



The effect of surface modification of zinc particles with phosphoric acid on the corrosion resistance of cold galvanizing coatings



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ARTICLE INFO

Keywords:

Cold galvanizing compound

Zinc rich coatings

Surface modification

EIS

Cathodic protection

Electric power

ABSTRACT

The surface modification of zinc particles using phosphoric acid was conducted to improve the corrosion resistance of Cold galvanizing coatings. The modified zinc particles were characterized by Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). Electrochemical impedance spectroscopy (EIS) and Scanning Vibrating Electrode Technique (SVET) were performed to investigate the corrosion protection mechanism of the coating. The electrochemical activity of zinc particles were found decreased because of the formation of $Zn_3(PO_4)_2 \cdot 4H_2O$ on the surface of the particle. Little lamellar-shaped phosphate was also observed after surface modification. The best anti-corrosion performance of the coating was achieved when using zinc particles modified with 1% phosphoric acid as the fillings. This improvement was accomplished by the combined effect of reduced electrochemical activity of surface modified zinc particles and block effect from lamellar-shaped phosphate.

1. Introduction

Conventional zinc-rich coatings (ZRCs) have been widely used in heavy duty industrial environments such as automotive industry and electric power for decades not only because of their good galvanic protection for steel but the weld ability due to electrical conductivity provided by the zinc dust [1]. Basically, they can be divided into two categories according to the film forming material. One is inorganic zinc-rich coating, using tetraethyl orthosilicate or silicate as film forming material, another category is organic coating, treating epoxy resin as film forming material in most situations. In organic zinc-rich coatings, one-component coatings and two-component coatings are distinguished based on whether there is hardener or not before the application of zinc-rich coatings.

One of the most remarkable characteristics of ZRCs is that the pigment solid content must be greater than the critical pigment volume concentration [2,3], which makes the coating porous. Research showed that in a zinc-rich coating containing 92% (w/w) zinc particles, the volume fraction of zinc particles was only 52% and 19.4% was occupied by air [4]. As a result, unlike normal organic coatings, the ZRCs' corrosion protective ability comes essentially from the cathodic protection provided by the preferential attack of zinc dust in earlier stages [5]. The

effect of barrier property may be increased during the corrosion progress when the corrosion products start sealing the pores in the coatings, when the coating transfers into a barrier-type coating [6].

Numerous studies have been carried out to improve the corrosion resistance of ZRCs. For example, the effects of size and shape of zinc particles have been studied by Kalendova [7] and Jagtap et al. [8], who found out that lamellar shaped zinc particles were more effective for electrical connecting and blocking of electrolytes, but were consumed too fast. The effect of pigment/binder ratio on the performance of zinc-rich coatings has also been investigated by Hare and Kurnas [9], who obtained that the pigment volume concentration has to be higher than the critical pigment volume concentration so that galvanic effect would be the dominant factor for corrosion protection capability. Kalendova et al. [10] evaluated the efficiency of inorganic nonmetal pigments, such as zinc phosphomolybdate and calcium borosilicate on the corrosion resistance of zinc-rich coatings. Remarkably, the reviewed literatures have demonstrated research achievements which have significantly improved the performance of zinc-rich coatings [3]. Bastos et al. [11,12] pretreated the zinc particles with several corrosion inhibitors such as cerium and lanthanum nitrates, benzotriazole and 2-mercaptobenzothiazole, trying to improve the corrosion resistance of primers. To this end, they concluded that this surface modification of

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zinc powder with these several corrosion inhibitors had no significant effects [13].

Especially, when the solid content of zinc in the dried film reaches 92% or above, the zinc-rich coating is also called cold galvanizing compound or coatings (CGCs) in industrial field. Unlike traditional zinc-rich coating that is usually used as primer in the anti-corrosion coating system; cold galvanizing compound can be applied without topcoat and has excellent ability to prevent hot dip galvanizing or steel from corrosion. In addition, it is convenient to apply because it is made up of one component. However, because of the high reaction activity of the zinc particles [3,13] and the porosity mentioned before, the pigments in the coatings, especially in cold galvanizing coatings, are largely consumed when exposed to the corrosive environment, making the life span of the CGCs much shorter than designed. One of the most promising strategies to solve the problem is zinc particles surface modification [14], which can partially or completely passivate the zinc particles and reduce their electrochemical activity, thus increasing the anti-corrosion ability of the coating. Notwithstanding, the effect of the surface modification of zinc particles in CGCs was not studied quite intensively, surface modification of zinc particles faces significant challenges in the corrosion field.

In this work, attempts were made to pre-treat zinc powders with different concentration of phosphoric acid. A layer of phosphate was supposed to cover the zinc particles, aiming at decreasing the electrochemical activity of zinc particles and improving the corrosion resistance of cold galvanizing coatings. Besides, the phosphate product was an effective anti-corrosive pigment that had been used for many years [15–17].

2. Experimental

2.1. Surface modification of zinc particles

Zinc particles were purchased from Umicore Hunan Fuhong Zinc Chemicals Co., Ltd, China, which were spherical in shape and average particle size ranged from 2 to 5 μm . The detailed chemical composition of zinc particles is listed in Table 1. SE200 acrylic resin was purchased from Shenyang Zhongke Engineering Technology Center for Corrosion Control, China. The zinc particles were chemically modified to reduce their electrochemical reactivity. The surface modification was carried out with phosphoric acid from Sinopharm Chemical Reagent Co., Ltd., whose chemical composition is also listed in Table 2. Ethanol solution (95 wt%, AR) was also employed as the surface modification medium which was also purchased from Sinopharm Chemical Reagent Co., Ltd. The modification solutions were prepared according to the formulation listed in Table 3. After adding a certain amount of phosphoric acid into ethanol, the solutions were stirred using magnetic stirrer for 15 min. The zinc particles were then added to the solution and stirred for 4 h at room temperature. Modified zinc powders were recovered by centrifugalization at 3000 rpm for 3 min and were then washed with deionized water. This step was repeated for several times to remove the residual chemicals around particles. Lastly the surface modified zinc particles were dried in a convection oven at 60 $^{\circ}\text{C}$ for 48 h. The grinding of recovered zinc particles was followed by filtration with 325 mesh sieve.

2.2. Preparation of coated steel panels

The resin used in the preparation of the coatings is SE200 acrylic

Table 1
Chemical composition of the zinc particles (weight%).

Zn	Fe	Cu	Cd	Pb
Balanced	0.0008	0.0003	0.0016	0.0018

Table 2
Chemical composition of the phosphoric acid (weight%).

Phosphoric acid	Mn	Fe	As	NO ₃	SO ₄	H ₂ O
Balanced	0.0002	0.0025	0.0001	0.0005	0.0035	15.0000

Table 3
Formulation of surface modification solution.

	Ethanol	phosphoric acid	zinc powders
1%	98g	2g	100g
3%	94g	6g	100g
5%	90g	10g	100g

resin. All ingredients including two other additives were dispersed at 1500 rpm with high speed dispersing machine. The coatings were applied on prepared Q235 low carbon steel sheet by air-spraying, the air pressure ranged from 0.6 to 0.8 MPa, and then the films were cured at room temperature for 7 days. Before the coating application, the steel sheets were sandblasted to insure the coating film adhere firmly to the steel substrate. The dry film thickness of coated panels was 75 μm –85 μm , which was measured by a portable thickness measurement system (PosiTector 6000, USA). The coating samples were numbered as Coating 0% which contains non-treated zinc particles; Coating 1%, Coating 3% and Coating 5% contains zinc particles treated with 1%, 3%, 5% phosphoric acid respectively.

2.3. Characterization

2.3.1. SEM (Scanning electron microscopy)

In order to observe the surface morphology of the pre-treated zinc particles and the surface and cross-sectional microscopic views of the coatings after experiments, scanning electron microscopy was carried out on XL30 type ESEM. Before SEM observations, the samples were coated 10 nm of Au.

2.3.2. SVET (Scanning vibrating electrode technique)

SVET measurements were performed on a sample of 1 cm \times 1 cm that was glued to an epoxy cylinder support. Beeswax was used to insulate the sample leaving only a window of a few squared millimeters that was exposed to the testing solution. Adhesive tape was applied around the epoxy support to make a solution reservoir. Measurements were made with Applicable Electronics and controlled by the Science Ware ASET 2.0 software. The vibrating micro-electrodes had a 10 μm spherical platinum black tip vibrated with amplitude of 10 μm at an average distance of 100 μm from the surface of the sample. Each scan comprised 40 \times 40 points and a duration of \sim 1600 s (with an acquisition of 1 s in each point).

2.3.3. EIS (Electrochemical impedance spectroscopy)

The electrochemical cells for EIS measurements were prepared by fastening a plastic tube to the surface with bolts and nuts. The tubes delimited an area of 12.56 cm^2 and were filled with the 3.5 wt% NaCl solution as corrosive electrolyte. A three-electrode arrangement was used with a saturated calomel reference electrode, a platinum counter electrode and the exposed sample area as working electrode. The cell was connected to 273A electrochemical workstation from EG & G and all measurements were performed at room temperature with the cells in the Faraday cage. Impedance measurements were done in the 100 kHz to 10 mHz frequency range with a total of 30 points distributed logarithmically; the sinusoidal perturbation was 10 mV at open circuit potential (OCP).

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