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Effects of oxidation temperature on the microstructure and photocatalytic activity of the TiO_2 coating

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Titanium coatings have been prepared on the surface of 1mm ZrO_2 balls by mechanical ball mill, then the coatings are oxidized to photocatalyst TiO_2 films at 400~600°C. XRD, SEM, EDS and OM were used to analyze the microstructure of the films. The photocatalytic activity of the samples is also evaluated. After that the effects of oxidation temperature on the microstructure and photocatalytic activity of the films has been discussed. Result shows that, oxygen elements are imported into the inner coatings by the gaps existed in the Ti coatings, which makes the Ti particles oxidized from surface to core, finally the films with TiO_2+Ti composite microstructure are obtained. The films have the best photocatalytic performance with degradation rate of methyl orange solution 79.08% by oxidation at 500°C, this owing to the existence of anatase and the composite microstructure.

Keywords: Mechanical ball milling, Photocatalytic activity, TiO_2, Photocatalytic thin films, Oxidation temperature

As is known to all, 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 UV irradiation[1-4]. Comparing with powder TiO_2, Supported TiO_2 film photocatalyst can be easily recycled, thus a large number of coating preparation technologies were used to prepare TiO_2 coatings (e.g., PDV, CDV, Sol-Geld, and Magnetron Sputtering). Although these technologies are mature enough, complex operations and rigorous conditions are necessary. Mechanical coating technology (MCT) is a new method to prepare thin films. The primary 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 coating on spherical or cylindrical substrates such as balls or tubes[5-8]. Using MCT, Lu Yun, has prepared TiO_2 films on alumina balls and analyzed the formation mechanism of the films [8-11].

In this paper, TiO_2 photocatalytic films were prepared on the surface of ZrO_2 balls by MCT, and its photocatalytic activities were evaluated. The mechanism and rules of the influence of oxidation temperature on microstructure and photocatalytic activity of the TiO_2 films were investigated.

Experimental Section

Titanium powders with 99.5% purity and an average diameter of 38μm were used as the coating metal, ZrO_2 balls with an average diameter of 1mm were used as substrates. A planetary ball mill was employed to perform the mechanical coating operation. Then, the ZrO_2 balls with Ti coating were oxidized in air at 400, 450, 500, 550, and 600°C for 20 h. The degradation rates of methyl orange solution under UV irradiation for 24 h at room temperature were measured by a spectrometer with a wavelength of 464 nm, which is near the peak of absorption spectrum of methyl orange solution. Before photocatalysis, all samples to be tested were put in dark to pre-adsorb for 12 h. The surface morphologies and microstructures of the samples were observed by SEM (JS-3400N), the elemental 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 phase component. The DSC curve of anatase was measured by STA449F3 DSC-TG thermal analyzer in Ar atmosphere at a heating rate of 20°C/min.

Results and Discussion

Surface morphology and structure of the 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. Figure 1 shows the photograph of the oxidized samples. We can see that a continuous layer of metallic coating covered the ball surface at Fig. 1(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 (Figs. 1 (b-f)), which means that the oxidation results are different.

The surface SEM photomicrographs of the oxidized films are illustrated in Fig. 2. 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 film has a low density as shown in Fig. 2(a), the flakes on the film's surface is out-of-shape and there exist many pores. But, with the increase of oxidation temperature, the flakes became smooth and the number of pores decreased, the films became more pyknotic (Fig. 2(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 disappear and the particles become flat, a bonding interface has formed between the particles.

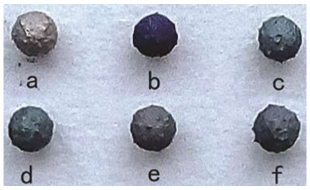

Fig. 1— Photograph of the samples fabricated by MCT and oxidized at: (a) room temperature (b) 400°C; (c) 450°C; (d) 500°C; (e) 550°C; (f) 600°C

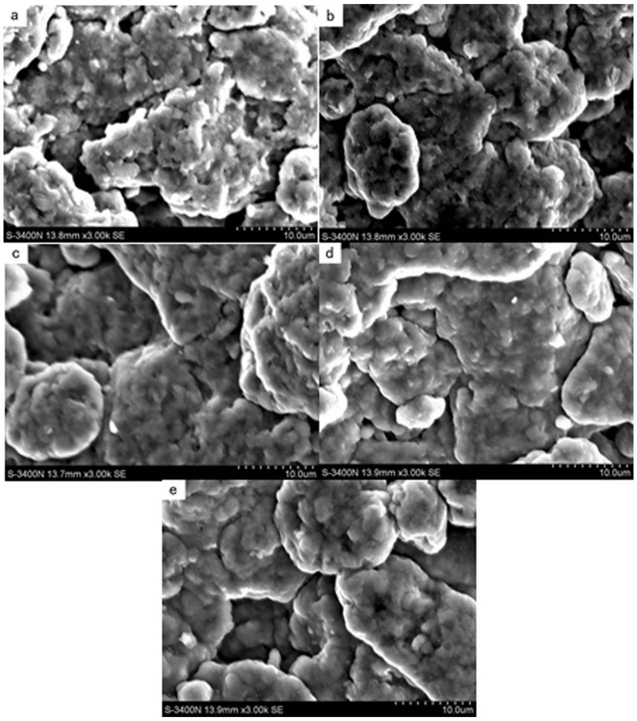

Fig. 2 — SEM micrographs of the films oxidized in air for 20 h at: (a) 400°C; (b) 450°C; (c) 500°C; (d) 550°C; (e) 600°C

The optical micrographs of sample cross section are shown in Fig. 3. Ball-milled for 15 h, an uneven coating with average thickness of 60 μm has formed on the surface of ZrO_2 balls (Fig. 3(a)). The bonding interface of coating and substrate is clear, which indicates that there is just a mechanical bonding. And the interface among particles is unconspicuous. Oxidized at 400~600°C, the interface among particles become obvious, as shown in Fig. 3(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. 4), it is found that the new phase is mainly composed of oxygen and titanium, which infers that the new phases are titanium oxide. As shown in Fig. 3, 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 inner through the gaps, as a result, not only the Ti particles on the outer layer but also the inner ones contact with oxygen and have been oxidized.

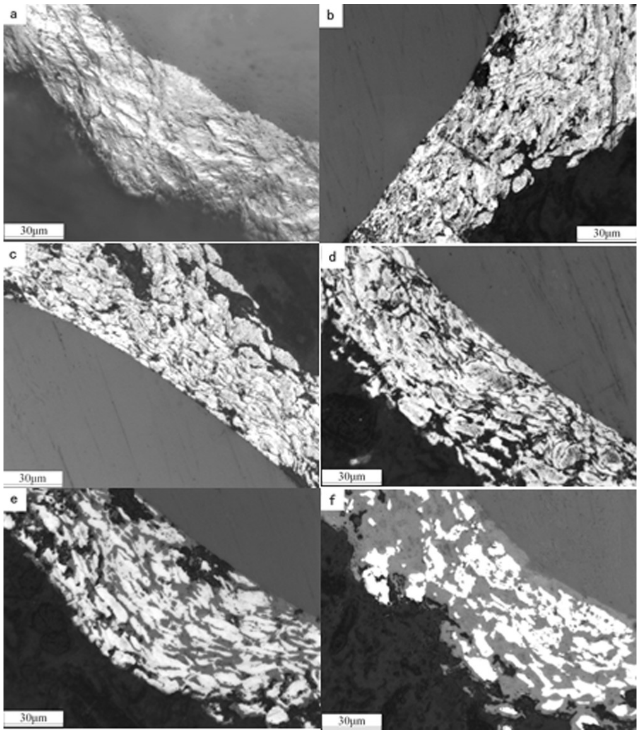

Fig. 3 — Micrographs of the film cross sections oxidized in air for 20 h at: (a) room temperature; (b) 400°C; (c) 450°C; (d) 500°C; (e) 550°C; (f) 600°C

Phase composition of the films

Figure 5 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 consiste of Ti and a little titanium oxide, and only a small mount of Ti was oxidized. With the increase of oxidation temperatures, the intensity of Ti peaks decrease, while that of rutile peaks increased at 2θ of about 28° and 70°. Oxidized at 600°C, the Ti peaks still existed at about 40°, which indicates that the particles have not been oxidized completely under this condition, this is consistent with what has been observed in Fig. 3. Although the intensity is weak, the diffraction peaks of anatase TiO_2 appeared at about 25° and 37° 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 can't be detected in the films oxidized at 550°C and 600°C. Because the anatase TiO_2 is a kind of metastable phase and will transform to rutile TiO_2 as the temperature rises. Figure 6 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 are 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 was obtained. There existed a little anatase TiO_2 in the film oxidized at 500°C, but does not at above 500°C.

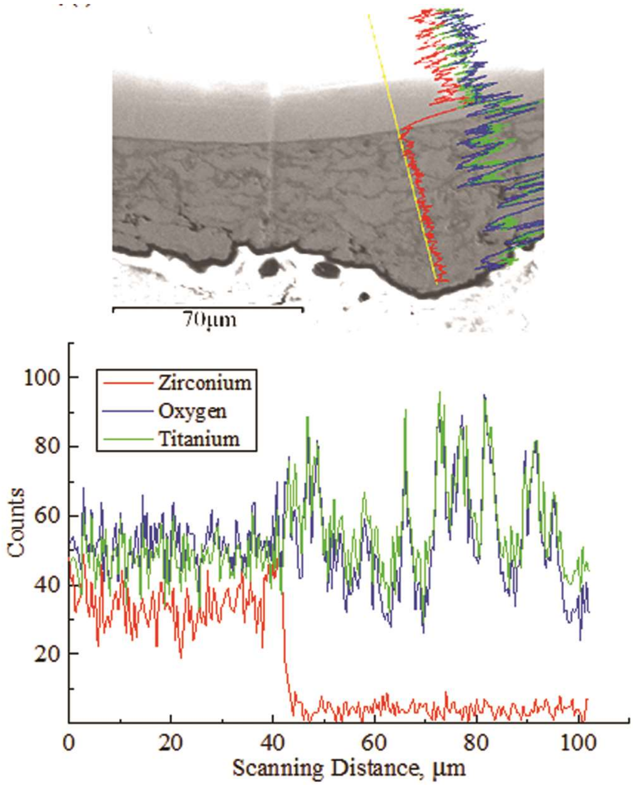

Fig. 4 — EDS pattern of the film oxidized in air at 500°Cfor 20h

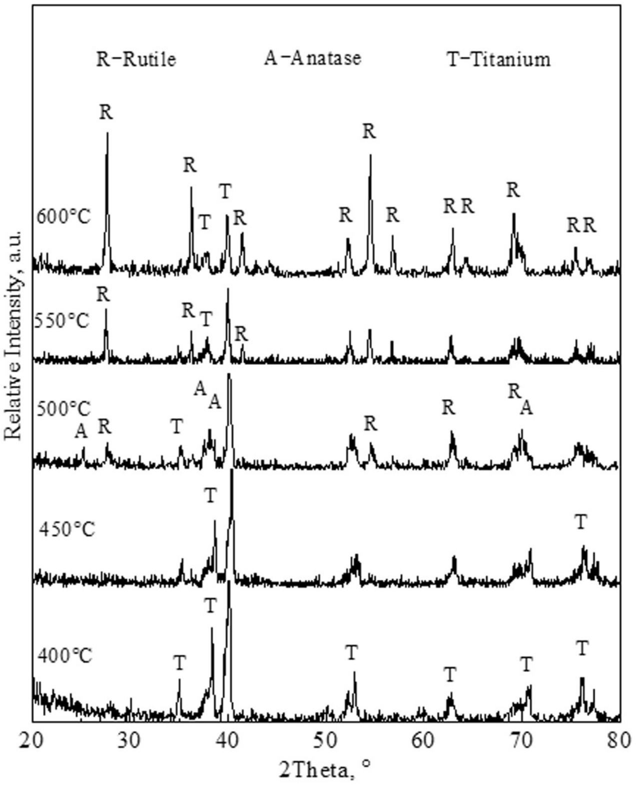

Fig. 5 — XRD patterns of films oxidized in air at different temperatures

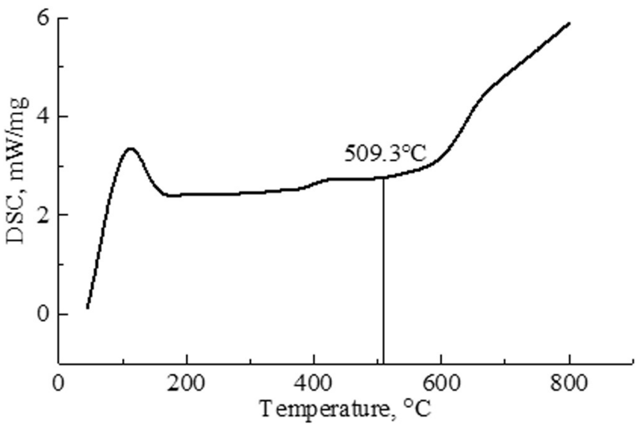

Fig. 6 — DSC pattern of anatase powder

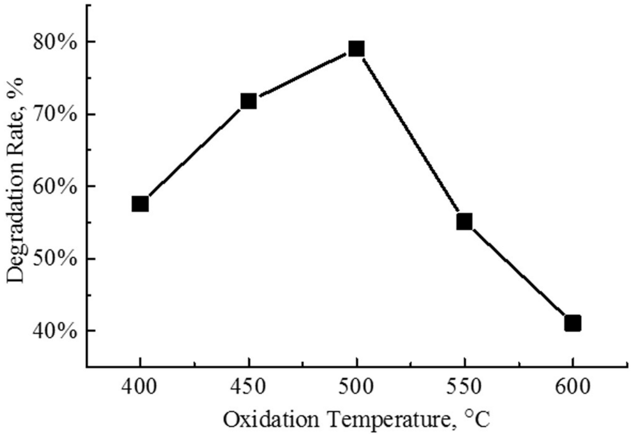

Fig. 7 — Dependence of methyl orange solution degradation rate on the oxidation temperature

Photocatalytic activity

Figure 7 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%. Oxidized below 500°C, the coatings have not been 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. Oxidized at 500°C, the TiO_2+Ti composite microstructure has been obtained. 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 [12, 13]. On the other hand, Oxidized at this temperature, some TiO_2 exist as anatase phase, which is also good for the photocatalytic activity, because the photocatalytic performance of anatase TiO_2 was significantly better than that of rutile type[1, 14]. Therefore the films oxidized at 500°C had 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. Oxidized at 600°C, the formed TiO_2 layer is so thick that the photogenerated electron-hole pairs have been blocked and can not be separated effectively, which ultimately leads to the worst photocatalytic performance with the degradation rate of 41.06%.

Conclusion

1) The coatings prepared by MCT have an average thickness of 60 μm. A large number of gaps exist in the metallic layer, oxygen could enter the inner coating through these gaps, which leads to the most 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 coating is oxidized at 400~600°C, the higher the oxidation temperature, the higher the TiO_2 content. Oxidized at 500°, TiO_2 mainly exists in rutile type, but contains 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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