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Photocatalytic Activity of TiO_2 Coatings Fabricated on Al_2O_3 by Mechanical Coating Technique

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Abstract: The titanium coatings were prepared on Al_2O_3 balls by mechanical coating technique (MCT), and then the coatings were oxidized to titanium oxides(TiO_2) films at 300-600 ℃. The effects of different milling time and oxidation temperature on thickness of films were studied. The composition and microstructure of the films were analyzed by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The results show that the thickest coatings with an average thickness of 20 μm were obtained at the milling time of 15 h. In addition, with the increase of the oxidation temperature, the oxidation of the film is increased. When the milling time is 15 h, the oxidation temperature is 500 ℃, and the addition of photocatalyst is 1 g/mL. The films have the best photocatalytic performance when the degradation rate of methyl orange solution reaches the maximum value of 74.9 %, and the films have a good reusability.

Key words: mechanical coating technique; photocatalytic activity; TiO_2; milling time; oxidation temperature

1 Introduction

TiO_2 has been widely researched due to its nontoxicity [1, 2], high catalytic efficiency[1-3], excellent chemical stability[1-4] and low energy consumption[5] in so many photocatalytic materials. TiO_2 can degrade most of the organic and inorganic pollutants in sewage into harmless or low toxic substances[6]. However, TiO_2 photocatalysts are often immobilized in films because the powder is easy to agglomerate, loses its activity, and difficult to recycle and reuse[2-5,7]. A large number of coating preparation technologies have been used to fabricate TiO_2 films such as physical-vapor deposition[8,9], chemical-vapor deposition[8,9], and the sol–gel method[8,10]. Unfortunately, these technologies are limited by complex operations and rigorous process[9,11].

The primary principle of mechanical coating technique (MCT) is cold welding. Fig.1 shows the schematic illustration of MCT. The Ti film of metal powder is formed in the pot of planetary ball mill based on the mechanical collision and friction of milling balls and metal powder[11,12]. With a higher efficiency and simple process, a metallic film can be easily formed on a circular or spherical substrates such as Al_2O_3 balls or bulks during MCT process [12-14]. Obviously, MCT provides a new direction for the preparation of TiO_2 films.

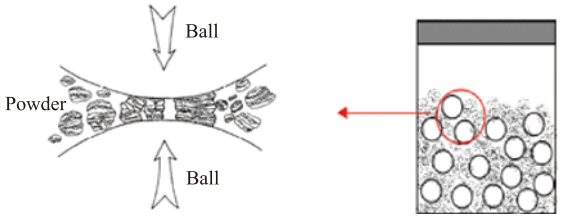

Fig.1 Schematic illustration of mechanical coating technique

In order to study the photocatalytic properties of TiO_2 films prepared by MCT. Ti films were prepared on the surface of Al_2O_3 by MCT. The composite films of Ti and titanium oxides were formed by oxidizing the Ti film at high temperature. And the photocatalytic activity was evaluated by ultraviolet-visible spectrophotometry.

2 Experimental

Titanium powder with a purity of 99.5 % and an average particle size of 75 μm was selected for the coating metal. Al_2O_3 balls with an average diameter of 6 mm were used as substrates. The MCT process was carried out in a planetary ball mill (ND7-

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2L) instrument. The ball-powder weight ratio was maintained at 2.5:1, and the rotation speed of the planetary ball mill was set at 250 rpm for 5, 10, 15 and 20 h, respectively. Then, the Al_2O_3 balls with Ti coatings were oxidized in air at 300, 400, 500 and 600 ℃ for 5 h, using box-type resistance furnace. The thickness of Ti films and the surface of the Titanium oxides films were observed by scanning electron microscopy (SEM, Hitachi S-3400). Moreover, the element distribution on the surface of balls were analyzed by the energy dispersive spectrometer (EDS). To study the photocatalytic activity of TiO_2 films, Al_2O_3 balls with titanium oxide films were added into 20 mL methyl orange solution, with a volume concentration of 10 mg/L and under the ultraviolet irradiation for 30 h. The different oxidation temperature, milling time and addition of photocatalyst were carried out. To study the stability of TiO_2 films, the degradation rates of methyl orange solution were measured by the 721A spectrometer.

3 Results and discussion

3.1 Surface morphology and cross-section of Ti coatings

Fig.2 shows the appearance of Ti coating samples at different milling time. After ball grinding for 5 h, the Ti coatings appears gray (Fig.2(a)). Because the Ti coatings is nonuniform pile on the Al_2O_3 ball at a short milling time.

The continuous layer of metallic coatings covered on the ball surface which is brown and smooth, when the milling time is 10 and 15 h, respectively (Fig.2(b) and 2(c)). However, there are many convex areas on the surfaces of Al_2O_3 balls at 20 h (Fig.2(d)), because the parts of Ti coatings have peeled off.

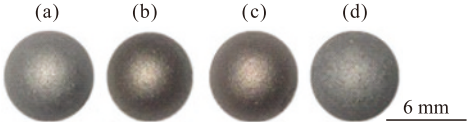

Fig.2 Photographs of the samples fabricated by MCT at different milling time: (a) 5 h, (b) 10 h, (c) 15 h, (d) 20 h

Fig.3 shows the cross-sectional micrographs of the Ti coatings at different milling time. The results show that the coatings thickness increases with the milling time. The peak value is reached when the milling time is 15 h (Fig.3(a)-(c)). It is an uneven coating with an average thickness of 20 μm. With the increase of milling time, the energy of pellets and Ti particles increases, and more Ti powder particles adhere to Al_2O_3 pellets, forming a continuous metal coating. Because of the cold welding between the Ti particles and the early coatings, the coatings thickness increased. When the milling time reaches 20 h, the coatings is partially delaminated. (Fig.3(d)). Because of the difference of thermal expansion coefficient between the Ti coatings and Al_2O_3 balls, the internal stress was formed into the coatings. The adhesion of the coatings in the surfaces of Al_2O_3 balls were weakened due to the internal stress. And the internal stress will be increased with the increase of ball milling time. In addition, after repeating plastic deformation, Ti powder particles and continuous metallic coatings became brittle due to the working hardening. The crack was formed when the brittle coatings were collided. The thickness of coatings will be reduced when the growth speed of coatings is less than the peeling speed.

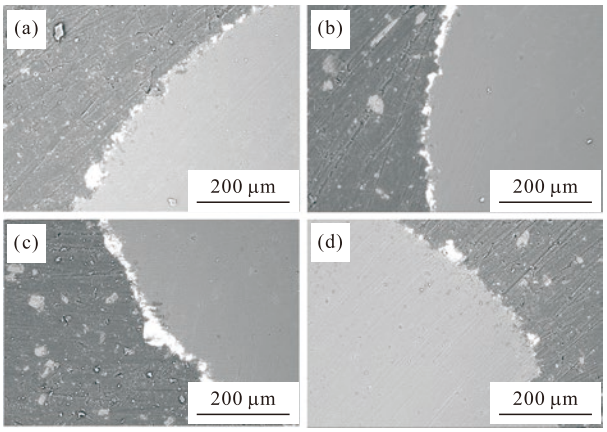

Fig.3 SEM of film's cross section under different ball milling time: (a) 5 h; (b) 10 h; (c) 15 h; (d) 20 h

3.2 The surface morphology and microstructure of the film

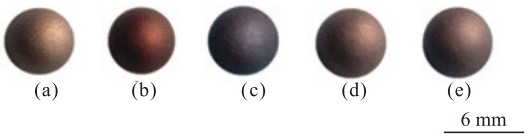

Fig.4 The films under different temperatures: (a) room temperature; (b)300 ℃; (c)400 ℃; (d)500 ℃; (e)600 ℃

Fig.4 shows the morphology of the samples. The samples were prepared by grinding Al_2O_3 balls with Ti power for 15 h and then oxidizing in air at different temperatures. With the increase of oxidation temperature, the metallic luster of balls disappeared and the color changed. The color of Fig.4(b) is brown, which is similar to TiO. The results showed that the Ti coatings began to oxidize. The color of Fig.4 (c) shows blue which is similar to Ti_3O_5. The color of sample Fig.4(d) and (e) become gray. The color change

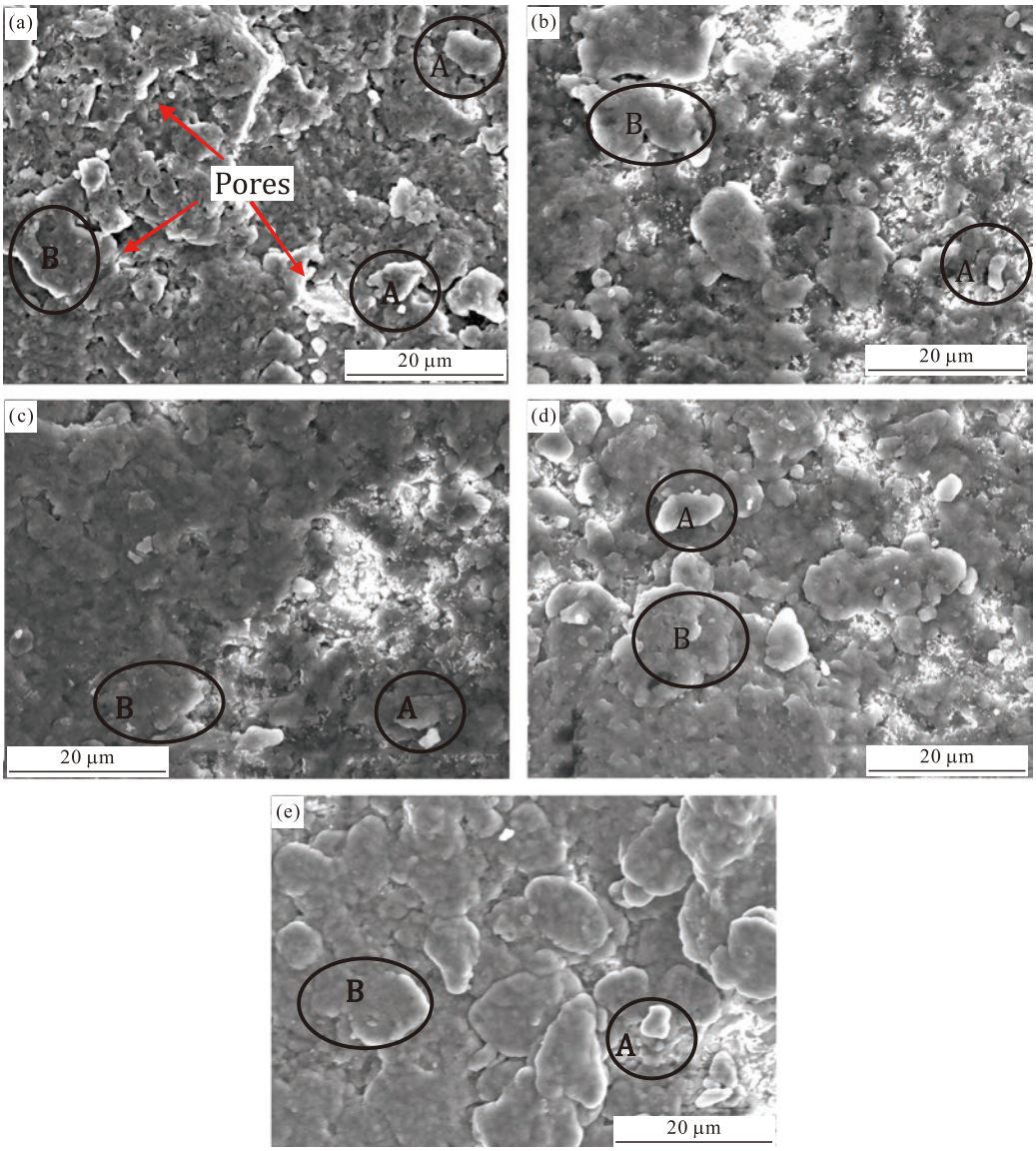

Fig.5 The microstructures of films under different temperatures: (a) room temperature; (b)300 ℃; (c)400 ℃; (d)500 ℃; (e)600 ℃

indicated that the oxidation of the titanium film was advanced with increase of oxidation temperature.

Fig.5 shows the surface SEM micrographs of the oxidized films. The surface of films has a great three-dimensional sense. There are a large number of granular substance (section A), flakes (section B) and pores on the surface of the films. It indicated that with the increase of oxidation temperature, the flake became smooth, the number of pores and particulate matters decreased, and the film became denser. (Fig.5 (b)-5(e)). Because fine particles bind together automatically to reduce surface energy, a rise in temperature can exacerbate the process. As a result, corners of the particles disappeared, and the particles became round, then, particles bonded together to form flakes.

Table 1 shows the surface elements of the films at different temperatures. All samples contain Al element.

Table 1 EDS analysis data of films under different temperatures/at%

Element	Room temperature	300 ℃	400 ℃	500 ℃	600 ℃
O	-	35.59	49.24	55.23	68.50
Al	3.11	3.27	2.16	1.78	-
Ti	96.89	61.14	48.60	42.99	31.50
O：Ti	-	0.58	1.01	1.28	2.17

Because the material of pot and balls is Al_2O_3, some Al_2O_3 particles were mixed into Ti powder, and then formed coatings in the process of ball milling. There is no O element in the unoxidized films. It indicated that the films are almost unoxidized. The content of O element and the atomic ratio of O to Ti were increased with the increasing of oxidation temperature. Because the increasing of temperature can intensify the

oxidation and form more titanium oxides.

3.3 Photocatalytic activity

3.3.1 Photocatalytic performance of the films at different temperatures and milling time

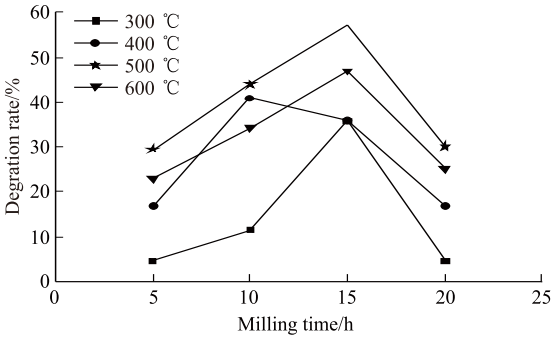

Fig.6 Dependence of photocatalytic activity on different temperature and ball milling time

Fig.6 shows the photocatalytic performance of the films at different temperatures and milling time. It indicated that the degradation rate increased and then decreased with the oxidation temperature increasing when the milling time is fixed. The films have the best photocatalytic performance at 500 ℃ when the degradation rate of methyl orange solution reach 57.1% and milling time is 15 h. Because of oxidizing treatment in lower temperature(less than 500 ℃), the coatings can't be oxidized sufficiently and there still exists a lot of Ti, as shown in Table 1. However, it forms titanium oxide +Ti composite films with the higher oxidizing temperature. The composite films have a higher photocatalytic activity relating to the efficiency of charge separation[15]. When titanium dioxide is combined with titanium, photo-generated electron of titanium dioxide many transfer to titanium, which can benefit for increased separation efficiency of photo-generated electron-hole pairs in titanium dioxide. Therefore, the photocatalytic activity is enhanced relatively. But, the degradation rate of methyl orange solution is decreased when the oxidation temperature is 600 ℃. At 600 ℃, the content of Ti decreased and the content of titanium oxide increased. The photogenerated electron-hole pairs have been blocked and couldn't been separated effectively, which leads to the decrease of degradation rate of methyl orange solution. When the oxidation temperature is 500 ℃, with the increase of milling time, the degradation rate first increases and then decreases, and reaches the peak at the milling time of 15 h (Fig.6). The thickness of the coatings increased with milling time. But the degradation rate of methyl orange solution decreased to 47% when milling time is 20 h. As shown in Fig.2, the part of coatings has peeled off. Therefore, the films on the Al_2O_3 balls are decreasing, which lead to the worst photocatalytic performance.

3.3.2 Photocatalytic performance of the films at different additions

Grind Al_2O_3 balls with Ti powder for 15 h and then the balls were oxidized at 500 ℃ in air. Fig.7 shows the photocatalytic performance of the films at different addition for 0.6, 0.8, 1.0 and 1.2 g/mL, respectively. The degradation rate of the methyl orange solution is 2% for the samples without films. It indicates the methyl orange solution is not degraded. It can be seen that the degradation rate increases with the addition of photocatalyst increasing when the addition of photocatalyst is below 1 g/mL, then, it decreases when the addition of photocatalyst is beyond 1 g/mL. The addition of photocatalyst of 1 g/mL shows the highest photocatalytic activity, which is 74.9%. Because more effective photons can be formed with the photocatalyst increasing, which can increase the degradation rate of methyl orange solution. However, the increase of photocatalysts will cause light scattering and occlusion between photocatalysts. They can reduce the generation of effective photons, leading to the decrease of the degradation rate of methyl orange solution. Therefore, when the addition of photocatalysts is 1 g/mL, the degradation rate of methyl orange solution reaches the maximum value.

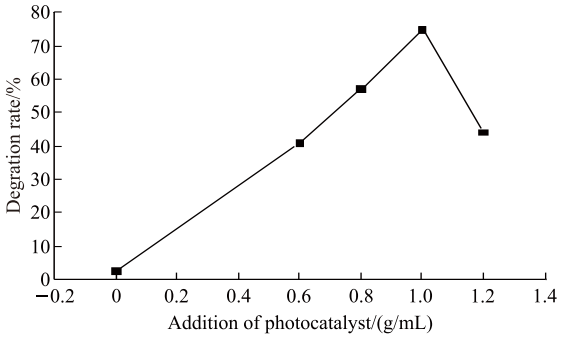

Fig.7 Dependence of photocatalytic activity and mass of film

3.3.3 The reusability of films

If the photocatalyst can be used repeatedly in wastewater treatment, it can not only improve the working efficiency, but also save the cost. Therefore, the study of photocatalytic film reusability has the vital practical significance in the field of photocatalysis technology. In this paper, the photocatalytic experiment was carried out to the films with the best photocatalytic performance for 5 times. Fig.8 shows the dependence of methyl orange solution degradation rate on the films

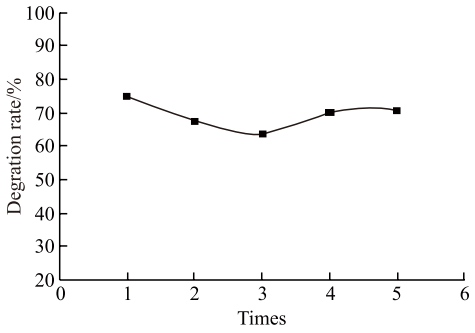

Fig.8 Dependence of photocatalytic activity and use times

reuse times. It can be seen that the degradation rate of methyl orange is above 60% after using the oxide film 5 times, which indicates that the film has a good reusability.

4 Conclusions

The Ti coatings can be fabricated by mechanical coating technique ,which have an average thickness of 20 μm when the milling time is 15 h.

The titanium oxide +Ti composite films have been obtained when the coating is oxidized at 300 - 600 ℃.The higher oxidation temperature, the higher titanium oxide content. The films are not dense enough and the surface of films has granular substance, flakes and pores.

The films have different photocatalytic performance with different of milling time, oxidized temperature and the addition of photocatalysts. The films have the best photocatalytic performance with the degradation rate of 74.9%, and a good reusability with the milling time of 15 h, oxidation temperature of 500 ℃ and the addition of photocatalysts of 1 g/mL.

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