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Microstructure-corrosion resistance relationship of direct and pulse current electrodeposited Zn-TiO_2 nanocomposite coatings

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Abstract

Zinc–TiO_2 nano-composite coatings were synthesized by Direct Current (DC) and Pulse Current (PC) electrodeposition techniques. The effects of the plating parameters on the microstructure, codeposition percentage of TiO_2 and corrosion behavior were investigated. The coatings morphology presents hexagonal grains perpendicularly oriented to the surface. Under DC conditions, TiO_2 content of the coatings decreased with increasing TiO_2 concentration of the electrolyte. Increasing applied current and TiO_2 concentration in the bath leads to a fine microstructure with corrosion currents as low as 2.7 $\mu A/cm^2$. Under PC conditions, incorporation rate of nanoparticles tends to increase with increasing pulse frequency and decreasing current density. Incorporation of TiO_2 increases microhardness of the zinc coatings by improving deposit structure.

Keywords: A. Films; B. Composites; C. Corrosion; D. TiO_2

1. Introduction

Zinc coatings have been found too weak to be used in aggressive environments such as those which contain industrial pollutants [1]. They are useful in the pH range of 6–12 and their corrosion rates are too high in strongly acidic or alkaline environments [2]. Another problem arises from the formation of the white rust. White rust formation can be prevented for a limited amount of time by coating in a chromate conversion coatings; however this process is avoided due to environmental hazards [3]. Also, the soft zinc coating on iron and steel is vulnerable to abrasion damage.

One of the best strategies to prepare zinc coatings with enhanced corrosion and wear resistance is to design novel zinc based composites. Pulsed direct current and direct current electrodeposition have been widely used for preparation of zinc composite coatings. These coatings possess unique properties, such as high corrosion resistance, self-lubricity, high temperature inertness and biological compatibility [4,5]. The nanoparticles like Al_2O_3, SiC, TiO_2, WC, PTFE, ZrO_2, SiO_2, CNTs, ceria and diamond are employed extensively to generate composite coatings with Zn. Several studies have established positive effects of incorporation of nanoparticles on corrosion properties of the zinc coatings [6–8].

In the conventional DC plating there is only one parameter, called the current density, which can be varied. In pulse electroplating, there are at least three parameters, including pulse height (current amplitude), relaxation time (T_{OFF}) and pulse time (T_{ON}) which values can be effectively optimized. Also, electrodeposition of composite coatings is affected by other factors such as stirring rate, concentration of particles in electrolyte, temperature and nature of particles. In the pulse current, the duty cycle (γ) corresponds to the percentage of the total time of a cycle and is given by [9,10]

$$\gamma = \frac{T_{ON}}{T_{ON} + T_{OFF}} = T_{ON} f$$

where f is pulse frequency and is defined as reciprocal of the time. Application of pulsed direct current technique is advantageous due

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to higher incorporation rate of micro and nanosized particles [11,12].

Despite a few reports on preparation of Zn–TiO_2 coatings, effects of bath parameters on the incorporation rate of TiO_2, microstructure of the coatings and their corrosion behavior is unclear. Up to our knowledge, there is no report concerning the effects of pulse frequency and duty cycle in the literature. Although Vlasa [13], Gomes [7] and Yang [14] have studied the corrosion behavior of the Zn–TiO_2 coatings, these studies are limited and there is a need for a comprehensive study on the microstructure–corrosion resistance relationship. Previously, we have reported fabrication of zinc–SiC nanocomposite coatings with desirable corrosion and morphological properties [15,16]. In the present work, effects of the applied current density, TiO_2 concentration in the bath, pulse frequency and duty cycle on the microstructure, TiO_2 content of the coatings and their corrosion behavior are investigated.

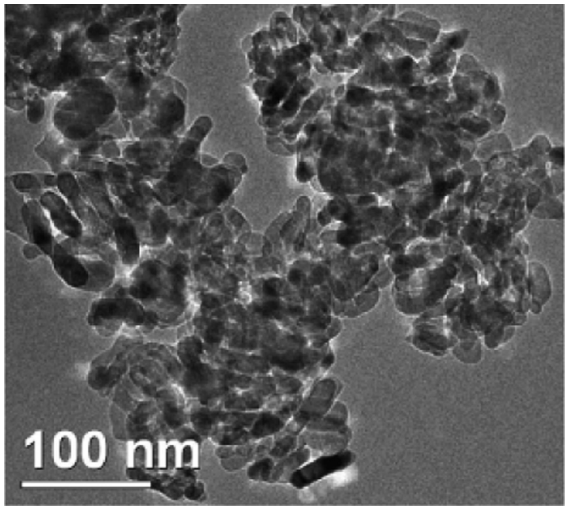

Fig. 1. TEM image of TiO_2 nanoparticles.

2. Experimental

The three electrode system with a cell volume of 300 ml was used to perform the experiments, using steel (St 37, 15 mm × 20 mm × 1 mm) as cathode and zinc (99/96% purity, 70 mm × 20 mm × 1 mm) as anode. The plating solution was mechanically stirred (250 rpm) using a magnetic stirrer. Anode was chosen more than 4 times larger than cathode to avoid anodic polarization. The distance between anode and cathode was 20 mm. Surface preparations involved abrasion of the specimens by 200♯grit SiC paper, ultrasonication in acetone, dipping in HCl (15%) and washing with distilled water.

Steel specimens were electrodeposited by the Zn–TiO_2 nanocomposite from a zinc sulfate bath. Bath composition is shown in Table 1. Boric acid, $ZnSO_4$ and sodium dodecyl sulfate (SDS) were added to distilled water and the solution was stirred for 2 h prior to adding TiO_2 nanoparticles. After adding TiO_2 nanoparticles the solution was stirred again for 12 h. TiO_2 nanoparticles with average size of 50 nm were provided from Merck (Fig. 1). Before starting coating process, the solution was ultrasonicated for 30 min to ensure even distribution of particles and avoid particles agglomeration.

Table 1
Chemical composition of the bath and the parameters of electrodeposition conditions.

Variable	Range
$ZnSO_4$	200 (g/l)
H_3BO_3	20 (g/l)
SDS	0.3 (g/l)
TiO_2 nanoparticles	0, 5, 10, 15 (g/l)
Temperature	25 (°C)
Peak current density (A/cm^2)	0.8, 0.10, 0.12
Pulse frequency (Hz)	0, 10, 50, 100
pH	4.5
Duty cycle	0, 25, 50, 75 (%)
Stirring rate	250 rpm

Specimens were electrodeposited under both DC and PC conditions. In PC, during the OFF-time the movement of nanoparticles from electrolyte to the cathode surface eliminates concentration gradient. Hence, more TiO_2 particles will be present at the cathode surface during the ON-time and consequently more nanoparticles are embedded in the coating. Besides wider range of deposit properties can be achieved through regulating the pulse amplitude and width. However, in most cases, the cost of a pulse rectifier is much greater than a DC unit. It is a highly regulated and sophisticated design that costs more to manufacture. The technology requires one to think and plan ahead with a series of procedures to follow in order to obtain the best results [9].

Potentiodynamic polarization measurements were carried out in a conventional three electrode cell, containing 200 ml of 1 M NaCl at the temperature of 25 °C. The measurements were performed at room temperature and in the non-stirred solution, where the applied sweep rate was 0.5 mV s^{-1}. Coated specimens were used as working electrode and saturated calomel electrode (SCE) and platinum electrode were used as the reference electrode and counter electrode. Polarization studies were conducted using Autolab-PGSTAT 10.

The hardness of the coatings was tested using the Leitz wetzlar Microhardness tester, employing a load of 25 g. The surface morphology and the composition of coatings were characterized with scanning electron microscopy (SEM) and energy dispersive analyzer system (EDX).

3. Results and discussion

3.1. Morphological studies

In this work, PC and DC electrodeposition methods were used for obtaining Zn–TiO_2 coatings. For DC coatings effects of TiO_2 content of solution and applied current density were studied. Increasing deposition current density and TiO_2 content of the bath resulted in very fine microstructures (Figs. 2 and 3).