FABRICATION AND PHOTOCATALYTIC ACTIVITY OF TiO_2/Ti COMPOSITE FILMS BY MECHANICAL COATING TECHNIQUE AND HIGH-TEMPERATURE OXIDATION

Y. Lu[1*], K. Matsuzaka[2], L. Hao[2], Y. Hirakawa[2], H. Yoshida[3], F. S. Pan[4]

[1]*Graduate School & Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, Japan*
[2]*Graduate school, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, Japan*
[3]*Chiba Industrial Technology Research Institute, 889 Kasori-cho, Wakaba-ku, Chiba, Japan*
[4]*College of Materials Science and Engineering, Chongqing University，Chongqing,400044,China*
**luyun@faculty.chiba-u.jp*

Keywords: mechanical coating technique, high-temperature oxidation, TiO_2/Ti composite films, photocatalytic activity.

Abstract

Mechanical coating technique was used to fabricate titanium (Ti) films on alumina (Al_2O_3) balls. The following high-temperature oxidation was carried out for oxidizing the Ti films to form TiO_2. The oxidation behavior of the films and the microstructure evolution of the oxidized films were investigated. The results showed that the inner and surface layers of the Ti films were oxidized simultaneously. When oxidizing at a relatively low oxidation temperature in a short time, TiO_2/Ti composite films were obtained. With increase in oxidation temperature and oxidation time, the thickness of TiO_2 increased and eventually Ti films were totally oxidized to TiO_2 films. Meanwhile, TiO_2 needles grew up and became columnar crystals which also grew up with the increase of the oxidation temperature and oxidation time. The photocatalytic activity of the oxidized films was examined and discussed. Compared with the single TiO_2 films, TiO_2/Ti composite films showed much higher photocatalytic activity. The highest photocatalytic activity was achieved when the thickness of TiO_2 films in TiO_2/Ti composite films was 27μm.

1 Introduction

Development and application of TiO_2 photocatalysts have been paid close attention to due to their high potential in environment purification, sterilization, and hydrogen generation, among others [1, 2]. To lower the recycling cost and increase the degradation efficiency of pollutants, investigations of TiO_2 photocatalysts are oriented toward the immobilization in the form of thin films [3, 4]. Numerous techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD), and sol-gel method, among others have been used to fabricate TiO_2 photocatalyst thin films to increase their photocatalytic activity [5-7]. However, some disadvantages limit the applications of these techniques. For example, complicated and large scale equipments are required and their processes can be operated only in vacuum for PVD and CVD. In addition, the production cost is relatively high.

In this condition, we developed ball milling and proposed a novel coating technique called mechanical coating technique (MCT) to fabricate TiO_2 photocatalyst films on alumina (Al_2O_3) balls [8, 9]. Collision, friction and abrasion are utilized effectively to form Ti films on ceramic grinding mediums during the fabrication. Subsequently, TiO_2 films were prepared by further oxidation of Ti films that had prepared before by MCT. Although the TiO_2 resultants had rutile crystal type, they showed relatively high photocatalytic activity [10]. To enhance the photocatalytic activity, clarifying the influence of the oxidation process on the microstructure and the photocatalytic activity of the oxidation films seems to be important.

In this work Ti films on Al_2O_3 balls was prepared by MCT. The following high-temperature oxidation was performed to oxidize the Ti films that were prepared by MCT. The oxidation behavior of Ti films at high temperatures and the microstructure evolution of the obtained films were investigated. The photocatalytic activity of the films was examined and discussed.

2 Experimental

2.1 Fabrication of Ti films

Ti powder with an average diameter of 30 μm and a purity of 99.1% was used as the coating material. Alumina (Al_2O_3) balls with an average diameter of 1 mm were used as the substrates. 40 g Ti powder and 60 g Al_2O_3 balls were charged into a bowl made of alumina with the dimension of Φ75 mm×70 mm (250 m*l* in volume). Then the mechanical coating was carried out by a planetary ball mill (Pulverisette 6, Fritsch). The rotation speed of the ball mill was set at 480 rpm and the milling time was 10 h. During the fabrication, milling operation was performed 10 min followed by 2 min intermittence to avoid the overheating of the bowl and the contents. The schematic diagram of MCT can be found in our published work [11].

2.2 Fabrication and characterization of TiO_2 films

The Ti film-coated Al_2O_3 balls prepared by MCT were heated in air to 973, 1073, 1173 and 1273 K at a speed of 15 K/min and then held at that oxidation temperature for 0.5~50 h. The mass gain of 40 Ti film-coated Al_2O_3 balls (The average weight: 136.4 mg) during the heating and the holding as the above oxidation process was examined by a thermal balance (TG-DTA 2000S, MAC science Co., Ltd.). The thicknesses of TiO_2 films were calculated by the mass gain. The chemical composition and the crystal types of the prepared samples were examined by XRD (JDX-3530, JEOL). Cu-*Ka* irradiation in the condition of 30 kV and 20 mA was adopted. Diffraction data were recorded in the 2θ angular range of 23~60 deg with a step width of 0.02 $deg \cdot s^{-1}$. The morphologies and the microstructures of the samples were observed by SEM (JSM-6510, JEOL).

2.3 Evaluation of photocatalytic activity

Photocatalytic activity of the samples was evaluated by measuring the degradation rate of methylene blue (MB) solution at room temperature. The samples were spread uniformly on the bottom of a cylinder-shaped cell with Φ20mm×50mm after ultrasonic cleaning. To obtain the same initial conditions of evaluating photocatalytic activity for all the samples, pre-adsorption of MB solution was carried out using 3 m*l* MB solution with a concentration of 20 μmol/*l* before evaluating photocatalytic activity. In this step, the cell with the samples and MB solution were kept in a totally dark place for 12 h. Subsequently, the samples after the pre-absorption were spread uniformly on the bottom of the cell again and 7 m*l* MB solution with a concentration of 10 μmol/*l* was poured into the cell. Then photocatalytic activity was evaluated under UV light irradiation with an intensity of 1 mW/cm^2 for 24 h. These evaluation conditions were referenced to Japanese Industrial Standard (JIS R 1703-2). The absorbance of MB solution was measured by a colorimeter (Sanshin Industrial Co., Ltd) with

UV irradiation with a wavelength of 660 nm, which was near the peak of absorption spectrum, 664 nm of MB solution used in the work. The gradient, k (nmol·L^{-1}·h^{-1}) of MB solution concentration-irradiation time curve was calculated by the least-squares method with the data from 1~12 h and used as the degradation rate constants.

3 Results and discussion

3.1 Microstructure evolution of the films during high-temperature oxidation

Fig. 1 shows the SEM images of the cross sections of the samples fabricated by MCT and the following high-temperature oxidation at 973 K. The light and dark areas of these films correspond to Ti and TiO_2 respectively. From Fig. 1 (a), numerous tiny pores were found in Ti films and the films had an average thickness of 46.71 μm. From Fig.1 (b)-(e), it can be seen that the inner layer and the surface layer of Ti films were oxidized simultaneously not as we thought before. It indicates that the films were not dense and therefore air penetrated into the films. That resulted in the simultaneous oxidation of the inner layer and the surface layer of the films. With the increase of oxidation time, the thickness of TiO_2 films on the surface increased. When it came to 50 h, TiO_2/Ti composite films were obtained. Meanwhile, the SEM images of the cross sections of the samples fabricated by MCT and the following high-temperature oxidation at 1073 and 1173 K are shown in Fig. 2 and Fig. 3 respectively. Compared with Fig. 1, it can be summarized that the oxidation rate of Ti films on the surfaces became greater with the increase of oxidation temperature after the same oxidation time. When oxidation temperature was 1073 and 1173 K, Ti films were completely oxidized to form single TiO_2 films after 40 and 10 h respectively. Fig. 4 shows the cross sections of the

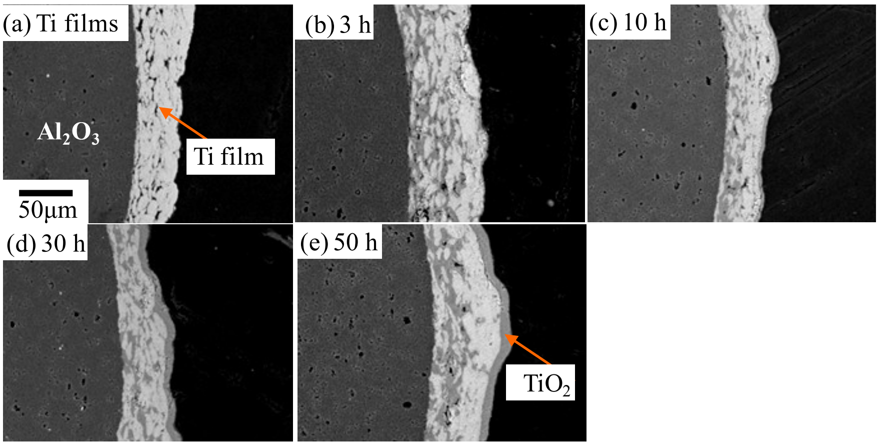

Figure 1. SEM images of the cross sections of Ti films after oxidized at 973 K.

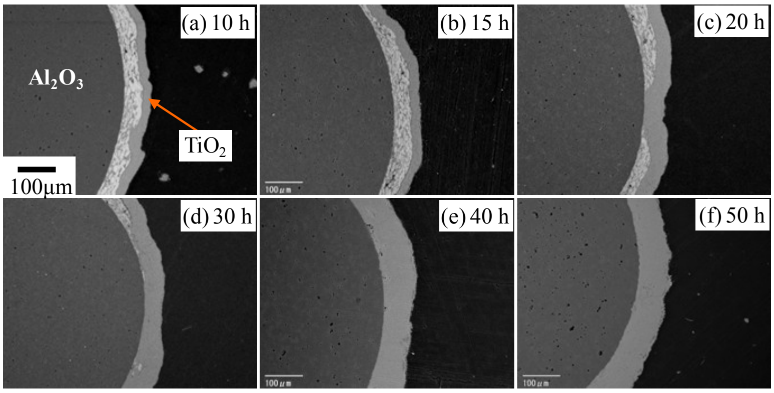

Figure 2. SEM images of the cross sections of Ti films after oxidized at 1073 K.

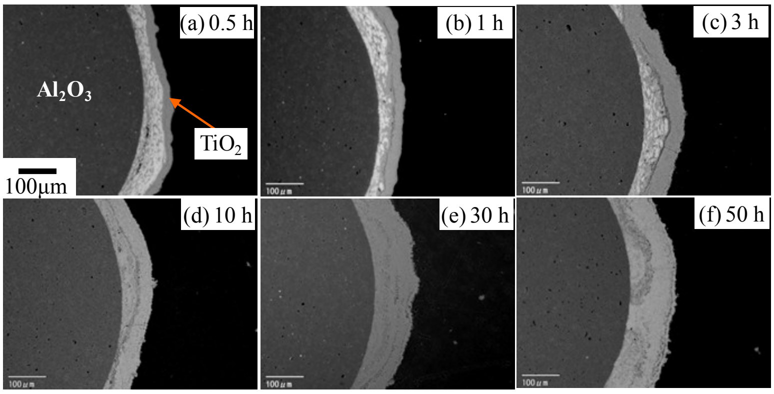

Figure 3. SEM images of the cross sections of Ti films after oxidized at 1173 K.

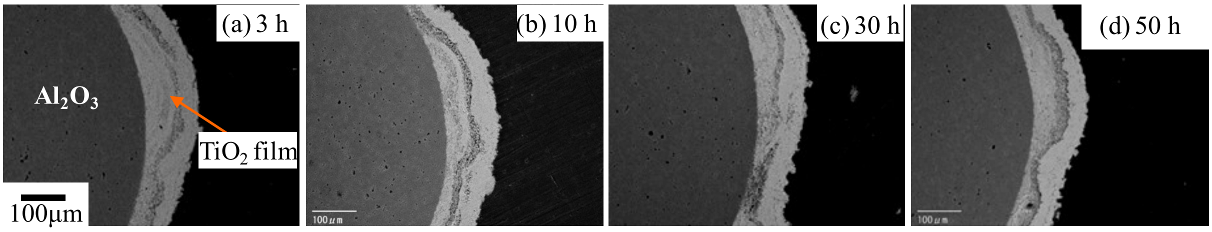

Figure 4. SEM images of the cross sections of Ti films after oxidized at 1273 K.

samples fabricated by MCT and the following high-temperature oxidation at 1273 K. It can be seen that single TiO_2 films were obtained when oxidation time was only 3 h and numerous tiny pores can also be seen in the films.

3.2 Phase evolution of the films during high-temperature oxidation

The XRD patterns of the samples fabricated by MCT and the following high-temperature oxidation at 973 and 1073 K are given in Fig. 5. When oxidation temperature was 973 K (Fig. 5 (a)), the peaks of Ti, rutile TiO_2 and anatase TiO_2 were detected. With the increase of oxidation time, the peaks of rutile TiO_2 became higher while those of Ti and anatase TiO_2 became lower. That means rutile TiO_2 and anatase TiO_2 were formed on the surfaces of the films during the oxidation of Ti films. Anatase TiO_2 as a metastable phase at high temperature converted to rutile TiO_2. When oxidation temperature increased to 1073 K (Fig. 5 (b)), only the peaks of rutile TiO_2 were detected which means relatively thick rutile TiO_2 films were formed on the surface of the films. From the above results, it can be concluded that anatase

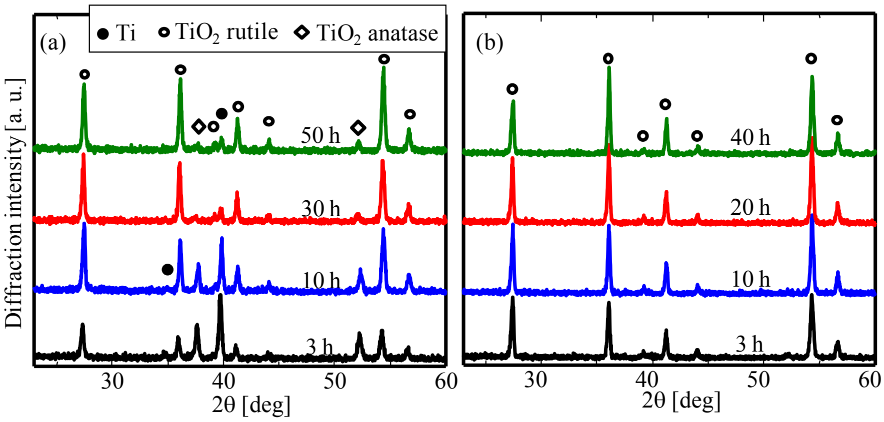

Figure 5. XRD patterns of the samples fabricated by MCT and high-temperature oxidation at (a) 973 K and (b) 1073 K.

TiO_2 cannot be obtained at high temperature of 1073 K and above. The above analysis is also good agreement with those from Fig. 1 and Fig. 2.

3.3 Mass and thickness evolution of the films during high-temperature oxidation

The mass gain as a function of oxidation time during high-temperature oxidation is shown in Fig. 6. When oxidation temperature was 973 K, the mass gain of the samples increased even oxidation time came to 50 h. It means the oxidation of Ti films did not finish. When oxidation temperature was 1073, 1173 and 1273 K, the mass gain of the samples increased firstly and then kept constant values. The constant values indicate that the oxidation of Ti films finished. The analysis on the mass gain is consistent with the microstructure evolution analysis of the films from Fig. 1 to Fig. 4.

Thickness of TiO_2 films on the surfaces of the films formed during the high-temperature oxidation can be calculated from the mass gain by

$$H_{TiO2} = \Delta w \frac{A_{TiO2}}{2A_O} \frac{1}{\rho_{TiO2}} \frac{1}{\pi D^2} \qquad (1)$$

Where Δw is the mass gain of every Al_2O_3 ball, A_O and A_{TiO2} are oxygen atomic weight and molecule weight of TiO_2, substituted by 16.00 and 79.88 respectively. ρ_{TiO2} is the density of TiO_2, substituted by 4.26 $g \cdot cm^{-3}$. D is the average diameter of Al_2O_3 ball, substituted by 1.093 mm. The thicknesses of TiO_2 films calculated by Eq. 1 and measured from the SEM images of the cross sections are given in Fig. 7. When oxidation temperature was 973 K or the early oxidation stage at higher oxidation temperature (no more than 30 h at 1073 K and 3 h at 1173), the calculated values were greater than the measured ones. It hints that the trapped oxygen was not only spent to form TiO_2 films on the surfaces of the films, but also used to oxidize the inner layer of Ti films. On the other hand, when oxidation temperature was increased to 1273 K or the later oxidation stage at 1073 and 1173 K (more than 30 h at 1073 K and 3 h at 1173), the calculated values were smaller than the measured ones. It is because numerous tiny pores were generated in the TiO_2 films after the complete oxidation of Ti films.

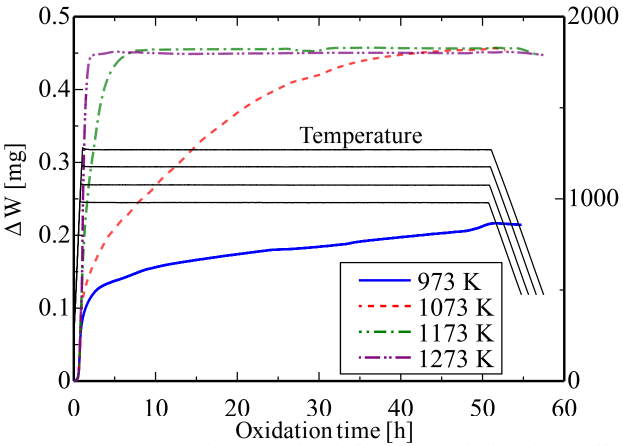

Figure 6. Mass gain of each Ti film-coated alumina ball during high-temperature oxidation.

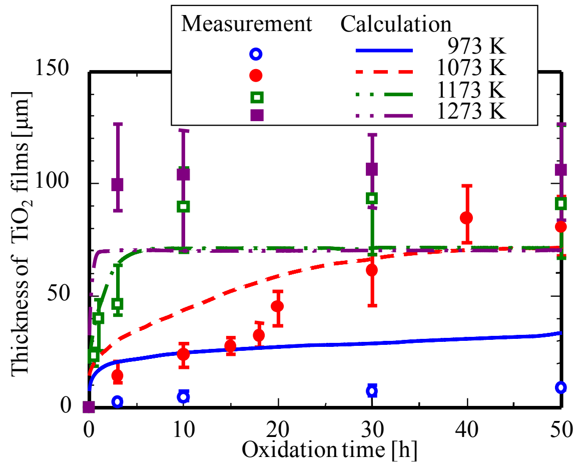

Figure 7. Relationship between thicknesses of TiO_2 films and oxidation time.

3.4 Morphology evolution of the films during high-temperature oxidation

The morphologies of the films fabricated by MCT and the following high-temperature oxidation at 973 and 1073 K are shown in Fig. 8 and Fig. 9. From Fig. 8 (b) and (c), nano-sized needles of TiO_2 were formed on the surfaces of Ti films. With the increase of oxidation time, the size of the needles became larger and columnar nanocrystals of TiO_2 were formed (Fig.8 (d) and (e)). When oxidation temperature was increased to 1073 K (Fig.9), the nano-sized needles of TiO_2 grew up rapidly and micron-sized columnar crystals of TiO_2 were formed with the increase of oxidation time.

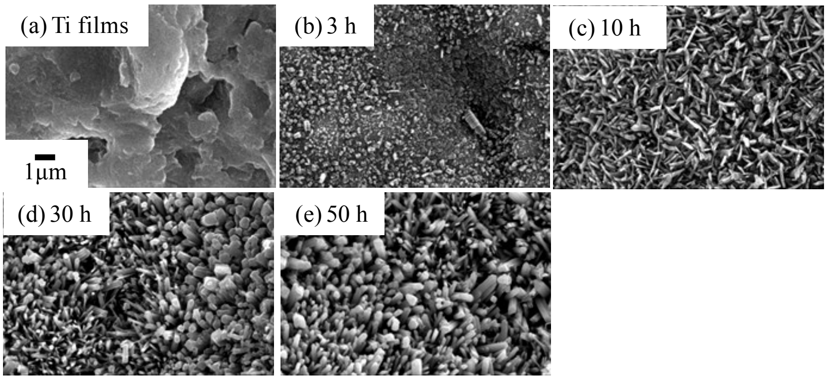

Figure 8. Morphologies of Ti films after oxidized at 973 K.

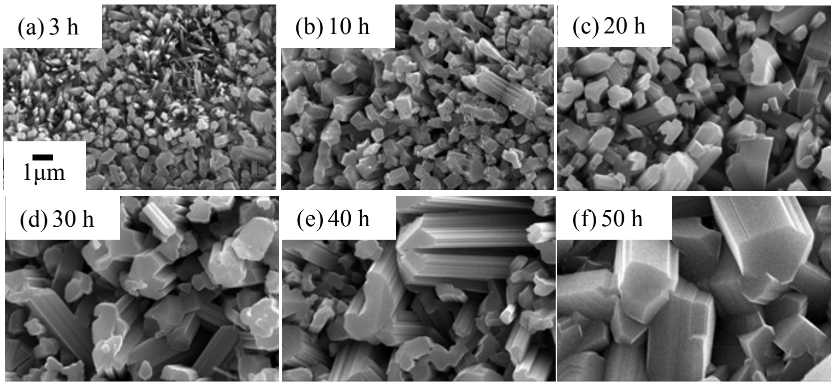

Figure 9. Morphologies of Ti films after oxidized at 1073 K.

3.5 Photocatalytic activity of the films

During photocatalytic activity evaluation of the films fabricated by MCT and the following high-temperature oxidation for 10 h, the concentration evolution of MB solution as a function of UV irradiation time is illustrated in Fig. 10. The concentration of MB solution with the Ti film-coated samples had a slight increase which means the Ti films had no photocatalytic activity. However, the concentration of the MB solution with the samples fabricated by MCT and the following high-temperature oxidation decreased in varying degrees. It means that the samples showed photocatalytic activity.

The degradation rate constants, *k* calculated from concentration-irradiation time curves are represented in Fig. 11. For the samples fabricated by MCT and the high-temperature oxidation at 973 and 1273 K, the degradation rate constants, *k* increased firstly and then nearly kept constant with the increase of oxidation time. On the other hand, *k* increased firstly and then decreased after their peak value for the samples fabricated by MCT and the high-temperature oxidation at 1073 and 1173 K. The samples fabricated by MCT and the following high-temperature oxidation at 1073 K for 15 h showed the highest photocatalytic activity for all the samples.

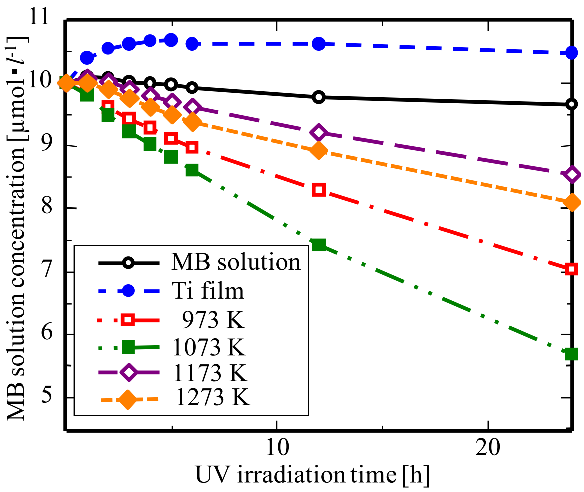

Figure 10. Concentration evolution of MB solution as a function of UV irradiation time.

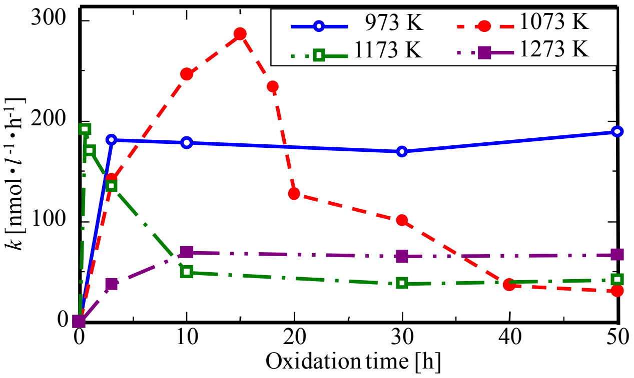

Figure 11. Degradation rate constants, *k* as a function of oxidation time.

The relationship between the degradation rate constants, the microstructure and the thickness of the films is shown in Fig. 12. It can be clearly seen that the samples with the TiO_2/Ti composite films showed much higher photocatalytic activity than those with single TiO_2 films. The improvement of photocatalytic activity is commonly considered to relate to the charge separation efficiency [12, 13]. When TiO_2 contacts with metals with higher work functions, photo-generated electrons in the conduction band of TiO_2 may transfer to the metal, which can decrease the recombination rate of electron-hole pair in TiO_2. Therefore, photocatalytic activity may be improved. When the thickness of TiO_2 films was 27 μm, the ratio of TiO_2 and Ti might be optimum at which the charge separation efficiency reached greatest. Therefore, the photocatalytic activity of the TiO_2/Ti composite films reached the greatest value (near 300 nmol·l^{-1}·h^{-1}).

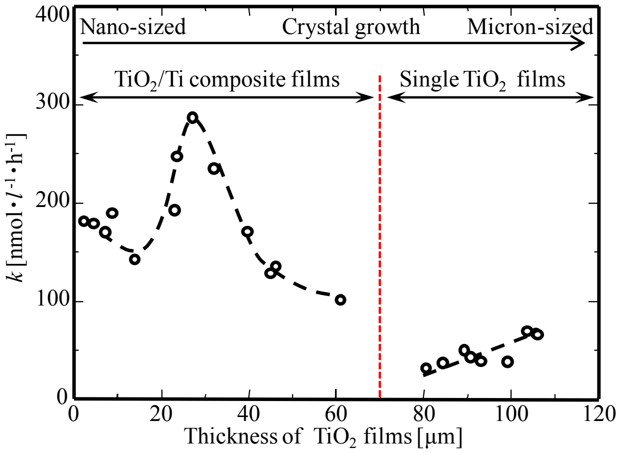

Figure 12. Relationship between degradation rate constants, *k* and thickness of TiO_2 films.

4 Conclusions

Single TiO_2 films and TiO_2/Ti composite films were fabricated by MCT and the following high-temperature oxidation. With the increase of oxidation temperature and oxidation time, the thickness of TiO_2 films on the surfaces of the samples increased and finally single TiO_2 films were obtained. Meanwhile, the nano-sized needles of TiO_2 grew up and micron-sized columnar crystals of TiO_2 were formed. Relatively higher photocatalytic activity of the samples was achieved. TiO_2/Ti composite films showed the highest photocatalytic activity. The formation of TiO_2/Ti composite microstructure is considered to be the main reason why the photocatalytic activity was improved.

References

[1] Fujishima A., Rao T.N., Tryk D.A. Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Review, 1, pp.1-21 (2000).

[2] Yoong L.S., Chong F.K., Dutta B.K. Development of copper-doped TiO_2 photocatalyst for hydrogen production under visible light. Energy, 34, pp.1652-1661 (2009).

[3] Arabatzis I.M., Stergiopoulos T., Andreeva D., Kitova S., Neophytides S.G., Falaras P. Characterization and photocatalytic activity of Au/TiO_2 thin films for azo-dye degradation. Journal of Catalysis, 220, pp. 127-135 (2003).

[4] Miyauchi M., Nakajima A., Watanabe T., Hashimoto K. Photocatalysis and photoinduced hydrophilicity of various metal oxide thin films. Chemistry of Materials, 14, pp. 2812-2816 (2002).

[5] Chen C.C., Yang W.J., Hsu C.Y. Fabrication of electron passes in nano-TiO_2 layer by high-velocity oxy-fuel method for dye-sensitized solar Cells. Superlattices and Microstructure, 46, pp. 461-468 (2009).

[6] Mills A., Elliott N., Parkin I.P., O'Neill S.A., Clark R.J. Novel TiO_2 CVD films for semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 151, pp. 171-179 (2002).

[7] Trapalis C., Todorova N., Anastasescu M., Anastasescu C., Stoica M., Gartner M., Zaharescu M., Stoica T. Atomic force microscopy study of TiO_2 sol–gel films thermally treated under NH_3 atmosphere. Thin Solid Films, 517, pp. 6243-6247 (2009).

[8] Lu Y., Yoshida H., Nakayama H., Hao L., Hirohashi M. Formation of TiO_2/Ti composite photocatalyst film by 2-step mechanical coating technique. Materials Science Forum, 675-677, pp. 1229-1232 (2011).

[9] Lu Y., Hao L., Toh K., Yoshida H. Fabrication of TiO_2/Cu composite photocatalyst thin film by 2-step Mechanical Coating Technique and its photocatalytic activity. Advanced Materials Research, 415-417, pp. 1942-1948 (2012).

[10] Yoshida H., Lu Y., Nakayama H., Hirohashi M. Fabrication of TiO_2 film by mechanical coating technique and its photocatalytic activity. Journal of Alloys and Compounds, 475, pp. 383-386 (2009).

[11] Hao L., Lu Y., Asanuma H., Guo J. The influence of the processing parameters on the formation of iron thin films on alumina balls by mechanical coating technique. Journal of Materials Processing Technology, 212, pp. 1169-1176 (2012).

[12] Sun P., Liu H.B., Yang H.B., Fu W.Y., Liu S.K., Li M.H., Sui Y.M., Zhang Y.Y., Li Y.X. Synthesis and characterization of TiO_2 thin films coated on metal substrate. Applied Surface Science, 256, pp. 3170-3173 (2010).

[13] Xu M.W., Bao S.J., Zhang X.G. Enhanced photocatalytic activity of magnetic TiO_2 photocatalyst by silver deposition. Materials Letters, 59, pp. 2194-2198 (2005).