Liquid phase deposition of titanium oxide film on stainless steel substrate

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ABSTRACT

In this study, liquid phase deposition (LPD) was used to prepare titanium oxide (TiO_2) films on stainless steel substrates. The raw materials used were ammonium hexafluorotitanate and boric acid. Various concentrations of boric acid and annealing conditions were employed to examine the influences on hydrophilicity, anti-corrosion and anti-abrasion. The optimum conditions were a boric acid concentration of 0.7 M and oxygen annealing at 800 °C for 1 h. The water contact angle was reduced from 82.62° to 2.51°, indicating that the hydrophilic properties of the stainless steel were enhanced after TiO_2 film deposition. Regarding corrosion, the corrosive current reduced from -4.75 A/cm^2 to -6.52 A/cm^2 by 3.65 wt.% of HCl. The Vickers hardness value (HV) of the stainless steel substrate increased from 254 to 820. Therefore, TiO_2 thin films prepared using LPD can improve the hydrophilic, anti-corrosion, and anti-abrasion properties of stainless steel substrates.

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1. Introduction

As technology advances, materials must become more diverse and versatile. In addition to their superior performance in specific areas, the operating environments of products should also be considered; for example, chemical stability is crucial for materials used in acidic or alkaline environments. Typically, the properties of industrial products can be enhanced using surface coating, which both expands the scope of application and increases the life expectancy of a material.

Titanium dioxide (TiO_2) is a ceramic material that exhibits the properties of n-type semiconductors. Its crystal structure is an octahedron composed of one titanium atom coordinated to six oxygen atoms. Common TiO_2 crystal structures include anatase, which demonstrates phase stability at low temperatures, and rutile, which demonstrates phase stability at high temperatures. The difference in phase transition temperatures between these two materials is approximately 600 °C [1]. TiO_2 is extensively applied because of its low price, accessibility, stable physical and chemical properties, wear resistance, safety, and non-toxicity [2]. TiO_2 films enable numerous applications in anti-bacterial products, anti-fog agents, water clarifiers, and air purifiers [3]. This experiment explored the self-cleaning property of stainless steel sheets. Self-cleaning was achieved by employing the hydrophilic and mechanical properties of TiO_2. In addition, the hardness and corrosion resistance of the stainless steel were enhanced. Currently, TiO_2 is prepared in vacuum environments such as reactive evaporation [4], reactive magnetron

sputtering [5], and chemical vapor deposition environments [6]. All such methods produce films that exhibit uniform thicknesses and favorable optical properties; however, conventional vacuum deposition processes are expensive and unsuitable for continual mass production, and thin films cannot be uniformly attached to substrates of irregular shapes using these processes. Recent nonvacuum processes for depositing TiO_2 films on stainless steel substrates have included the sol–gel method [7] and liquid phase deposition (LPD). The LPD method was used herein to fabricate TiO_2 films, ensuring affordability, uniformity, favorable adhesion, mass producibility, and the formation of large area; such multi-functional films can be fabricated regardless of substrate shape.

LPD is a low-temperature (25 °C–80 °C) fabrication process that facilitates high selectivity levels, large area, simplicity, adjustable film composition, and can be applied to mass production [8,9]. It is based on the slow hydrolysis of a metal-fluoro complex $[MF_n]^{m-n}$ that typically uses boric acid as a fluoride scavenger [10]. C. X. Lei et al. [11] have developed LPD-TiO_2 films on stainless steel for photogenerated cathodic protection applications. Most studies have indicated that hydrophilic films only become hydrophilic after being exposed to UV light [12]; thus, the application of photocatalytic self-cleaning is limited. However, few studies reported the no UV radiation hydrophilic surface of LPD-TiO_2 film on stainless steel substrates. In this study, ammonium hexafluorotitanate [$(NH_4)_2TiF_6$] and boric acid (H_3BO_3) were used as the starting materials in the TiO_2 deposition to examine the characteristics of LPD-TiO_2 films on stainless steel substrates. Consequently, this study involved applying the LPD method to prepare TiO_2 hydrophilic films that required no UV radiation. The annealing effects of hydrophilic, anti-corrosion, anti-abrasion properties of LPD-TiO_2 film stainless steel substrates were also investigated.

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2. Experiment

2.1. LPD-TiO₂ film deposition

Stainless steel plates (SUS304) that comprised 18.01 wt.% chromium and 7.98 wt.% nickel were used as the substrates in this study. The tested sides of the specimens were mechanically polished to a mirror finish by using Al_2O_3 powder and ultrasonically cleaned for 15 min each in acetone and deionized water. The average surface roughness of the bare stainless steel substrate was 4.19 nm. The deposition system comprised a temperature-controlled water bath that provided a uniform deposition temperature at an accuracy of ±0.1 °C and a Teflon vessel that contained the deposition solution. A solution that contained 20 mL of $(NH_4)_2TiF_6$ (0.2 M) was saturated using TiO_2 powder and mixed with 20 mL of H_3BO_3 (0.4–0.8 M) for depositing the TiO_2 films. The deposition temperature was maintained at 60 °C during the deposition. The thickness of all samples was kept at 100 nm. Following deposition, the stainless steel substrate was rinsed in deionized water and dried in purified nitrogen gas. Finally, the samples were annealed at 600 °C–900 °C in oxygen for 1 h, and the increasing and decreasing temperature rates were set at 5 °C/min.

2.2. Characterizing LPD-TiO₂ films

The thicknesses and refractive indices of the LPD-TiO₂ films were measured using ellipsometry. X-ray diffraction (XRD) measurements were used to examine the constituent phases of the TiO_2 films. Field emission scanning electron microscopy (FE-SEM) was employed to determine film thickness and morphology. The depth profile of the LPD-TiO₂ film was analyzed using X-ray photoelectron spectroscopy (XPS). The surface roughness of the films was examined using atomic force microscopy (AFM) techniques. The water contact angles were measured at room temperature using a contact angle meter and the sessile drop method.

2.3. Potentiodynamic polarization test

Potentiodynamic polarization measurements were executed in a conventional three-electrode cell that was open to air and contained 500 mL of electrolyte. Measurements were performed in 3.65 wt.% HCl solution at 25 °C. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated based on the intersection of the cathodic and anodic Tafel curves by using the Tafel extrapolation method.

The polarization resistance (R_p) was determined using the Stern–Geary equation [13]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{corr}(\beta_a + \beta_c)} \tag{1}$$

where β_a and β_c are the anodic and cathodic Tafel slopes. The corrosion rate (r_{corr} in mm/y) was calculated using the following equation [14]:

$$r_{corr} = 0.00327 \frac{i_{corr} M}{nd} \tag{2}$$

where M, n, and d are the molar mass, charge number, and density of the tested metal, respectively.

2.4. Vickers hardness test

The specimens were mounted in bakelite, ground using a diamond-grinding wheel and then carefully polished using diamond paste to produce an optical finish. The specimens were then subjected to Vickers diamond pyramid indentations at an indentation load of 98 mN. All the indentation tests were conducted using a commercial low-load hardness tester and a loading time of 10 s at room temperature. For each
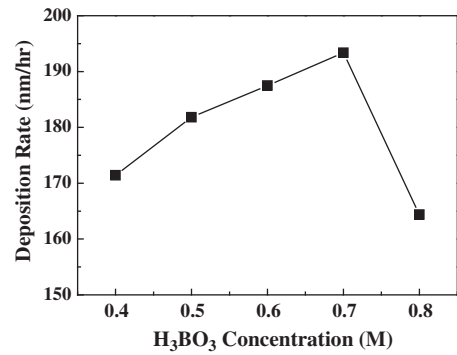

Fig. 1. Deposition rate of LPD-TiO₂ as a function of H_3BO_3 concentration.

substrate, a total of 5 Vickers indentations were made. After indentation, the lengths of both diagonals of each indentation were immediately measured using optical microscopy at 300× and an error of measurement of ±0.5 μm.

3. Results and discussion

3.1. Influences of boric acid on the deposition rate of LPD-TiO₂ films

Fig. 1 shows the deposition rate of LPD-TiO₂ films on a stainless steel substrate as a function of H_3BO_3 concentration. The deposition rate increased as the H_3BO_3 concentration increased, reaching a maximal value at 0.7 M. The deposition rate is linearly related to concentration in the range of 0.4–0.7 M. The deposition rate falls dramatically as the concentration of H_3BO_3 rises above 0.7 M, owing to the precipitation of TiO_2 powder in the deposition solution. Therefore, the deposition rate drops seriously when 0.8 M H_3BO_3 is used. Fig. 2 shows the SEM results for the surface morphologies of the as-deposited LPD-TiO₂ films on stainless steel substrates, employing various H_3BO_3 values. Various boric acid concentrations were used to deposit the TiO_2 films. The as-deposited LPD-TiO₂ films on stainless steel substrates displayed some cracks, although the quantity of the cracks decreases as the concentration of H_3BO_3 increases. It is from the proportion of HF in the deposition solution decreases. Related chemical reaction formulas show that boric acid suppresses the HF generated in the solution. The HF typically corrodes the TiO_2 films during deposition, causing cracks on the film surfaces. Therefore, high concentrations of boric acid generated compact and uniform films.
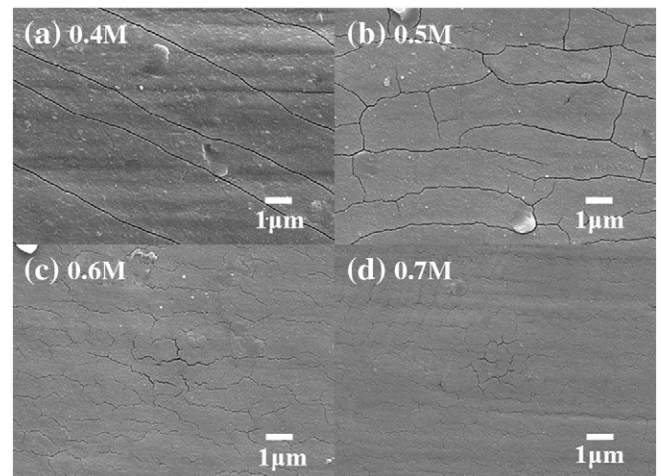

Fig. 2. FE-SEM surface morphologies of as-deposited LPD-TiO₂ films on stainless steel substrates.