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An evaluation of the anticorrosion properties of the spinel nanopigment-filled epoxy composite coatings applied on the steel surface

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ABSTRACT

MnAl$_2$O$_4$ nanopigment was synthesized through co-precipitation method. The composition and morphology of the pigment were investigated by X-ray diffraction and scanning electron microscope. Electrochemical impedance spectroscopy (EIS) and linear polarization techniques were utilized to investigate the corrosion inhibition performance of the pigment. Scanning electron microscope (equipped by energy dispersive spectroscopy) was utilized in order to evaluate the surface morphology and composition of the steel samples exposed to the solutions without and with nano-MnAl$_2$O$_4$ pigment. Solubility of nano-MnAl$_2$O$_4$ pigment in the 3.5 wt% NaCl solution was evaluated by inductively coupled plasma test method. Results obtained from X-ray diffraction analysis revealed that nano-MnAl$_2$O$_4$ pigment was synthesized successfully. Results obtained from inductively coupled plasma and electrochemical measurements showed that nano-MnAl$_2$O$_4$ pigment could significantly reduce the corrosion rate of the steel sample immersed in the 3.5 wt% NaCl solution through releasing inhibitive species. Epoxy nanocomposite coatings containing 3 wt% Al$_2$O$_3$ and MnAl$_2$O$_4$ nanoparticles were produced. The epoxy nanocomposites were applied on the steel surface and then their corrosion protection properties were evaluated by EIS. Results showed that the MnAl$_2$O$_4$ nanopigment filled coating showed higher corrosion resistance than the coating loaded with Al$_2$O$_3$ nanoparticle.

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1. Introduction

Organic coatings are employed in order to protect the metal structures against corrosion [1–4]. The coatings act as physical barrier between the metal surface and the corrosive environment restricting the corrosive species diffusion into the metal surface. However, the electrolyte permeation into the coating matrix causes coating damage and creation of pores. This means that the degraded coating could not provide long term corrosion protection properties. Therefore, different kinds of anticorrosive pigments can be added to the coating matrix to improve its anticorrosion properties [5–7]. The corrosion protection properties of the pigments depend on the chemical nature, shape and size of the pigments. The anticorrosive pigments can be divided into three main categories including inhibitive, barrier and sacrificial pigments [8–12]. Among different kinds of pigments, the electrochemically active

pigments are employed in order to obtain coatings with promising corrosion protection performance [13,14].

Chromates and zinc phosphates are the most common types of inhibitive pigments which have been widely used to enhance the corrosion protection properties of the organic coatings. These pigments are slightly soluble in water. As a result, they could release inhibitive species into the coating matrix when exposed to the corrosive electrolyte. The released ions diffuse to the coating/metal interface restricting the aggressive ions access to the active sites of the metal surface. The electrolyte diffusion into the metal surface is responsible for the increase of pH as a result of the following cathodic reaction: $2H_2O + O_2 + 2e \leftrightarrows 4OH^-$. Therefore, the inhibitive species could react with OH^- ions and form insoluble compounds on the steel surface blocking the active sites. However, chromates and zinc phosphates produce carcinogenic and toxic compounds. Therefore, in the last decades, it has been attempted to replace them with the more environmentally friendly alternatives [15–18].

In recent years, nano size pigments are employed in order to enhance the anticorrosion properties of the organic coatings. Nanoparticles, due to their small size and high specific area, could enhance the corrosion protection properties of the coating through

increasing its barrier properties. In our previous works we have investigated the anticorrosion performance of the nano-SiO_2 [19], nano-ZnO [20] and nano-Al_2O_3 [21] particles filled epoxy coatings applied on the steel substrate. They found that all of the mentioned nanoparticles could effectively enhance the barrier characteristics of the epoxy coating through filing the voids and free volumes presented in the coating\structure and increasing the electrolyte pathways length. Recently the researchers' attention has directed to using inhibitive nanopigments in the organic coating matrix.

Deflorian et al. [22] investigated the inhibition effect of CeO_2 nanoparticles on the corrosion of mild steel. They found that this nanoparticle could protect the steel substrate from corrosion through releasing inhibitive spices and their adsorption on the active sites of the steel surface can restrict the corrosive spices access to the surface.

Moreover, the electrochemically active nanoparticles could release more inhibitive species than the micro-sized pigments leading to better corrosion protection properties [23–26]. Recently, the researchers' attentions have been directed to development of nanomaterials based on metal oxides. Nano size aluminum (III) oxide is a nontoxic anticorrosive pigment which has been employed for the improvement of the coating corrosion resistance. The coating barrier performance can be enhanced in the presence of nano-Al_2O_3 particles. However, nano-Al_2O_3 particles, due to its slight solubility in water, could not provide corrosion inhibitive properties [21]. One approach to achieve inhibitive action from the metal oxide based nanoparticles is doping them with the inhibitive cations. In this regard, a wide range of spinel anticorrosive pigments have been developed by doping metal oxide with inhibitive components [27,28].

The aim of this study is synthesis of $MnAl_2O_4$ nanopigment through co-precipitation method. The composition and morphology of the pigment were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The nanopigment extract was prepared in the 3.5 wt% NaCl solution. Then, the steel samples were immersed in the solution containing nanopigment extract. The corrosion inhibition properties of the nanopigment were studied by different electrochemical techniques on the steel surface. The surface morphology of the sample immersed in the 3.5 wt% NaCl solution containing nano-$MnAl_2O_4$ pigment was evaluated by SEM analysis. Also, the epoxy nanocomposites containing 3 wt% nanoparticle were prepared and applied on the steel substrate. The corrosion protection properties of the nanopigments filled composite coatings were evaluated by EIS analysis.

2. Experimental

2.1. Materials

Manganese nitrate [Mn $(NO_3)_3 \cdot 4H_2O$], sodium hydroxide (NaOH) and aluminum nitrate [Al $(NO_3)_3 \cdot 9H_2O$] were prepared from Merck Co. Mild steel panels (St-37) were provided from Foolad mobarakeh Co. (Iran). The steel sample has the following composition (wt%): Fe (97.7), C (0.19), Si (0.415), Mn (1.39), P (<0.005), S (<0.005), Cr (0.026), Mo (0.018), Co (0.429) and Cu (0.0481). Samples were polished with sand papers of 600, 800 and 12,000 grades followed by acetone degreasing.

2.2. Nano-$MnAl_2O_4$ pigment synthesis

The nano-$MnAl_2O_4$ pigment was prepared by a co-precipitation method. For this purpose, 1 mol of manganese nitrate [$Mn(NO_3)_3 \cdot 4H_2O$] and 2 mol of aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] were used. Manganese and aluminum nitrates were dissolved in deionized water with the molar ratio of 1:2. The mixture

was stirred for 10 min. It was slowly titrated with 3 M sodium hydroxide at room temperature until the pH became alkaline. The suspension was then stirred for 2 h at room temperature. The final pH of the suspension was adjusted to 12. The reaction products were collected using a centrifugal separator. The residue was washed by deionized water for four times to remove Na^+, NO_3^- ions and other impurities. Then, the residue was dried at 100 °C for 24 h to remove the additional moisture. Finally, the resulted nanopigment was calcinated at 800 °C at a rate of 10 °C per minute.

2.3. Pigment extracts preparation

The pigment extract was prepared in the 3.5 wt% NaCl solution. For this purpose, 1 g of nano-$MnAl_2O_4$ and nano-Al_2O_3 pigments was stirred in 1 L of 3.5 wt% NaCl solution for 24 h. Then, the solutions were centrifuged at 4500 rpm. Also, the 3.5 wt% NaCl solution without pigment was prepared as a reference solution.

2.4. Epoxy nanocomposite preparation

The $MnAl_2O_4$ and Al_2O_3 nanopigments were added into the epoxy resin with a concentration of 3 wt% and ground by using a three-roll grinder. Then, the appropriate amount of polyamide hardener was added to the epoxy nanocomposites. The epoxy coatings were applied on the steel sheets by an adjustable film applicator. The steel substrates were abraded with sand papers of 600, 800 and 1200 grades followed by acetone degreasing. All of the coatings were cured in a ventilate oven at 120 °C for 30 min. The dry thickness of the coatings was about 50 ± 5 μm.

2.5. Techniques

2.5.1. Nano-$MnAl_2O_4$ pigment characterization

The composition of the nano-$MnAl_2O_4$ pigment was characterized with an X-ray diffractometer (XRD) (MXP3; Bruker AXS K.K.) at a CuK radiation. The morphology of the pigment was also investigated by a 1455VP model scanning electron microscope (SEM). Nanoparticles dispersion in the epoxy coating matrix was studied by field emission scanning electron microscopy (FE-SEM, Mira).

2.5.2. Solubility of the nanopigments

The type and concentration of the ions released from the $MnAl_2O_4$ and Al_2O_3 nanopigments in the 3.5 wt% NaCl solution was studied by inductively coupled plasma (ICP) model Vista (Varian).

2.5.3. Surface analysis

The steel panels were immersed in the solutions without and with nano-$MnAl_2O_4$ and nano-Al_2O_3 pigments for 24 h. Then, samples were rinsed with distilled water and dried. The surface morphology of the samples was evaluated by SEM model 1455VP (LEO).

2.5.4. Electrochemical studies

The electrochemical properties of the steel samples immersed in the 3.5 wt% NaCl solutions without and with nano-Al_2O_3 and nano-$MnAl_2O_4$ pigments extracts were examined by EIS and polarization techniques. EIS and polarization measurements were carried out by an Ivium Compactstat. The electrochemical cell used for this purpose included graphite (auxiliary electrode), Ag/AgCl (reference electrode) and mild steel panels (working electrode). The EIS measurements were performed on 1 cm^2 area of the steel panel at open circuit potential (OCP). The perturbation and frequency range of the measurements were ± 10 mV and 10 kHz to 10 mHz, respectively. Polarization test was done at sweep rate of 1 mV/s in the range of ± 100 mV from the OCP.