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Low-temperature liquid phase deposited TiO_2 films on stainless steel for photogenerated cathodic protection applications

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ABSTRACT

The low-temperature synthesis of anatase TiO_2 films was an imperative requirement for their application to corrosion prevention of metals. In this paper, a liquid phase deposition (LPD) technique was developed to prepare TiO_2 films on SUS304 stainless steel (304SS) at a relatively low temperature (80 °C). The as-prepared films were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photon spectroscopy (XPS). It was observed that a dense and crack-free anatase TiO_2 film with a thickness about 300 nm was obtained. The film contained some fluorine and nitrogen elements, and the amounts of these impurities were greatly decreased upon calcination. Under the white light illumination, the electrode potential of TiO_2 coated 304SS rapidly shifted to a more negative direction. Moreover, the photopotential of TiO_2/304SS electrode showed more negative values with increased film thickness. In conclusion, the photogenerated cathodic protection of 304SS was achieved by the low-temperature LPD-derived TiO_2 film.

1. Introduction

Ever since Fujishima and Honda [1] reported the water decomposition reaction at a TiO_2 electrode under illumination in 1972, the unique performances of TiO_2 photoelectrochemistry have got an intensive study in many areas such as pollutant degradation [2], superhydrophilic materials [3] and dye-sensitized solar cells (DSSC) [4]. Very recently, a novel application of TiO_2 photoelectrochemistry to the corrosion prevention of metals was also proposed in a few studies [5–7]. When a metal coated with TiO_2 film is illuminated by ultraviolet (UV) light, the photogenerated conduction band (CB) electrons in TiO_2 will be injected into the underlying metal substrate, which drives the potential of metal shift toward the negative direction. In that case, the corrosion prevention of metals known as photogenerated cathodic protection is achieved.

Until now, various techniques for preparing TiO_2 films applied to cathodic protection of metals were developed. Among these, the sol–gel-derived TiO_2 coatings were commonly used on copper [5] and stainless steel [8,9] for corrosion prevention. In recent studies, using the titanium foils as substrates, both the anodization method [10,11] and hydrothermal [12,13] technique were also developed to prepare the TiO_2 photoanodes. However, the TiO_2 film synthesized by the above methods were usually subjected to a post-annealing treatment at a higher temperature (above 450 °C), which would cause certain unfavorable changes in the structure and composition of the coated substrates. Therefore, the low temperature synthesis of crystalline anatase TiO_2 films without high temperature post-heat treatment is imperatively required.

Liquid phase deposition (LPD) is a method that can obtain crystalline TiO_2 films from aqueous solutions at low temperatures (25–100 °C) [14]. It is based on the slowly hydrolysis of a metal-fluoro complex $[MF_n]^{m-n}$ with the boric acid as the common fluoride scavenger [14]. After the pioneering works by Deki and co-workers [15,16], the TiO_2 films on various substrates prepared by LPD method were widely studied [17–19]. Recently, the liquid deposited TiO_2 film on glassy carbon electrode was also developed for degradation application [20]. However, to the best of our knowledge, few studies reported the photogenerated cathodic protection of metals by low-temperature LPD-derived TiO_2 films. In this paper, a dilute precursor solution containing $(NH_4)_2TiF_6$ and H_3BO_3 was chosen to synthesis the crystalline TiO_2 films by LPD process at 80 °C. The results showed that a dense and crack-free anatase TiO_2 film containing certain fluorine and nitrogen impurities was successfully obtained. Under illumination by the white light, the electrode potential of TiO_2/304SS exhibited a rapid shift to the negative direction, which was a typical characteristic of the photogenerated cathodic protection.

2. Experimental

2.1. Liquid phase deposition of TiO_2 films

SUS304 stainless steel plates (10 mm × 30 mm × 1 mm) were used as substrates in this study. The tested sides of the specimens

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were mechanically polished to a mirror finish with Al_2O_3 powder, and then ultrasonically cleaned in acetone, ethanol and de-ionized water for 15 min, respectively. The precursor bath solutions were prepared by mixing 0.02 M $(NH_4)_2TiF_6$ and 0.06 M H_3BO_3 at the same volume. The pH of the above mixing solution was kept natural without further adjustment (pH 3.73). During the deposition process, 304SS substrates were placed vertically into the precursor solutions and the whole system was kept at 80 °C for 3 h. After the film deposition, the specimens were gently washed and naturally dried in the air. The above processes were repeated when a thicker film was needed. In addition, the precipitates during LPD process were also collected and dried at 80 °C used for X-ray diffraction analysis. For comparison, some specimens were chosen to anneal at 300 °C and 500 °C in the air for 3 h, with the heating rate of 5 °C/min.

2.2. Characterization of the LPD-derived films

The surface and cross section morphologies of LPD-derived films on 304SS were observed using scanning electron microscopy (FE-SEM, LEO1530). The crystalline structure of precipitates collected from LPD process were measured via X'pert X-ray diffractometer (XRD, X'pert PRO, Panalytical, Netherlands) using Cu Kα_1 radiation (λ = 1.54056 Å) at 40 kV and 30 mA, with 2θ ranged from 10° to 80°. The phase composition of the LPD-derived films was determined by Raman spectroscopy (Renishaw, UV–vis Raman System 1000) with 514.5 nm laser excitation. The surface chemical composition analysis of LPD-derived film was performed using X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000) with an Al Kα radiation source. All of the specimens were subjected to Ar etching of 30 nm from the top-surface before the data collection during the XPS measurement. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV. Moreover, the quantitative analysis was carried out to obtain the concentrations of each element using the sensitivity factors supplied with the instrument.

2.3. Photoelectrochemical measurements

The photoelectrochemical measurements were performed using Model 263A potentiostat/galvanostat (EG&G Instruments, Inc., USA, Princeton Applied Research) connected to an SBP300 grating spectrometer with an LPX 150 W Xe lamp as the source of illumination. The TiO_2 coated 304SS with an active area of 1 cm^2 was served as working electrode, while a platinum toil and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. A polytetrafluoroethene (PTFE) container was used as the photoelectrochemical cell and had a quartz window to transmit the light. The electrolyte used in the photoelectrochemical test was 0.5 M NaCl solution. The open circuit potential of TiO_2/304SS electrode was measured both in the dark and under the illumination of the white light with wavelengths ranging from 200 nm to 750 nm. In addition, the tafel polarization of the TiO_2/304SS electrode was also measured between −250 mV and +250 mV at the open circuit potential with the scanning rate of 0.167 mV/s. Before the measurement of polarization, the specimens were immersed into the electrolyte solution and the open circuit potential of each specimen was monitored until a constant value was observed.

3. Results and discussion

3.1. Structure and morphology of LPD-derived films

The surface morphology of the film on 304SS was shown in Fig. 1. It can be observed that the LPD-derived film mainly constituted of rod-like crystals with a dense and crack-free morphology. Fig. 2 showed the cross section of SUS304 substrate coated with TiO_2 thin films obtained by three repeated LPD process. The total film thickness was about 0.9 μm. For one cycle of LPD process, the typical film thickness was about 300 nm. The powder XRD pattern of as-collected precipitates was shown in Fig. 3. The diffraction peaks of the precipitates matched well with the anatase TiO_2 (PDF No. 21-1272). The broadening of diffraction peaks was attributed to the relatively small size of the nanoparticles in the TiO_2. More-

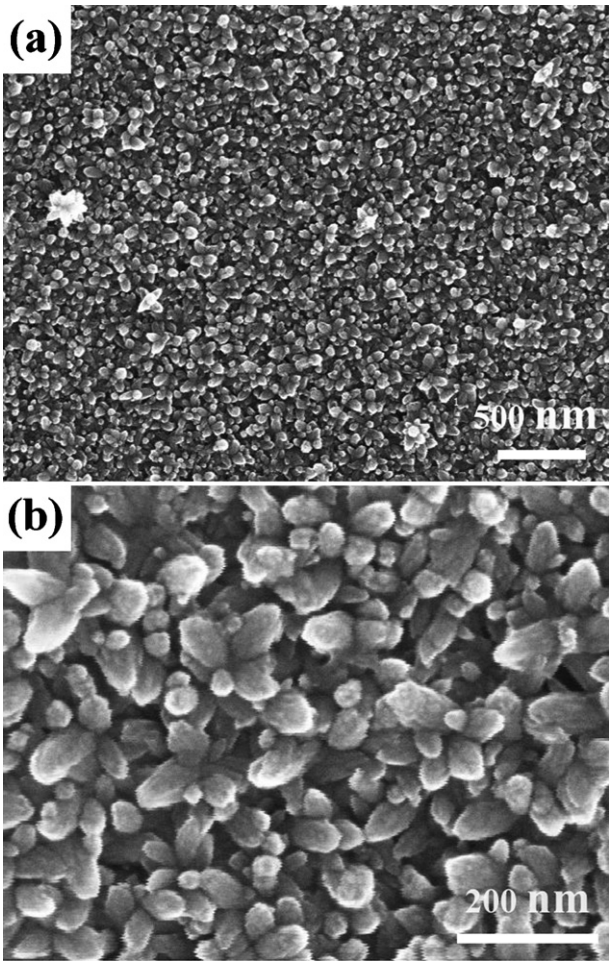

Fig. 1. Surface morphology of the LPD-derived film on 304SS: a dense and crack-free morphology shown in low-magnification image (a); rod-like crystals shown in high-magnification image (b).

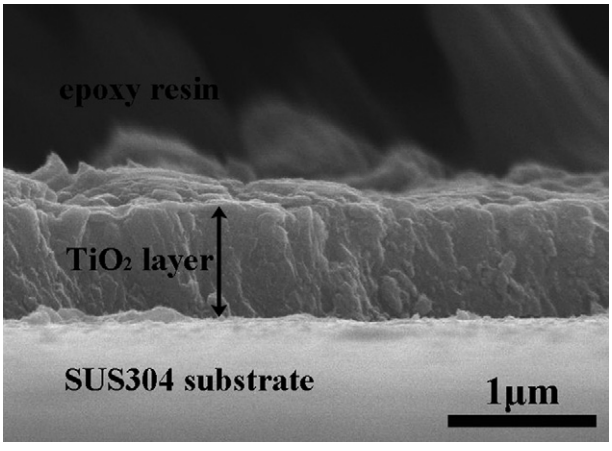

Fig. 2. The cross section morphology of SUS304 substrate coated with TiO_2 thin film by three repeated LPD processes.