



Full Length Article

Corrosion protective performance of amino trimethylene phosphonic acid-metal complex layers fabricated on the cold-rolled steel substrate via one-step assembly

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ABSTRACT

Seeing that amino trimethylene phosphonic acid (ATMP) possesses very strong complexation ability to metal ions and the phosphonic acid group has good affinity for the oxidized iron surface, herein a simple and rapid film-forming method (one-step assembly method) was developed to construct the ATMP-Zn complex conversion layers (ATMP-Zn layers for short) on the cold-rolled steel (CRS) substrate. Zinc ions were found to participate in the formation process of ATMP-based composite film, which made the Zn-containing ATMP film significantly different in appearance, thickness, microstructure and film-forming mechanisms from the Zn-free ATMP film. There was mainly iron (III) phosphonate in the Zn-free ATMP film, whereas there were Zn²⁺-ATMP complex and a certain amount of ZnO in the ATMP-Zn composite film. In addition, electrochemical test results clearly indicate that corrosion resistance of ATMP-Zn composite film was greatly enhanced due to the presence of Zn component. Moreover, the corrosion resistance performance could be controlled by adjusting film-forming time, pH and ATMP concentration in the film-forming solutions. The present study provides a new method for the design and fabrication of high-quality environmentally-friendly conversion layers.

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1. Introduction

The study on corrosion and protection of iron and steel workpieces has been an old and new research topic since the corrosion not only leads to the degradation or failure of products or devices but also causes a series of economic and security problems [1–3]. Seeing that the corrosion and protection of metals are related to the behavior of surface films, chemical conversion treatment method, as a typical method for fabricating protective films directly on the surface of a metal substrate through a chemical or electrochemical process, has been widely applied to surface anti-corrosion treatment of iron, aluminum, titanium, zinc and various steels [4,5]. Usually, the as-formed chemical conversion layer can be seen as an integral part of the metallic substrate and work as an insulating barrier of exceedingly low solubility between the metal and the surrounding environment, thereby providing the greater corrosion resistance to the metal and the increased adhesion of coatings applied to the metal. The typical examples are phosphate coatings on steel [6] or zinc [7] and chromate coatings

on aluminum [8]. Nevertheless, chromate passivation process and phosphating process have been strictly restricted or even forbidden due to the toxicity and environmental pollution [9–11]. Given this, it is imperative to develop environmentally friendly, non-toxic, and high-efficiency chemical conversion coating techniques applicable to the surface treatment of many metals, including the commonly used iron and steels.

The formation process of traditional conversion layers involves the corrosion of metal substrate and the deposition of insoluble salts or oxides on the surface. For nearly 30 years, self-assembly techniques have found wide application in the development of new chemical conversion layers, marked by preparation and application of sets of silane conversion coating products [12,13]. Besides, Schiff base [14], alkylthiol [15] and alkyl phosphate self-assembled thin films [16] also show good anti-corrosion ability to metal substrates in corrosive environments. More recently, our group have demonstrated that some alkyl phosphates, such as mono-n-butyl phosphate, mono-n-hexyl phosphate [17], and bis-2-ethylhexyl phosphate [18], can spontaneously adsorb onto the iron surface in water solutions, forming a type of self-assembled thin films with good corrosion protective performance. However, it should be noted that the common self-assembled thin films are very thin (on nano scale) and contain some defects. These

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disadvantages make them hardly serve as the chemical conversion layers. So far, silane-based self-assembled film has been one of the few successful examples of applying self-assembly method to fabricate chemical conversion layers. Even so, there is no doubt that self-assembly method provide researchers the theoretical basis for design new chemical conversion layers, and the key to success is selecting an appropriate self-assembly system.

Recently, a one-step film-forming method based on the assembly of the coordination complexes between natural polydentate ligands and metal ions on solid substrates has attracted our attention [19–21]. The film formers, Tannic acid (TA) and phytic acid (PA) with polyfunctional groups, can produce a layer of compact organic film on the steel substrate due to the affinity of $-\text{OH}$ groups for the iron surface (especially for the oxidized iron surface) and protect the steel base from being corroded. In particular, when they coexist with certain metal ions, such as Zn^{2+} , Fe^{3+} and Ca^{2+} , TA and PA are able to complex with the metal ions, and further deposit in the form of TA-metal or PA-metal chelates onto the surface of metal substrate, forming the protective films with the very high anti-corrosion performance [22,23]. Inspired by this, in this paper we planned to use amino trimethylene phosphonic acid (ATMP), a multi-complexing agent with three $-\text{PO}(\text{OH})_2$ groups, as a film former to construct ATMP-metal conversion layers on the cold rolled substrate in the presence of Zn^{2+} ions. ATMP is a commonly used scale inhibitor in cooling water systems and sometimes used as a green cathodic inhibitor [24–27], but there have not been any report about whether it can be used to fabricate chemical conversion layers thus far. Herein, taking advantage of very strong complexation ability of ATMP to Zn^{2+} ions and the good affinity of $-\text{PO}(\text{OH})_2$ groups for the oxidized iron surface, we developed a simple but effective method to fabricate ATMP-Zn conversion layers on the cold-rolled steel (CRS) substrate. ATMP- Zn^{2+} complexes can be deposited on the CRS substrate via one-step assembly under co-existence of ATMP with Zn^{2+} ions. Moreover, microstructure, thickness, and corrosion resistance of ATMP-Zn coating can be adjusted by changing assembly time, pH and ATMP concentration. The present method paves a new path to develop new chemical conversion treatment techniques.

2. Experimental section

2.1. Materials and chemical reagents

Cold-rolled steel (CRS) plate samples of 100 mm \times 100 mm \times 0.5 mm were purchased from Changan Gangde Co. and used as metal substrate to construct chemical conversion layers on them. The major components of the CRS plate were Fe (97.61%), C (1.00%), Al (0.43%), Mn (0.24%), Si (0.50%), Ni (0.12%) and S (0.11%) with atomic percentage. Amino trimethylene phosphonic acid (ATMP) was purchased from Aldrich Ltd. Six hydrated zinc nitrate, sodium chloride, ethanol, and sodium hydroxide were provided by Sinopharm Chemical Reagent Co., Ltd. All the reagents used were of analytical reagent grade.

2.2. Fabrication of ATMP film and ATMP-Zn layer on CRS substrates

Before use, the CRS sample was polished with 1200 grit emery paper, rinsed with ultrapure water and ethanol, and dried in a flow of N_2 . ATMP aqueous solution with an appropriate concentration was prepared by dissolving 1 mL of 50 wt% ATMP concentrated solution in 500 mL of ultrapure water. The film-forming solution (namely Zn^{2+} -containing ATMP aqueous solution) was obtained through the addition of 1 g solid $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into the ATMP aqueous solution. The concentrations of Zn^{2+} and ATMP were 0.044 wt% and 0.2 wt% in the mixed solution respectively. The pH

of the film-forming solution was adjusted to pH4 with NaOH aqueous solution. The pretreated CRS plate was immersed in the film-forming solution for 20 min to allow the formation of ATMP-Zn layer, and then removed from the solution and washed with deionized water for 2 min, followed by drying in a flow of N_2 . In this way, ATMP-Zn layer was fabricated on the CRS substrate. Similarly, Zn-free ATMP film was also prepared using the same method.

2.3. Surface analysis and characterization

ATMP film and ATMP-Zn layer were constructed on CRS substrates by using the above-mentioned method and the CRS plates modified by ATMP film and ATMP-Zn layer were cut into small pieces of 10 mm \times 10 mm \times 0.5 mm as the test samples. The ATR-FTIR spectra of ATMP-based coatings on CRS samples were recorded by a Bruker TENSOR 27 FTIR in spectral range 500–4000 cm^{-1} . Surface morphological observations, as well as energy dispersive spectrometer (EDS) elemental analyses, were carried out using a JSM-6390LV scanning electron microscope (SEM) (JEOL, Japan). The X-ray photoelectron spectroscopy (XPS) were performed using a Perkin Elmer PHI 5300 system fitted with an Mg Ka X-ray source and analyzed by XPS software (XPS peak 4.1). The spectra were referenced using the most intense hydrocarbon C1s photoelectron peak (C-C/C-H) taken at 284.6 eV.

2.4. Corrosion protective performance

Corrosion resistance properties of ATMP-Zn layers were evaluated by electrochemical methods, including open-circuit potential (OCP) method, polarization curve and electrochemical impedance spectroscopy (EIS). The typical three-electrode cell system was used to carry out electrochemical measurements with 3.5 wt% NaCl solution as corrosive solution. The CRS plate samples coated with the ATMP-based layers served as the working electrodes, a platinum plate as the counter electrode and Ag-AgCl electrode (EEGs) as reference electrode, respectively. The exposed area of the working electrode to the corrosion medium was 12.56 cm^2 . EIS measurements were performed in the frequency range from 100 kHz to 50 mHz with a sinusoidal wave of ± 5 mV amplitude by using an HZ-7000 electrochemical workstation. Herein, OCP and the EIS measurements were performed based on a standard procedure of ASTM G3-89. Polarization curves were scanned from cathodic side to anodic side with a slow sweep speed of 0.2 mV/s and recorded by a CHI 604 electrochemical workstation. Before each experiment, the working electrode was stabilized for several minutes in the electrolyte solution to acquire a stable open-circuit potential.

3. Results and discussion

3.1. FTIR characterizations

Reflection FTIR technique was used to identify and study whether ATMP molecules were able to self-assemble onto the CRS substrate in water. The FTIR spectra of the different CRS plate samples were measured after being treated by immersing in ATMP-containing solutions in the presence or absence of Zn^{2+} ions for a designated period of time. Certainly, the FTIR spectrum of naked CRS plate sample was presented as comparison, which showed an approximately flat line with no obvious characteristic peaks (see Fig. 1a). Meanwhile, CRS samples treated in the ATMP-containing solutions, regardless of presence or absence of Zn^{2+} ion, demonstrated the several prominent absorbance peaks that matched well with those of the pure ATMP substance (see Fig. 1b and c). Specifically, the peak at 1170 cm^{-1} was ascribed to

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