Fabrication of TiO₂ film by mechanical coating technique and its photocatalytic activity

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1. Introduction

In recent years, investigations on the fabrication and functional characteristics of TiO₂ film have been widely reported due to its potential applications as photocatalyst [1–5], gas sensor [6], solar cell [7] and others [8,9]. Numerous techniques have been used in the formation/fabrication of films on substrates of various materials with physical vapor deposition (PVD) [10] or chemical vapor deposition (CVD) [11]. However, large and complicated equipment is required; also these techniques can be only operated in a high vacuum condition. In addition, it is very difficult to form a film on spherical substrates such as balls or buttons by PVD or CVD technique. Therefore, a simple and economic film-coating technique is urgently expected.

The mechanical coating technique (MCT) was proposed and conducted to form metallic titanium film on alumina balls or buttons in the previous study [12]. The idea of MCT was from the mixing powders in powder metallurgy process, in which metallic adhesions on the surfaces of alumina balls in a pot of a planetary ball mill occur because of mechanical friction and abrasion. From that work, it was found that MCT is a simple and useful technique for forming a metallic film on round or spherical substrates such as alumina balls or buttons. It is thus expected to be a good candidate process for the formation of a metallic oxide film such as TiO₂ film.

In the present study, TiO₂ film on alumina balls was fabricated by MCT and oxidation process. The surface and microstructure of the film was examined. Photocatalytic activity of the film was evaluated by measuring the decomposition rate of methylene blue (MB) solution at room temperature. Influence of oxidation temperature on the microstructure and the photocatalytic activity was discussed. The film has an uneven surface and a composite microstructure with rutile TiO₂ and titanium. The photocatalytic activity goes up and reaches a peak at 723 K with increasing the oxidation temperature.

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2. Experimental

2.1. Fabrication of titanium film and oxidation process

In the present study, titanium powders with 99.9% purity and an average diameter of 35 μm were used as the coating metal. Alumina balls with an average diameter of 1 mm were used as substrates. A planetary ball mill (P5/4, Fritsch) was used for MCT [13]. Titanium powders of 40 g and alumina balls of 60 g were placed in a pot mill of 250 ml, and MCT was carried out with a rotation speed of 300 rpm for 10 h. Then, the alumina balls with the titanium film (M10-Ti) by MCT were oxidized in air at 573, 623, 673, 723, 773 and 873 K for 20 h to form TiO₂ film. These processes are denoted by M10-573-20, M10-623-20, M10-673-20, M10-723-20, M10-773-20, M10-873-20 and M10-973-20, respectively.

2.2. Analysis of the microstructure and photocatalytic activity

The TiO₂ film fabricated by the above processes was examined by scanning electron microscope (SEM, JEOL, JSM-6100) and the crystal form was analyzed by X-ray diffraction (XRD, JEOL, JDX-3530) through spreading and arranging the balls on a hold (15 mm × 15 mm). Cu Kα radiation under conditions of 30 kV and 30 mA was used for XRD.
Photocatalytic activity of the samples of the alumina balls with the TiO$_2$ 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 $\phi$ 20 mm × 50 mm after washing the alumina balls for removing adhesion things in the processes. To get the same starting condition of evaluating photocatalytic activity for all the samples, the pre-adsorption of MB solution was carried out using 3 ml of MB solution with 20 $\mu$mol/ml 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.

After that, the samples were again spread uniformly on the bottom of the cell and 7 ml of MB solution with 10 $\mu$mol/ml was poured. Then, 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) [14]. The absorbance of MB solution was measured by a colorimeter (mini Photo 10, Sanshin Kogyo) with UV radiation with a wavelength of 660 nm, which is near the peak of absorption spectrum, 664 nm of MB solution used in the present work. The gradient, $k$ [nmol l$^{-1}$ h$^{-1}$] of the time–MB solution concentration line was calculated out by the least-squares method removing the data of the first 1 h, and is used as the degradation constant.

3. Results and discussion

3.1. The fabricated TiO$_2$ film

Fig. 1 shows a photograph of the samples with the film. The color of the samples changed with increasing oxidation temperature and lost the metallic luster of titanium (see (a) M10-Ti). The color change indicated that the oxidation of the titanium film was advanced with oxidation temperature. The sample of M10-573K-20 showed the brown color similar to TiO. It hints that the oxidation at 573 K was insufficient. In the cases of samples, M10-673-20, M10-723-20, M10-773-20 and M10-873-20, the color became gray and

![Fig. 1. A photograph of the samples fabricated by MCT and oxidation process: (a) M10-Ti; (b) 573 K; (c) 623 K; (d) 673 K; (e) 723 K; (f) 773 K; (g) 873 K; (h) 973 K.](image1)

![Fig. 2. SEM micrographs of the film: (a) M10-Ti; (b) M10-673-20; (c) M10-723-20; (d) M10-773-20; (e) M10-873-20; (f) M10-973-20.](image2)
the metallic luster disappeared with increasing oxidation temperature. It was probably due to growing of the TiO$_2$ grains or increasing thickness of the film with oxidation temperature. Besides, for the sample of M10-973-20, the color changed to light yellow. It can be understood that the film was completely oxidized to TiO$_2$ in this oxidation condition.

3.2. Microstructure and crystal form of the TiO$_2$ film

SEM photomicrographs of the surfaces of the TiO$_2$ film were shown in Fig. 2. It is found that the film as shown in Fig. 2(a) has the uneven and differed surface microstructure in comparison with the films fabricated by CVD or PVD. The growth process of the microstructure with increasing oxidation temperature can be seen from Fig. 2(b)–(e). While it is likely that the surface microstructure of the film after the oxidation grows in size (see Fig. 2(b)–(e)), a small surface microstructure about 300 nm was observed in the case of M10-973-20. Also, the thickness of the film was estimated to be about 10 $\mu$m from SEM micrographs as the previous study [12].

Fig. 3 shows XRD patterns of the samples. The intensity of the titanium peaks decreased with increasing oxidation temperature and disappeared at temperature of 973 K at about 41$^\circ$. Conversely, the peaks of rutile TiO$_2$ appeared in the cases of over oxidation temperature of 673 K at about 28$^\circ$, and the intensity increased with oxidation temperature. From these results, it is found that the film is a composite microstructure with rutile TiO$_2$ and titanium for the samples obtained in the range of oxidation temperature from 673 to 873 K.

3.3. Photocatalytic activity

Fig. 4 shows the changes of MB solution concentration with UV irradiation time of evaluating photocatalytic activity of the TiO$_2$ film. It is found that MB solution concentration has a little increase due to the absorbance in the cases of the titanium film (M10-Ti) and the TiO$_2$ film oxidized at 573 K (M10-573-20). On the other hand, the other samples have obvious photocatalytic activity.

The degradation constant, $k$ calculated from the time–MB solution concentration line (see Fig. 4) is shown in Fig. 5. It is found that the degradation constant increases and reaches a peak at 723 K with increasing oxidation temperature until 723 K, and then decreases.

Regarding the experimental results shown in Figs. 3 and 5, we may be able to make the following three aspects the discussion. First, in the range of low oxidation temperature below 623 K, a low photocatalytic activity was due to insufficiency of the oxidation on the film. Secondly, in the range of oxidation temperature from 623 to 773 K, a high photocatalytic activity was depended on the composite microstructure of rutile TiO$_2$ and metallic titanium in the film [15]. Although it is usually considered that a photocatalytic activity of TiO$_2$ of rutile form is low, a high photocatalytic activity was obtained because of the composite microstructure with rutile TiO$_2$ and titanium in the present study. Besides, in the range of high oxidation temperature over 773 K, photocatalytic activity became low when the oxidation occurred deeply. It was due to a decrease in the volume of titanium in the film by the oxidation.
4. Conclusion

The TiO₂ film on surface of alumina balls was obtained by MCT and oxidation process in air. The film has an uneven surface and a composite microstructure with rutile TiO₂ and titanium. The photocatalytic activity increased and reached a peak at 723 K with increasing oxidation temperature. The increase of the photocatalytic activity is related with the composite effect.

References