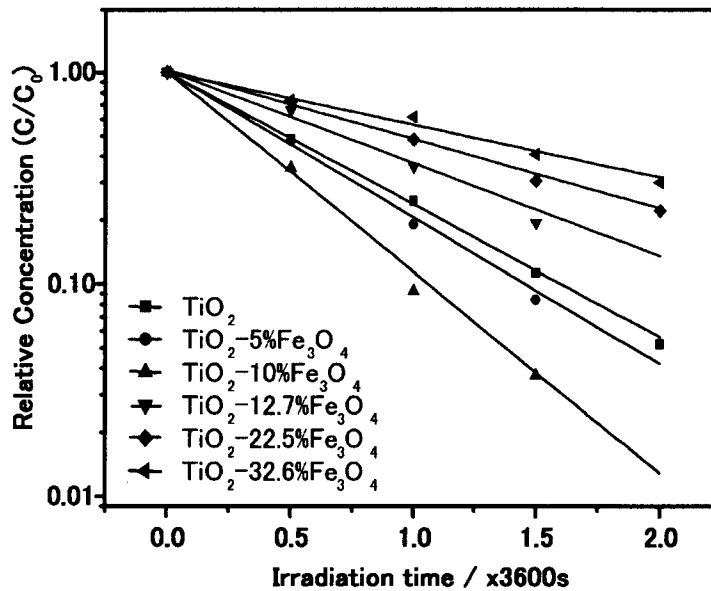


Fig.4.19. Photocatalytic decomposition characteristics of the acetaldehyde by the sprayed TiO₂ and TiO₂-Fe₃O₄ coatings.

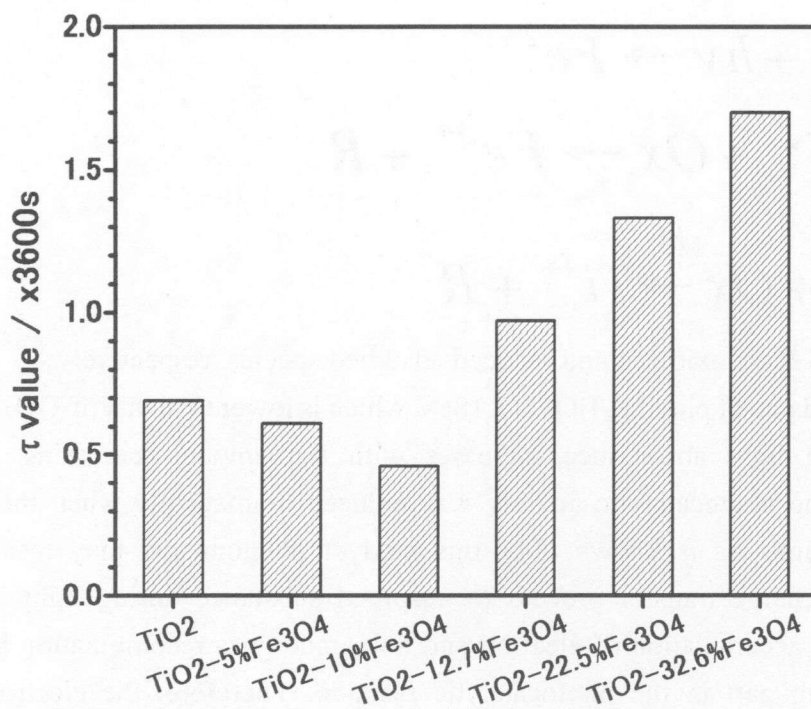


Fig.4.20. τ values of the plasma sprayed TiO₂ and TiO₂-Fe₃O₄ coatings.

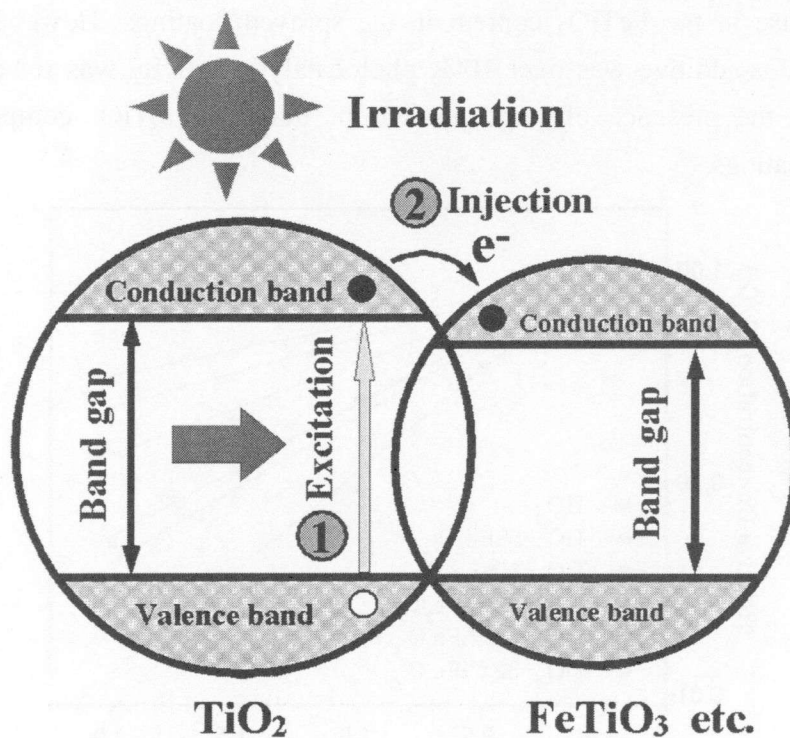


Fig.4.21. A proposed two-steps electron transfer model for the good photocatalytic activity of TiO₂-10%Fe₃O₄ coating.

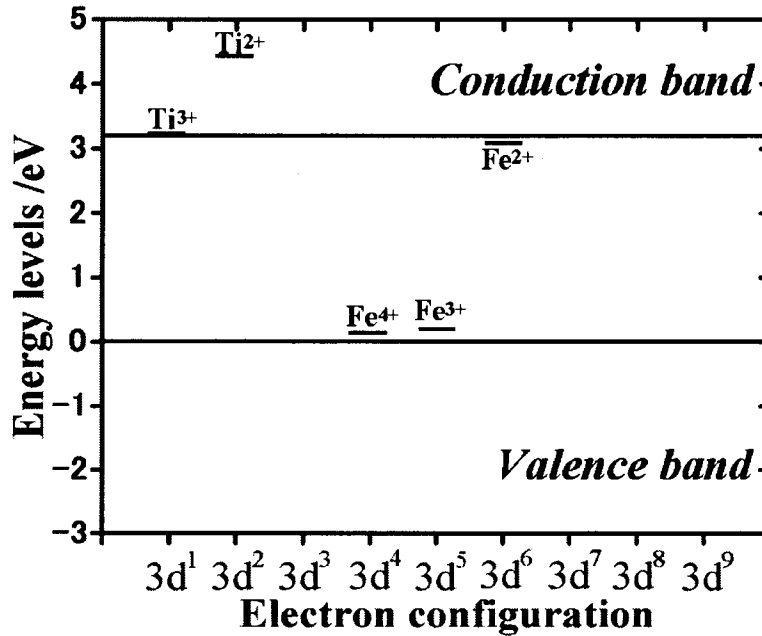


Fig.4.22. Energy levels of various redoxes in anatase TiO₂.

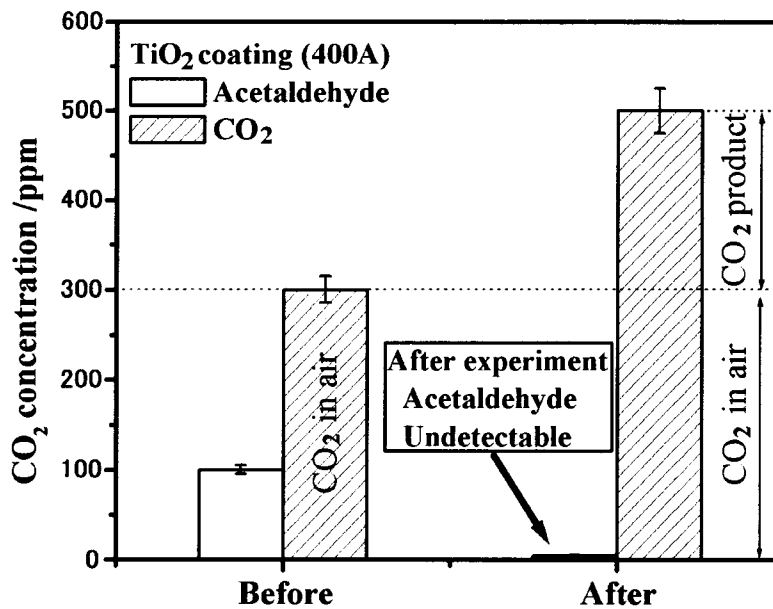


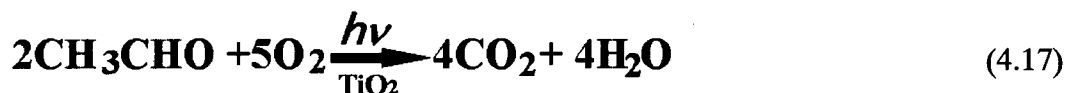
Fig.4.23. Variation of CO₂ concentration before and after photo-degradation experiment.

4.3.8. Generation of CO₂ in Photo Degradation Processes

Figure 4.23 shows the variation of CO₂ concentration before and after photo-degradation experiment (an example). In the figure, “after experiment” was the time

when the acetaldehyde was undetectable in evaluation experiment of photocatalytic activity of sprayed coating.

If 100ppm acetaldehyde decomposes completely to CO₂ and H₂O, the concentration of CO₂ should be 200ppm according to the reaction (4.17).



After photo-degradation experiment, 200ppm CO₂ increased (Fig.4.23), which implied that the acetaldehyde decomposed completely using plasma sprayed TiO₂ coating.

4.4. Conclusions

The anatase-rutile phase transformation temperature of TiO₂ and TiO₂-Fe₃O₄ feedstock powders was studied systematically. TiO₂ and TiO₂-Fe₃O₄ coatings were prepared on stainless steel substrate by plasma spray. The results clearly showed that the anatase-rutile transformation temperature of TiO₂-Fe₃O₄ powders was in the range of 973K to 1123K, which was at least 50K lower than that of pure anatase TiO₂ powder. The TiO₂-Fe₃O₄ coatings consisted of anatase TiO₂, rutile TiO₂, and pseudobrookite Fe₂TiO₅ phase which appeared when the content of Fe₃O₄ 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-steps electron transfer model. Moreover, initiated electrons could separate with holes easily because Fe²⁺ can be regarded as a trap of initiated electrons. 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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CHAPTER 5

Evaluation of Plasma Sprayed TiO₂-FeTiO₃ Coatings

5.1. Introduction

Titanium-substituted iron oxides are widespread in nature and represent an important mineral resource for the commercial extraction of both iron and titanium [1]. The FeTiO₃ structure, which is of rhombohedral crystal structure, is derived from α -Fe₂O₃ by replacing every other layer of the Fe atoms in (0001) planes by a layer of Ti atoms [2, 3]. Ilmenite is an incongruently melting material with the melting point of approximate 1683K [4]. Although high temperature electrical conductivity and magnetic properties of ilmenite FeTiO₃ have been investigated in detail [2–6], very little work has been done as a chemical catalyst and photocatalyst [7]. The characterization of photocatalytic performance of TiO₂-FeTiO₃ composite cannot be found until now.

To elucidate the influence of FeTiO₃ on the photocatalytic activity of plasma sprayed TiO₂-Fe₃O₄ coatings, FeTiO₃ and TiO₂-FeTiO₃ powders were designed. The phase composition, microstructure and photocatalytic activity of plasma sprayed FeTiO₃, TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ coatings were discussed in detail in this chapter. The photocatalytic activity of TiO₂, TiO₂-30%FeTiO₃ and FeTiO₃ powders was also evaluated.

5.2. Materials and Experimental Procedures

5.2.1 Feedstock Powders and Substrate

FeTiO₃ particles with average size of 1.4 μ m were agglomerated to FeTiO₃ feedstock powder with average size of 32.5 μ m. To manufacture TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ feedstock powders, TiO₂ particle with average size of 0.2 μ m was mechanically and uniformly mixed with 1.4 μ m FeTiO₃ particles with corresponding weight ratio. The average size of TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ was 30.4 μ m and 28.9 μ m, respectively. The x-ray diffraction patterns of the FeTiO₃, TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ feedstock powders are shown in **Fig.5.1**. The morphology of TiO₂-30%FeTiO₃ powder is given in **Fig.5.2**, which was very similar to FeTiO₃ and

$\text{TiO}_2\text{-50\%FeTiO}_3$ powder. The substrate was stainless steel (JIS SUS304).

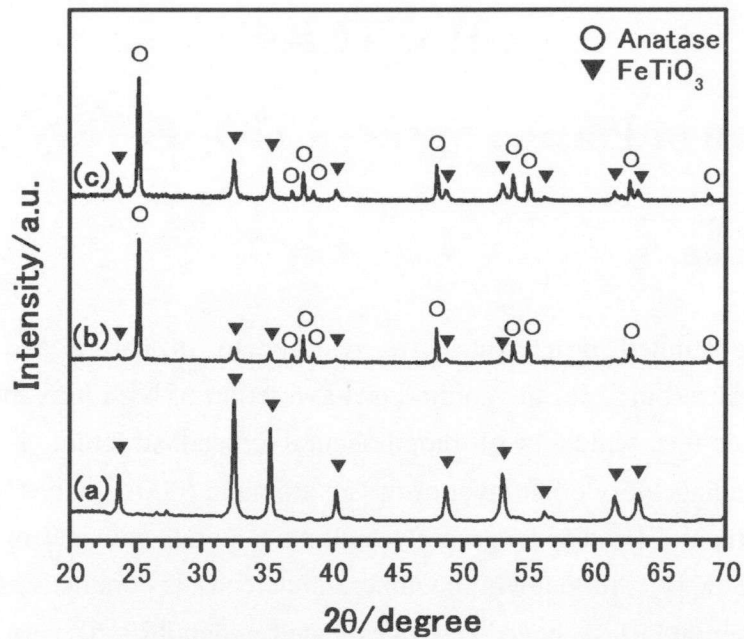


Fig.5.1. X-ray diffraction patterns of the FeTiO_3 (a), $\text{TiO}_2\text{-30\%FeTiO}_3$ (b) and $\text{TiO}_2\text{-50\%FeTiO}_3$ (c) feedstock powders.

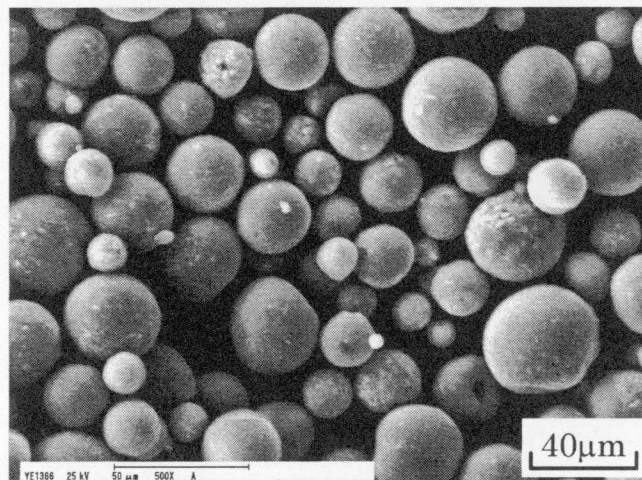


Fig.5.2. The morphology of $\text{TiO}_2\text{-30\%FeTiO}_3$ powder.

5.2.2. Plasma Spraying Equipment

The thermal spraying equipment was a plasma spraying system (Plasmadyne-Mach1 manufactured by Plasmadyne Company). Argon was applied as primary gas, and helium was applied as secondary gas. The thermal spraying parameters are given in **Table 5.1**.

Table 5.1 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, 600, 800
Arc voltage (V)	28~30
Spraying distance (mm)	70

5.2.3. Characterization of Powders and Sprayed Coatings

Electron probe surface roughness analyzer (ERA-8800FE, Elionix Co. Ltd., Japan) 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 feedstock powders and the sprayed coatings was investigated by x-ray diffraction using Cu-K α radiation ($\lambda=1.5406\text{\AA}$) and graphite crystal monochromator (M03XHF, MAC Science Co. Ltd.). To evaluate powder deposition efficiency, the relative deposition speed of powder was also calculated by Equation (2.2) given in Chapter 2. The photocatalytic activity of sprayed coatings was evaluated using the acetaldehyde degradation set-up, and the τ value was calculated by Equation (2.6).

5.3. Results and Discussion

5.3.1. Typical Microstructure of FeTiO₃ and TiO₂-FeTiO₃ Coatings

Figure 5.3 shows the cross sections of TiO₂-30%FeTiO₃ coatings sprayed under the arc current of 400A, 600A and 800A. It indicates that the coating became denser with the increasing of arc current. As clearly shown in **Fig.5.4**, many primary particles existed in the coating sprayed under the arc current of 400A for the low energy transfer from plasma jet. The relative deposition speed of TiO₂-30%FeTiO₃ powder, which was approximate to 4 μm /pass, had no significant variation comparing with that of TiO₂ powder as shown in **Fig.5.5**. With the increase of arc current to 600A or 800A, the relative deposition speed of TiO₂-30%FeTiO₃ powder (RDSP) increased obviously.

Figure 5.6 shows the cross sections and surface morphologies of FeTiO₃ and TiO₂-50%FeTiO₃ coatings sprayed under the arc current of 400A. It indicated that the FeTiO₃ powder was more melted than the TiO₂-50%FeTiO₃ powder, which also can be inferred from **Fig.5.5**.

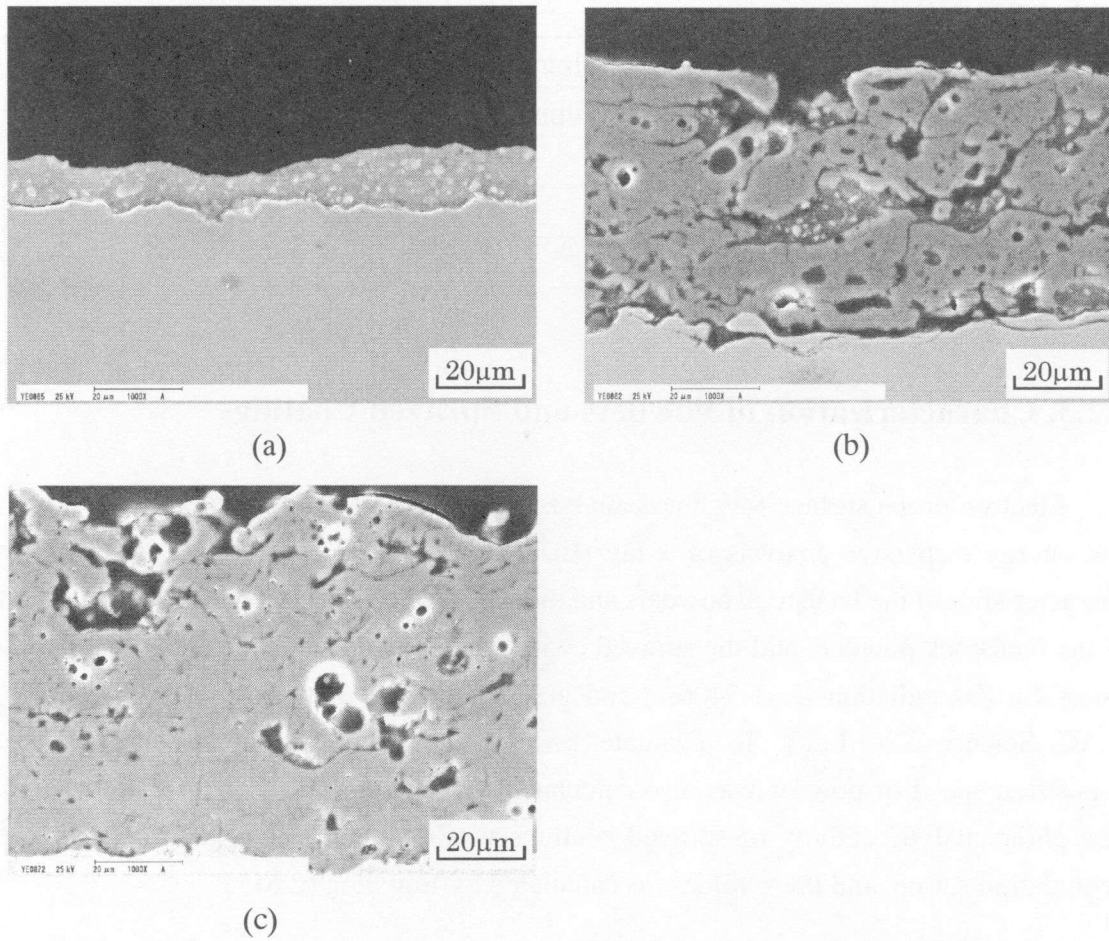


Fig.5.3. Cross sections of $\text{TiO}_2\text{-30%FeTiO}_3$ coatings sprayed under the arc current of 400A(a), 600A(b) and 800A(c).

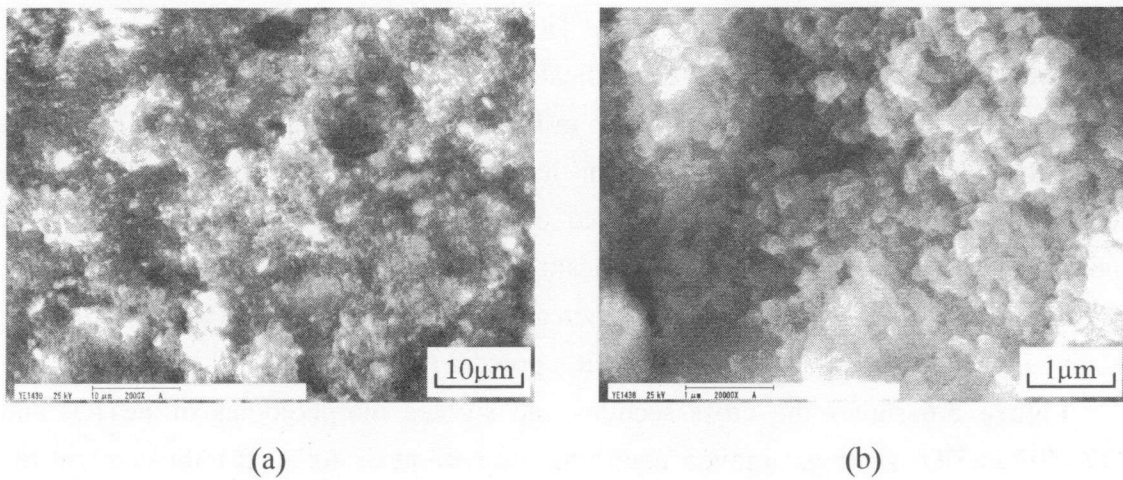


Fig.5.4. Surface morphologies of $\text{TiO}_2\text{-30%FeTiO}_3$ coating sprayed under the arc current of 400A ((a) low magnification, (b) high magnification.).

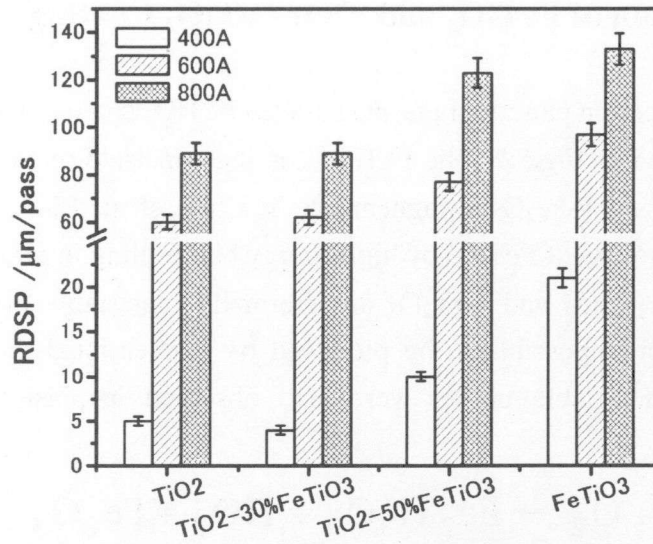


Fig.5.5. Relative deposition speed of TiO_2 , TiO_2 -30% FeTiO_3 , TiO_2 -50% FeTiO_3 and FeTiO_3 powder under the arc current of 400A, 600A and 800A.

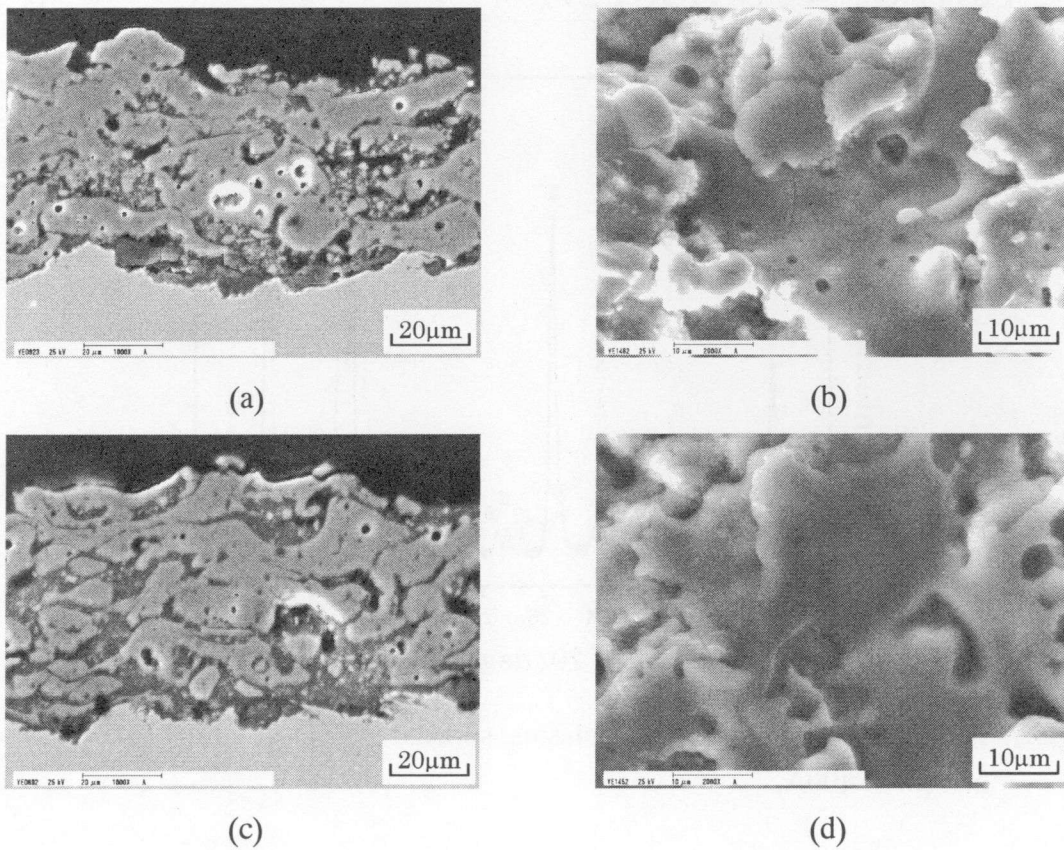


Fig.5.6. Cross sections and surface morphologies of FeTiO_3 (a, b) and TiO_2 -50% FeTiO_3 (c, d) coatings under the arc current of 400A.

5.3.2. Composition of FeTiO₃ and TiO₂-FeTiO₃ Coatings

The x-ray diffraction pattern of plasma sprayed FeTiO₃ coating under the arc current of 400A is illustrated in Fig.5.7. The FeTiO₃ coating consisted of rutile TiO₂, FeTiO₃, Fe₂TiO₅, Fe₂Ti₃O₉ and γ-Fe₂O₃ (Maghemite). Y. Chen et al. [2~4] reported that the thermal oxidation process of FeTiO₃ by high energy ball milling in air consists Reactions (5.1)~(5.3). The Fe₂Ti₃O₉ and γ-Fe₂O₃ 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 FeTiO₃ coatings.

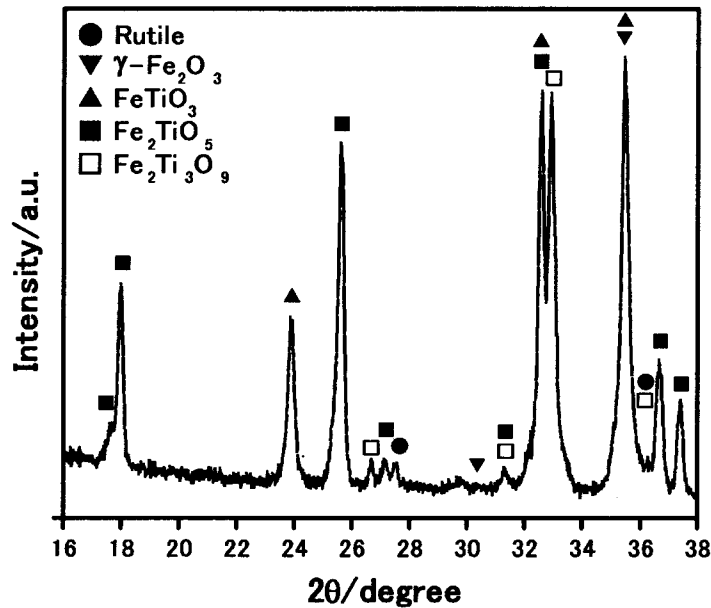
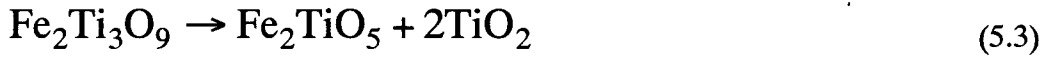
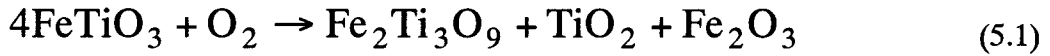


Fig.5.7. X-ray diffraction pattern of plasma sprayed FeTiO₃ coating under the arc current of 400A.

The TiO₂-30%FeTiO₃ coating under the arc current of 400A consisted of anatase TiO₂, rutile TiO₂ and FeTiO₃ as illustrated in Fig.5.8. Under the arc current of 400A, large part of anatase TiO₂ and FeTiO₃ still existed in it, and Fe₂TiO₅ and Fe₂Ti₃O₉ phase were

undetectable. With the increasing of arc current to 600A or 800A, Fe₂TiO₅, Fe₂Ti₃O₉ and Fe₂O₃ phases appeared in the sprayed coatings.

With the increase of the weight content of FeTiO₃ to 50% in the TiO₂-FeTiO₃ feedstock powder, Fe₂Ti₃O₉ and Fe₂TiO₅ phases appeared in spite of the low arc current of 400A as illustrated in Fig.5.9.

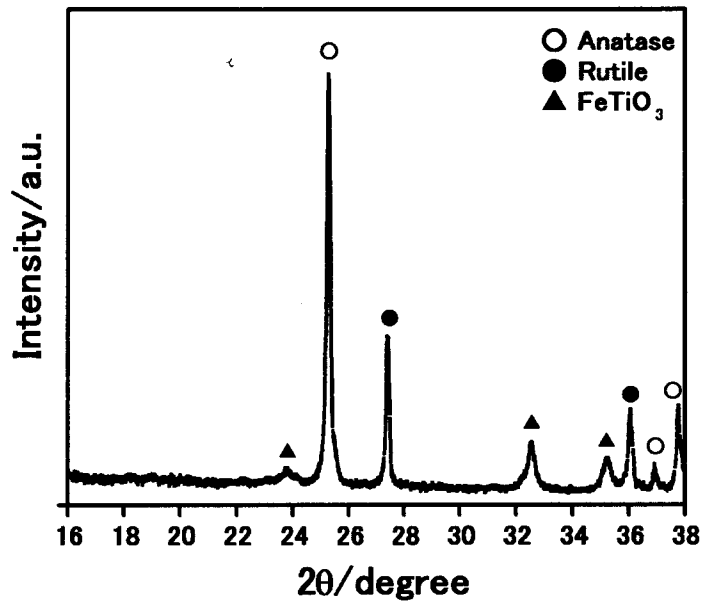


Fig.5.8. X-ray diffraction pattern of plasma sprayed TiO₂-30%FeTiO₃ coating under the arc current of 400A.

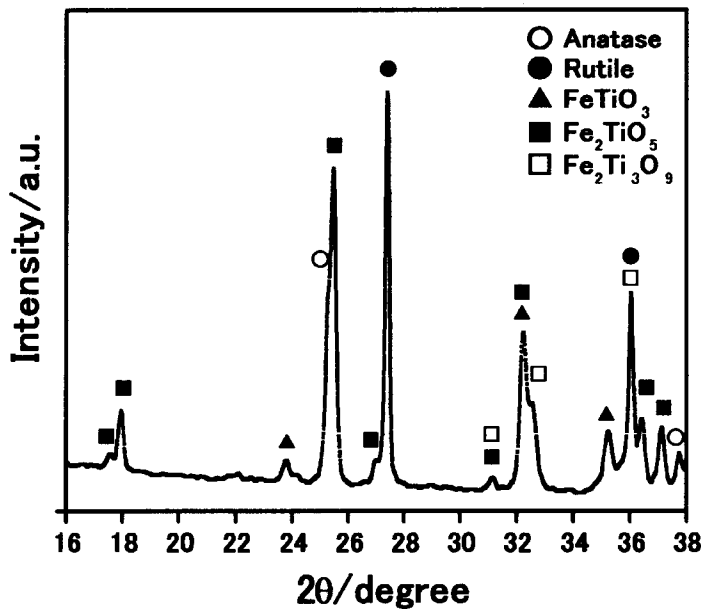


Fig.5.9. X-ray diffraction pattern of plasma sprayed TiO₂-50%FeTiO₃ coating under the arc current of 400A.

5.3.3. Photocatalytic Activity of FeTiO₃ and TiO₂-FeTiO₃ Coatings

Figure 5.10 illustrates the decomposition characteristics of the acetaldehyde by TiO₂, TiO₂-30%FeTiO₃ and FeTiO₃ feedstock powders.

Although FeTiO₃ can absorb visible light, the initiated electron may easily recombine with hole generated in FeTiO₃. Thus the pure FeTiO₃ powder did not show photocatalytic activity. The photocatalytic activity of TiO₂ powder was higher than that of TiO₂-30%FeTiO₃ powder. Because the TiO₂-30%FeTiO₃ powder was manufactured by agglomeration of TiO₂ particle with FeTiO₃ particle using polyvinyl alcohol (PVA) as binder, the TiO₂ was separated with FeTiO₃ particle by binder. Therefore, it is inferred that the initiated electron in the conduction band of TiO₂ can not inject to the conduction band of FeTiO₃, which resulted in the relative low photocatalytic activity of TiO₂-30%FeTiO₃ feedstock powder comparing with that of agglomerated TiO₂ powder. However, the PVA (C, H, O organic substance) have little influence on the properties of the sprayed coating, because PVA vaporizes over 550K and decomposes in plasma spraying processes.

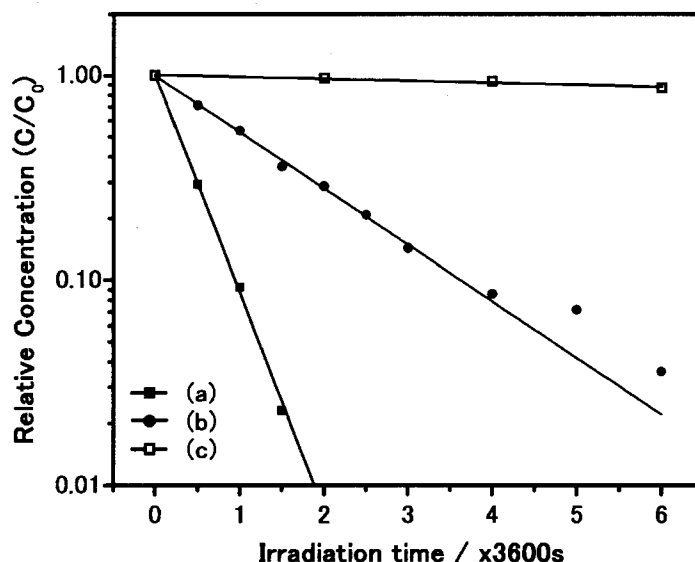


Fig.5.10. Decomposition characteristics of the acetaldehyde by agglomerated TiO₂ (a), TiO₂-30%FeTiO₃ (b), and FeTiO₃ (c) feedstock powders.

Figure 5.11 illustrates the decomposition characteristic of the acetaldehyde by plasma sprayed FeTiO₃ coating under the arc current of 400A. The τ values of the plasma sprayed FeTiO₃ coatings are shown in **Fig.5.12**. The results reveal that the FeTiO₃ coatings nearly had not photocatalytic activity.

The decomposition characteristics of the acetaldehyde by plasma sprayed TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ coatings are illustrated in **Fig.5.13**, and their τ values are shown in **Fig.5.14**. Because the TiO₂-30%FeTiO₃ coating sprayed under the arc current of 400A consisted of TiO₂ and FeTiO₃ only, and did not contain the unfavorable phase of Fe₂TiO₅ as discussed in Section 5.3.2 and large part of PVA combusted for the high temperature of plasma jet according to the EDAX analysis results, the photocatalytic activity was better than that of the other sprayed coatings.

As a result, the compositions of the sprayed coatings have great influence on the photocatalytic activity. Although pure FeTiO₃ compound has not photocatalytic property, the existence of FeTiO₃ could improve the photocatalytic activity of anatase TiO₂ if FeTiO₃ contacts coherently with TiO₂, which was explained using two-steps electron transfer model given in Chapter 4.

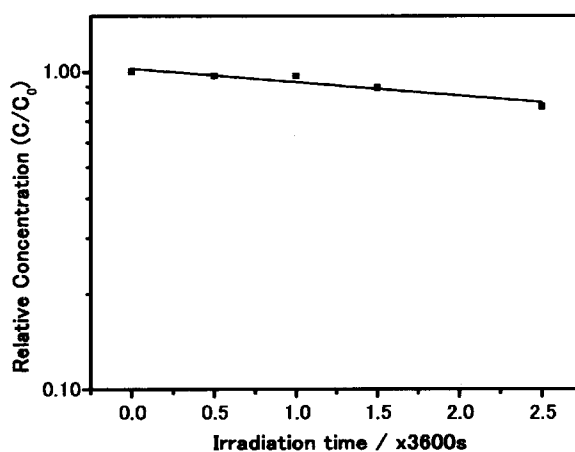


Fig.5.11. Decomposition characteristic of the acetaldehyde by FeTiO₃ coating sprayed under the arc current of 400A .

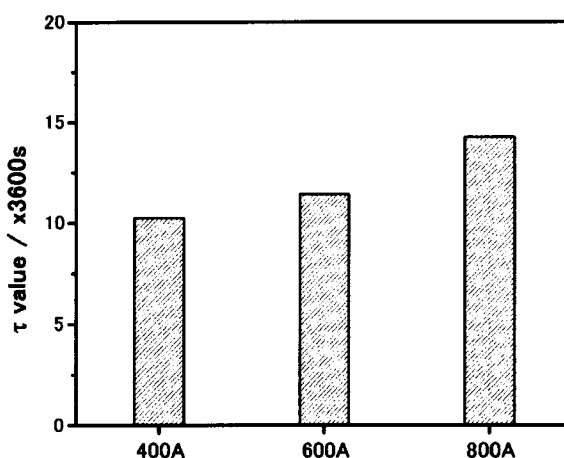


Fig.5.12. τ values of plasma sprayed FeTiO₃ coatings under the arc current of 400A, 600A and 800A.

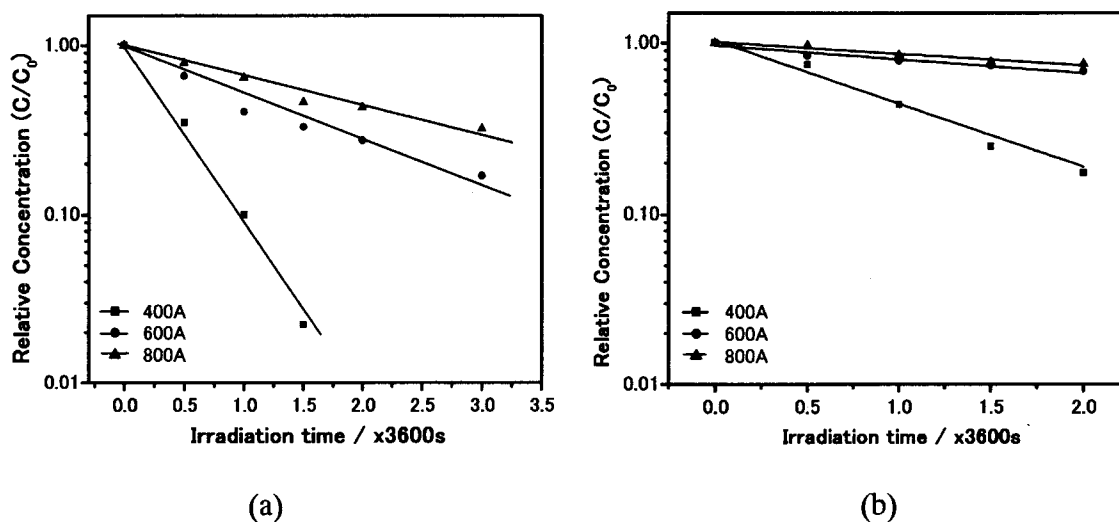


Fig.5.13. The decomposition characteristics of the acetaldehyde by the sprayed TiO₂-30%FeTiO₃ coatings (a) and TiO₂-50%FeTiO₃ coatings (b) under the arc current of 400A, 600A and 800A.

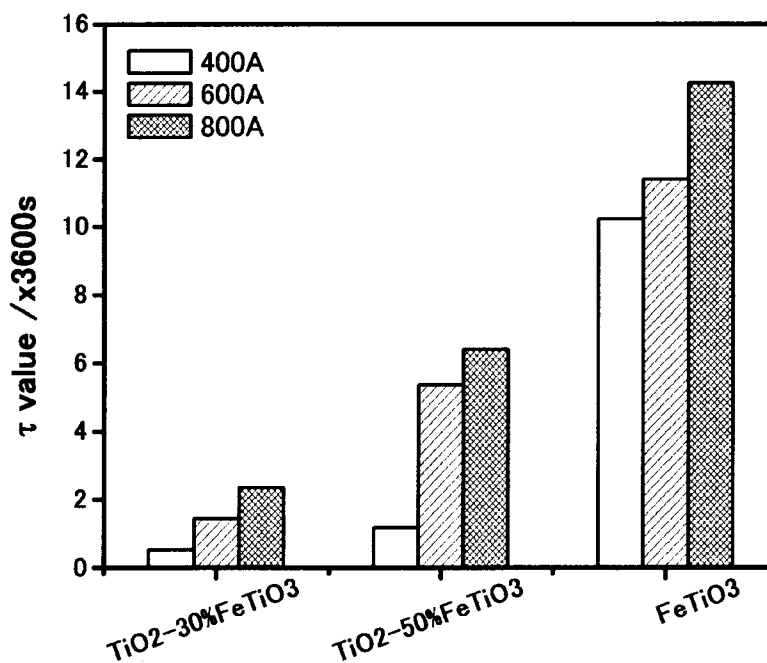


Fig.5.14. τ values of plasma sprayed FeTiO₃, TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ coatings under the arc current of 400A, 600A, 800A.

5.4. Conclusions

The composition and photocatalytic activity of plasma sprayed FeTiO₃, TiO₂-30%FeTiO₃ and TiO₂-50%FeTiO₃ coatings were investigated. The influence of FeTiO₃ compound on the photocatalytic activity of TiO₂ coating was clarified. The TiO₂-30%FeTiO₃ coating sprayed under the arc current of 400A had good photocatalytic activity because the coating did not contain the unfavorable Fe₂TiO₅ phase. However, the relative deposition speed of TiO₂-30%FeTiO₃ powder under the arc current of 400A, which was approximate to 4μm/pass, was very low. Although pure FeTiO₃ compound nearly did not show photocatalytic performance, the existence of FeTiO₃ could improve the photocatalytic activity of anatase TiO₂ if FeTiO₃ contacts coherently with TiO₂, which was explained using two-steps electron transfer model given in Chapter 4.

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CHAPTER 6

Photoelectrochemical Characteristics of TiO₂ and TiO₂-Fe₃O₄ Electrodes

6.1. Introduction

The radiant energy on the earth surface from the sun is 420 to 1260 J/m² [1]. Recently, electrochemical reactions on semiconductor electrodes have been investigated extensively. The “photo-sensitized electrolytic reaction” on an illuminated semiconductor electrode is one of the most interesting features of semiconductor electrochemistry[2~5], and the idea of using multiple-band-gap cells in order to capture a greater fraction of the solar spectrum has motivated much work in the area of photovoltaic solar cells [2].

Photocatalysis by semiconductor is the result of the interaction of electrons and holes generated in an activated solid with the surrounding medium [6]. The activation behavior has similarity to that of Si solar cell. As discussed in Chapter 4, multiple-band-gap photocatalytic reaction cell formed in composite TiO₂-10%Fe₃O₄ coating. Moreover, FeTiO₃ is a kind of p-type semiconductor [7~9], and TiO₂ is a kind of n-type semiconductor [10, 11], thus solid p-n junction formation in the sprayed coating is possible in thermal spraying processes.

The formation of 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 thin splat/lamellae, the stacking of which constitutes the deposit (**Fig.6.1**) [12, 13]. It is easy to deposit composite coatings by plasma spraying technique if the feedstock powders are composite materials. The composite substances may react with each other and then produce new compounds in plasma spraying processes; and the interface between two kinds of compounds is very large because the droplets spread to very thin lamellae (micron order). Therefore, the formation of microelectrochemical cell between two individual splats is reasonable. One splat is photo-anode and another is regarded as photo-cathode.

With respect to these suppositions, investigations on the photoelectrochemical characteristics of plasma sprayed TiO₂ and TiO₂-10%Fe₃O₄ electrodes were motivated.

The photocatalytic activity of TiO₂ and TiO₂-10%Fe₃O₄ coatings was evaluated. TiO₂-10%Fe₃O₄ splat was formed and its element distributions were analyzed. These results are presented in this chapter.

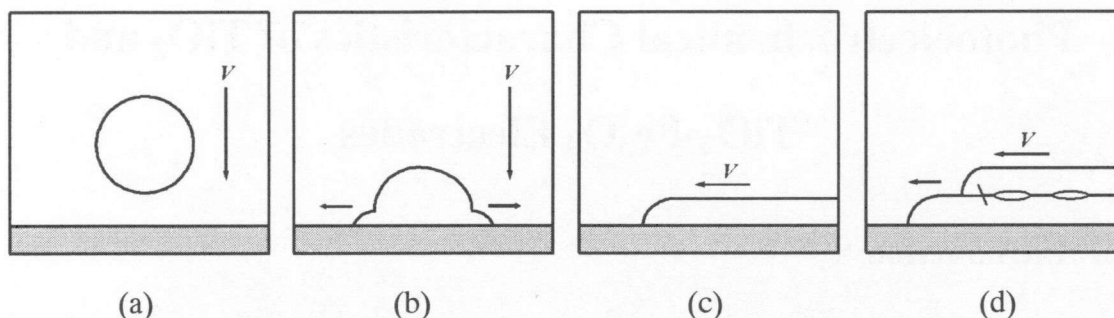


Fig.6.1. Coating formation processes by thermal spraying. (a) Flying of melted particle, (b) Impacting of droplet, (c) Flattening of droplet, (d) Solidification and stacking of splat.

6.2. Materials and Experimental Procedures

6.2.1 Feedstock Powders and Substrates

The feedstock powders were agglomerated TiO₂ powder and TiO₂-10%Fe₃O₄ composite powder. The substrate for electrode or coating preparation was stainless steel (JIS SUS304). However, to analyze the Fe element distribution in the splat, the substrate for splat formation was copper, or else the Fe element from steel substrate will disturb the EDAX analysis.

6.2.2. Plasma Spraying Equipment

The thermal spraying equipment was a plasma spraying system (Plasmadyne-Mach1 manufactured by Plasmadyne Company). The thermal spraying parameters are given in **Table 6.1**.

Table 6.1 Plasma spraying parameters.

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

6.2.3. Splat Preparation Set-up and Procedures

The schematic diagram of the set-up used for splat formation is shown in **Fig.6.2**. To get the individual splat, the diameter of the holes of mask was 1mm. The distance from plasma gun to the substrate was 70mm, which was the same with the spraying distance applied for coating or electrode preparation.

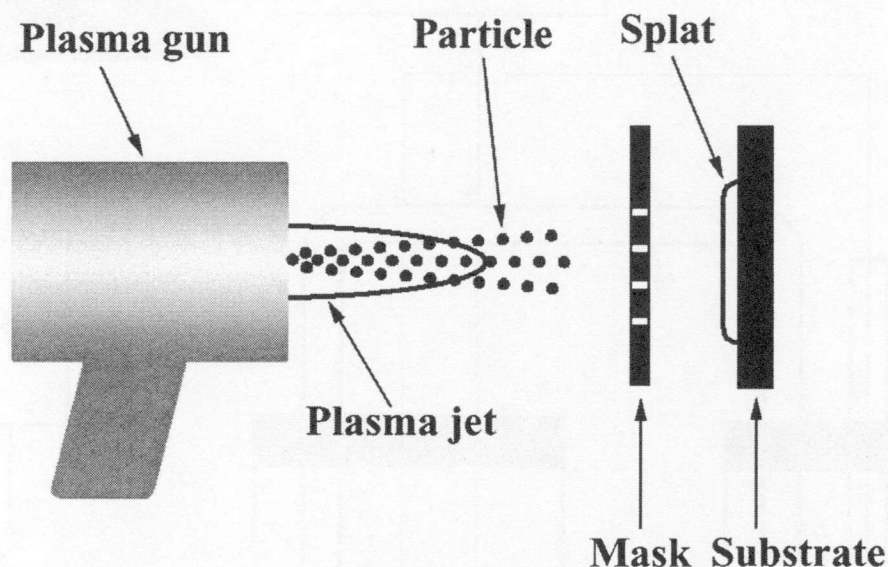
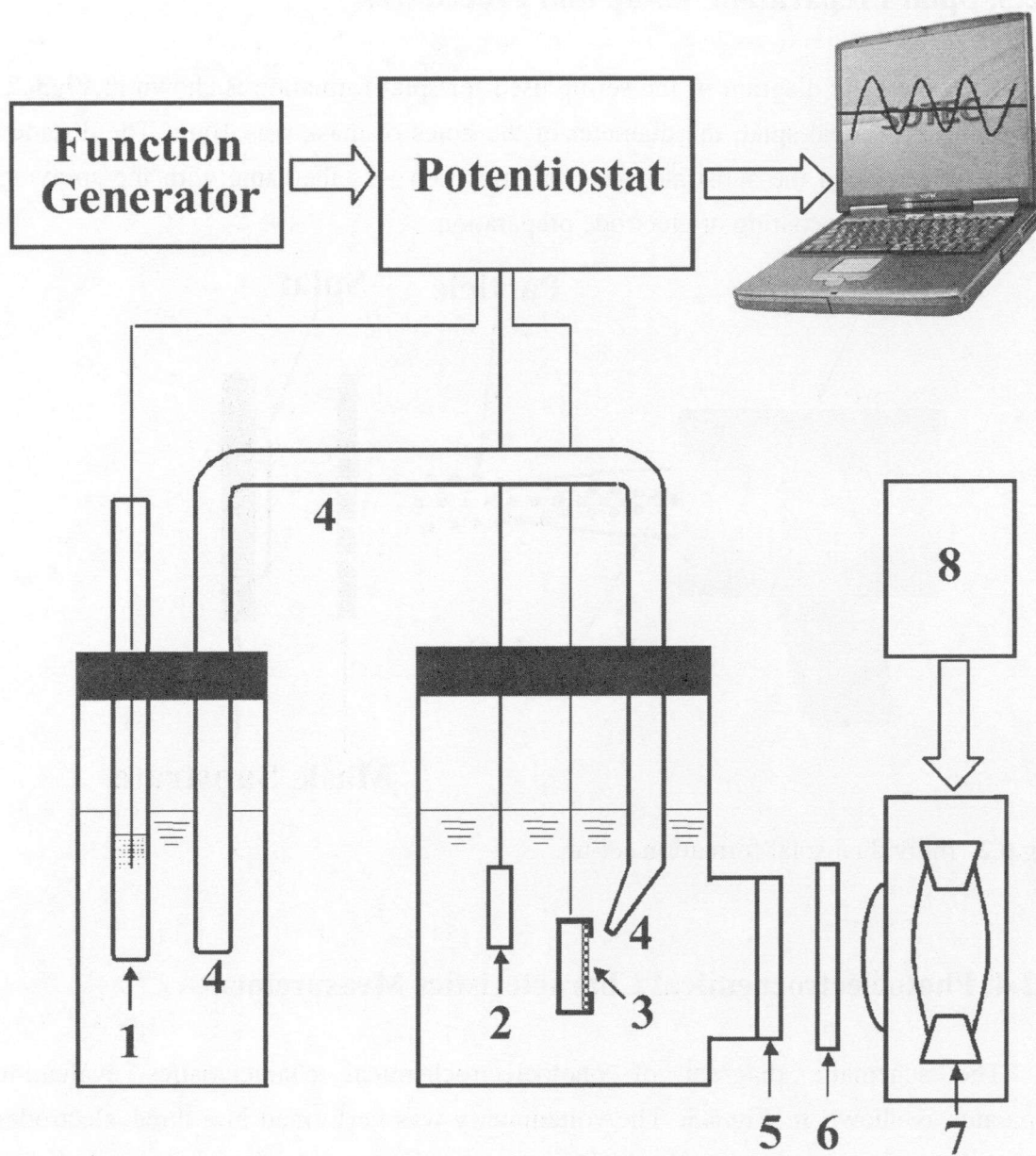


Fig.6.2. Individual splat formation set-up.

6.2.4. Photoelectrochemical Characteristics Measurement

The schematic diagram of photoelectrochemical characteristics evaluation apparatus is shown in **Fig.6.3**. The voltammetry was performed in a three electrodes glass cell at room temperature, in which a commercial saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate (30×30mm) as the counter electrode. The electrolyte was 0.1N NaOH solution and deaerated by purging with Ar gas for 30 minutes before the experiments. The photocurrent against potential at each sprayed electrode (10×10mm) was measured using a scanning potentiostat and recorded by a personal computer through an AD converter (NR-110, KEYENCE company). The sweep speed of the potential was 2mV/s in every experiment except in the transient photocurrent measurement experiment. A 500W xenon lamp was used as light source and the light intensity was measured by a UV radiometer (UVR-2, TOPCON, Tokyo, Japan) with UD-40 detector.



- | | |
|--------------------------------|-------------------|
| 1. Saturated calomel electrode | 5. Quartz window |
| 2. Counter electrode | 6. Optical filter |
| 3. Working electrode | 7. Xe lamp |
| 4. NaOH solution | 8. Power supply |

Fig.6.3. Photoelectrochemical characteristics measurement set-up.

6.2.5. Photocatalytic Activity Evaluation Method

The photocatalytic activity of the sprayed coatings was evaluated through the degradation of acetaldehyde under 1mW/cm² ultraviolet light irradiation. The τ value was calculated by Equation (2.6). The details are given in Chapter 2.

6.2.6. General Characterization

The microstructure and phase characterization of the sprayed coatings and splat were performed by electron probe surface roughness analyzer, energy dispersive analysis of x-ray (ERA-8800FE, Elionix Co. Ltd., Japan) and x-ray diffraction (M03XHF, MAC Science Co. Ltd.).

6.3. Results and Discussion

6.3.1. Structure and Composition of TiO₂ and TiO₂-10%Fe₃O₄ Coatings

The surface morphologies and cross sections of TiO₂ and TiO₂-10%Fe₃O₄ coatings prepared by plasma spraying under the arc current of 600A are shown in Fig.6.4. In the figures, “U”, “P” and “M” denote un-melted zone, partially melted zone and melted zone, respectively. The TiO₂ powders were not melted fully. The TiO₂ coatings were not very dense, contained many holes. Un-melted or partially melted TiO₂-10%Fe₃O₄ particles in the TiO₂-10%Fe₃O₄ coating were fewer than TiO₂ particles in TiO₂ coating. The reasons are given in Chapter 4 in detail. Because the electric resistance is a factor to affect the photocurrent, the coating thickness (for electrode preparation) was about the same. In this study, the thickness of the sprayed coating used for electrode was approximate to 70 μ m as confirmed from Fig.6.4(b) and (d).

The EDAX analysis results of TiO₂ and TiO₂-10%Fe₃O₄ coatings sprayed under the arc current of 600A are illustrated in Fig.6.5. The Fe/(Ti+Fe) ratio in the sprayed TiO₂-10%Fe₃O₄ coating equaled to 0.12, which was directly comparable to that of the feedstock powder.

The x-ray diffraction patterns of plasma sprayed TiO₂ and TiO₂-10%Fe₃O₄ coatings are shown in Fig.6.6. As shown in Fig.6.6(b), the sprayed TiO₂-10%Fe₃O₄ coating consisted of rutile phase, anatase phase and iron titanium oxide. Furthermore, the x-ray diffraction intensity of the anatase TiO₂ was very low, which evidenced the melting state of TiO₂-10%Fe₃O₄ feedstock powder too.

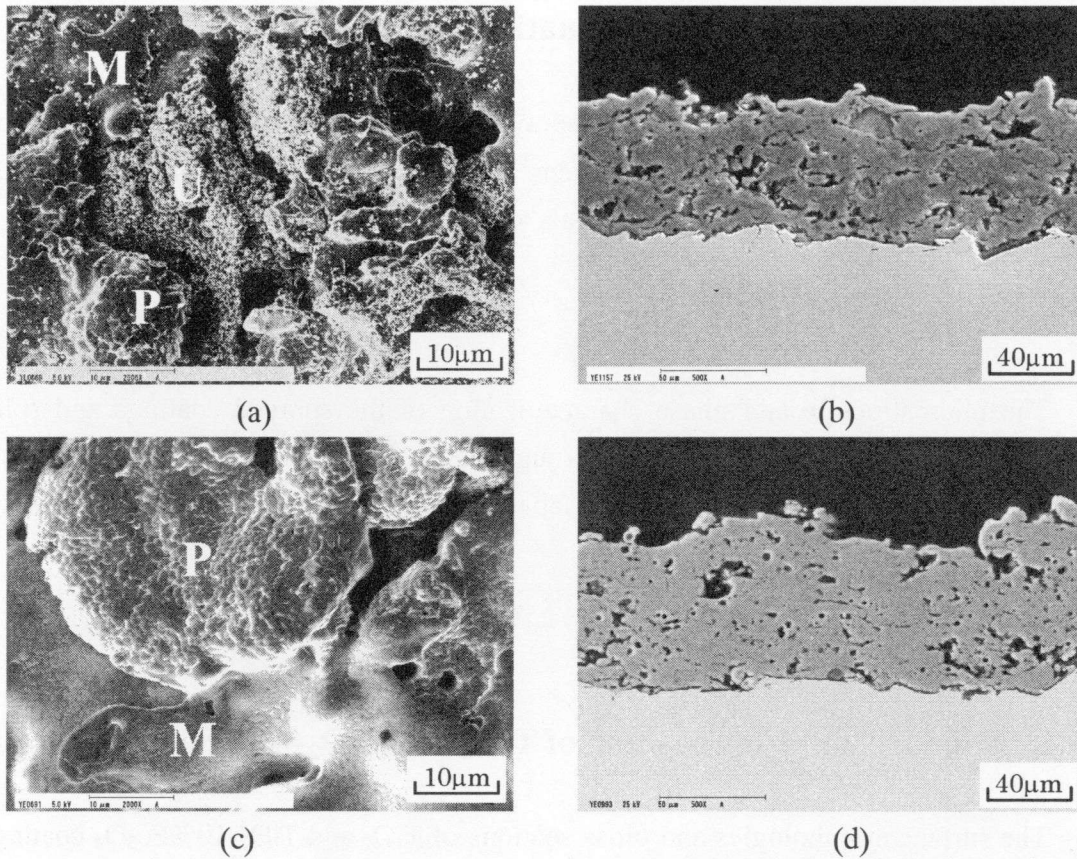


Fig.6.4. SEM views of coatings sprayed under 600A. (a) and (b) morphology and cross section of TiO_2 coating, respectively, (c) and (d) morphology and cross section of $\text{TiO}_2\text{-10}\%\text{Fe}_3\text{O}_4$ coating, respectively. (Notes: “U”, “P” and “M” denote un-melted zone, partially melted zone and melted zone, respectively.)

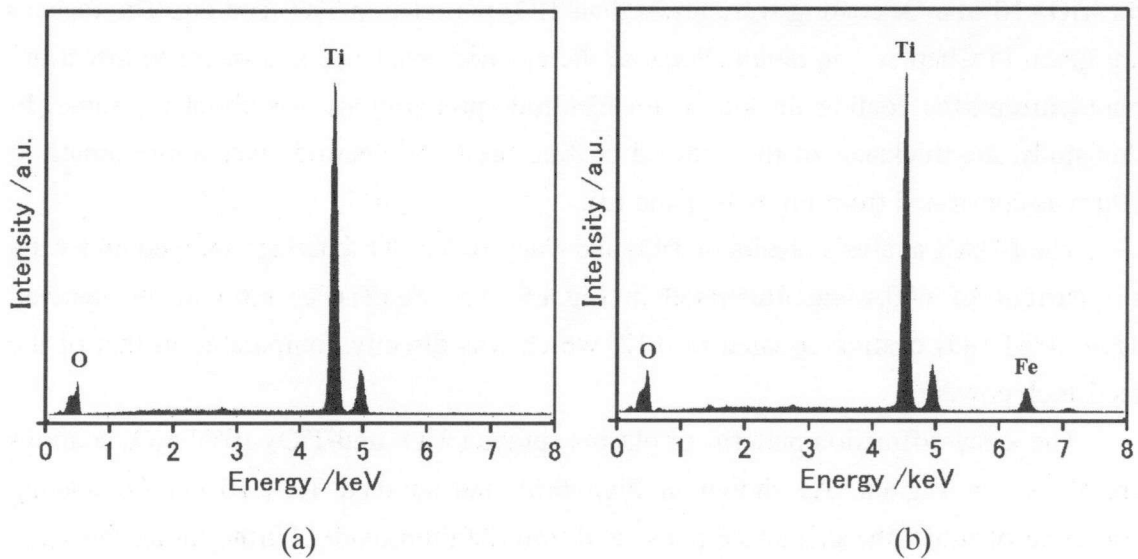


Fig.6.5. EDAX analysis results of TiO_2 (a) and $\text{TiO}_2\text{-10}\%\text{Fe}_3\text{O}_4$ (b) coatings plasma sprayed under the arc current of 600A.

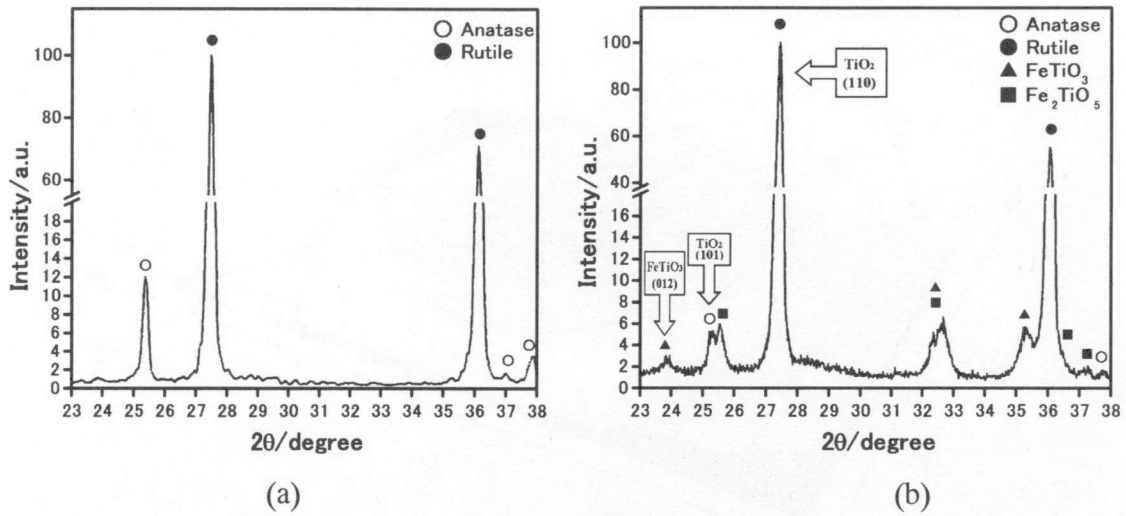
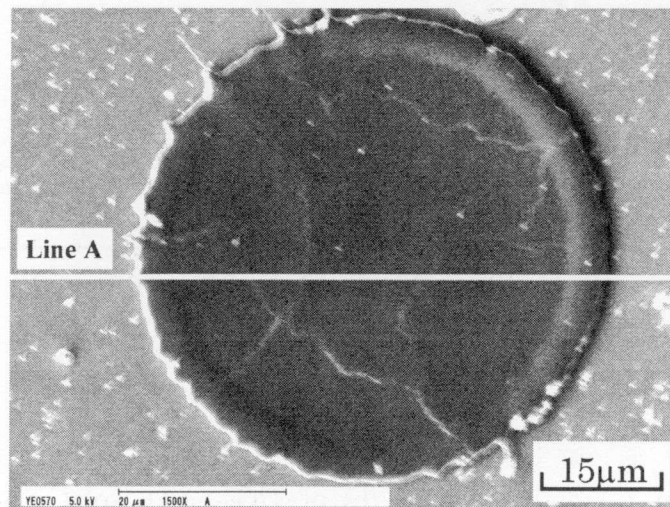


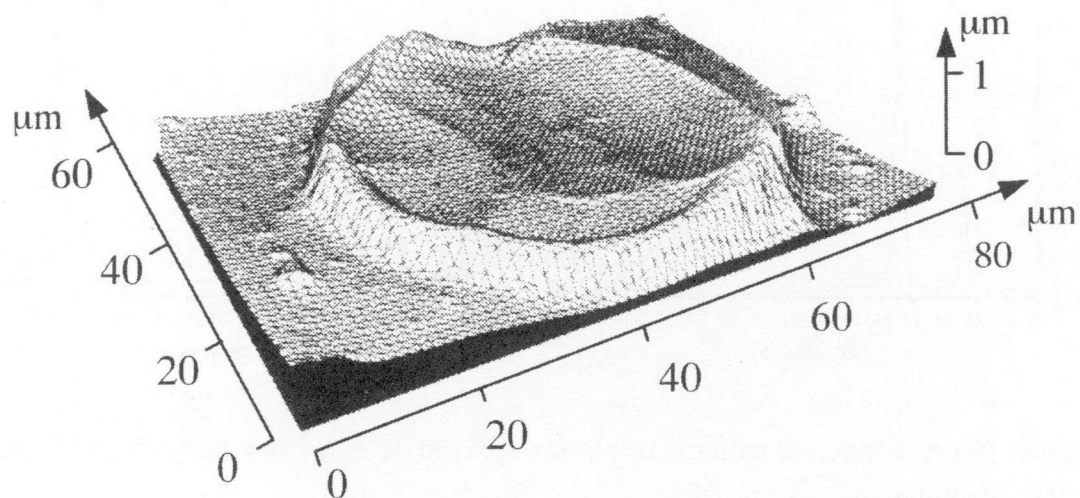
Fig.6.6. X-ray diffraction patterns of plasma sprayed TiO_2 (a) and $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ (b) coatings.

6.3.2. Characterization Results of $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ Splat

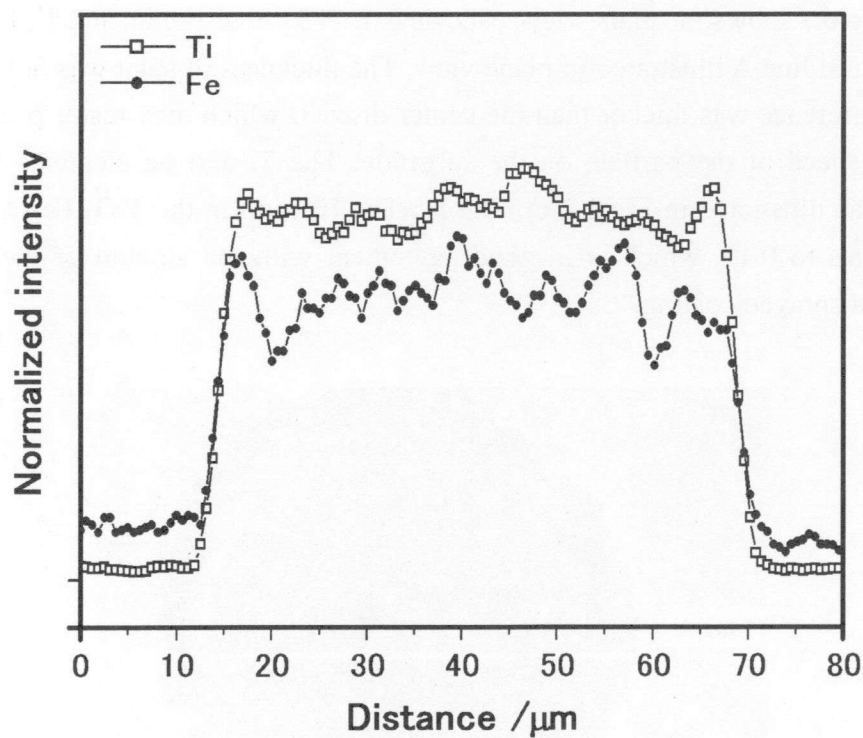
Figure 6.7 shows the plane view, 3-D view of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ splat, and Ti, Fe elements distribution of line A illustrated in plane view. The thickness of splat was not over $1\mu\text{m}$. The circumference was thicker than the center district, which may result from the high impacting speed of the particle on the substrate. The Ti and Fe elements distributed uniformly as illustrated in Fig.6.7(c). The $\text{Fe}/(\text{Fe}+\text{Ti})$ ratio in the $\text{TiO}_2\text{-Fe}_3\text{O}_4$ splat was approximates to 0.12, which is in good agreement with the amount of the feedstock powder and sprayed coating.



(a)



(b)



(c)

Fig.6.7. Plane view (a) and 3-D view (b) of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ splat, and Ti, Fe element distributions (c) of line A illustrated in plane view.

6.3.3. Photocatalytic Activity of TiO₂ and TiO₂-10%Fe₃O₄ Coatings

The photocatalytic decomposition characteristics of acetaldehyde by prepared TiO₂ and TiO₂-10%Fe₃O₄ coatings are illustrated in Fig.6.8. The photocatalytic degradation efficiency (reciprocal of τ value) of TiO₂-10%Fe₃O₄ coating was approximately two times than that of TiO₂ coating as shown in Fig.6.9. The good photocatalytic activity of TiO₂-10%Fe₃O₄ coating resulted possibly from the good light absorbance and the good electron transfer character of the coating. With respect to electron transfer action, the details are given in Chapter 4. When the TiO₂-10%Fe₃O₄ coating 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-steps electron transfer mechanism, the lifetime of initiated electron-hole pair becomes longer.

Another reason for the good photocatalytic activity of TiO₂-10%Fe₃O₄ coating is given in Section 6.3.5.

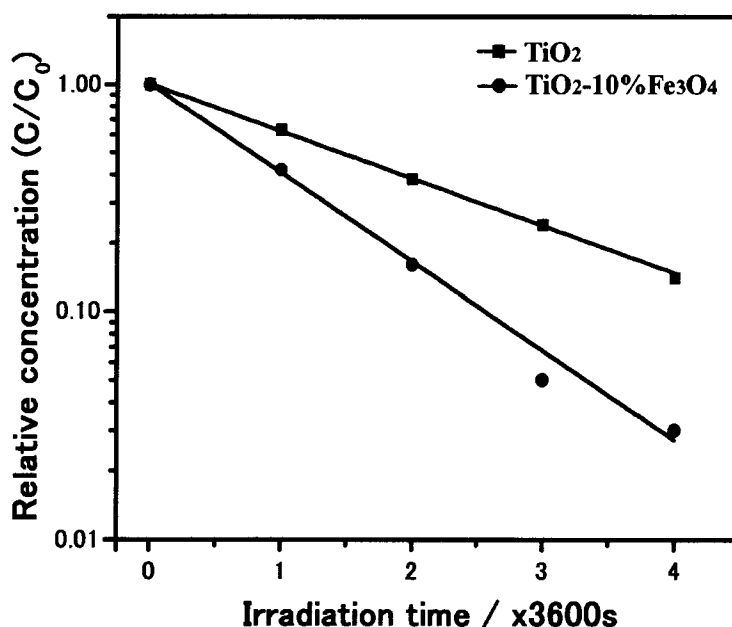


Fig.6.8. Photocatalytic decomposition characteristics of the acetaldehyde by the TiO₂ and TiO₂-10%Fe₃O₄ coatings sprayed under the arc current of 600A and spraying distance of 70mm.

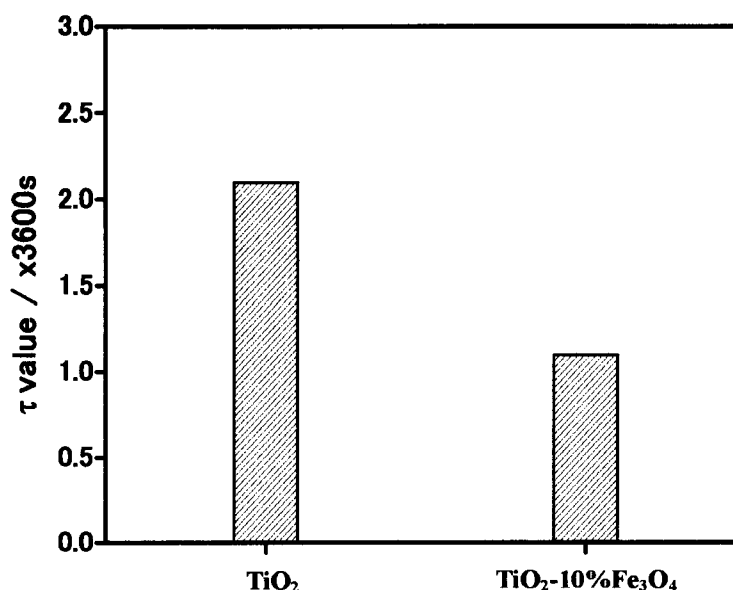


Fig.6.9. τ values of TiO₂ and TiO₂-10%Fe₃O₄ coatings sprayed under the arc current of 600A and spraying distance of 70mm.

6.3.4. Photoelectrochemical Characteristics of TiO₂ and TiO₂-10%Fe₃O₄ Electrodes

The use of n-type wide-bandgap semiconductor (SC) as photo-electrode in photoelectrochemical cells has been widely developed since A. Fujishima and K. Honda reported in 1972 that water could be photo-electrolyzed at an n-TiO₂ electrode illuminated with UV light. It is well established that water photoelectrolysis in a photoelectrochemical cell (PEC) is the result of two processes. Firstly, photons are absorbed by the SC and generate electron-hole pairs. Secondly, those pairs are separated by the electrostatic field, the electrons migrating toward the bulk and the holes toward the surface. The study of the transient photocurrent-time behaviour, frequently observed with semiconductor electrodes in a PEC, has been used by different authors as an interesting tool for the analysis of the mechanisms of charge at the SC/electrolyte interface [14]. **Fig.6.10** shows a typical photocurrent-time profile of TiO₂ electrode with hand-chopped light. An anodic photocurrent spike appeared immediately after the light was turned on, and then decreased continuously with time until a steady state photocurrent reached. When the light was turned off, the photocurrent decreased quickly down to zero. The initial anodic photocurrent spike was due to instantaneous photo-induced electron transitions to the conduction band as discussed by P. Salvador et

al. [14] and C. Liu et al. [15]. This kind of phenomenon was also observed for single crystal TiO₂ and polycrystalline TiO₂ [14–16].

Figure 6.11 illustrates the photocurrent-potential curves with and without light irradiation of the TiO₂ electrode prepared under arc current of 600A. The photocurrent increased obviously from the applied potential of -0.6V to -0.3V, and then increased slightly till to 0.4V, and finally broke. The photo-response characteristic of the sprayed electrode was comparable to that of single crystal TiO₂, but the breakdown voltage was approximately 0.5V (vs. SCE), which is similar to the plasma sprayed electrode prepared by R. Wang [17]. The short-circuit current (J_{sc}) of TiO₂ electrode was 1.05mA/cm² under 30mW/cm² light illumination from xenon lamp, and it increased linearly with the light intensity as shown in **Fig.6.12**. It implied that the light absorption coefficient (α) was very small.

Figure 6.13 illustrates the photocurrent-potential curves with and without light irradiation of the TiO₂-10%Fe₃O₄ electrode prepared under arc current of 600A. The photocurrent increased slightly from the applied potential of -0.6V to 0.4V, and then broke over 0.5V. The short-circuit current (J_{sc}) of TiO₂-10%Fe₃O₄ electrode was 0.07mA/cm² under 30mW/cm² light illumination from xenon lamp, which was notably lower than that of TiO₂ electrode. However, the bubbles (came from water photolysis) formation speed from TiO₂-10%Fe₃O₄ electrode was obviously higher than that from the latter.

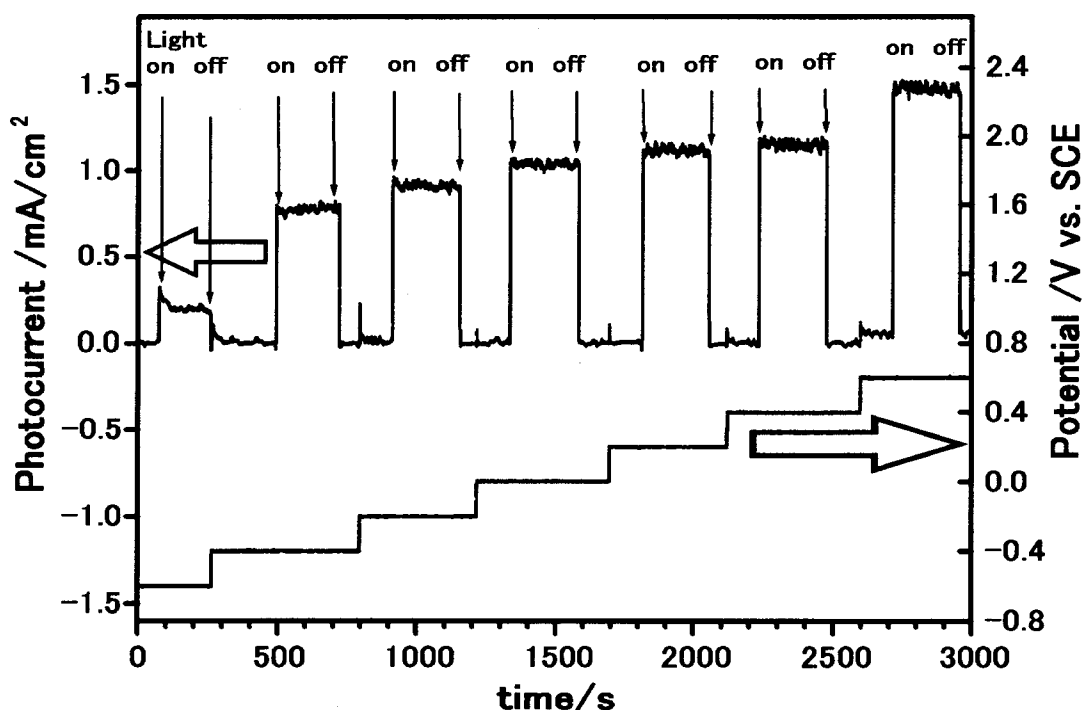


Fig.6.10. Typical photocurrent-time profile of TiO₂ electrode with hand-chopped light.

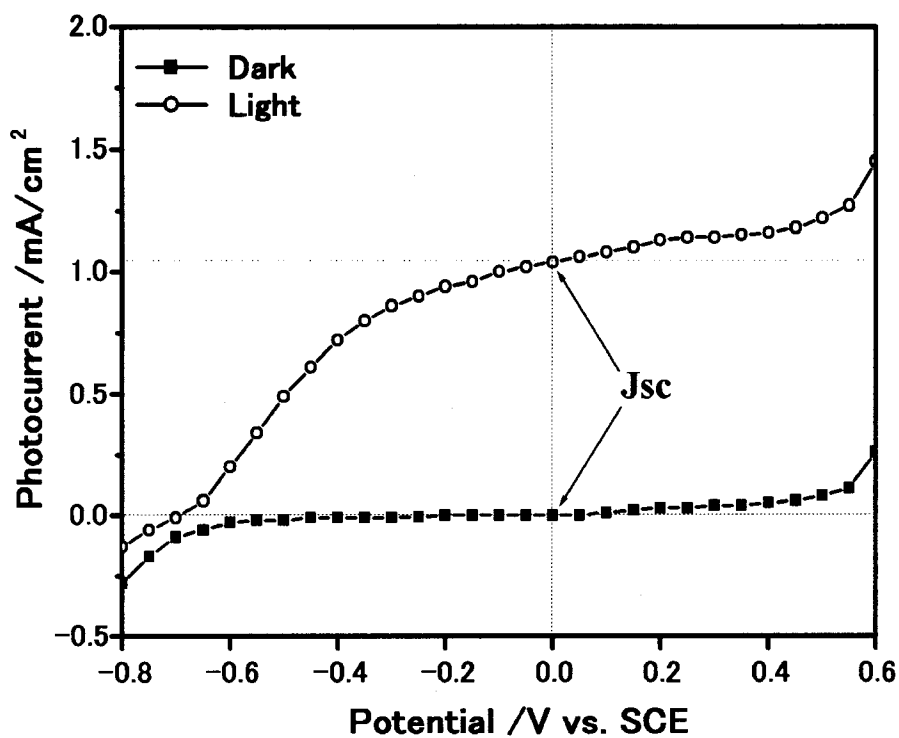


Fig.6.11. Photocurrent-potential curves with and without light irradiation of the TiO_2 electrode prepared under arc current of 600A.

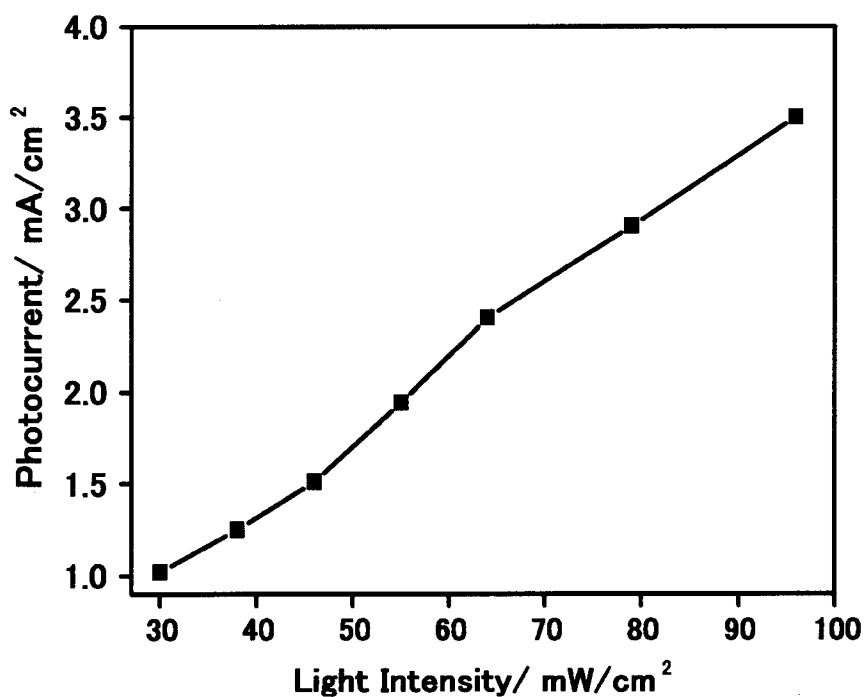


Fig.6.12. Relation between short-circuit photocurrent and light intensity of TiO_2 electrode.

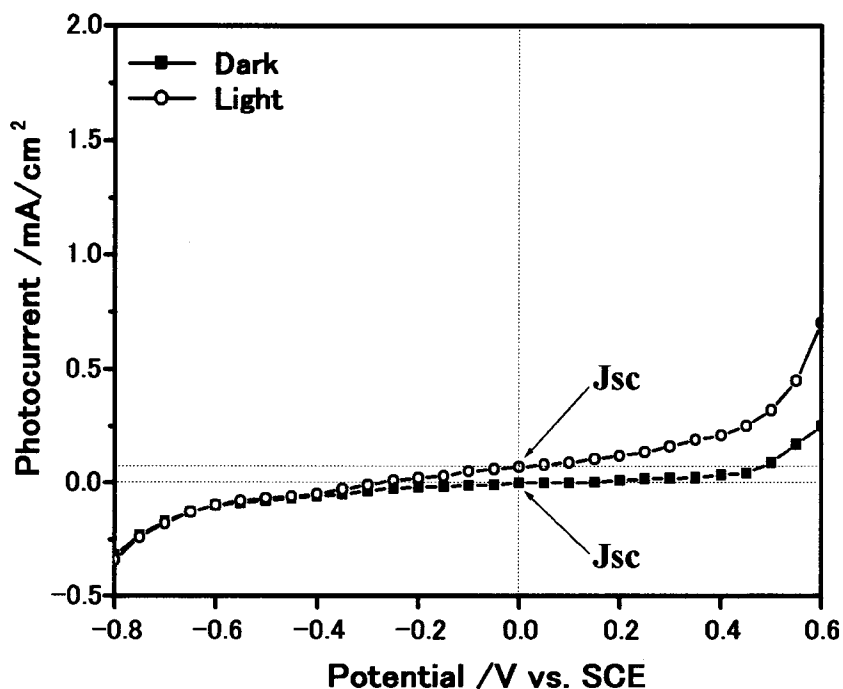


Fig.6.13. Photocurrent-potential curves with and without light irradiation of TiO₂-10% Fe₃O₄ electrode prepared under arc current of 600A.

6.3.5. P-N Junction Formation Model

According to the x-ray diffraction pattern, the n-type TiO₂ semiconductor particle reacted with Fe₂O₃ or Fe₃O₄ particle and concurrently produced p-type FeTiO₃ in the TiO₂-10%Fe₃O₄ coating, thus solid p-n junction formation in the sprayed coating is possible in thermal spraying process.

The bubbles (came from water photolysis) formation speed from TiO₂-10%Fe₃O₄ electrode was higher than that from TiO₂ electrode. Furthermore, H₂ and O₂ generation coincided on TiO₂-10%Fe₃O₄ electrode. Moreover, the short-circuit current (J_{sc}) of TiO₂-10%Fe₃O₄ electrode was notably lower. These facts implied that the FeTiO₃/TiO₂ island acted as micro-photoelectrolysis cell in a short circuit configuration in TiO₂-10%Fe₃O₄ coating. Therefore, the existence of solid p-n junction between p-type FeTiO₃ and n-type TiO₂ was confirmed.

According to the above mentioned results and the special particle flattening phenomenon in plasma spraying process, a p-n junction formation model in plasma sprayed TiO₂-10%Fe₃O₄ coating is illustrated in Fig.6.14(a). In fact, an agglomerated

$\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ powder contains many micro TiO_2 particles with average diameter of $0.2\mu\text{m}$, therefore, it is reasonable that one small splat flattened from primary TiO_2 particle may generate a micro p-n junction with FeTiO_3 , and then it is inferred that a $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ splat shown in Fig.6.7(a) comprised a lot of micro p-n junctions. Fig.6.14(b) shows the schematic diagram of electron-hole separation process in a p-n junction. The micro- TiO_2 and FeTiO_3 constituted innumerable micro-cell.

For the formation of micro p-n junction, which may spatially separate the photo generated electrons and holes as like Si solar cell, the photocatalytic activity of $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ coating was improved significantly as shown in Fig.6.8. Therefore, it is concluded that plasma spraying is a promising technique to deposit high performance photocatalytic coating for its special advantage.

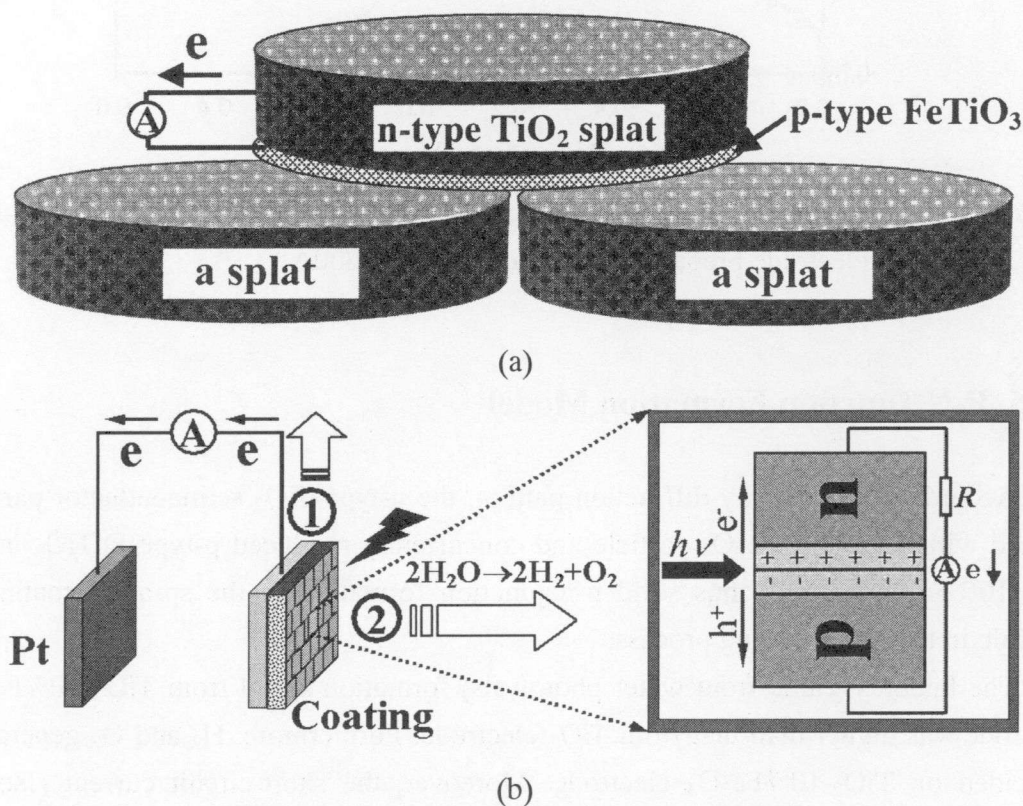


Fig.6.14. A proposed p-n junction formation model in $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$ coating (a) and schematic diagram of electron-hole separation process in p-n junction (b).

6.4. Conclusions

Photoelectrochemical characteristics of plasma sprayed TiO_2 and $\text{TiO}_2\text{-10\%Fe}_3\text{O}_4$

electrodes were investigated. The photo-response of the sprayed TiO₂ electrode was comparable to that of single crystal TiO₂, but the breakdown voltage was approximate to 0.5V (vs. SCE). The short-circuit current of TiO₂ electrode was 1.05mA/cm², which was 15 times than that of TiO₂-10%Fe₃O₄ electrode under 30mW/cm² light illumination from xenon lamp. FeTiO₃ compound obviously improved the photocatalytic activity of the TiO₂ coating for the formation of p-n junction, which may spatially separate the photo-generated electrons and holes. From these investigations, it is concluded that plasma spraying is a promising technique for manufacturing high performance photocatalytic coating.

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CHAPTER 7

Summary

In this dissertation, TiO₂ and composite TiO₂ coatings were deposited on stainless steel by plasma spraying technique. The microstructure, phase composition, photo absorbance and photocatalytic activity of sprayed coatings were investigated systematically. The photoelectrochemical characteristics of TiO₂ and TiO₂-10%Fe₃O₄ electrodes were studied in detail. Two-steps electron transfer model and p-n junction formation model were proposed. The content of each chapter is summarized as follows:

In **Chapter 1**, fundamental and general aspects of heterogeneous photocatalysis were briefly introduced after the emphasis of the importance of sustainable development. An overview of TiO₂ photocatalyst and the recent topics in photoelectrochemistry were described. The necessity for coating photocatalyst and the advantage of plasma spraying technique were given.

In **Chapter 2**, TiO₂ coatings were prepared by plasma spraying technique using agglomerated anatase TiO₂ powder. The content of anatase TiO₂ in the sprayed coatings was approximate to 7-15%. The anatase to rutile phase transformation temperature of agglomerated anatase TiO₂ powder was about 1173K. TiO₂ coating sprayed under the arc current of 400A had good photocatalytic activity for the relative high content of anatase phase in it. However, the relative deposition speed of powder, which was approximate to 5μm/pass, was very low. For the high temperature of plasma jet, it is not easy to fabricate high performance photocatalytic coatings by plasma spray using the pure anatase TiO₂ powder applying the technique of inhibiting anatase phase transformation.

In **Chapter 3**, phase composition, microstructure and photocatalytic activity of plasma sprayed TiO₂-10%Fe₃O₄, TiO₂-10%Al₂O₃, and TiO₂-10%Y₂O₃ composite coatings were characterized and discussed in detail. The addition of Fe₃O₄ to TiO₂ improved the anatase-rutile transformation. The anatase content of TiO₂ in the sprayed coating was affected by the melting degree of TiO₂ particle in thermal spraying process. Although the content of anatase TiO₂ was very low in the sprayed TiO₂-10%Fe₃O₄ coating, the photocatalytic activity was better than that of TiO₂ coating under the same spraying conditions, which implied the photocatalytic activity was not only controlled by anatase content of TiO₂. The relative deposition speed of TiO₂-10%Fe₃O₄ powder was 2.6 times comparing with that of TiO₂ powder under the arc current of 400A and

spraying distance of 70mm. However, the addition of Al_2O_3 and Y_2O_3 particle to TiO_2 particle had not favorable effect on the photocatalytic activity of TiO_2 coating. Therefore, the influence of additive on the photocatalytic activity of TiO_2 is greatly controlled by not only the kind of additive, but also by the synthetic process.

In **Chapter 4**, the influence of Fe_3O_4 content on the properties of TiO_2 coating was investigated. The results showed that the $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings consisted of anatase TiO_2 , rutile TiO_2 , and pseudobrookite Fe_2TiO_5 phase which appeared when the content of Fe_3O_4 additive was equal to or over 10%. With relative low amount addition of Fe_3O_4 , ilmenite FeTiO_3 phase existed in the sprayed coatings. The content of anatase TiO_2 in the sprayed coatings decreased with the increasing of Fe_3O_4 content. The photocatalytic activity was improved with an increase of FeTiO_3 content in the coating, which was explained by the good photo absorbance capacity and by two-steps electron transfer model. Moreover, initiated electrons could separate with holes easily because Fe^{2+} can be regarded as a trap of initiated electrons. However, the presence of large amount of Fe_2TiO_5 compound substantially reduced the photocatalytic efficiency of the sprayed $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings for the unfavorable electron-hole transfer process.

In **Chapter 5**, the composition and photocatalytic activity of plasma sprayed FeTiO_3 , $\text{TiO}_2\text{-30}\%\text{FeTiO}_3$ and $\text{TiO}_2\text{-50}\%\text{FeTiO}_3$ coatings were investigated. The influence of FeTiO_3 compound on the photocatalytic activity of TiO_2 coating was clarified. The $\text{TiO}_2\text{-30}\%\text{FeTiO}_3$ coating sprayed under the arc current of 400A had good photocatalytic activity because the coating did not contain the unfavorable Fe_2TiO_5 phase. However, the relative deposition speed of $\text{TiO}_2\text{-30}\%\text{FeTiO}_3$ powder under arc current of 400A, which was approximate to $4\mu\text{m/pass}$, was very low. Although pure FeTiO_3 compound nearly did not show photocatalytic performance, the existence of FeTiO_3 phase would improve the photocatalytic activity of anatase TiO_2 if FeTiO_3 contacts coherently with TiO_2 .

In **Chapter 6**, photoelectrochemical characteristics of plasma sprayed TiO_2 and $\text{TiO}_2\text{-10}\%\text{Fe}_3\text{O}_4$ electrodes were examined. The photo-response of the sprayed TiO_2 electrode was comparable to that of single crystal TiO_2 , but the breakdown voltage was approximate to 0.5V (vs. SCE). The short-circuit current of TiO_2 electrode was 1.05mA/cm^2 , which was 15 times than that of $\text{TiO}_2\text{-10}\%\text{Fe}_3\text{O}_4$ electrode under 30mW/cm^2 light illumination from xenon lamp. FeTiO_3 compound obviously improved the photocatalytic activity of the TiO_2 coating for the formation of p-n junction, which may spatially separate the photo-generated electrons and holes. From these investigations, it is concluded that plasma spraying is a promising technique for manufacturing high performance photocatalytic coating.

In **Chapter 7**, it gives a summary of whole dissertation.

Publication Lists

● Main Papers

- [1] **F. -X. Ye**, A. Ohmori and C. -J. Li, Formation of p-n junction by plasma spraying technique to enhance the photocatalytic activity of TiO₂, *Journal of Materials Science Letters*, (2003) (In press).
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- [3] **F. -X. Ye** and A. Ohmori, The influence of FeTiO₃ formation on the photocatalytic property of plasma sprayed TiO₂ coatings, *Journal of High Temperature Society*, Vol. 29(4) (2003) 160-163.
- [4] **F. -X. Ye** and A. Ohmori, Fabrication of advanced photocatalytic TiO₂ coatings by thermal spraying technique, *Thermal Spraying Technique*, Vol. 23(1) (2003) 45-51 (In Japanese).
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● International Conferences

- [1] **F. -X. Ye** and A. Ohmori, Photoresponse and donor concentration of plasma sprayed TiO₂ and TiO₂-ZnO electrodes, *Proceedings of the International Thermal Spray Conference 2004, 10-12 May 2004, Osaka, Japan*, (In press).

Publication Lists

- [2] **F. -X. Ye**, A. Ohmori and C.-J. Li, Investigation on the photocatalytic efficiencies of plasma sprayed $\text{TiO}_2\text{-Fe}_3\text{O}_4$ coatings, *Proceedings of the International Thermal Spray Conference 2003, 5-8 May 2003, Orlando, Florida, USA*, 169-174.
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