Formation of TiO$_2$/Ti Composite Photocatalyst Film by 2-step Mechanical Coating Technique

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Abstract: In the present work, 2-step mechanical coating technique (2-step MCT), an advanced MCT, was proposed and carried out to form TiO$_2$/Ti composite photocatalyst film with anatase TiO$_2$. The microstructures and photocatalytic activity of the composite film were investigated. The results show that the proposed 2-step MCT is a simple process for forming TiO$_2$/Ti composite film. The composite film has a microstructure with a nonuniform thickness, like random distribution islands. The TiO$_2$/Ti composite film has high photocatalytic activity, which is related with crystallinity and volume of the TiO$_2$ in the composite film.

Introduction

In recent years, research, development and application of TiO$_2$ photocatalyst have been widely reported owing to its high potential for environmental improvement [1-2]. Usually, film formation processes have been used for photocatalysts with high performance [3]. Numerous techniques have been used in the formation/fabrication of films on substrates of various materials with physical vapor deposition (PVD) and chemical vapor deposition (CVD) [4]. However, large and complicated equipments are required; besides, several of these techniques are operated only in condition of high vacuum. In addition, it is very difficult to form a uniform film on spherical substrates such as balls or buttons by PVD or CVD techniques. Therefore, a simple and economic film-coating technique is urgently expected.

We have proposed and performed a new process named mechanical coating technique (MCT) for forming TiO$_2$ photocatalyst film. In the process of MCT, the friction and abrasion are used effectively for forming Ti film based on the opposite conception of mixing powders in powder metallurgy process [5-6]. First, Ti film was formed on Al$_2$O$_3$ balls by turning the pot, in which, Ti powder and Al$_2$O$_3$ balls were put, and by using the friction and abrasion between Ti powder and the Al$_2$O$_3$ balls. Then TiO$_2$ photocatalyst film was formed by oxidizing the Ti film at high temperature. From that work, it is found that MCT is a simple and useful technique for forming a metallic film on round or spherical substrates such as Al$_2$O$_3$ balls or buttons. Although the resultant TiO$_2$ photocatalyst film was rutile crystal structure, it still had photocatalytic activity.

In the present work, an advanced MCT, 2-step mechanical coating technique (2-step MCT) was proposed for forming TiO$_2$/Ti composite photocatalyst film with anatase TiO$_2$ based on the idea of MCT. The microstructures and photocatalytic activity of the composite film were investigated. Influences of milling time and the impact by adding impact ceramic balls on photocatalytic activity were discussed.
Experimental

Formation of the composite film. In the present work, 2-step MCT shown in Fig.1 was proposed. In the first step of the proposed 2-step MCT, Ti film was formed on the Al$_2$O$_3$ balls by MCT as in the previous works [6-7]. Ti powder with 99.1% purity and an average diameter of 30 µm was used as the coating metal. Al$_2$O$_3$ balls with an average diameter of 1 mm were used as the substrates. A planetary ball mill (P5/4, Fritsch) was used for MCT as in the previous works [6-7]. 40 g Ti powder and 60 g Al$_2$O$_3$ balls were put in a pot of 250 ml, and formation of Ti film on the Al$_2$O$_3$ balls was carried out with a rotation speed of 300 rpm for 10 h. The Al$_2$O$_3$ balls with Ti film obtained from this process were denoted by M10-Ti. After that, as the second step, 15 g Al$_2$O$_3$ balls with Ti film (M10-Ti) and 13 g nano-TiO$_2$ powder (ST-01, Ishihara Sangyo Kaisha, Ltd., Japan) with anatase form and an average diameter of 7 nm were put in a pot, then MCT for forming the composite film was carried out for 1, 3, 6 and 10 h. Also, to compare the effect of different TiO$_2$ powder, micro-TiO$_2$ powder (020-78675, Kishida Chemical Co. Ltd., Japan) with anatase form and an average diameter of 0.45 µm was also introduced in the second step. The received materials and the apostrophes in the present work are listed in Table 1. Also, to form strong composite film by the high impact in the second step, Al$_2$O$_3$ or WC balls with a diameter of 10 mm as impact balls were put in the pot. The sample markers for the above processes are denoted as shown in Table 2, respectively.

Analysis of the microstructure and photocatalytic activity. The surface microstructure of the composite film formed by the above processes was examined by scanning electron microscope (SEM)(JEOL, JSM-5300LV) and the crystal form was analyzed by X-ray diffraction (XRD)(JEOL, JDX-3530) with Cu-Kα radiations under conditions of 30 kV and 20 mA, and by spreading the Al$_2$O$_3$ balls coated with the composite film on a holder.

Photocatalytic activity of the samples coated with the composite film was evaluated by measuring the decomposition rate of methylene blue (MB) solution (water solution) at room temperature. The samples were spread uniformly on the bottom of a cylinder-shaped cell with Φ18 x 50 mm after washing the balls to remove adhesion substances on the Al$_2$O$_3$ balls' surface in the processes. To get the same starting condition of evaluating photocatalytic activity for the all samples, the pre-adsorption of MB was carried out on the samples using 3 ml MB solution with 20 µM (where µM = µmol • l$^{-1}$) before evaluating photocatalytic activity. In this step, the samples and MB solution were put into the cell and kept for over 12 h in a dark place. Then, the samples were again spread uniformly on the bottom of the cell and 7 ml MB solution with 10 µM was poured into the cell. After that, photocatalytic activity was evaluated under an intensity of the ultraviolet radiation of 1 mW • cm$^{-2}$ for 24 h at room temperature. These conditions were referenced to Japanese industrial standard (JIS R 1703-2) [8]. The absorbance of MB solution was measured by a

![Fig.1 A schematic drawing of 2-step MCT.](image-url)
colorimeter (mini photo 10, Sanshin Industrial Co., Ltd.) with UV radiation of a wavelength with 660 nm, which is near the peak of absorption spectrum, 664 nm of MB solution used in the present work. The gradient, \( k \text{ nmol l}^{-1} \text{ h}^{-1} \) of the time-MB solution concentration curve was calculated out by the least-squares method using the data from 1 to 12 h, and was used as the degradation constant.

Results and Discussion

**TiO$_2$/Ti Composite photocatalyst film formed by 2-step MCT.** Figure 2 shows a photograph of the samples with the composite film by 2-step MCT. The color of the samples changed after the second step and lost the metallic luster and became navy blue comparing with the case of Ti film. In the cases of adding the impact balls, the samples also had the color change. It hints that TiO$_2$/Ti composite film was formed. The Ti film has uniform composition comparatively as shown in Fig. 3(a) in the case of Ti film. On the other hand, from Fig. 3(b)-(c), there are many convex areas on surfaces of the composite film. The dark areas are TiO$_2$, and the light areas are Ti. Besides, many pores were also found on the surfaces by SEM. Figure 4 shows a cross section of Al$_2$O$_3$ ball with the composite film adding the impact by WC balls in the second step. The composite film has a microstructure, which is nonuniform pile of TiO$_2$ on the Ti film. It is probably that first the Al$_2$O$_3$ balls coated by Ti film roll TiO$_2$ particles up and collide each other, and then, the TiO$_2$ particles rolled up are pushed into the Ti film owing to the collision process, after that the Al$_2$O$_3$ balls with the composite film repeat the collisions each other. The composite films with different TiO$_2$ powders and the impact by WC balls in the second step are compared in Fig. 5. The composite film has more nonuniform piles of TiO$_2$ in the case of the micro-TiO$_2$ powder. From the above results, it is found that the composite film has a microstructure with many convex areas on the surface, which are formed by nonuniform piles of TiO$_2$ on Ti film. The convex microstructure is more obvious in the cases of the micro-

Fig. 2 A photograph of the balls with TiO$_2$/Ti composite photocatalyst film by 2-step MCT.

Fig. 3 SEM micrographs of the surfaces for TiO$_2$/Ti composite photocatalyst film by 2-step MCT without impacting balls.

Fig. 4 A SEM micrograph of cross-section for ?10W-CM6K.

Fig. 5 SEM micrographs of the surfaces for TiO$_2$/Ti composite photocatalyst film.

Fig. 6 XRD patterns of TiO$_2$/Ti composite photocatalyst film by 2-step MCT with TiO$_2$-S and WC balls

Fig. 7 XRD patterns of TiO$_2$/Ti composite photocatalyst film by 2-step MCT with TiO$_2$-K and WC balls
TiO$_2$ powder and with the impact balls. Also, the composite film had a high hardness (the maximum value of dynamic hardness reached 472) on the cross section (in the case of Φ10W-CM6K) near that of alumina. It means that adding of the impact balls makes the composite film strong.

XRD patterns of the composite films with the impact by WC balls for the two cases of different TiO$_2$ powders show in Fig.6 and Fig.7, respectively. In the case of nano-TiO$_2$, peaks of Ti and anatase TiO$_2$ can be found from Fig.6. In the case of micro-TiO$_2$, although anatase TiO$_2$ was not detected in Fig.7, peaks of anatase TiO$_2$, which became broad, were detected from the rest powder after the second step. It means that TiO$_2$ powder was pulverized and crystallinity of TiO$_2$ was decreased by adding the impact balls in the second step. From the above results, it can be concluded that the TiO$_2$/Ti composite film formed by the 2-step MCT, and TiO$_2$ in the composite film has anatase crystal form.

Photocatalytic activity of the composite film. The degradation constants $k$, which are the gradient of the time-MB solution concentration curve, are shown in Fig. 8. The degradation constant goes up and reaches a peak around MCT time of 3 h, and then decreases with increasing MCT time for the case of the nano-TiO$_2$ powder and without the impact in the second step. The photocatalytic activity is increased by adding the impact balls in the second step for the case of micro-TiO$_2$ powder. However, photocatalytic activity is decreased as a whole by adding the impact in the second step. It is related with the pulverization and crystallinity of TiO$_2$ by adding the impact balls in the second step.

Conclusions

The proposed 2-step MCT is a simple and economic process to form the TiO$_2$/Ti composite film. The composite film has a microstructure with many convex areas on the surfaces, which are formed by nonuniform piles of TiO$_2$ on Ti film. Also, TiO$_2$ in the composite film keep anatase crystal form. The TiO$_2$/Ti composite film had high photocatalytic activity. Adding of the impact balls in the second step makes the composite film strong.

References