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Investigation on the inhibition synergism of new generations of phosphate-based anticorrosion pigments

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ABSTRACT

The role of zinc aluminum molybdenum orthophosphate hydrate and zinc calcium strontium aluminum orthophosphate silicate hydrate as new generations of phosphate-based anticorrosion pigments in corrosion protection of mild steel exposed to 3.5% sodium chloride solution was studied using electrochemical techniques as well as surface analysis. Compared to conventional zinc phosphate, superiority of the modified pigments was shown through taking advantage of electrochemical impedance spectroscopy, polarization curves and electrochemical noise measurements. Moreover, a good trend was also observed between electrochemical noise data and the results obtained from electrochemical impedance spectroscopy and potentiodynamic polarization. Protective films deposited on the surface were detected using SEM/EDX in the presence of zinc aluminum molybdenum orthophosphate hydrate and zinc calcium strontium aluminum orthophosphate silicate hydrate releasing more inhibiting species. The effect of immersion time on the film formation was studied through the electrochemical methods. XPS technique was also employed to analyze the sample surface exposed to 3.5% NaCl solution containing combination of the modified pigments. In addition to the surface analysis data, various parameters extracted from the electrochemical measurements revealed corrosion inhibition synergism of the two pigments.

1. Introduction

Several approaches have been proposed in recent years to produce the coatings revealing enhanced anticorrosion properties [1–4]. One of the efficient ways to enhance protective performance of organic coatings is to incorporate inorganic anticorrosion pigments belonging to the electrochemically active class. By taking the compounds into consideration as reservoir, solubility can play role of a discharge valve which makes the inhibitor species kinetically available [5–8]. When the pigment particles come into contact with water taken up by the coating film, some inhibiting species could be released reinforcing the coating/substrate interface and plugging the pores. Toxic chromium-containing anticorrosion pigments exhibiting excellent inhibitive performance have been extensively used for a long time. Due to the heavy restrictions on the use and disposal of chromate containing materials, a big attempt has been made with the hope of finding proper replacements [9–13]. Zinc phosphate as widely used alternative to chromates has been reported to possess undesirable performance. Hence, several physical and chemical modifications have been already proposed to improve its solubility, affecting the release of inhibiting ions [14–20]. Through taking advantage of various electrochemical methods, the inhibitive mechanisms of some compounds representing second and third generations of phosphate-based anticorrosion pigments were studied in the previous publications [21–25]. This work aims to investigate the synergistic effect of zinc aluminum molybdenum orthophosphate hydrate (ZAM) and zinc calcium strontium aluminum orthophosphate silicate hydrate (ZCP) on the corrosion behavior of mild steel exposed to 3.5% NaCl solution through various electrochemical techniques as well as surface analysis.

Common electrochemical tools, in particular EIS and potentiodynamic polarization methods, have been widely employed to provide insight into the inhibition performance of various anticorrosion pigments. In the recent decade, an increasing interest toward applying brand new techniques such as electrochemical noise method (EN) among corrosion researchers could be spotted. EN is traced back to stochastic pulses occurring in the corrosion potential or galvanic current of a freely corroding cell. It is a non-intrusive technique giving both kinetic and mechanistic

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information [26–28]. In this study, different aspects of EN parameters are focused to study inhibition mechanisms of the modified anticorrosion pigments. Furthermore, it is intended to seek the correlation between EN data and the results of EIS. The SEM/EDX and XPS techniques facilitated further study of film formation as the inhibition mechanism in the presence of the two modified pigments. The effect of immersion time on the film formation was also investigated using the electrochemical methods. Moreover, XPS as a surface specific analytical technique providing information on chemical composition was used to characterize sample surface in contact with the combination of ZCP and ZAM extracts.

2. Experimental

2.1. Materials

Mild steel (CK45) plates with dimension of 3 cm × 3 cm × 2 mm were used as substrate in this work. The mild steel specimen surface was abraded with abrasive papers starting from 120 to 1200 grit size. The samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. One surface of the samples was connected to a copper wire for electrical connection. To seal the edges and back sides of the steel panels, they were covered with a beeswax-colophony mixture, leaving an area of 1 cm^2 unmasked.

The commercial grade anticorrosion pigments used in this study were zinc phosphate, zinc aluminum molybdenum orthophosphate hydrate and zinc calcium strontium aluminum orthophosphate silicate hydrate and zinc aluminum phosphate which are known under the trademarks ZP, ZAM and ZCP, respectively, according to datasheets published by the supplier (Heubach Ltd.). SEM images for pigment powders are depicted in Fig. 1. In order to prepare extracts, 2 gr of each pigment was stirred in 1 L 3.5% w/w NaCl aqueous solution for 24 h then filtered to achieve saturation conditions. To make the ZAM + ZCP extract, 1gr of each pigment was also added to 1 L 3.5% NaCl solution. The concentration of the species dissolved in the pigment extracts was measured by inductively coupled plasma-optical emission spectrometry (Varian Vista Pro ICP-OES).

2.2. Methods

The electrochemical measurements were performed on 1 cm^2 of the mild steel panels exposed to the 3.5% NaCl solutions containing various pigment extracts at 25 °C without de-aeration. Within 24 h immersion, electrochemical measurements were carried out employing Autolab instrument model PGstat 302N. During the measurements, the cell was placed in a Faradic cage to minimize possible external electromagnetic interference. To perform EIS and polarization measurements, a conventional three electrode cell including mild steel specimen as working electrode, a platinum counter electrode and a saturated Ag/AgCl reference electrode was used. Impedance spectra were plotted at open circuit potential (OCP) within the frequency domain 10 kHz to 0.01 Hz using perturbation sine wave of 10 mV amplitude peak to peak. Polarization curves were provided at a scan rate of 1 mV s^{-1} from −200 mV to +200 mV of OCP. The electrochemical noise measurements were performed using a three electrode cell containing two nominally identical mild steel panels and a saturated Ag/AgCl reference electrode. The EN data were gathered within a period of 1024 s at 1-s interval, which led to a frequency range from close to 1 mHz to 0.5 Hz determined by the expressions $f_{max} = 1/$

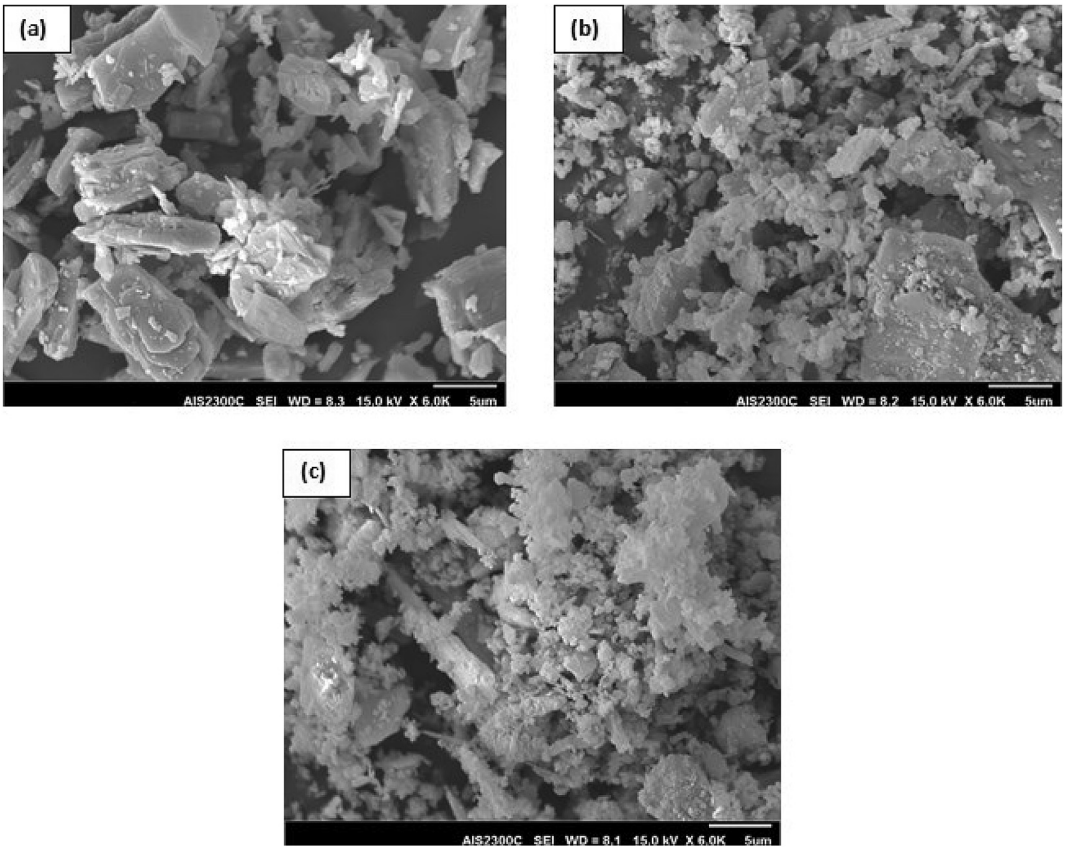

Fig. 1. SEM images for (a) ZP powder, (b) ZAM powder and (c) ZCP powder.