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ZrO_2/TiO_2 films prepared by plasma electrolytic oxidation and a post treatment

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ABSTRACT

ZrO_2/TiO_2 films with high surface area and improved catalytic structures were prepared by the combination of plasma electrolytic oxidation technology with a sulfuric acid acidification and calcinations post treatments. The metal oxides composition, metal oxides phase and morphologies of the obtained films were determined by X-ray diffraction, energy dispersive spectroscopy and scanning electron microscopy. The post treatment conditions had significant influence on the phase composition and morphologies of the films. Both anatase and rutile phases of TiO_2 in the film were observed by XRD. After the post processing, the surface of the film was covered by high crystalline TiO_2 particles and the film surface is rough, leading to an increased surface area. With the increase of sulfuric acid concentration, the crystal form of the TiO_2 particles transformed from cubic to spindle-like. Moreover, a tendency to form a multilevel structure was displayed with the increase of the calcinations temperature. The degradation of methylene blue under ultraviolet radiation indicated that the film with a post treatment showed a high photocatalytic activity. When catalyzed by the film prepared with a 750 °C calcination temperature, the degradation of the methylene blue reached 93.18%. Meanwhile, the regeneration experiments showed the prepared film catalyst had a good reusability.

1. Introduction

TiO_2 mixed with certain kinds of transition metals have been widely studied to improve the photocatalytic efficiency. Among them, introduction of Zr atoms as dopants into the TiO_2 matrix has been studied in various forms, such as nanoparticles [1–2], powders [3–5], mesoporous and nanocomposites films [6]. Researches have shown that the ZrO_2/TiO_2composite system had excellent catalytic performance for dehydrogenation [7], organic synthesis, transformation [8]and photocatalytic reaction [9,10]etc. There are many researches on the preparation of ZrO_2/TiO_2 oxide catalysts. The main methods include: sol-gel and coprecipitation [11–16]. Zhang et al. [17] reported that the photocatalytic activity of (N, Zr)-codoped TiO_2 is three times that of N-doped sample. They proposed that Zr^{4+} ions in substitutional mode and NO_x on the surface extended the absorption into the visible-light region. When excess Zr^{4+} cations are incorporated, $ZrTiO_4$ will form and the $TiO_2/ZrTiO_4$ interface also contributes to the separation of photo generated charge carriers. Fu et al. [18] revealed that B and Zr co-doping can raise the photocatalytic ability of the undoped TiO_2 by a fold. Moreover, Zr^{4+} ions replace Ti^{4+} ions and form impurity levels, which could improve visible light response.

Despite a large number of studies have shown that nanoparticles and powders catalyst have excellent catalytic effect, it is not easy to recycle and be reused. In order to resolve this problem, more and more researches focused on the preparation of catalyst film on various substrates. Plasma electrolytic oxidation (PEO), also called micro-arc oxidation, has attracted widely attention for its high efficiency in fabricating metal oxides films with exceptional properties on light metals (Al, Mg, Ti etc.). It consists in anode or anode–cathode processing valve metals under spark or arc electric discharges. Multi components metal oxides film can be prepared by PEO. For example, the formation of oxide films contain calcium phosphate on aluminum and titanium substrates for biomedical purposes [19,20]; Magnetic ceramic film that contains iron or nickel compound [21]; Catalytic films of nickel, copper, molybdenum and platinum compounds [22–24]. In addition, the experimental results show that Al_2O_3, TiO_2, Cr_2O_3, ZrO_2, TiC, B_4C and BN can enhance the strength of the film [25]. Recently, extensive attentions had been put on the preparation of metal oxides catalyst film with PEO, because the film prepared by PEO was considered had excellent adhesion [26,27], wear resistance [28] and anti-corrosion performance [29].

TiO_2 films prepared by PEO technology in acid electrolyte or phosphate electrolyte have proved to have good catalytic performance [30, 31]. However, the surface area of the PEO film was still limited when used as a catalyst. Patcas et al. [32] reported that the surface areas of films prepared on Ti, Mg and Al were just 0.5– 0.7 m^2/g. Currane et al. [33] reported that the surface area of the PEO film on Al was 4.15 m^2/g. The surface area on this level is obviously not good for a catalyst. In addition, study has shown that ZrO_2/TiO_2 composite

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photocatalytic film can be prepared using in-situ $Zr(OH)_4$ colloidal particle by MAO technique [6]. Although the photocatalytic activity of this kind of films was improved, it is still poor and one of the reasons to limit the photocatalytic activity for this kind of films is the small surface areas. Therefore, new methods need to be proposed to overcome this limitation.

Herein, to improve the surface area of TiO_2/ZrO_2 films prepared on titanium substrates by PEO with a post sulfuric acid treatment and calcinations were conducted. We found that these post treatments could significantly change the microstructure, phase and surface area of the films. Also, the photocatalytic properties of the films were tested. A good photocatalytic activity and reusability of the prepared TiO_2/ZrO_2 films was proved.

2. Material and methods

2.1. Preparation of oxide films

A Ti-6Al-4V alloy plate was used as an anode. Prior to PEO treatment, the rectangular samples with dimensions 2 cm × 1 cm × 0.2 cm were polished with 400 to 2000 grit abrasive papers and degreased using acetone followed by rinsing with distilled water, and then dried in warm air. While a stainless steel plate was used as the counter electrode. The compositions of the electrolytes used for the PEO treatments were 10 g/L Na_3PO_4 + 4 g/LKOH + 4 g/L ZrO_2. The size of the ZrO_2 particles used here is 0.2– 0.4 μm. Electrolyte temperature was kept below 35 °C using magnetic-stirring and water-cooling systems. A homemade DC power supply with a maximum output of 1500 V/5 A was used as a power source. PEO treatment was carried out under potential static mode at 370 V for 30 min.

After PEO treatment, the samples were cleaned thoroughly with distilled water and dried in warm air. Then the samples with a PEO film were soaked in sulfuric acid solutions with different concentration (1–6 mol/L) for 24 h. After cleaning in distilled water and drying in warm air, samples were calcined at 450–750 °C for 5 h. To distinguish the PEO films formed in different conditions, the corresponding names of the films with and without post-processing (Including acid treatment and heat treatment) were named PPEO and PEO, respectively.

2.2. The analysis of the ZrO_2/TiO_2 films

Scanning electron microscope (SEM 1530VP, LEO, Germany) was employed to study the surface morphology of the PEO films. The elemental composition of the PEO films was investigated by energy dispersive spectroscopy (EDS) affiliated with SEM. The phase composition of the PEO film was investigated by X-ray diffraction(XRD, D/MAX-3A), using Cu-Kα radiation with a step size of 0.05°and a scan range from 20° to 90° (in 2θ).

2.3. Evaluation of photocatalytic activity

The photocatalytic activity of films was determined by degrading methylene blue (MB) solution. 50 ml of MB solution (15 mg/L) was added to a 100 ml double-walled quartz cell, and the catalytic film (3 cm^2) was placed at the bottom of the cell. A cut-off filter was also employed to eliminate any radiation with shorter wavelengths. The distance between the UV lamp (500 W high-voltage mercury lamp) and the surface of the MB solution was 15 cm. In each experiment, prior to UV-irradiation, the solution and the catalyst were left in the dark for 30 min (as a reference point) until adsorption/desorption equilibrium was reached. A fixed quantity of solution was removed every 1 h to measure the absorption and then the concentration. The absorptivity measurements were carried out at a fixed wavelength of 664 nm, because the maximum light absorption of the MB solutions occurred at this wavelength.

3. Results and discussion

3.1. Elemental analysis of PPEO films

In order to study the influence of the post processing on the film compositions, EDX spectra were examined. From Table 1, we can see that both the plasma electrolytic oxidation film and post plasma electrolytic oxidation films mainly consisted of Ti, O, Zr. On the surface of PEO film, for the depositing of a lots of ZrO_2 powders, Zr was the dominant element. Because these ZrO_2 powders did not combine well with the substrate and a large number of Zr^{4+} ions would lost during acid treatment. So after post processing, the Zr decreased significantly. The atomic weight of Ti and Zr is 47.87 and 91.22, respectively. Based on atomic weight percentage, we can know the mole ratio of TiO_2 and ZrO_2 was about 1:1 on the surface of PEO film. After post processing, the surface of the film is mostly composed by TiO_2. The EDX analysis results were in accordance with the SEM (Fig. 1) and XRD analysis (Fig. 2) results. Compared with the morphologies and the crystal phases of the PPEO films, the elementary composition of the film changed little (Tables 1 and 2) with the acid concentration and calcinations temperature. The oxygen increased for several percent. The increase of the oxygen element was caused by the oxidation of Ti substrates exposed to surface after acid treatment. One interesting thing was that the content of Zr element gradually increased with the calcination temperature, while the content of Ti gradually decreased. That meant we could adjust the ratio of TiO_2 and ZrO_2 of the film by controlling the calcination temperature, and therefore adjusting the catalytic activity of PPEO films [6,34].

3.2. Morphologies of the ZrO_2/TiO_2 films

It could be found that the surface of PEO film exhibited a low porous microstructure (Fig. 1(a)). Some powders scattered on the surface of the PEO film, and these scattered powders should come from the ZrO_2 added in the electrolyte. Just as we can see, the porosity of the PEO film is limited. The porosity of the PEO film was originated not only the reaction channels between electrolytes and substrates, but also the channels through which molten oxides ejected during the PEO process [32]. According to the porosity forming mechanism of the PEO film reported by Curran [33], a consequence of oxygen entrapment in molten titanium vicinity of localized electrical discharges, which occur during PEO film formation. The pore network facilitates the formation of relatively thick films, by allowing electrolyte to penetrate deep into the growing layer during the process. And the strong spark discharge on the surface of anode generates high pressure and temperature, 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. The surface micrographs of the film treated with 2 mol/L sulfuric acid solution without calcination was exhibited in Fig. 1(b). Compared with the original PEO films, the surface of the film treated with 2 mol/L sulfuric acid solution without calcination had less porous. This was caused by the corrosion the sulfuric acid and most of the discharged channels disappeared. The surface micrographs of the films immersed in different concentrations of H_2SO_4 solutions (1 mol/L, 2 mol/L, 4 mol/L, and 6 mol/L) for 24 h, followed by a calcination treatment (550 °C, 5 h) were totally different with PEO film and

Table 1
EDS surface results of PEO and PPEO films treated in different concentrations of H_2SO_4.

H_2SO_4 concentration	Ti (wt%)	Zr (wt%)	O (wt%)
PEO	33.61	42.49	23.90
1 mol/L	57.53	7.99	34.48
2 mol/L	56.07	7.60	36.32
4 mol/L	57.16	7.40	35.44
6 mol/L	55.09	5.29	39.62