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Fabrication of poly(alkyl-aniline)-SiC/zinc bilayer coatings and evaluation of their corrosion resistance properties

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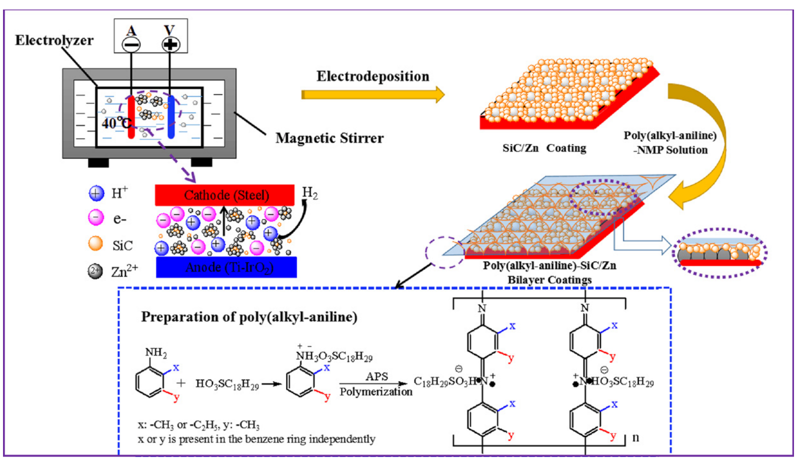
GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this work is to study the structure and corrosion resistance of poly(alkyl-aniline)-SiC/zinc (Zn) bilayer coatings. Herein, the poly(alkyl-aniline) such as poly(o-toluidine) (POT), poly(m-toluidine) (PMT) and poly(o-ethylaniline) (POEA) were chemically synthesized, and the structures of poly(alkyl-aniline) powders were characterized by various optic techniques. The composite SiC/zinc (Zn) coating was electrodeposited on the surface of carbon steel, and the structures and morphologies were detected by Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and scanning electron microscopy (SEM). Thereafter, the resultant poly(alkyl-aniline) were chemically deposited on the surfaces of SiC/Zn coating using solution evaporation method, and thus a series of bilayer coatings were obtained. The corrosion resistances of bilayer coatings were investigated in 3.5% NaCl solution by using Tafel polarization technique and electrochemical impedance spectroscopy. The outer POEA film exhibits a lower corrosion behavior with respect to POT and PMT, which significantly reduces the corrosion rate of SiC/Zn coating and prolongs the service life of zinc matrix. The conclusion depicted that the micro/nanostructure of SiC/Zn surface is beneficial to the complete and good embedding of outer POEA film, the formed POEA-SiC/Zn bilayer coatings possesses a uniform, compact and smooth surfaces which facilitates POEA film to develop its excellent barrier and passivation

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properties to against corrosion. The corrosion protection mechanism conferred by poly(alkyl-aniline)-SiC/Zn bilayer coatings was also discussed.

1. Introduction

Zinc (Zn) galvanized coatings which are one of metallic coatings acts both as a physical barrier and a sacrificial anode protects exposed steel and cast iron from corrosion [1]. In general, Zn coating is easy to darken and spot when touched and their service life is relatively short. The works [2,3] reported that the incorporation of different types of inorganic nanoparticles in Zn matrix can improve the appearance defects and prolong their service life. Compared to pure Zn coating, the composite electrodeposited coatings show evidently improved properties such as higher hardness, wear resistance, good microstructure, chemical compatibility and corrosion resistance [4–6]. Sajjadnejad et al. [7] prepared Zn-TiO_2 nanocomposite coatings on the steel substrate by electrodeposition technique, and the results revealed that incorporation of TiO_2 nanoparticles into Zn matrix result to form a compact and smooth surface and improved the corrosion resistance. However, Zn coatings in the air especially in humid environments are susceptible to be corroded, this is why Zn or composite Zn coatings need to be passivated at first. At present, chromation has been commonly used to improve the corrosion resistance of the electrodeposited coatings [8]. Although the formation of white-rust can be avoided by chromate passivation of Zn surfaces, the chromium in chromates is a heavy metal which could bring serious hazards to humans and environments. Therefore, looking for an effective method that can substitute the chromate passivation has become essential in the electrodeposition zinc industry.

In recent years, conducting polymers have been widely investigated due to their unique properties such as corrosion protection [9]. The advantage of conducting polymer coatings compared to the paints and cadmium containing coatings is that they do not contain toxic substances that are harmful to the environment. Therefore, polymer coatings have become a good substitute for materials containing heavy metals or hexavalent chromium coatings. The most studied polymers are polypyrrole (PPy) and polyaniline (PANI) applied on the surface of oxidizable metals or alloys [10]. Generally, the anodic protection has been considered as a mechanism by which conducting polymers prevent corrosion [11]. Anodic protection occurs once the oxidative behavior of polymer coatings inducing passivation of the metal substrates, and the metals are protected by a thin oxide layer beneath the polymer coatings [12]. Lehr et al. [13] and Sheng et al. [14] found that Zn-PPy bilayer system is a very effective protective coating for steel and magnesium alloy. Tüken et al. [15] suggested that the inner Zn acts as sacrificial anode against the corrosion of mild steel and the outer PANI behaves as a physical barrier to prevent the permeation of corrosion medium. Consequently, the assembly of conducting polymers onto the surface of the galvanized steels to fabricate the bilayer coatings is a promising approach for protection of Zn or its composite electrodeposited coatings.

Silicon carbide (SiC) is a very stable inorganic material because of its high thermal conductivity, high mechanical strength and microhardness, low friction coefficient, excellent wear resistance and corrosion resistance at extreme environments, and it has been widely used in the reinforcement phase of composite materials or coatings [16]. Moreover, we know that PANI prevents corrosion of metals mainly depending on its physical barrier and reversible redox properties, but the poor solubility of it in common organic solvents have restricted its practical applications in many fields. It is well known that the ring substituted modification of PANI usually can improve the solubility of polymers [17]. Based on that, Bilal et al. [18] and our group [19] have confirmed the excellent structure and corrosion resistance of PANI derivatives such as poly(o-toluidine). In this context, the aim of the work is to study the differences of structure and corrosion resistance of alkyl-substituted PANIs (poly(alkyl-aniline)). As far as we know, there are limited literatures comparing study poly(alkyl-aniline) to protect the galvanized steels against corrosion. Meanwhile, it is easy to cause partial dissolution of Zn surface by the anodic oxidation of galvanized steel [20], and this method will bring a disadvantage effect on the corrosion resistance and adhesion strength of outer polymer coatings. Therefore, in order to avoid the above defects and expand the industrial applications of bilayer coatings, based on our more recently method for preparation of poly(o-ethylaniline)-SiC/Zn bilayer coatings [21], the poly(alkyl-aniline)-SiC/Zn bilayer coatings were also fabricated. Firstly, POT, PMT and POEA were synthesized by chemical oxidative polymerization method, SiC/Zn surface was deposited on the carbon steel substrate by electrodeposition technique. And then, the poly(alkyl-aniline) was applied on the surfaces of SiC/Zn composite coating to obtain POT-SiC/Zn, PMT-SiC/Zn and POEA-SiC/Zn bilayer coatings, respectively. The structures of polymers and electrodeposited coatings were investigated and analyzed. The corrosion resistances of the bilayer coatings were evaluated in 3.5% NaCl solution by Tafel polarization technique and electrochemical impedance spectroscopy, and the corrosion protection mechanism was also discussed in detail.

2. Experimental

2.1. Materials

O-toluidine (OT), M-toluidine (MT) and O-ethylaniline (OEA) monomers were obtained from Shanghai Macklin Biochemical Co., Ltd and it was distilled to colorless before use. Dodecylbenzene sulfonic acid (DBSA) was acquired from Linyi Yongtai Chemical Co., Ltd. Ammonium persulfate (APS) and zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS) was provided by Sinopharm Chemical Reagent Co., Ltd. The SiC with an average size of 40 nm, supplied by Shanghai Chaowei Nanotechnology Co., Ltd. Nmethyl-2-pyrrolidone (NMP) was provided by Tianjin Guangfu Fine Chemical Research Institute. The other reagents were purchased from different resources and used without further purification.

2.2. Synthesis of poly(alkyl-aniline)

Poly(alkyl-aniline) includes poly(o-toluidine) (POT), poly(m-toluidine) (PMT) and poly(o-ethylaniline) (POEA) were synthesized by chemical oxidative polymerization method, a given amount of DBSA and monomers were mixed according to the molar ratio of 1:1. The typical synthesis process of POT is as follow: 9.79 g of DBSA was dissolved in deionized water and added into 3.69 ml of OT monomer to form a mixture emulsion under a series of ultrasonic vibrating, magnetic and vigorous stirrings, and then 100 mL of 0.3 M APS solution was added dropwise into the above mixture. The resulting mixture was allowed to react for 10 h below 5 °C. After that, the precipitate was collected on a Buchner funnel and multiple washed with ethanol and deionized water. Finally, the products were dried in an oven at 60 °C for 24 h and then fine grinded by agate mortar. Similarly, PMT and POEA were also synthesized by the same method.