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Photo-catalytic Decomposition of Tetrachloroethylene (C₂Cl₄) by Plasma Sprayed TiO₂ Coatings[†]

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Abstract

TiO₂ coatings were prepared on a stainless mesh net by plasma spraying using agglomerated TiO₂ powder. Since TiO₂ powders are well known as photo-catalytic materials, the photo-catalytic TiO₂ coatings on mesh net are used for purification of water containing tetrachloroethylene (C₂Cl₄). It was found that TiO₂ agglomerated powders could be deposited on mesh net and approximately 35% anatase ratio could be obtained by 400A plasma spraying.

It was possible to obtain approximately 100 μm thicknesses on the stainless mesh net substrate when plasma spraying was carried out at 800A, while the coating thickness drastically decreased at 400A. In terms of photo-catalytic properties, retaining the anatase phase ratio in the TiO₂ coatings is essential to achieve photo-catalytic decomposition of 10ppm C₂Cl₄ solution. It was found that the anatase ratio decreased gradually with increasing arc current and pass count, while the coating thickness increased with increasing arc current. This means that 0.2μm agglomerated powders showed a lower susceptibility to heat effects and provided higher photo-catalytic activity.

It was cleared that the anatase ratio had large influence on the photo-catalytic activity. These coatings showed photo-catalytic degradation of C₂Cl₄ solution. As a result of photo-catalytic experiments, it was shown that tested C₂Cl₄ solution is decomposed in moderately shorter times, to the extent that 10ppm C₂Cl₄ was decomposed to less than 1ppm after 7.2ks of 400A plasma sprayed coating. Thermal spraying on stainless mesh net could imply both new applications and possibilities for photo-catalytic degradation of C₂Cl₄ solution.

KEY WORDS : (Agglomerated powder), (TiO₂), (Plasma spraying), (Anatase), (Rutile), (Tetrachloroethylene (C₂Cl₄)), (Photo-catalytic property)

1. Introduction

Volatile chlorinated organic compounds, such as tetrachloroethylene (C₂Cl₄) have been widely used as industrial solvents. Groundwater and soils supplies can become contaminated as a result of leaking underground storage tanks and improper disposal practices. The destruction of persistent organic chemicals in water is not only very important, it is an extreme environmental problem because these chemicals are toxic, carcinogenic and extremely persistent in the environment [1, 2].

From these points of view, the development of environmental cleanup methods should be carried out in order to degrade these contaminants.

The use of TiO₂ photo-catalyst for environmental cleanup has been of great interest, since TiO₂ is stable, harmless, not-expensive and potentially can be activated by solar energy [3].

The photo-excitation of Titanium dioxide (TiO₂) particles generates electron/hole pairs due to the adsorption of 390-nm or lower wavelength UV light. It is commonly acknowledged that such holes generate highly

reactive radicals, such as ·OH, which oxidize pollutant molecules [3].

However, in many cases, the powders have to be fixed on the target substrate for practical applications.

Although there have been many reports [4-8] about the preparation of thin film TiO₂ coatings such as sol-gel or similar thin film processes, a heat treatment for fixing is necessary in the sol-gel processes, hence the coating speed becomes very low. On the other hand, there are currently a few techniques which can deposit thick coatings. Plasma spraying is a typical example of these techniques, thermal sprayed coatings produce thick layers in short times. In addition, thermal sprayed coatings can be easily prepared on many type of materials such as metal plate and metal mesh net and ceramics.

Additionally, it is anticipated that if TiO₂ coatings can be deposited on stainless mesh net in short times, the fixed TiO₂ coating will show photo-catalytic activity for purification of water. By spraying on the mesh net, a high surface area of photo-catalytic reaction sites is expected to efficiently perform in liquid water containing C₂Cl₄. In

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terms of effective purification treatment of C₂Cl₄ solution, it is preferable that the C₂Cl₄ solution will flow smoothly under working photo-catalytic reaction.

However, none of the spraying conditions have been specified for achieving TiO₂ coatings on stainless mesh net. Therefore, TiO₂ deposition on stainless mesh net by thermal spraying was tried and one of the major objectives in this study is to investigate the basic behavior of the TiO₂ deposition on a mesh net substrate. It is expected that easy phase transformation to rutile phase occurs above the 973K during spraying [9,10], however, retaining the anatase phase is essential to achieve high photo-catalytic activity.

In this research, the influence of plasma spraying condition on the microstructure and transformation to rutile phase were investigated using agglomerated powder and then evaluating photo-catalytic activities.

2. Experimental

A Cu undercoat was first sprayed to increase adhesion strength between topcoats (TiO₂) and substrates.

The plasma spraying was carried out by Plasma Dyne Gun. Argon was employed as primary plasma gas and helium as a secondary gas. Table 1 shows plasma spraying conditions.

Fig. 1 shows the surface morphology of anatase TiO₂ powders with an average size of 33.7 μm. Polyvinyl alcohol (PVA) was used as a binder and feedstock powders were synthesized from 0.2 μm particles. X-ray diffraction with Cu K_α radiation was employed to detect anatase and rutile phases. From the X-ray diffraction results, the anatase phase ratio of the TiO₂ coating was estimated by the following equation (1) [10].

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

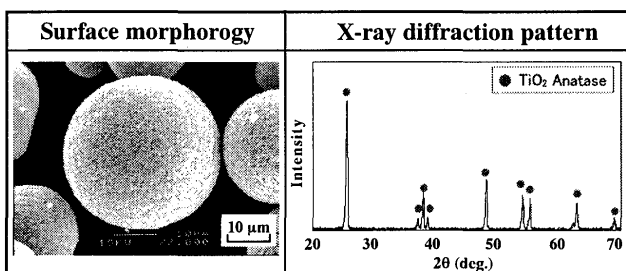


Fig. 1 Surface morphology and X-ray diffraction pattern of anatase-TiO₂ powders.

Table 1 The conditions of plasma spraying.

Flow rate (l/min) : Ar	57.7
Flow rate (l/min) : He	9.3
Spraying distance (mm)	70
Spraying atmosphere	Air
Arc current (A)	400~800
Arc voltage (V)	35~72
Traverse speed of gun (mm/s)	90
Spraying pass count	1, 4

In this research, the photo-catalytic decomposition experiment using a high pressure Hg lamp was introduced in the stirring reactor as shown in Fig. 2. The 10ppm tetrachloroethylene (C₂Cl₄) dissolved in water was selected as the test chemical solution to be treated. τ (ks) was used as decomposition time to evaluate photo-catalytic activity of TiO₂ coatings and τ value was defined as time when the concentration of C₂Cl₄ becomes C₀/e [11]. (C₀ : primary concentration of C₂Cl₄ before black light irradiation, e: a natural logarithm, C₀/e means that C₀ divided by e). A lower τ value means higher photo-catalytic activity and higher decomposition rate of dissolved C₂Cl₄ in water.

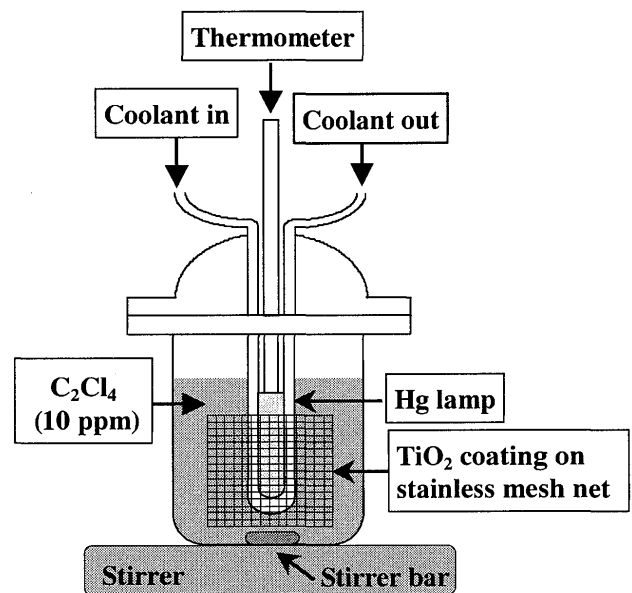


Fig. 2 Photo-catalytic reactor for decomposition of Tetrachloroethylene (C₂Cl₄) dissolved in water.

3. Results and Discussion

P₂₀₀ agglomerated powders were sprayed on stainless mesh net substrates by plasma spraying apparatus. Fig. 3 shows surface morphologies and cross sectional images of plasma sprayed TiO₂ coatings on mesh nets.

P₂₀₀ agglomerated anatase powders could be deposited on the mesh without clogging the filter in all sprayed conditions.

The thickness of TiO₂ coatings formed by plasma spraying was strongly dependent on arc current and pass count. It was possible to obtain approximately 100 μm thickness on the mesh net at 800A for 1pass, while at 400A the coating thickness drastically decreased. The average thickness was 10 μm at 400A.

According to the surface morphology as shown in Fig. 3 (f), TiO₂ coating formed by melt deposition on substrate was clearly observed. By comparing between Fig. 3 (d) and Fig. 3 (f), the spraying morphology on the mesh net could be clearly distinguished.

In contrast to Fig. 3 (d), the sprayed powders mainly retained spherical shapes on mesh net substrates as well as

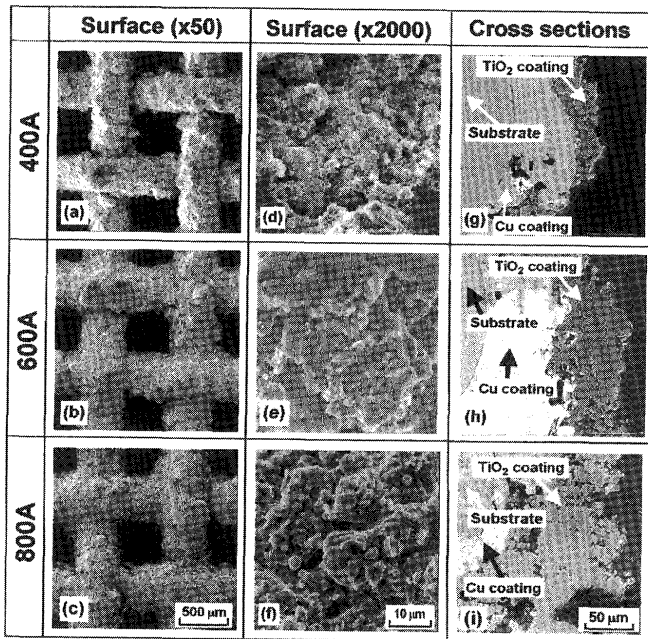


Fig. 3 The cross sectional images and surface morphologies of TiO₂ coatings formed by plasma spraying.

agglomerated powder since sprayed powders were not melted in the case of 400A spraying. However, in the case of more than 600A, non-melted powders tend to bounce off substrates, while partially and completely melted powders tended to bond to the substrate and consequently, the deposited coating on the mesh net was mainly formed by partially and completely melted powders. In addition, non-melted anatase powders tend to bond on melted rutile since both non-melted anatase powders and melted rutile powders were sprayed simultaneously toward to the substrate. Fig. 3 (e) shows a typical case of this kind of phenomenon.

Thus, individual non-melted agglomerated powders were clearly observed in Fig. 3 (d) after 1 pass spraying, whereas agglomerated spherical powder was not clearly observed in the deposited coating when 800A spraying was carried out because the melted bond has changed completely as a result of high speed impacting and the high temperature on the hard substrate surface.

The coating thickness increased with increasing plasma arc current and displayed a maximum 100 μ m thickness in the case of 800A as shown in Fig. 3 (i) since partially and completely melted powders were preferentially deposited on the hard substrate.

The agglomerated TiO₂ powders were assumed to break into primary particles on the hard substrate through high speed impacting and then were reheated up to high temperature by the plasma jet. In addition, agglomerated powders are partially melted in thermal plasma flame before arriving at the substrate. Therefore, it is anticipated that plasma spraying provided easy transformation into rutile phase.

Fig. 4 shows the anatase ratio of plasma sprayed TiO₂

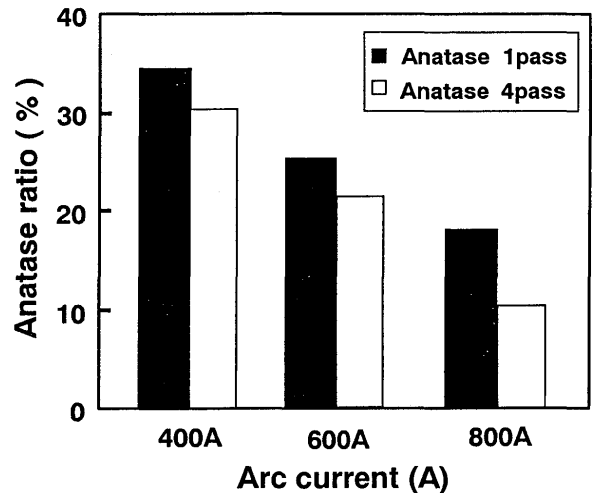


Fig. 4 The influence of arc current and spraying pass count on anatase ratio.

coatings (1pass, 4pass). The anatase ratio changed from 35% to 20% with increasing arc current. It is well known that anatase particles are easily transformed into the rutile phase above 973K [3,4].

The deposited anatase powders in 1 pass spraying tend to transform to rutile phase with the plasma jet of a subsequent pass, in addition, the deposited melted powders are mainly transformed to rutile phase since partially and completely melted rutile powders were preferentially deposited on the substrate. Therefore, the anatase ratio which could exhibit high photo-catalytic activity gradually decreased with increasing pass count as shown in Fig. 4.

The diagnostic system of DPV-2000 was often used to measure the velocity and temperature of spraying powders. Even when the plasma arc current was 400A, the transformation to rutile phase easily occurs during plasma spraying since the temperature of dynamic sprayed particles in the plasma jet was approx. 1600K according to the diagnostics system of DPV-2000.

However, approx. 35% anatase ratio could be detected as shown in Fig. 4. This implies that non-melted particles and not-transformed particles were deposited onto the mesh net substrate although anatase particles were reheated up to 1600K. Although anatase particles were reheated up to 1600K, the residence time of sprayed powders in the plasma jet is seen to less than 1 sec, and in addition, the deposited particles on the substrate are exposed to the plasma flame for very short times because the plasma jet passes away just after impacting on the substrate.

According to measured particle temperatures, the agglomerated powders are assumed to partially melted before arriving at the substrate. The amount of melting of the agglomerated powders is assumed to increase with increasing arc current.

Fig. 5 shows photo-decomposition properties of the C₂Cl₄ solution. The higher anatase ratio showed a higher

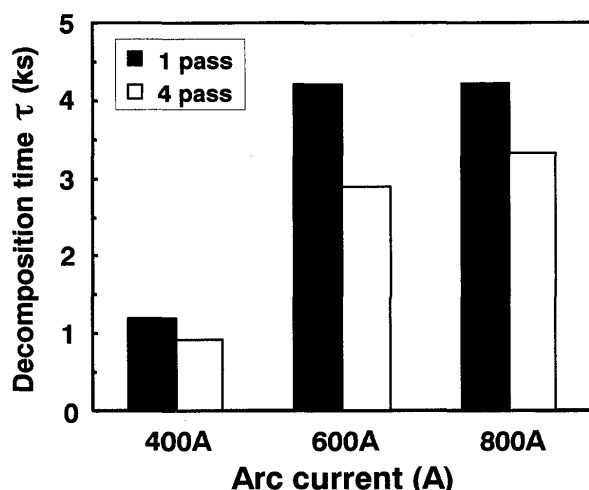


Fig. 5 The relation between decomposition time and spraying condition (arc current, spraying pass count).

photo-catalytic activity and it was found that this anatase ratio had a large influence on the photo-catalytic properties.

Of the all thermal sprayed TiO_2 coatings, the measured τ value in the TiO_2 coatings with 400A plasma spraying was the lowest. It was assumed that the surface area of the anatase phase on deposited coatings formed at 400A exhibited relatively larger values compared with other coatings. As a result of, 10ppm C_2Cl_4 solution was decomposed to less than 1ppm after 7.2ks in the case of 400A.

When plasma spraying using 30nm-agglomerated powders was carried out with stainless mesh net, little anatase phase remained after plasma spraying.

Since it is reported that transformation to rutile phase easily occurs in the case of fine nano powders, in terms of photo-catalytic activity, plasma spraying using 200nm-agglomerated powders could be recommended for the purpose of C_2Cl_4 solution degradation.

If a large decrease of the anatase ratio did not occur on increasing the pass count, increasing the coating thickness could be recommended as a result of this investigation. Thick TiO_2 coatings are suitable as actual photo-catalytic applications for long-term periods, when sprayed photo-catalytic coatings are used in natural environments.

The efficient degradation data could be obtained by stirring water containing C_2Cl_4 under irradiating ultraviolet rays. However, τ values drastically increased up to approx. 6.8ks when photo-catalytic experiments were performed without stirring liquid water containing C_2Cl_4 for 400A plasma spraying. Therefore, the stirred water is needed for efficient photo-catalytic degradation of C_2Cl_4 solutions.

For the purpose of finding out adequate conditions, the influence of mesh size was investigated by using different mesh size nets. With increasing mesh size, the

photo-catalytic properties decreased.

There are little photo-catalytic data about thermal sprayed TiO_2 coatings and literature regarding photo-catalytic degradation of C_2Cl_4 solution could not be found.

It is suggested that plasma sprayed TiO_2 coatings can be recommended for degradation of C_2Cl_4 solution. The investigation of the degradation of C_2Cl_4 solutions by using HVOF sprayed coatings must be investigated in more detail in the future.

4. Conclusions

1. It was possible to obtain approximately 100 μ m coating thicknesses on the stainless mesh net substrate when plasma spraying was carried out at 800A, while the coating thickness drastically decreased at 400A. In terms of photo-catalytic properties, retention of the anatase ratio in the TiO_2 coatings is essential to achieve photo-catalytic degradation of 10ppm C_2Cl_4 solution
2. The anatase phase had a large influence on photo-catalytic decomposition when TiO_2 coatings were used to degrade C_2Cl_4 solution, i.e. the TiO_2 coatings formed by plasma spraying at 400A showed higher anatase ratios, which exhibited the highest photo-catalytic activity. As a result, 10ppm C_2Cl_4 in solution was decomposed to less than 1ppm after 7.2ks by 400A plasma spraying

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