Photocatalytic activity of TiO₂/Ti composite coatings fabricated by mechanical coating technique and subsequent heat oxidation

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Abstract
Titanium (Ti) coatings were fabricated on alumina (Al₂O₃) balls by mechanical coating technique (MCT) with Ti powder. The Ti coatings were then oxidized to titanium dioxide (TiO₂) coatings at different temperatures. The oxidation behavior and microstructure evolution of these coatings were investigated. The results showed that the inner and surface layers of the Ti coatings were oxidized simultaneously. When oxidizing at a relatively low temperature for a short time, TiO₂/Ti composite coatings were obtained. Increasing the oxidation temperature or time increased the thickness of the TiO₂ layer and eventually Ti coatings were totally oxidized to TiO₂ coatings. During oxidation, TiO₂ needles formed at a lower temperature grew to generate columnar crystals. The photocatalytic activity of these coatings was examined. Compared with TiO₂ coatings, the TiO₂/Ti composite coatings showed much higher photocatalytic activity. The highest activity was observed for the TiO₂/Ti composite coatings prepared by MCT and subsequent oxidation at 1073 K for 15 h and then the thickness of the TiO₂ layer was 27 μm.

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1. Introduction

Researchers have focused on developing and applying TiO₂ photocatalysts because of their potential in environment purification, sterilization, and hydrogen generation [1,2]. To lower the recycling cost and increase the efficiency of pollutant degradation, TiO₂ photocatalysts are often immobilized in films [3,4]. Many techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD), and the sol–gel method have been used to fabricate TiO₂ films [5–7]. However, these techniques are limited by disadvantages including complicated large-scale equipment, complex process, and high production cost.

TiO₂ exists in three different crystalline habits: rutile, anatase and brookite. It is generally believed that anatase is more reactive as photocatalyst than rutile and brookite [8]. However, rutile has been found rarely active for the photodegradation of organic species in aqueous solutions [9]. In addition, anatase and brookite as metastable phases are readily transformed to stable form rutile when they are heated. Therefore, rutile TiO₂ can be applied to photodegradation at elevated temperatures. The investigation on photocatalytic activity of rutile TiO₂ is of practicable significance.

We have developed a new coating method to fabricate TiO₂ photocatalyst coatings on alumina (Al₂O₃) balls called mechanical coating technique (MCT) [10,11]. Al₂O₃ balls
were used not only as the supplier of impact force to form coatings, but also as the coatings’ substrates. Collision, friction and abrasion are used to effectively form Ti coatings on Al₂O₃ balls [10]. The Ti coatings are then oxidized to form TiO₂ coatings. Although the resulting TiO₂ coatings contained rutile crystals, they showed relatively high photocatalytic activity [12]. Compared with other fabrication techniques for TiO₂ coatings or films, simple equipments are needed in MCT, the preparation procedure is simpler and the production cost is lower. To enhance the photocatalytic activity of these TiO₂ coatings, it is important to clarify the influence of the oxidation behavior on microstructure and photocatalytic activity.

In the present work, Ti coatings are fabricated on Al₂O₃ balls using MCT. The Ti coatings are then oxidized at elevated temperatures. The oxidation behavior at elevated temperatures, microstructure evolution, and photocatalytic activity of these obtained coatings were examined and discussed.

2. Experimental

2.1. Fabrication of Ti coatings

Ti powder (Osaka Titanium technologies, Japan) with an average diameter of 30 μm and purity of 99.1% was used as the coating material. Al₂O₃ balls (Nikkato, Japan) with an average diameter of 1 mm were used as the substrates. 40 g Ti powder and 60 g Al₂O₃ balls were added to an alumina bowl with dimensions of φ35 mm x 70 mm and a volume of 250 ml. The mechanical coating operation was then carried out with a planetary ball mill (Pulverisette 6, Fritsch). The rotation speed of the planetary ball mill was set at 480 rpm and the milling time was 10 hours. Milling was performed for 10 minutes and then stopped for 2 minutes to prevent the bowl from overheating. The process of MCT has been described in detail previously [13,14].

2.2. Fabrication and characterization of TiO₂ coatings

The Ti-coated Al₂O₃ balls after mechanical coating operation were heated in air to 973, 1073, 1173 and 1273 K at a rate of 15 K min⁻¹ and then maintained at each target temperature for 0.5, 1, 3, 5, 10, 20, 30, 40 and 50 h. The mass gain of 40 Ti-coated Al₂O₃ balls during the above oxidation treatment was examined by a thermal balance (TG-DTA 2000S, MAC science Co., Ltd.). The thicknesses of TiO₂ coatings were calculated by the mass gain.

The chemical composition and the crystal types of the prepared samples were examined by X-ray diffraction (XRD, JDX-3530, JEOL) using Cu-Kα irradiation at 30 kV and 20 mA. Diffraction data were recorded in the 2θ range of 23–60 deg with a step width of 0.02' s⁻¹. The samples for XRD were prepared as follow. A piece of glass with the dimension of 40 mm x 50 mm x 2 mm was used as the holder. Then the double-sided adhesive tape with the dimension of 17 mm x 26 mm was stuck on the center area of the glass holder. Finally, the Al₂O₃ samples were laid and stuck on the tape as densely as possible. The surface morphologies and cross-section microstructures of the samples were observed by scanning electron microscopy (SEM, JSM-6510, JEOL). The thicknesses of these coatings were also measured in the cross-section SEM images.

2.3. Evaluation of photocatalytic activity

Methylene blue (MB) as a common organic dye is frequently used as the target degradation pollutant in the photocatalytic activity evaluation of TiO₂. Photocatalytic activity of the samples was evaluated by measuring the degradation rate of MB solution at room temperature. Samples after ultrasonic cleaning were spread uniformly on the bottom of a cylinder-shaped cell with φ20 mm x 50 mm. To obtain the same initial conditions for all the samples, MB solution (3 ml, 20 μmol l⁻¹) was preadsorbed onto the samples before evaluating photocatalytic activity. The cell containing the samples and MB solution were kept in the dark for 12 h to allow adsorption. The samples were then spread uniformly on the bottom of the cell again, and MB solution (7 ml, 10 μmol l⁻¹) was poured into the cell. The photocatalytic activity of each sample was evaluated under ultraviolet (UV) light (wavelength < 400 nm) with an intensity of 1 mW cm⁻² for 24 h. These conditions are the same as those in Japanese Industrial Standard (JIS R 1703-2). The absorbance of MB solution was measured by a colorimeter (Sanshin Industrial Co., Ltd., Japan) with UV irradiation at a wavelength of 660 nm, which is near the absorption maximum (664 nm) of MB solution [15]. The gradient (k) (nmol l⁻¹ h⁻¹) of MB solution concentration versus irradiation time was calculated by the least squares method with the data from 1–12 h and used as the degradation rate constant.

3. Results and discussion

3.1. Microstructure evolution of these coatings during heat oxidation

Fig. 1 shows the cross-sectional SEM images of these coatings fabricated by the MCT and subsequent heat oxidation at 973 K in air for different oxidation times. The light and dark areas of these coatings were confirmed to be Ti and TiO₂ by XRD analysis, respectively. Fig. 1(a) shows numerous small pores in Ti coatings, which had a thickness of about 50 μm. The inner and surface layers of the Ti coatings were found to be oxidized simultaneously (Fig. 1(b–e)). It indicates that the coatings were porous and can be penetrated by air. As the oxidation time increased, the thickness of the TiO₂ layers was increased. From the above analysis, it can be confirmed that TiO₂/Ti composite coatings were prepared after the Ti coatings were oxidized at 973 K.

The cross-section SEM images of these coatings fabricated by the MCT and subsequent heat oxidation at 1073 and 1173 K are shown in Figs. 2 and 3, respectively. Compared with the samples oxidized at 973 K (Fig. 1), the oxidation level of the Ti coatings was increased with an increase in oxidation temperature. When the oxidation temperatures were 1073 and 1173 K, Ti coatings were...
completely oxidized to form TiO$_2$ coatings when oxidation time became 40 and 10 h, respectively. Fig. 4 shows the cross-section SEM images of the coatings fabricated by the MCT and subsequent heat oxidation at 1273 K. Porous TiO$_2$ coatings were obtained after just 3 h of oxidation.

3.2. Phase evolution of the coatings during heat oxidation

The XRD patterns of the Ti coatings oxidized at 973 and 1073 K are presented in Fig. 5. When the oxidation temperature was 973 K (Fig. 5(a)), the diffraction peaks of
Fig. 3. Cross-section SEM images of Ti coatings oxidized at 1173 K for (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 10 h, (e) 30 h and (f) 50 h.

Fig. 4. Cross-section SEM images of Ti coatings oxidized at 1273 K for (a) 3 h, (b) 10 h, (c) 30 h and (d) 50 h.
Ti, and rutile TiO₂ and anatase TiO₂ were detected. As the oxidation time was increased, the peaks of rutile TiO₂ became higher while those of Ti and anatase TiO₂ got lower. Combined with the results and analysis from Figs. 1–4, the weaker peaks of Ti indicate that the thickness of TiO₂ layer became larger and the thickness of Ti got smaller. As the thickness of surface TiO₂ layer increased, the detection of Ti became difficult. Meanwhile, both rutile and anatase TiO₂ were formed on the surface of the Ti coatings during oxidation treatment.

When the oxidation temperature was increased to 1073 K (Fig. 5(b)), the peaks of rutile TiO₂ were detected while those of Ti coatings were not found. It means that relatively thick rutile TiO₂ layers formed on the surface of the Ti coatings. The peaks of anatase TiO₂ were not detected, which indicates that anatase as a metastable phase cannot be formed or has been transferred to rutile at the high temperature. The above results shows that anatase phase can be obtained at 973 K while cannot be prepared at 1073 K.

3.3. Mass and thickness evolution of the coatings during heat oxidation

The mass gain of the coatings during heat oxidation is shown in Fig. 6. When the oxidation temperature was 973 K, the mass gain increased even after oxidized for 50 h, which indicates that the oxidation of the Ti coatings has not been completed. For oxidation at 1073, 1173 and 1273 K, the mass gain increased first and then remained constant. A constant mass gain indicates that the Ti coatings were completely oxidized. The mass gain of the coatings is consistent with their microstructure evolution (Figs. 1–4).
The thickness of the TiO$_2$ coatings formed during heat oxidation can be calculated from the mass gain by

$$H_{\text{TiO}_2} = \Delta W \left( \frac{A_{\text{TiO}_2}}{2A_0} \right) \left( \frac{1}{3\rho_{\text{TiO}_2}} \right) \left( \frac{1}{\pi D^2} \right)$$  \hspace{1cm} (1)

where $\Delta W$ is the mass gain of one Al$_2$O$_3$ ball, $A_0$ and $A_{\text{TiO}_2}$ are the oxygen atomic weight (16.00) and molecule weight of TiO$_2$ (79.88), $\rho_{\text{TiO}_2}$ is the density of TiO$_2$ (4.26 g·cm$^{-3}$) and $D$ is the average diameter of Al$_2$O$_3$ ball (1.093 mm). The thicknesses of the TiO$_2$ coatings calculated using Eq. (1) and measured from the cross-section SEM images are illustrated in Fig. 7. When the oxidation temperature was 973 K or during early oxidation stages at 1073 and 1173 K, the calculated values were greater than the measured values. This hints that the trapped oxygen was not only used to form TiO$_2$ coatings on the surfaces of the coatings, but also to oxidize the inner layer of the Ti coatings. In contrast, when the oxidation temperature was 1273 K or at later oxidation stages at 1073 and 1173 K, the calculated values were smaller than the measured values. This should relate to the presence of numerous small pores in the TiO$_2$ coatings. In other words, the real density of TiO$_2$ coatings should be smaller than the theoretical density of TiO$_2$.

Fig. 8. Morphologies of the coatings after oxidized at 973 K for different oxidation times. (a) Ti coatings before oxidation, and after oxidation for (b) 3 h, (c) 10 h, (d) 30 h and (e) 50 h.

Fig. 9. Morphologies of the coatings after oxidized at 1073 K for (a) 3 h, (b) 10 h, (c) 20 h, (d) 30 h, (e) 40 h and (f) 50 h.
3.4. Morphology evolution of the coatings during heat oxidation

The surface morphologies of the coatings fabricated by the MCT and subsequent heat oxidation at 973 and 1073 K are shown in Figs. 8 and 9, respectively. Fig. 8(b) and (c) indicates nano-sized TiO₂ needles formed. With increasing oxidation time, the size of the needles increased and columnar TiO₂ nanocrystals formed (Fig. 8(d) and (e)). When the oxidation temperature was increased to 1073 K (Fig. 9), nano-sized TiO₂ needles grew rapidly and micron-sized columnar TiO₂ crystals formed as the oxidation time was increased. The formation and growth of nano-sized TiO₂ needles and micron-sized columnar TiO₂ crystals have been discussed in many papers [16–18]. It should result from the preferential growth of TiO₂ crystals along the specific direction. It will not be involved here.

3.5. Photocatalytic activity of TiO₂ coatings and TiO₂/Ti composite coatings

The change in concentration of MB solution in the presence of the coatings oxidized for 10 h at different temperatures as a function of UV irradiation time is illustrated in Fig. 10. The concentration of MB solution for the blank (marked with MB solution in Fig. 10) hardly decreased, which means that the MB solution did not degrade under UV irradiation. In addition, the concentration of MB solution in the presence of the Ti-coated samples (marker with Ti coatings in Fig. 10) showed a slight increase under UV irradiation, which means that MB was not degraded under the action of Ti coatings and UV irradiation. In other words, Ti coatings have no photocatalytic activity. However, the concentration of MB solution in the presence of the samples by the MCT and subsequent heat oxidation decreased to varying degrees. It indicates that MB was degraded under the action of UV irradiation and the samples fabricated by the MCT and subsequent heat oxidation. In other words, the TiO₂ coatings and TiO₂/Ti composite coatings showed photocatalytic activity toward MB.

Degradation rate constants, k, calculated from plots of concentration versus irradiation time curves are presented in Fig. 11. For the TiO₂ coatings and TiO₂/Ti composite coatings fabricated by the MCT and subsequent heat oxidation at 973 and 1273 K, k first increased and then remained almost constant with extending oxidation time. In contrast, k first increased and then decreased for the samples fabricated by the MCT and subsequent heat oxidation at 1073 and 1173 K. The samples fabricated by the MCT and subsequent heat oxidation at 1073 K for 15 h showed the highest photocatalytic activity.

The relationship between k, microstructure and measured thickness of the TiO₂ coatings is shown in Fig. 12. The TiO₂/Ti composite coatings showed much higher photocatalytic activity than TiO₂ coatings. Improved photocatalytic activity is commonly considered to relate to the efficiency of charge separation [19,20]. When TiO₂ is in contact with a metal with a higher work function, photogenerated electrons in the conduction band of TiO₂...
may transfer to the metal, which can decrease the recombination rate of electron–hole pairs in TiO$_2$, thereby improving photocatalytic activity. After the Ti coatings were oxidized at 1073 K for 15 h, the thickness of TiO$_2$ layer became 27 μm, at which the highest efficiency of charge separation is reached. As a result, the highest $k$ for the TiO$_2$/Ti composite coatings (near 300 nmol l$^{-1}$ h$^{-1}$) was achieved at this thickness.

4. Conclusions

TiO$_2$ coatings and TiO$_2$/Ti composite coatings were fabricated by the MCT and subsequent heat oxidation. With an increase in oxidation temperature or time, the thickness of the TiO$_2$ layer on Ti coatings increased, and finally single TiO$_2$ coatings were obtained. Nano-sized TiO$_2$ needles and micron-sized columnar TiO$_2$ crystals formed in the coatings. The TiO$_2$/Ti composite coatings prepared by MCT and subsequent oxidation at 1073 K for 15 h showed the highest photocatalytic activity for degradation of MB. The improved photocatalytic activity of the coatings should be related to the formation of TiO$_2$/Ti composite microstructure that decreased the recombination velocity of electron–hole pairs in TiO$_2$.

References