Fabrication and Photocatalytic Activity of Photocatalyst Coatings by Mechanical Coating Technique and the Oxidation at Relatively Low Temperatures

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Keywords: mechanical coating technique, heat oxidation, TiO$_2$, composite coatings, photocatalytic activity.

Abstract. Titanium (Ti) coatings on alumina (Al$_2$O$_3$) balls fabricated by mechanical coating technique (MCT) were oxidized at relatively low temperatures. Crystal structure and microstructure of the coatings were investigated. Photocatalytic activity of the coatings was evaluated and discussed. The results showed that TiO$_2$ films on Ti or Ti/TiO$_2$ coatings were fabricated by the MCT and subsequent heat oxidation. The TiO$_2$ is anatase phase if the heat oxidation temperature is under 773 K. The TiO$_2$ is the mixed phases of anatase and rutile if the heat oxidation temperature is in the range of 673–973 K. Besides, rutile TiO$_2$ is formed if the heat oxidation temperature is beyond 1073 K. Photocatalytic activity of anatase TiO$_2$ is higher than rutile TiO$_2$.

Introduction

Development and application of TiO$_2$ photocatalysts has been paid much attention because of their potential in environment purification, sterilization, and hydrogen generation [1,2]. To reduce the recycling cost and increase the efficiency of pollutant degradation, TiO$_2$ photocatalysts are often immobilized in films [3,4]. Numerous techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD), and the sol-gel method have been used to fabricate TiO$_2$ films [5-7]. However, these techniques are limited by disadvantages including complicated large-scale equipment, vacuum for PVD and CVD, and high production cost.

We have developed a novel coating method to fabricate TiO$_2$ photocatalyst coatings on Al$_2$O$_3$ balls called mechanical coating technique (MCT) [8, 9]. Collision, friction and abrasion are used to effectively form Ti coatings on ceramic grinding media. The Ti coatings are then oxidized to form TiO$_2$ coatings or TiO$_2$/Ti composite coatings. Although the resulting TiO$_2$ coatings contained rutile crystals, they showed relatively high photocatalytic activity [10, 11].

It is known that TiO$_2$ has three crystal phases named brookite (B), anatase (A) and rutile (R) [12]. Most researchers at photocatalytic field are focusing on anatase TiO$_2$ [13]. On the other hand, efforts to investigate photocatalytic activity of rutile TiO$_2$ or mixed-phase of these crystal phases are continued [14].

In this work, Ti coatings on Al$_2$O$_3$ balls are fabricated by the MCT. The Ti coatings are then oxidized at relatively low temperatures than those in our previous work [11]. Crystal structure and microstructure of the coatings were investigated. Photocatalytic activity was evaluated and discussed.
Experimental

Source materials and fabrication of Ti coatings by MCT. Ti powder with an average diameter of 30 µm and purity of 99.1% was used as the coating material. Al₂O₃ balls with an average diameter of 1 mm were used as substrates. A planetary ball mill (type: P6, Fritsch, Germany) was employed to perform the mechanical coating operation. The MCT has been described in detail previously [3, 4], which was used to prepare Ti coatings. First, Ti powder (40 g) and Al₂O₃ balls (60 g) were charged into an Al₂O₃ bowl with a volume of 250 mL (dimensions of Φ75 mm×70 mm). The rotation speed of the planetary ball mill was set at 480 rpm and the mechanical coating operation was carried out for 10 h with a 10-min milling operation and a following 2-min cooling interval to prevent the bowl from overheating. After this operation, Ti coatings on Al₂O₃ balls were obtained.

Heat oxidation and characterization of the coatings. The Ti-coated Al₂O₃ balls prepared by MCT were then heated to relatively low temperatures. Heat oxidation was performed using an electric furnace in air atmosphere at temperatures of 573, 673, 773, 873, 937, and 1073 K. The samples were held at elevated temperature for 3 h and then cooled in the furnace.

The prepared samples were labeled as follows. "M10-Ti" is the sample prepared with Ti powder by MCT at 480 rpm for 10 h. "M10-xK-3h" are the final oxidized products of the M10-Ti samples, heat oxidation at the elevated temperature of x K for a period of 3 h.

Before the characterization of the samples, they were treated by ultrasonic cleaning (frequency: 40 kHz) in acetone for 15 min to remove any substances that did not strongly adhere to the surfaces of the Al₂O₃ balls. An XRD analyzer (JDX-3530, JEOL, Japan) with Cu-Kα radiation at 30 kV and 20 mA was used to determine the compositions and crystal structures. The surface morphologies and cross-sectional microstructures of the samples were observed by SEM (JSM-5300, JEOL, Japan).

Evaluation of the photocatalytic activity. Photocatalytic activity of the samples was evaluated by measuring the degradation rate of methylene blue (MB) solution at room temperature by referring to Japanese Industrial Standard (JIS R 1703-2), which has been described in detail previously [7, 9]. 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 obtained from 1–12 h and used as the degradation rate constant.

Results and discussion

The coatings by MCT and heat oxidation. Fig. 1 shows the appearance photograph of M10-Ti and M10-xK-3h samples. The Ti coatings (M10-Ti) show metallic color. In contrast, the M10-xK-3h
samples appear various colors, which are golden, blue, silver, purple, and white with increasing the heat oxidation temperature. It is known that the colors of TiO$_2$ are related to the thickness of TiO$_2$ films if the thickness is nano-size [15]. These mean that the TiO$_2$ films, which have different thickness and nano-size were formed by heat oxidation at the relatively low temperatures. Fig. 2 shows the XRD patterns of the coatings on Al$_2$O$_3$ balls prepared by MCT and heat oxidation. It can be seen that only the diffraction peaks of Ti are detected for the M10-Ti. On the other hand, the peak of anatase TiO$_2$ started to appear at 38.57° from the sample oxidized at 673 K. Further, the peaks of rutile TiO$_2$ are detected at 27.45° from the sample oxidized at 973 K. As a result, the TiO$_2$ is anatase phase if the heat oxidation temperature is under 773 K. The TiO$_2$ has the mixed phases of anatase and rutile structures if the heat oxidation temperature is in the range of 673–973 K. Besides, rutile TiO$_2$ is formed if the heat oxidation temperature is beyond 1073 K. SEM images of the surfaces of the samples are presented in Fig. 3. Any reaction compound is not detected from the samples oxidized at temperatures under 773 K. A few reaction compounds as point-shape appeared from the samples oxidized at temperatures under 873 K. With an increase of oxidation temperature, reaction compounds increase in number and growth to form the needle structure. It can be concluded that the observed reaction compounds are rutile TiO$_2$, according to the needle-like structure and the XRD results above [16]. Fig. 4 shows SEM images of the cross sections of the samples. The oxidized layer can not be detected from the samples oxidized at oxidation temperatures under 873 K. If the oxidation temperature reach to 973 K, the oxidized layer on the coatings can be observed. Also, the party inner layer of the coatingshad been oxidized, which forms a TiO$_2$/Ti-TiO$_2$ structure.
Photocatalytic activity of the oxidized coatings. Fig. 5 shows degradation rate constant of the samples. All the samples show photocatalytic activity. Besides, photocatalytic activity of anatase TiO$_2$ is higher than rutile TiO$_2$.

Summary

TiO$_2$ films on Ti or Ti-TiO$_2$ coatings were fabricated by the MCT and subsequent heat oxidation. The TiO$_2$ is anatase phase if the heat oxidation temperature is under 773 K, and is the mixed phases of anatase and rutile structures if the heat oxidation temperature is the rage of 673–973 K. Besides, rutile TiO$_2$ is formed if the heat oxidation temperature is beyond 1073 K. Photocatalytic activity of anatase TiO$_2$ is higher than rutile TiO$_2$.

References