Ultrasound-assisted synthesis of wear-resistant Zn-Ferrocene composite coatings with high anticorrosive properties in alkaline environments

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ABSTRACT

Zn coatings are widely applied due to their low cost and negative potential in steel construction and reinforcing steel bars in concretes. However, Zn coatings have been found to perform unsatisfactorily in moist and alkaline environments. In the aqueous alkali environments that inevitably form when concretes fail, galvanized reinforcing steel bars have extremely low corrosion resistance and, consequently, are subject to corrosion. Facing these problems, various additives, including organic and inorganic compounds, have been introduced into Zn coatings to obtain enhanced corrosion resistance, with fewer experiments focusing on organometallic compound composited coatings. As a typical organometallic compound, ferrocene possesses high resistance to corrosive media, such as acids and alkalis. This makes ferrocene an extremely appropriate additive for composite Zn coatings. In this study, Zn-Ferrocene composite coatings were synthesized via electrodeposition with ultrasound assistance. Ferrocene was successfully incorporated using electrochemical control, with a maximum ferrocene content determined to be 19.4% of the C present in the composite coating. The surface morphologies and crystalline structures of the resultant coatings were significantly altered to thin, flake-like hexagonal crystals, a characteristic that was associated with the electrodepositing atomic matrix. The addition of ferrocene greatly improved the wear resistance of the composite coatings, with a 25% mass loss of pure zinc within the coating. The best properties were obtained at an ultrasound assistance level of 15 W. In addition, the corrosion mechanism of the composite coatings was studied at the molecular level. It was found that the corrosion resistance of the composite coatings in alkaline solutions was noticeably enhanced, with an R_{ct} value doubled showing the charge transfer process was inhibited. These results indicate that ultrasound-assisted Zn-Ferrocene composite coatings hold much promise for their potential use in reinforced steel bars in concretes and other abrasive environments.

1. Introduction

For several decades, zinc coatings have been commonly applied in steel construction due to their high corrosion resistance, affordability, and ease of fabrication [1]. Galvanized coatings can provide barrier and cathodic protection to exposed steel from hostile environments [2,3]. In particular, as one of the anti-corrosion technologies of developed concretes, the addition of galvanized reinforced steel bars has been proposed to enhance the corrosion resistance of concretes. However, when

concretes fail, alkaline environments form around galvanized reinforced steel bars [4]. The service life of zinc coatings is thus strictly limited in these hostile environments. Similar situations also occur in some abrasive environments, which can lead to serious corrosion that threatens both operational and occupational safety [3,5,6].

Given the excellent performance of composite coatings, there has recently been a considerable expansion of experimentation focusing on the fabrication of these coatings [7–9]. Researchers have made extensive efforts to create zinc composite coatings that exhibit specialized

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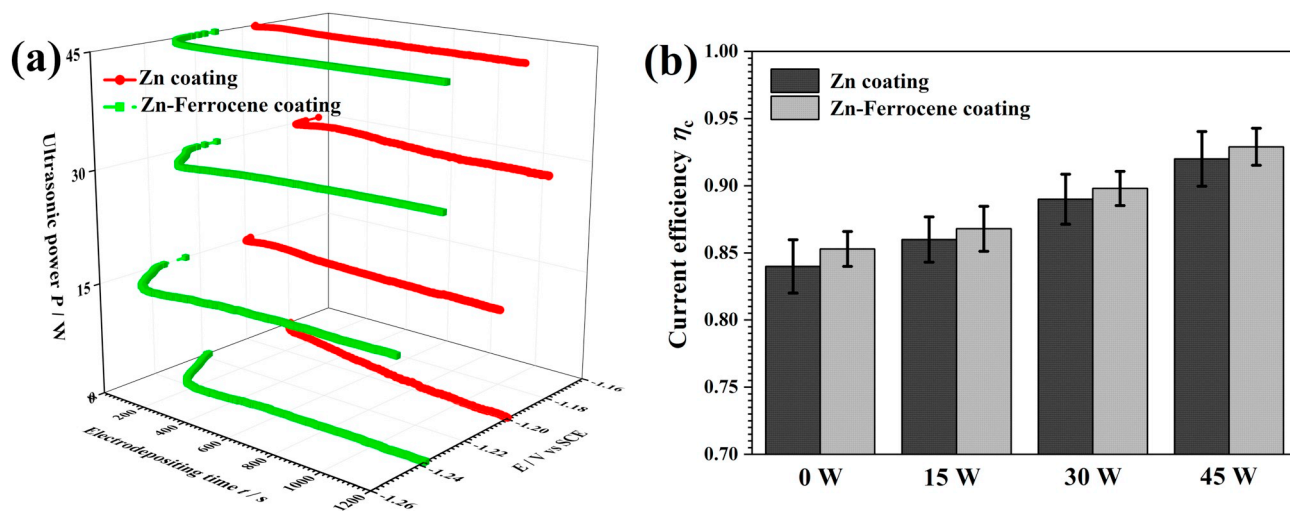
Fig. 1. The (a) electrodepositing potential and (b) current efficiency of Zn coatings electrodeposited with 0 W, 15 W, 30 W, and 45 W of ultrasonic assistance.

functions in different hostile environments [10–12]. For example, the zinc-organic composite coatings Zn-DCOIT and Zn-chitosan were fabricated for their antibacterial properties [13–15]. Zn-PTFE and Zn-polytetrafluorethylene coatings were also electrodeposited for their exploitable tribological properties [16]. Zinc-inorganic nanocomposite coatings, such as Zn-SiC, Zn-Al$_2$O$_3$, and Zn-ZrO$_2$, were also investigated for their potential enhanced wear resistance [17–20]. Interesting results were also found by electrodepositing Zn-Ag and Zn-Cu/Ag nanocomposite coatings with enhanced antibacterial properties [21–23].

Although many attempts have been made to create both organic and inorganic composite zinc coatings, with excellent results, some problems still remain to be solved, such as hydrogen embrittlement for organic additives and the low composite content of inorganic nanoparticle additives. Facing these challenges associated with new deposition methods, the current study focused on searching for new additives that would lead to enhanced properties. Organometallic compounds have not been widely reported as additives in metal coatings for enhanced properties, making them an unexplored additive target. Ferrocene is a typical organometallic compound that is composed of two cyclopentadienyl anions located on both sides of the iron (II) cation [24]. Ferrocene has been observed to display high resistance towards bases, acids, and alkalis, as well as displaying high wear resistance [25], making it an appropriate additive for functional zinc coatings [26]. Using ordinary motionless electrodeposition, ferrocene composite coatings with low additive contents can be obtained, but the properties are unsatisfactory [27]. Recently, ultrasound was introduced into the electrodeposition process to better disperse the additives and improve both the coating deposition rate and the inclusion rate of composite particles. It was found that with suitable ultrasonic assistance, various degrees of property enhancement could be acquired.

In this study, we explored the possibility of using organometallic ferrocene as a functional additive in zinc electrolytes in order to obtain a Zn-Ferrocene composite coating. We further evaluated its properties, including wear resistance and corrosion resistance in alkaline solutions. Stirring and ultrasound were also introduced into the electrodeposition process in order to not only help ferrocene co-deposit but also to promote the uniform dispersion of ferrocene in the composite coatings. The influence of ultrasonic power on Zn-Ferrocene coatings was further investigated.

2. Material and methods

2.1. Electrodeposition of Zn-Ferrocene composite coatings

Electrodeposition of Zn and Zn-Ferrocene composite coatings was

performed in a glass cell. A pure Zn sheet with the dimensions 50 mm × 20 mm × 5 mm served as the anode, a 20# carbon steel (0.19 wt% C, 0.31 wt% Si, 0.55 wt% Mn, 0.04 wt% P0.043 wt% S, and residual Fe, purchased from YangXin Company, Henan, China) sheet of 50 mm × 13 mm × 2 mm served as the cathode, and a saturated calomel electrode (SCE, Leici, Shanghai, China) was applied as the reference electrode, connected by a salt bridge. The electrodeposition was controlled by a DJS-292E Potentiostat (Leici, Shanghai, China). Ultrasound was supplied by Y92-IIN Ultrasonic Processor (Xinzhi, Ningbo, China) at a vibration frequency of 20 kHz. An RH-D-W-S25 magnetic stirring apparatus (IKA, Germany) was used to provide a stable stirring velocity during electrodeposition.

A nontoxic sulfate electrolyte containing 250 g L^{-1} ZnSO$_4$·7H$_2$O, 80 g L^{-1} Na$_2$SO$_4$, 26 g L^{-1} H$_3$BO$_3$, and 40 g L^{-1} Al$_2$(SO$_4$)$_3$·18H$_2$O was used in this experiment. All electrolyte contents were purchased from the Sinopharm Company, China. To obtain a Zn-Ferrocene composite coating, a 10 g L^{-1} ferrocene solution (particle size ~ 1 μm, Sinopharm Company, China) was added to the electrolyte and stirred for 4 h before use. Prior to electrodeposition, the 20# carbon steel substrate was ground with sandpaper to 2000#, oscillated in ethanol for 10 min and then surface-activated in 1 mol L HCl for 5 s. The steel sheet was then immediately connected to the electrodeposition cell and immersed in the nontoxic sulfate electrolyte for Zn coating, or ferrocene-added electrolyte for the Zn-Ferrocene composite coating. The electrodepositing current density was set at 20 mA cm^{-2}, with a deposition time of 20 min and a stirring speed of 600 rpm. The assisted ultrasonic supply cycle was t$_{on}$ = t$_{off}$ = 1 s, and the ultrasound power ranged from 0 to 45 W in 15 W increments.

During deposition, the electrodepositing potential was recorded by the potentiostat. The mass of the sheet both before and after electrodeposition was measured by an analytical balance (Sartorius, Germany). The current efficiency, η$_c$, could then be calculated according to the literature [14].

2.2. Characterization of Zn-Ferrocene composite coatings

The surface morphologies and elemental distributions of the coatings were observed using a scanning electron microscope (SEM, S-3400 N, Hitachi, Japan) with an energy-dispersive spectrometer (EDS, INCAx, Oxford, UK) system. The crystal structure of the coatings was analyzed by X-ray diffraction (XRD, Rigaku D/max-Ultima IV, Japan) under the following conditions: 40 kV, 30 mA, graphite-filtered Cu Ka radiation (l = 0.1542 nm). Surface roughness was then determined using an Atomic Force Microscopy (AFM, Multimode 8, Bruker, USA).