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The Effects of Oxidation Temperature on the Microstructure and Photocatalytic Activity of the TiO_2 Coating

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Titanium coatings were prepared on the surface of 1mm ZrO_2 balls by mechanical ball mill, then the coatings were oxidized to photocatalytic TiO_2 films at 400 ~ 600 °C. X-Ray Diffraction, Scanning Electron Microscope, Energy Dispersive Spectroscopy and Optical Microscope were used to analyze the microstructure and crystal form of the films. The photocatalytic activity of the samples was also evaluated. After that, the effects of oxidation temperature on the microstructure and photocatalytic activity of the films were discussed. The results show that the fabricated coatings are uneven, with average thickness of 60 μm. In the process of oxidation, oxygen is imported into the inner coatings by the gaps existed in the Ti coatings, which makes the Ti particles oxidize from surface to core, finally the films with TiO_2 + Ti composite microstructure are obtained. The films oxidized at 500 °C have the best photocatalytic performance with the degradation rate of methyl orange solution 79.08 %, this owing to the existence of anatase and the TiO_2+Ti composite microstructure. The result will provide theoretical basis for the fabrication of efficient photocatalytic film.

Keywords: mechanical ball milling, photocatalytic activity, TiO_2, photocatalytic thin films, oxidation temperature.

1. INTRODUCTION

TiO_2 is a kind of n-type semiconductor materials with a band gap of 3.2eV (anatase), it can be used in sewage treatment, air purification and other fields because of the high photocatalytic activity under ultraviolet irradiation [1 – 4]. Comparing with powder TiO_2, supported TiO_2 film photocatalyst can be easily recycled and reused, thus a large number of coating preparation technologies were used to fabricate TiO_2 coatings (e.g., Physical Vapor Deposition, Chemical Vapor Deposition, Sol-Gel, and Magnetron Sputtering). Although these technologies are matured enough, complex operations and rigorous conditions are necessary. This is one of the reasons why TiO_2 based sewage treatment method couldn't have a large scale application. Mechanical coating technology (MCT) is a new method to prepare thin films. The basic principle of MCT is the cold welding, which makes the particles adhere to the milling ball surface and form coatings when mechanical ball milling is processing. With a higher efficiency and a lower cost, MCT can be easily used to form coatings on spherical or cylindrical substrates such as balls or tubes [5 – 8]. It's no doubt that MCT provides new ideas to prepare supported TiO_2 film, moreover, the prepared TiO_2 coatings have a spherical appearance, which is good for photocatalytic reaction. Using MCT, Lu Yun has prepared TiO_2 films on alumina balls and analyzed the formation mechanism of the films [8 – 11]. As for the oxidation process and the influence of oxidation temperature on photocatalytic activity of the TiO_2 films, they didn't discuss deeply.

In this paper, TiO_2 photocatalytic films were prepared on the surface of ZrO_2 balls by MCT, and its photocatalytic activity was evaluated. The mechanism and rules of oxidation process were studied, the influence of oxidation temperature on the microstructure and photocatalytic activity of TiO_2 films was also investigated. The results are a great theoretical support for subsequently fabricating efficient photocatalytic film.

2. EXPERIMENTAL DETAILS

Titanium powder with 99.5 % purity and an average diameter of 38μm was used as the coating metal, ZrO_2 balls with an average diameter of 1mm were used as substrates, because Ti coatings are easy to fabricate on the ZrO_2 grinding balls. A planetary ball mill (ND7-2L) was employed to perform the mechanical coating operation, 57.14 g ZrO_2 balls and 20.86 g Ti powder were added into a 250ml alumina bowl. The rotation speed of the planetary ball mill was set at 300 r/min and the milling time was 15 hours. Then, the ZrO_2 balls with Ti coating were oxidized in air at 400, 450, 500, 550, and 600 °C for 20 h. Photocatalytic activity of the samples was evaluated by measuring the decomposition rate of methyl orange solution (water solution) at room temperature. 10 g ZrO_2 balls with titanium oxide films were added in 20 ml, volume concentration of 10 mg/L of methyl orange solution. The degradation rates of methyl orange solution under UV irradiation for 24 h were measured by the 721 A spectrometer. The wavelength of the spectrometer was set to 464 nm, which is near the peak of absorption spectrum of methyl orange solution, as shown in Fig. 1. Before photocatalysis, all samples to be tested were put into dark to pre-adsorb for 12 h. The surface morphologies and microstructures of the samples were observed by SEM (S-3400), the element distribution was examined using an energy dispersive spectrometer being part of SEM. An optical microscope (DMM-400C) was used to observe the cross section of the coatings. An XRD (DMAX2500) with Cu-Kα radiation at 25 kV and 15 mA was used to analyze

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phase component, scanning speed 0.03°/s, at range of 20 ~ 80°. The DSC curve of anatase was measured by STA449F3 DSC-TG thermal analyzer in Ar atmosphere at a heating rate of 20 °C/min.

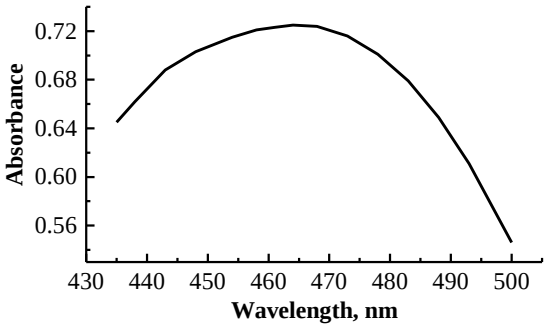

Fig. 1. The absorption spectra curve of methyl orange solution

3. RESULTS AND DISCUSSION

3.1. Surface morphology and structure of coatings

ZrO_2 balls were mixed with Ti power and milled for 15 h, and then the balls were oxidized in air at different temperatures. Fig. 2 shows the photograph of the samples. We can see that a continuous layer of metallic coating covered the ball surface at Fig. 2 a, however the metallic luster disappeared when the coatings were oxidized in air at different temperatures. With the increase of oxidation temperature, the color of coatings changed from dark blue to ash black (Fig. 2 b – f), which means that the oxidation results are different.

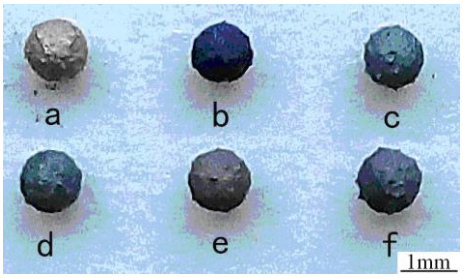

Fig. 2. Photograph of the samples fabricated by MCT and oxidized at: a – room temperature; b – 400 °C; c – 450 °C; d – 500 °C; e – 550 °C; f – 600 °C

The surface SEM micrographs of the oxidized films are illustrated in Fig. 3. It's shown that the metal particles bond together and form flakes. Several flakes stack each other form coating. However, the coatings are not dense enough. Between and inside the flakes, there are a large number of pores and gaps. Oxidized at 400 °C, the films have a low density as shown in Fig. 3 a, the flakes on the film's surface are out-of-shape and there are many pores in the films. But, with the increase of oxidation temperature, the flakes become smooth and the number of pores decrease, the films become more compact (Fig. 3 b – e). Because fine particles tend to agglomerate or bond together automatically in order to reduce surface energy, while, heating can intensify this process. Therefore, the sharp corners of the particles disappeared and the particles became flat, a bonding interface has formed between the particles after sintering.

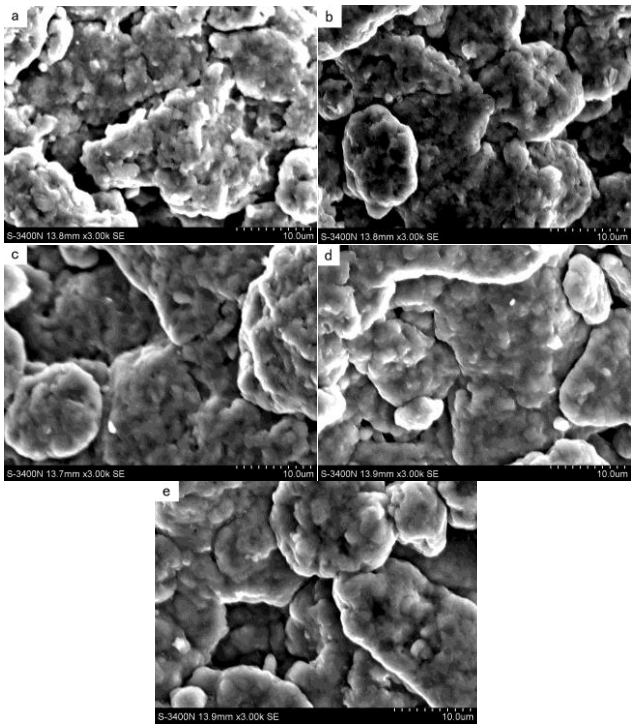

Fig. 3. SEM micrographs of the films oxidized in air for 20 h at: a – 400 °C; b – 450 °C; c – 500 °C; d – 550 °C; e – 600 °C

The optical micrographs of samples' cross section are shown in Fig. 4. Ball-milled for 15 h, an uneven coating with average thickness of 60μm was formed on the surface of ZrO_2 balls (Fig. 4 a).

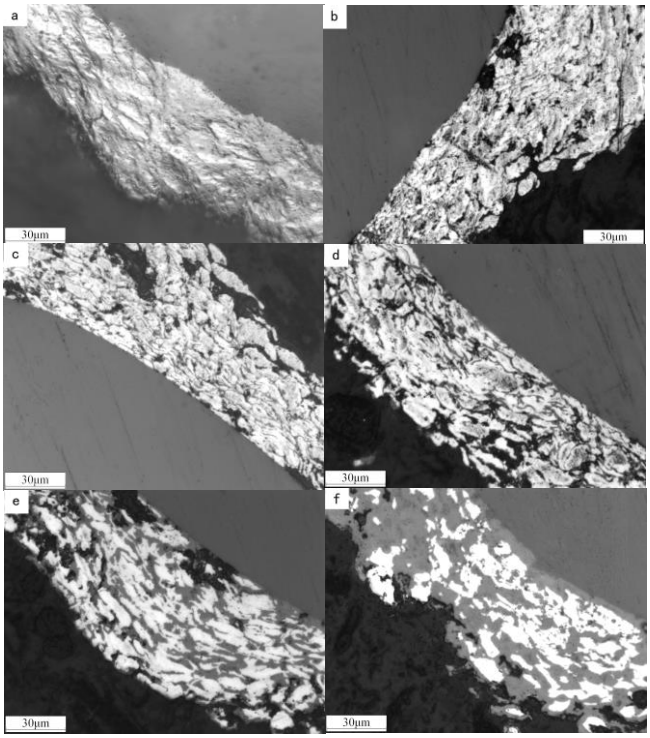

Fig. 4. Micrographs of the films' cross section oxidized in air for 20 h at: a – room temperature; b – 400 °C; c – 450 °C; d – 500 °C; e – 550 °C; f – 600 °C

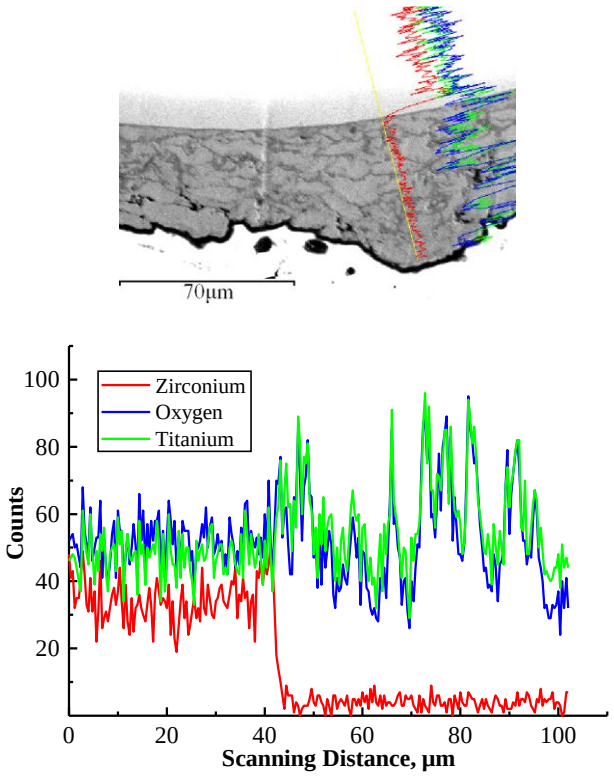

Fig. 5. EDS pattern of the film oxidized in air at 500℃for 20h

The bonding interface between coating and substrate is clear, which indicates that there is just mechanical bonding. And the interface among particles is inconspicuous. Oxidized at 400 ~ 600 °C, the interface among particles become obvious, as shown in Fig. 4 b – d. A kind of gray new phase has been observed at the interface which is different from the interior of Ti particles. By linear SEM-EDS (Fig. 5), it is found that the new phase is mainly composed of oxygen and titanium, which infers that the new phase is titanium oxide. As shown in Fig. 4, with oxidation temperature increasing, the white Ti areas shrink; the gray oxide areas enlarge, and reach to the maximum at 600 °C. The results indicate that the oxidation starts at the surface of each particle in the coatings, and penetrates into the interior. In the coatings, there are many tiny gaps between the Ti particles, so, oxygen can enter the coating internal through the gaps, as a result, oxidation does not just start at the outermost layer, not only the Ti particles on the outer layer but also the inner ones contact with oxygen and will be oxidized.

3.2. Phase composition of the films

Fig. 6. shows XRD patterns of the films oxidized at different temperatures for 20 h. The diffraction peaks of ZrO_2 can not be detected, which suggests that the prepared films are continuous and thick enough, X ray can't penetrate it. When the oxidation temperature is below 500 °C, the films consist of Ti and a little titanium oxide, and only a small amount of Ti was oxidized. With the increase of oxidation temperatures, the intensity of Ti peaks decrease (PDF2: 89-5009), while that of rutile peaks increase at 2θ of about 28° and 70° (PDF2: 87-0710). Oxidized at 600 °C, the Ti peaks still exist at about 40°, which indicates that the particles have not been oxidized completely under this condition, this is consistent with what have been observed in Fig.4. Although the intensity is weak, the diffraction peaks of anatase TiO_2 appear at about 25° and 37° (PDF2: 71-1168) when oxidized at 500 °C, which shows that there is a little anatase TiO_2 in the film. With the temperature rising, the content of anatase gradually decreases, as a result, the anatase TiO_2 peaks couldn't be detected in the films oxidized at 550 °C and 600 °C.

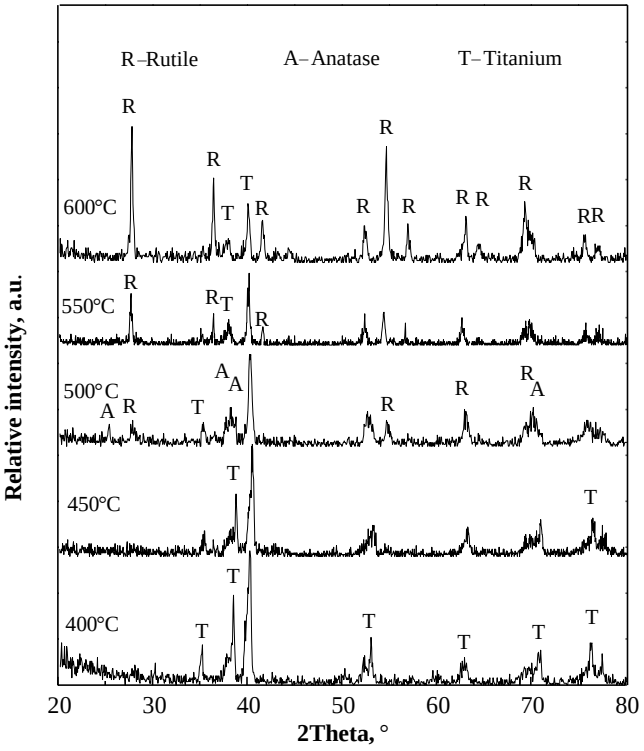

Fig. 6. XRD patterns of films oxidized in air at different temperatures

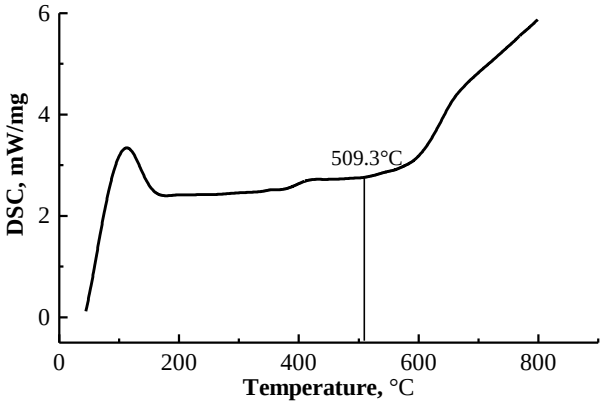

Fig. 7. DSC pattern of anatase powder

Because anatase TiO_2 is a kind of metastable phases and will transform to rutile TiO_2 as the temperature rises. Fig. 7 shows the DSC curve of anatase. It can be seen that the transformation from anatase to rutile started at about 509.3 °C. So when the samples were oxidized at 550 °C and 600 °C, anatase reduced and its diffraction peaks disappeared in relevant XRD patterns. Thus, it can be

concluded that, oxidized at 400 ~ 600 °C, the films with TiO_2 + Ti composite microstructure are obtained and TiO_2 mainly exist in rutile. After oxidized at 500 °C, there is a little anatase TiO_2 in the films, but does not at above 500 °C.

3.3. Photocatalytic activity

Fig. 8 shows the dependence of methyl orange solution degradation rate on the oxidation temperature. We can see that the degradation rate increases with the oxidation temperature increase below 500 °C, but it decreases beyond 500 °C. Oxidized at 500 °C, the films have the best photocatalytic performance with a degradation rate of methyl orange solution 79.08 %. Below 500 °C, the coatings can't be oxidized sufficiently and there still exists much more Ti. But, as the temperature rises up, the content of TiO_2 increases and the photocatalytic activity is enhanced relatively.

It's well known that anatase TiO_2 has more crystal defects and dislocations than rutile, which leads to an easier separation of photogenerated electron-hole pairs, and the electron hole produced by anatase is easier to be captured, besides, anatase has a stronger adsorption ability to the organic matter. So the photocatalytic performance of anatase TiO_2 is significantly better than that of rutile [12, 13]. When oxidized at 500 °C, the TiO_2 + Ti composite microstructure has been obtained, according to the publication, the TiO_2 + Ti composite microstructure is benefit for the separation of photogenerated electron-hole pairs at the surface of TiO_2, thus it can improve the photocalatytic activity [14, 15]. On the other hand, oxidized at this temperature, some TiO_2 exists as anatase phase, which is also a great increase in photocatalytic activity, therefore the films oxidized at 500 °C have the best photocatalytic performance. However, with the further increase of oxidation temperature, the content of TiO_2 increased, correspondingly that of Ti decreased, and anatase TiO_2 transformed to rutile type at 500 ~ 600 °C.

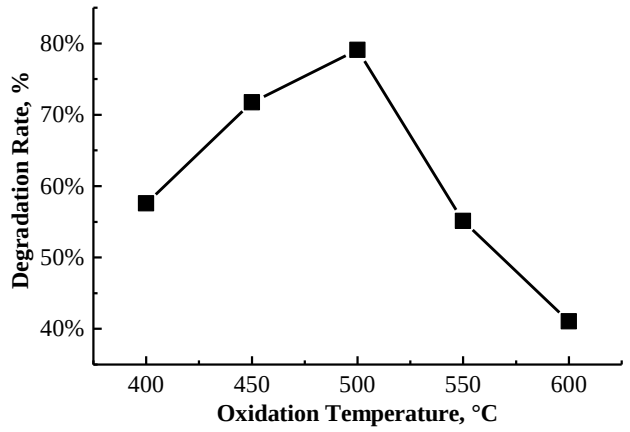

Fig. 8. Dependence of methyl orange solution degradation rate on the oxidation temperature

Oxidized at 600 °C, the formed TiO_2 layer is so thick that the photogenerated electron-hole pairs have been blocked and couldn't been separated effectively, which finally leads to the worst photocatalytic performance with the degradation rate of 41.06 %.

4. CONCLUSIONS

1. The coatings prepared by MCT have an average thickness of 60 μm. A large number of gaps exist in the metallic coating. Oxidation didn't just start at the outermost layer, oxygen could enter the inner coating through these gaps, which leads to the Ti particles in the coatings gradually being oxidized from the surface to the core.
2. TiO_2 + Ti composite microstructure has been obtained when the coatings are oxidized at 400 ~ 600 °C, the higher the oxidation temperature, the higher the TiO_2 content. TiO_2 mainly exists in rutile type, but oxidized at 500 °C, the films contain a small amount of anatase TiO_2.
3. The films prepared at 400 ~ 600 °C have different photocatalytic performance, oxidized at 500 °C, the films have the best photocatalytic performance with the degradation rate of 79.08 %, due to the TiO_2 + Ti composite microstructure and the existing of anatase TiO_2.

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