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Influence of oxidation process on photocatalytic activity of photocatalyst coatings by mechanical coating technique

Yun Lu [a,*], Kouta Kobayashi [b], Sujun Guan [b], Liang Hao [c,**], Hiroyuki Yoshida [d], Hiroshi Asanuma [a], Jinxiang Chen [e]

[a] Graduate School & Faculty of Engineering, Chiba University, 1–33, Yayoi-cho, Inage-ku, Chiba, 2638522, Japan
[b] Graduate School, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, 2638522, Japan
[c] College of Mechanical Engineering, Tianjin University of Science and Technology, No.1038, Dagu Nanlu, Hexi District, Tianjin, 300222, PR China
[d] Chiba Inductrial Technology Research Institute,889, Kasori-cho, Wakaba-ku, Chiba, 2640017, Japan
[e] International Institute for Urban Systems Engineering, Southeast University, Nanjing, 210096, PR China

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ABSTRACT

Titanium (Ti) coatings on alumina (Al_2O_3) balls fabricated by mechanical coating technique (MCT) were oxidized in air at a series of relatively low temperatures with the oxidation time of 3 h and 50 h. Crystal structure and microstructure of the coatings were investigated. Photocatalytic activity of the coatings was evaluated and discussed. The results showed that titanium dioxide (TiO_2) films on Ti or Ti/TiO_2 coatings were fabricated by the MCT and subsequent heat oxidation. The oxidized coatings started to show the mixed-phase of anatase and rutile, at the temperature of 873 K for 3 h and 773 K for 50 h. With extending the oxidation time from 3 h to 50 h, the oxidative effect of relatively lower temperatures of 773 K to 973 K almost reached to that of higher temperatures, which is similar to the time–temperature equivalence principle. Photocatalytic activity of anatase TiO_2 at 673 K is higher than that of mixed-phase or rutile TiO_2 under UV irradiation.

1. Introduction

TiO_2 has been widely used as photocatalyst for the potential in environment purification, sterilization, and hydrogen generation due to its high photocatalytic activity, excellent chemical stability, and without any toxicity [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 some disadvantages such as complicated large-scale equipments, vacuum for PVD and CVD, and high production cost. A novel coating method of MCT has been successfully used to fabricate TiO_2 photocatalyst coatings on Al_2O_3 balls [8,9]. Collision, friction and abrasion are used to effectively form metal coatings, such Ti, Fe, Zn on ceramic grinding media[9–11]. With subsequent oxidation process, the Ti coatings are oxidized to form TiO_2 coatings or TiO_2/Ti composite coatings [12].

It is known that the crystal phases of TiO_2 most occur in the thermodynamically stable rutile (R) and metastable anatase (A), and the crystal phase could be transformed from anatase to rutile by changing the treatment conditions [13–15]. Many researchers at photocatalytic field are focusing

* Corresponding author. Tel.: +81 43 290 3514; fax: +81 43 290 3039.
** Corresponding author. Tel.: +86 22 60272123; fax: +86 22 60273495.
E-mail addresses: luyun@faculty.chiba-u.jp (Y. Lu), haoliang@tust.edu.cn (L. Hao).

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on anatase TiO_2 [16,17]. On the other hand, efforts to investigate photocatalytic activity of rutile TiO_2 or mixed-phase of these crystal phases are continued [18–22].

In this work, Ti coatings on Al_2O_3 balls are fabricated by the MCT. The Ti coatings are then oxidized in air at a series of relatively low temperatures, compared with the previous work [12], with the oxidation time of 3 h and 50 h. Crystal structure and microstructure of the coatings were investigated. Photocatalytic activity was evaluated and discussed.

2. Experimental

2.1. Source materials and fabrication of Ti coatings by MCT

Ti powder (Osaka Titanium technologies, Japan) with an average diameter of 30 μm and purity of 99.1% was used as the coating material. Al_2O_3 balls (Nikkato, Japan) 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. First, Ti powder (40 g) and Al_2O_3 balls (60 g) were charged into an Al_2O_3 bowl with a volume of 250 mL (dimensions of Φ 75 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 the operation of MCT, Ti coatings on Al_2O_3 balls were obtained.

2.2. Heat oxidation and characterization of the coatings

The Ti coatings fabricated by MCT were then heated at a series of relatively low temperatures of 573, 673, 773, 873, 937, and 1073 K, using an electric furnace. The samples were held at each elevated temperature for oxidation with 3 h and 50 h, then cooled to room temperature in the furnace.

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

2.3. 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 had been described in detail previously [8,9]. The degradation rate constant 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 gradient (k) (nmol L^{-1} h^{-1}).

3. Results and discussion

3.1. The coatings by MCT and heat oxidation

Fig. 1 shows the appearance photograph of M10-Ti and M10-*x* K-*y* h samples. The Ti coatings (M10-Ti) show metallic color. In contrast, the M10-*x* K-*y* h samples appear various colors, which are golden, blue, silver, gray, and white with increasing the heat oxidation temperature with holding at each oxidation temperature for 3 h. While the holding time extented to 50 h for each oxidation temperature, the colors change to be light-golden, purple, light-purple, gray, light-blue, and white. The color of TiO_2 is related to the thickness of TiO_2 films if the thickness is nano-size [23], which hints the samples of TiO_2 films with different thicknesses and nano-size were formed by heat oxidation at the relatively low temperature with different holding times.

Fig. 2 shows the XRD patterns of the coatings on Al_2O_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. With the oxidation time of 3 h, the crystal structures of samples changed with the oxidation temperature are (1) anatase phase started to appear at 38.57° from the sample oxidized at 673 K, (2) mixed-phase of anatase and rutile started to appear at 873 K, and (3) anatase started to disappear at 1073 K. While extented the oxidation time to

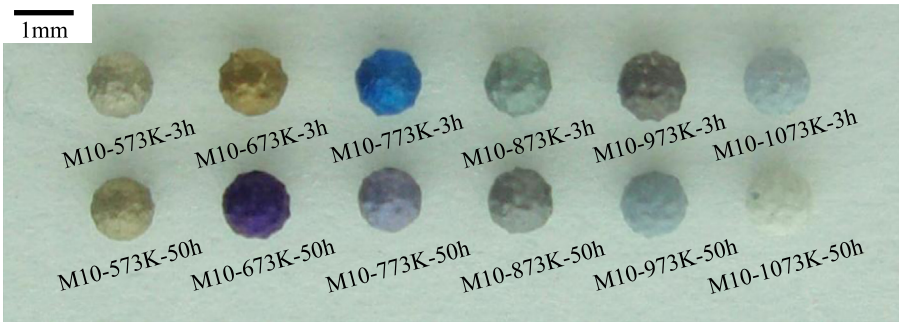

Fig. 1. The appearance photograph of the samples. : (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)