Preparation and characterization of ZrO$_2$/TiO$_2$ composite photocatalytic film by micro-arc oxidation

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Abstract: ZrO$_2$/TiO$_2$ composite photocatalytic film was produced on the pure titanium substrate using in-situ Zr(OH)$_4$ colloidal particle by the micro-arc oxidation technique and characterized by scanning electron microscope (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and ultraviolet-visible (UV-Vis) spectrophotometer. The composite film shows a lamellar and porous structure which consists of anatase, rutile and ZrO$_2$ phases. The optical absorption edge of film is shifted to longer wavelength when ZrO$_2$ is introduced to TiO$_2$. Furthermore, the photocatalytic reaction rate constants of degradation of rhodamine B solution with ZrO$_2$/TiO$_2$ composite film and pure TiO$_2$ film under ultraviolet irradiation are measured as 0.0442 and 0.0186 h$^{-1}$, respectively.

Key words: pure titanium; micro-arc oxidation; Zr(OH)$_4$; colloidal particle; ZrO$_2$/TiO$_2$; composite photocatalytic film

1 Introduction

TiO$_2$ photocatalysis is currently accepted as one of the most promising technologies for destruction of organic pollutions in the environment because it is cheap, chemically and biologically inert, non-toxic, photostable, and highly photo-reactive [1–4]. The immobilization of TiO$_2$ is so critical for the practical photocatalytic application. Micro-arc oxidation (MAO) is a processing technique which can convert the surfaces of valve metals, such as aluminum, magnesium and titanium, into ceramic coatings [5–7]. The technique is considered to be appropriate for immobilizing the TiO$_2$ photocatalyst, because the distinct properties of TiO$_2$ formed via MAO include chemical durability, large specific surface area, remarkable thickness and good adhesion to metal substrate. Furthermore, the complex TiO$_2$ film can be formed by adjusting electrolyte composition. There are only few reports on growing composite TiO$_2$ photocatalytic films by MAO method. HE et al [8] prepared the WO$_3$/TiO$_2$ photocatalytic films on pure titanium substrate via MAO technique in tungstate electrolyte. BAYATI et al [9] used the MAO method to synthesize V$_2$O$_5$/TiO$_2$ photocatalytic films. JIANG et al [10] fabricated the TiO$_2$/YAG:Ce$^{3+}$ compound photocatalytic films upon titanium alloy by micro-arc oxidation.

On the other hand, the fast recombination of photogenerated electron-hole pairs deteriorates the photocatalytic activity of TiO$_2$, which limits the commercialization of this technology [11]. Some semiconductors have been used to couple with TiO$_2$ in order to improve its photocatalytic activity. Among these semiconductors, ZrO$_2$ is considered an appropriate semiconductor coupled with TiO$_2$ because it is beneficial for the increase of surface area, the stabilization of anatase and the existence of stable electron-hole pairs [12–14]. As far as we know, ZrO$_2$/TiO$_2$ composite photocatalytic film has not been prepared by MAO technique to date. In this work, ZrO$_2$/TiO$_2$ composite photocatalytic film is prepared using in-situ Zr(OH)$_4$ colloidal particle by MAO technique and the photocatalytic activity of the film is investigated.
2 Experimental

2.1 Preparation of film

The equipment used during the MAO process consists of an AC power supply, an electrolyte cell, a stirring system, a cooling system and an exhaust system. The pure titanium (99.5%) sheets with dimensions of 20 mm × 20 mm × 2 mm were polished by emery paper (150#–1200# grit), degreased by acetone and then rinsed by distilled water before the MAO process. The pure titanium sheet was selected as the anode and the stainless steel plate was used as the cathode. The electrolyte consisted of K$_2$ZrF$_6$ (7.1 g/L), NaOH (5 g/L) and NaF (1 g/L). In order to compare the microstructure and photophysical property of the ZrO$_2$/TiO$_2$ composite film with those of pure TiO$_2$ film which was prepared in the electrolyte consisting of Na$_3$PO$_4$·12H$_2$O (9.5 g/L), NaOH (1 g/L) and NaF (1 g/L). The electrolytes used to prepare ZrO$_2$/TiO$_2$ composite film and pure TiO$_2$ film were marked as electrolytes A and B, respectively. The electrolyte temperature was kept under 40 °C through circulating water cooling system during the complete MAO process. The positive voltage, negative voltage, frequency, duty cycle and treatment time for both the ZrO$_2$/TiO$_2$ composite film and the pure TiO$_2$ film were 300 V, −40 V, 700 Hz, 0.3 and 6 min, respectively. The as-prepared films were rinsed by distilled water, dried in hot air and then kept in a drying chamber.

2.2 Analysis of film

The phase composition and crystalline structure of films were determined by XRD analysis using a D/Max-IIIB diffractometer with Cu K$_\alpha$ radiation. A Quanta 200 scanning electron microscopy (SEM) was used to characterize the morphological feature of the films. The composition of films was analyzed with an energy dispersive X-ray (EDX) detector incorporated into the SEM. A Shimadzu UV−2550 UV-Vis spectrophotometer with an integrating sphere attachment recorded the diffuse reflectance spectra (DRS) of films.

2.3 Evaluation of photocatalytic activity

The photocatalytic activity of films was determined by degrading aqueous solutions of rhodamine B. The samples were submerged into 10 mL of rhodamine B solution (10 mg/L) in the dark for 30 min prior to irradiation in order to achieve adsorption/desorption equilibrium. An ultraviolet lamp (36 W) with a maximum irradiation peak at 254 nm was used as light source, the solution was constantly supplied with air during the irradiation process, a fixed quantity of solution was removed every 2 h to measure the absorbance. The absorbance of rhodamine B solution was tested at the wavelength of 550 nm with a UV-Vis spectrophotometer.

3 Results and discussion

3.1 XRD analysis

The XRD patterns of films prepared in different electrolytes are shown in Fig. 1. The characteristic peaks of Ti are detected from pure titanium substrates. A mixed phase of anatase, rutile and ZrO$_2$ occurs in the ZrO$_2$/TiO$_2$ composite film. The mechanism for formation of ZrO$_2$/TiO$_2$ composite film can be interpreted as follows. At first, the reaction between K$_2$ZrF$_6$ and NaOH occurs in the electrolyte:

$$K_2ZrF_6 + 4NaOH \rightarrow Zr(OH)_4 \downarrow + 2KF + 4NaF \quad (1)$$

Zr(OH)$_4$ is the colloidal particle, whose isoelectric point is 6.8, which means that Zr(OH)$_4$ is electropositive when the pH of electrolyte is lower than 6.8 and Zr(OH)$_4$ is electronegative when the pH of electrolyte is higher than 6.8 [15]. So, Zr(OH)$_4$ colloidal particle should be electronegative in the alkaline electrolyte. When the MAO process begins, an oxidation reaction occurs on the surface of titanium substrate [16]:

![Fig. 1 XRD patterns of films prepared in different electrolytes: (a) ZrO$_2$/TiO$_2$ composite film prepared in electrolyte A; (b) Pure TiO$_2$ film prepared in electrolyte B](image-url)
\[ \text{Ti} \rightarrow \text{Ti}^{4+} + 4e \quad (2) \]

Meanwhile, the Zr(OH)\textsubscript{4} particles and OH\textsuperscript{-} anions move toward the anode surface because of the strong electrical field between anode and cathode, and then the following reactions occur due to the strong spark discharge on the surface of anode \[16,17\]:

\[ \text{Zr(OH)}_4 \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O} \quad (3) \]

\[ \text{Ti}^{4+} + 4\text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \quad (4) \]

The crystalline phase of the pure TiO\textsubscript{2} film is anatase, because it is very difficult for the metastable anatase phase to transform to thermodynamically stable rutile phase due to less heat produced by mild spark discharge on the surface of anode. The ratio of rutile to anatase in the ZrO\textsubscript{2}/TiO\textsubscript{2} composite film is very high. Furthermore, the photocatalytic activity of rutile is lower than that of anatase. At the same time, because the conductive band of anatase phase locates at a higher energy position than that of rutile phase by about 0.20 eV, the photo-generated electron can transfer from rutile to anatase, which effectively inhibits the recombination of photo-generated electron-hole pairs \[18,19\]. Therefore, the ZrO\textsubscript{2}/TiO\textsubscript{2} composite film should have a higher photonic efficiency compared with pure TiO\textsubscript{2} film.

### 3.2 Microstructures

The surface micrographs of films prepared in different electrolytes are shown in Fig. 2. Obviously, the surface of ZrO\textsubscript{2}/TiO\textsubscript{2} composite film exhibits a lamellar and porous microstructure. Furthermore, on the surface of film, there are many bright particles which are agglomerated. The EDX analysis of the bright particle marked in Fig. 2(b) is shown in Fig. 3, and the contents of elements are presented in Table 1. The bright particle mainly contain 22.95\% Zr, 11.13\% Ti and 65.91\% O (mole fraction), which is similar to the chemical compositions of the mixture of ZrO\textsubscript{2} and TiO\textsubscript{2}. The holes in the film are not only the reaction channels between electrolyte and substrate but also the channels through which molten oxide ejects during the MAO process. The strong spark discharge on the surface of anode generates high temperature and pressure, which results that the titanium substrate melts and then enters into the reaction channels, and is oxidized. The oxidized titanium rapidly ejects from the channels and solidifies because of the cold quenching of electrolyte. Meanwhile, the Zr(OH)\textsubscript{4} particles translate to the ZrO\textsubscript{2} particles on the surface of anode and then combine with the oxidized titanium to form the mixture of ZrO\textsubscript{2} and TiO\textsubscript{2}. Although the surface of pure TiO\textsubscript{2} film also exhibits a porous microstructure, the surface of pure TiO\textsubscript{2} film is relatively smooth compared with the ZrO\textsubscript{2}/TiO\textsubscript{2} composite film. Mild spark discharge means fewer discharge channels on the surface of pure TiO\textsubscript{2} film compared with the ZrO\textsubscript{2}/TiO\textsubscript{2} composite film, which results that the surface of pure TiO\textsubscript{2} film is relatively smooth compared with the ZrO\textsubscript{2}/TiO\textsubscript{2} composite film.

The cross-section micrographs of films prepared in different electrolytes are shown in Fig. 4. There is no...
obvious discontinuity between the films and the substrate, which proves that the films are well adhered to the titanium substrate. This is beneficial to long-term degradation of organic compounds. However, there are two considerable differences in cross-section micrographs of two films. The thicknesses of the ZrO$_2$/TiO$_2$ composite film and the pure TiO$_2$ film are approximately 10 and 3 $\mu$m, respectively. Furthermore, compared with the pure TiO$_2$ film, there are many micro-pores in the inner layer of the ZrO$_2$/TiO$_2$ composite film. The growth of the MAO film is the result of melting and solidifying of oxide through the discharge channels, therefore, more discharge channels mean faster growth rate and the ZrO$_2$/TiO$_2$ composite film should be thicker than the pure TiO$_2$ film during the same period.

The differences of the surface and cross-section morphologies between the two films are attributed to more violent spark discharge during the MAO process of ZrO$_2$/TiO$_2$ composite film. For ZrO$_2$/TiO$_2$ composite film, the lamellar and porous microstructure, agglomerated ZrO$_2$/TiO$_2$ mixed particles and micro-pores in the inner layer of film should be responsible for providing more surface sites, in which more organic compounds and photons can be absorbed compared with the pure TiO$_2$ film.

3.3 UV-Vis absorption spectra

The UV-Vis absorption spectra of films prepared in different electrolytes are shown in Fig. 5. Obviously, the optical absorption edges of the ZrO$_2$/TiO$_2$ composite film and the pure TiO$_2$ film are about 421 and 412 nm, respectively. A slight shift towards longer wavelength in absorption band is detected when ZrO$_2$ is introduced to TiO$_2$. This behavior is in a good agreement with achievement of Ref. [20]. Zr ions may enter into the lattice of TiO$_2$ because of violent spark discharge during the MAO process, which leads to the lattice deformation as reported by WANG et al [21]. Therefore, some structural defects such as vacancies in the lattice would correspond to point $A$ in Fig. 2(b).

### Table 1 Contents of surface element of bright particles

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass fraction/%</th>
<th>Mole fraction/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>28.64</td>
<td>65.91</td>
</tr>
<tr>
<td>Ti</td>
<td>14.48</td>
<td>11.13</td>
</tr>
<tr>
<td>Zr</td>
<td>56.87</td>
<td>22.95</td>
</tr>
</tbody>
</table>

Fig. 4 Cross-section micrographs of films prepared in different electrolytes: (a) ZrO$_2$/TiO$_2$ composite film prepared in electrolyte A; (b) Pure TiO$_2$ film prepared in electrolyte B

Fig. 5 UV-Vis absorption spectra of films prepared in different electrolytes: (a) ZrO$_2$/TiO$_2$ composite film prepared in electrolyte A; (b) Pure TiO$_2$ film prepared in electrolyte B
be produced particularly on the surface to partially offset the lattice strain [22]. The enhanced concentration of the oxygen vacancies in binary oxides system forms a defect band that further changes the energy of conduction band [23]. However, the ZrO_2/TiO_2 composite film exhibits lower absorption in the visible light region compared with the pure TiO_2 film, because ZrO_2 has a lower ability of absorbing visible light compared with TiO_2 and the excessive ZrO_2 can cover the surface of composite films, resulting that very little visible light is absorbed by ZrO_2/TiO_2 composite film.

3.4 Photocatalytic activity

No detectable degradation of rhodamine B occurs without MAO films under UV light radiation. It is proved that the photocatalytic decomposition of rhodamine B solution agrees with the apparent first-order model [24]:

\[ \ln \frac{C_0}{C} = kt \]  

(5) where \( C_0 \) is the initial concentration of the rhodamine B solution at \( t=0 \); \( C \) is the concentration of the rhodamine B solution at latter time \( t \); \( t \) is the irradiation time and \( k \) is the reaction rate constant. Figure 6 illustrates the relationship of \( \ln \frac{C_0}{C} \) versus irradiation time for two films. The photocatalytic reaction rate constants of degradation of rhodamine B solution with ZrO_2/TiO_2 composite film and pure TiO_2 film under UV irradiation are measured as 0.0442 and 0.0186 h^{-1}, respectively. A comparison between the photocatalytic activities of the two films emphasizes the photocatalytic enhancement in the ZrO_2/TiO_2 composite film, which can be mainly attributed to the mixed phase, more surface sites and formation of structural defects. The ZrO_2/TiO_2 composite film has the mixed phase of anatase, rutile and ZrO_2, which results that the photo-generated electron can transfer from rutile to anatase. This effectively inhibits the recombination of photo-generated electron-hole pairs. The lamellar and porous microstructure, agglomerated ZrO_2/TiO_2 mixed particles and micro-pores in the inner layer should be responsible for providing more surface sites, in which more absorbed organic compounds can be degraded by OH^{-}. Furthermore, some oxygen might be escaped from the surface of the lattice to trap the photo-generated holes because of the formation of vacancies on the surface [22]. In addition, metal oxides with more structure defects on surface are able to substantially ionosorb oxygen, in the form of O^{2-} species, which are involved in electron capture in aqueous phase reactions, to let photoholes react with surface OH^{-} groups [25]. Another reason of the enhanced photocatalytic activity is zirconia modified titania with higher surface acidity, the surface sites with higher acidity may prove to be better adsorption sites or hole traps [20].

\[ \text{Fig. 6 Relationship of } \ln \frac{C_0}{C} \text{ versus irradiation time for films prepared in different electrolytes: (a) ZrO}_2/\text{TiO}_2 \text{ composite film prepared in electrolyte } \text{A}; \text{ (b) Pure TiO}_2 \text{ film prepared in electrolyte B} \]

4 Conclusions

ZrO_2/TiO_2 composite film with a lamellar and porous morphology was successfully produced in the electrolyte consisted of in-situ Zr(OH)_4 colloidal particle by the MAO technique. The composite film consists of anatase, rutile and ZrO_2 phases. The optical absorption edges of the ZrO_2/TiO_2 composite film and the pure TiO_2 film are about 421 and 412 nm, respectively. It is also revealed that the photocatalytic activity of ZrO_2/TiO_2 composite film enhances approximate three times compared with pure TiO_2 film under UV irradiation. Future works will be focused on the further improvement of photocatalytic activity of ZrO_2/TiO_2 composite film under ultraviolet and visible irradiations by adjusting process parameters, such as power voltage, reaction time and electrolyte composition.

References


ZrO$_2$/TiO$_2$ 复合光催化膜的微弧氧化法制备及表征

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摘 要: 采用微弧氧化方法和原位生成的 Zr(OH)$_x$ 胶体颗粒，在纯钛基体上制备 ZrO$_2$/TiO$_2$ 复合光催化膜。采用 SEM、EDX、XRD、UV-Vis DRS 等分析手段，对膜层进行分析表征。结果表明：复合膜显示出层状和多孔的结构。孔径图中，金红石和 ZrO$_2$ 组成；相对于纯 TiO$_2$ 膜，复合膜的光吸收截止边缘产生红移。ZnO$_2$/TiO$_2$ 复合膜层和纯 TiO$_2$ 膜层在紫外光照射下，对罗丹明 B 的光催化催速率常数分别为 0.0442 和 0.0186 h$^{-1}$。

关键词: 纯钛; 微弧氧化; Zr(OH)$_x$ 胶体颗粒; ZrO$_2$/TiO$_2$ 复合光催化膜

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