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Improvement in corrosion protection properties of TiO_2 coatings by chromium doping

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ABSTRACT

A series of chromium-doped TiO_2 coatings was prepared for corrosion protection of 316L stainless steel substrates. The morphology, crystalline phase and composition of the coatings were systematically investigated. The corrosion protection performances of the coatings in the presence and absence of simulated sunlight illumination were evaluated through electrochemical measurements. The chromium-doped TiO_2 coatings showed a remarkable improvement in photogenerated cathodic protection properties under illumination. In addition, during a long-time dark immersion process, the chromium-doped TiO_2 coatings could provide an active corrosion protection for metal substrates due to the self-healing property of chromium ions.

1. Introduction

Nano-structured TiO_2 thin film is a technologically important material because of its unique photoelectrochemical properties and good chemical stability, which can be used in many high-tech applications including water splitting for solar energy conversion, dye-sensitized solar cells, environmental remediation, coating materials for self cleaning windows, and photocatalytic processes [1–6]. Recently, intensive efforts have been focused on the development of TiO_2 coatings for photogenerated cathodic protection of metals under ultraviolet (UV) illumination [7–11]. The principle of photogenerated cathodic protection lies in the fact that if a layer of TiO_2 coated on a metallic substrate is exposed to a UV irradiation, the photogenerated electrons are injected from the semiconductor to the metal substrate and adjust its Fermi level. As a result, the potential of the metal is shifted to a more negative value than the potential at which the metal begins to oxidize, thus the metal can be protected from corrosion. Yuan and Tsujikawa first reported the potential of a TiO_2 coated copper substrate drastically shifted toward the corrosion immunity region under illumination providing the corrosion protection effect [12]. The main advantage of this method is that the TiO_2 thin film is not consumed during the protection process and can be regarded as a non-sacrificial anode. Following this, many investigations were carried out on other substrates such as carbon steel [7] and stainless steel [9–11] using the TiO_2 coating as the semiconductor photo-anode.

There are three main drawbacks associated with the use of pure TiO_2 thin film: high recombination rate of electron–hole pairs, low efficiency of photoelectric conversion under natural sunlight illumination and no functionality of photogenerated cathodic protection under dark conditions. To overcome these limitations, Li et al. reported that N-doped TiO_2 nanotube layers with a highly ordered structure on titanium had been verified to provide an effective photogenerated cathodic protection for metals under regular sunlight illumination [13]. In addition, composite coatings prepared by coupling electron storage materials (e.g. SnO_2 and WO_3) with TiO_2 can have cathodic protection effects under both UV illumination and dark conditions [8,14]. However, these protection systems cannot maintain the cathodic protection for metals in a long-time dark condition. Consequently, an efficient and durable TiO_2 coated corrosion prevention system which can be carried out with or even without the photo effect is highly required.

Recently, there has been an upsurge of interest in doped TiO_2 coatings with transition metals [15–18]. Doped transition metal ions exhibit an isomorphic replacement of Ti^{4+} ions in TiO_2 and decrease the band gap energy, enabling TiO_2 to absorb visible light. Furthermore, doped ions can be used as electron or hole trapping centers to improve the separation efficiency of photo-induced electron–hole pairs of titania. Sol–gel technique is the preferred method to incorporate transition metal ions into TiO_2 coatings because of its low process cost and easy control of compositions [16–19]. Chromium has been reported as an effective doping metal to modify TiO_2 for enhancing its photocatalytic activity [19], and we make use of this advantage in the photocatalysis field to verify its effectiveness in the photogenerated cathodic protection performance of TiO_2 under illumination.

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The sol–gel derived TiO_2 coatings may contain cracks and defects, through which corrosive species can be diffused to the coating/metal interface, inducing a local corrosion process. It is reported that the incorporation of corrosion inhibitors in the coatings can achieve active corrosion protection performance, since inhibitors can suppress localized corrosion when the defects appear [20–25]. Chromium ions contained in chromate passive film are found to have a significant inhibiting action on corrosion process, because they can be released from the coating and heal the defects or corrosion sites [26–31]. Therefore, the development of the chromium-doped TiO_2 coating can provide not only mechanical covering of the protected surface with a dense barrier film, but also self-healing properties which allow continued protection even after partial damage of the film. This protection mechanism of such a coating appears to be essential for its long-time protection property in the absence of illumination.

In this research, sol–gel derived TiO_2 coatings doped with different chromium-ion concentrations were produced and applied to 316L stainless steel substrates. The crystalline phase, composition and morphology of the coatings were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and energy dispersion X-ray spectroscopy (EDX). The variations in open circuit potential (OCP), potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and accelerated corrosion tests were employed to measure the corrosion protection property of the coatings. The main purpose of this work was to study the role of chromium doping on the active corrosion protection performance of the TiO_2 coating in the presence and absence of simulated sunlight illumination.

2. Materials and experimental methods

2.1. Preparation chromium-doped TiO_2 sol

All reagents used in the experiments were of analytical grade and purchased from Chinese Chemical Reagent Co. The chromium-doped TiO_2 sol was prepared with the following procedure: tetra-*n*-butyl titanate [$Ti(O\text{-}n\text{-}Bu)_4$] used as titania precursor was added into a mixture of ethanol (EtOH) and triethanolamine (TEA) at room temperature, denoted as Solution A. The mole ratio of $Ti(O\text{-}n\text{-}Bu)_4$/EtOH/TEA was 1/24/1. Chromium nitrate [$Cr(NO_3)_3\cdot 9H_2O$] used as the Cr(III) additive was dissolved into H_2O and then mixed with EtOH, denoted as Solution B. The mole ratio of $Ti(O\text{-}n\text{-}Bu)_4/H_2O$/EtOH was 1/9/17. Solution B was added drop by drop into Solution A under vigorous stirring. Acetylacetone (Hacac), a chelating agent, was dropped into the mixed solution with further stirring for 3 h at room temperature. The mole ratio of $Ti(O\text{-}n\text{-}Bu)_4$/Hacac was 1/0.2. The resulting transparent sol was aged for 5 days before usage. In this study, the sols with different mole ratios of Cr/Ti were prepared, such as 0.2%, 1% and 5%. Pure TiO_2 sol was also prepared for a comparison.

2.2. Preparation of chromium-doped TiO_2 coatings

Stainless steel 316L specimens (47 × 11 × 2 mm), used as substrate materials, were ground with No. 400-2000 emery papers gradually, polished with Al_2O_3 powders, and then degreased in acetone, ethanol and distilled water for 10 min, respectively, and finally air-dried. The coating on the metal substrate was prepared by using a dip-coating method. The substrate was immersed in the sol for 3 min and withdrawn at a speed of 12 mm/min. After air-drying, the sample was dried in the oven at 100 °C for 10 min. The operation from dipping to drying was repeated twice in order to increase the coating thickness. Finally, the sample was heat-treated in a muffle furnace at 250 °C for 30 min, and at 450 °C for 1 h. The coatings doped with different chromium-ion concentrations were named 0.2%, 1%, and 5% Cr–TiO_2 coating, respectively.

2.3. Characterization

The surface morphology of the prepared coatings was evaluated by scanning electron microscopy (SEM) (HITACHI S-4800). Elemental chemical analysis of the coatings was performed by energy dispersive X-ray spectroscopy (EDX) connected to the SEM.

The crystalline phase of the prepared coatings was characterized by X-ray diffraction (XRD) analyses performed using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda \approx 1.54$ Å) over a 2θ range from 10° to 80°, at a scan rate of 5°/min.

The composition of the prepared coatings was studied by X-ray photoelectron spectra (XPS) recorded on a Perkin–Elmer PHI5000C X-ray photoelectron spectrometer, using Mg $K\alpha$ ($h_\upsilon = 1253.6$ eV) X-ray as the excitation source. The binding energy was corrected by taking the C 1s level as 284.6 eV.

2.4. Electrochemical measurements

Each electrochemical measurement was performed at room temperature in 3.5 wt.% NaCl solution using Princeton Applied Research Model 2273 potentiostat. A saturated calomel electrode (SCE) and a platinum foil served as reference electrode and counter electrode, respectively. 316L stainless steel specimens coated with undoped and chromium-doped TiO_2 thin films were used as working electrodes. The test area of working electrode was 0.25 cm^2 and the rest of the surface was embedded in epoxy resin.

The variations in open circuit potential (OCP) of different Cr–TiO_2 coatings were investigated in the presence and absence of illumination. A 500 W high pressure Xe lamp (output wavelength $\lambda = 320–780$ nm) was used as a light source to simulate sunlight. The potentiodynamic polarization curves of the coated and uncoated stainless steel samples were recorded after 1 h of immersion in the solution, within the range from −150 mV to at least +500 mV vs. the open circuit potential at a scan rate of 0.166 mV/s. The electrochemical impedance spectroscopy (EIS) was performed at different immersion times using sine wave signals of 10 mV amplitude with the measuring frequency ranging from 10^5 Hz down to 10^{-2} Hz. The impedance plots were fitted using ZSimpWin software with an appropriate equivalent circuit. All electrochemical measurements repeated for three times to confirm the reproducibility of the results and were carried out in a Faraday cage to avoid external electromagnetic interference.

2.5. Accelerated corrosion tests

The coated stainless steel samples were scratched in the middle of the coating surface with a knife-edge and then immersed in 2 M NaCl solution at 60 °C. The samples were removed from the solution after 14 h of immersion and the surface appearances were imaged with a digital camera. The tests were used to evaluate the corrosion protection performance of the coatings under this special condition.

3. Results and discussion

3.1. SEM observations

Fig. 1 presents SEM micrographs of pure TiO_2 and 1% Cr–TiO_2 coatings. In Fig. 1a and b, the surface of pure TiO_2 coating contains some cracks and a few pinhole-like defects due to contraction and