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Study of the active corrosion protection properties of epoxy ester coating with zeolite nanoparticles doped with organic and inorganic inhibitors

Leili Rassouli[a], Reza Naderi[a,*], Mohammad Mahdavian[b,*]

[a] School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

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ABSTRACT

This work intends to investigate the role of NaX zeolite nanoparticles as reservoir of Zn^{2+} and 2-mercaptobenzimidazole in prolonging the lifetime of an epoxy ester coating. Based on the XPS and SEM/EDX surface analysis and electrochemical data in solution phase, the synergistic inhibition effect of the organic and inorganic species released from the zeolite particles resulted in deposition of a dense protective layer mainly composed of zinc hydroxide, organic inhibitor and organic/inorganic complex on the surface. Accordingly, a synergistic corrosion protection was detected when the NaX zeolite particles doped with Zn^{2+}/mercaptobenzimidazole were incorporated in the epoxy ester coating.

1. Introduction

One of the fundamental and economical methods for corrosion protection of metallic substrates is organic coating [1,2]. The barrier properties of organic coatings can decline the penetration rate of aggressive electrolyte to the metal surface [3]. Nevertheless, the presence of defects in the coating film may facilitate easier diffusion of corrosive species and decrease the corrosion protection properties [4]. Development of active protection through loading inhibitors in the coating matrix with or without mediator has frequently been reported as an effective strategy, increasing the coating lifetime [5,6]. In order to control the inhibitor leaching and to maintain the stability and integrity of coatings, inhibitors are suggested to be isolated from the matrix by some containers, *e.g.* layered double hydroxide (LDH), halloysites, cerium molybdate containers, clay and zeolite [1,5,7–13]. Due to the sensitivity to pH change [14,15], ion exchange capacity [16], mechanical fracture [8], the solubility of pigments [17] and UV radiation [18], inhibitors release from the containers to decline the corrosion rate in active zones. Through studying the effect of halloysite nanotubes loaded with different organic inhibitors including benzotriazole (BTA), 2-mercaptobenzimidazole (MBI), and 2-mercaptobenzothiazole (MBT) on the self-healing properties of acrylic and polyurethane paints on copper, Abdullayev et al. [19] found that the coating formulated with MBI shows the best protection due to the most efficient container capacity [19]. The role of reservoirs doped with inorganic inhibitors in the active anti-corrosion properties of coatings was also investigated. SiO_2/CeO_2 nanoparticles [20], zeolite fillers [9,21] and nano-clay [22] were used as Ce(III) reservoirs to modify the protective properties of sol–gel coatings. Montemor et al. [1] reported a synergistic inhibition effect through addition of a mixture of layered double hydroxides and cerium molybdate nanocontainers filled with 2-mercaptobenzothiazole to an epoxy coating on galvanized steel. According to the literature, the efficiency of the synergistic effect of organic and inorganic inhibitors depends on the valency of cation and its tendency to form a complex with organic molecules [23].

Zeolites are aluminosilicate crystals with negative charge due to the $SiO_4{}^{4-}$ and $AlO_4{}^{5-}$ tetrahedral arrangement [24–26]. The micro/nano-porous structure of zeolite consists of channels, voids, and cages with a high specific surface area [9,24,25,27]. The negative charge of zeolite is neutralized with loosely held cations which can be exchanged with other cations [28]. The NaX zeolite with low Si/Al ratio has high ion exchange capacity [27]. The organic and inorganic inhibitors can be loaded into the zeolite particles due to inherent properties of the reservoir such as molecular adsorption and ion exchange capacity [27,29]. In order to control the corrosion of AA2024-T3 substrate, Dias et al. [30] formulated

* Corresponding authors.
E-mail addresses: rezanaderi@ut.ac.ir (R. Naderi), mahdavian-m@icrc.ac.ir (M. Mahdavian).

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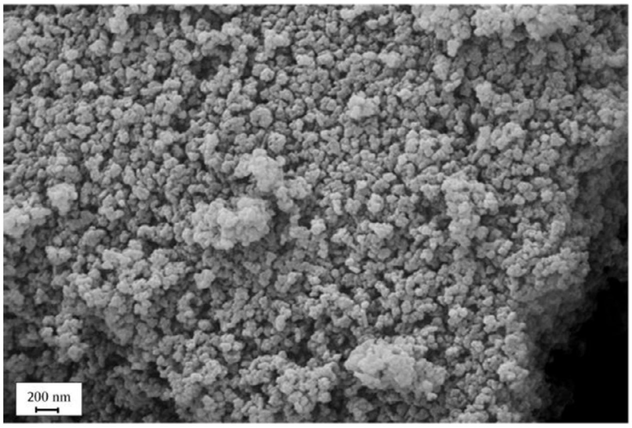

Fig. 1. FESEM image of zeolite particles.

Table 1
The characteristic of zeolite particles.

Sample code	EDS (Wt. %)				Si/Al ratio
	O	Na	Al	Si	
Z	35.7	14.6	22	27.7	1.26

sol–gel coatings with the zeolite microparticles containing a mixture of lanthanum and molybdate. The self-healing properties of an epoxy coating modified with Ce-MCM-22 zeolites on Mg–Li alloy was reported by Wang et al. [31]. Ferrer et al. [29] increased the corrosion resistance of AA2023-T3 through the application of a hybrid sol–gel epoxy coating containing the NaY zeolite particles double doped with cerium and diethyldithiocarbamate (DEDTC).

The NaX zeolite particles were doped with zinc cation and 2-mercaptobenzimidazole in this study. In other words, the zeolite was used as a host for inorganic and organic inhibitors due to its ion exchange capacity and absorption properties. At first step, the effect of inhibiting species released from the zeolite particles on the corrosion of bare steel specimens in 3.5% sodium chloride solution was studied. In this regard, the inhibition synergism of the released organic and inorganic compounds was examined using EIS and polarization measurements as well as SEM/EDX and XPS surface analysis. Then, the inhibitor-doped zeolite particles were included in the formulation of an epoxy ester coating to provide active corrosion protection. This work is novel over the previously published works as there is no research investigating the synergistic effect of organic and inorganic inhibitors released from the NaX zeolite particles in the formulation of a polymeric coating.

2. Experimental

2.1. Materials

The Z_1 zeolite which was synthesized according to our previous work [32], was used in this study. The cage shape morphology of this zeolite was shown in Fig. 1. The results of EDX analysis in Table 1 indicated NaX composition for the zeolite nanoparticles. The low Si/Al ratio induced the high ion exchange capacity due to more negative charge [24,33].

2-mercaptobenzimidazole (Fig. 2 [34]) and zinc nitrate as organic and inorganic inhibitors were supplied by Merck. Moreover, the epoxy ester resin and coating additives (driers) were obtained from Polyresin Co. (Iran).

2.1.1. Preparation of inhibitor-doped zeolite

Zinc nitrate, MBI and a combination of the two inhibitors with the molar ratio of 1:1 were doped with zeolite particles. For this

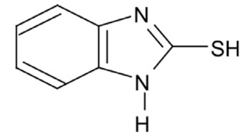

Fig. 2. The chemical structure of 2-mercaptobenzimidazole.

purpose, 1 g zeolite particles was stirred in 1L of 2 mM zinc nitrate solution, 2 mM MBI solution and 1 mM Zn nitrate +1 mM MBI solution for 24 h at ambient temperature. The doped particles were filtered, washed with distilled water and finally dried at 60 °C.

2.1.2. Preparation of extract for solution phase study

1 g of inhibitor-doped zeolite particles was stirred in 1L of 3.5 wt. % NaCl aqueous solution for 24 h at ambient temperature. After filtration, the extract was used for solution phase study.

2.1.3. Epoxy ester coating preparation

According to the coating formulation summarized in Table 2, the zeolite particles were ultrasonically dispersed in toluene for 30 min. The combination was then homogenized with epoxy ester resin for 30 min. Some additives including leveling agent, wetting agent and defoamer were incorporated in the coating formulation at this stage. After addition of driers, the mixture was applied by a film applicator on the steel substrates ($15 \times 10 \times 0.1$ cm^3). Prior to the coating application, the substrates were abraded by 600 to 1200 grit size abrasive papers, washed with distilled water and degreased with acetone. The elemental analysis of the steel substrate is shown in Table 3. The coated panels were dried at room temperature for 5 days and cured at 70 °C for 1 h. To prepare the coating with an artificial defect, a 1 cm scratch was applied on the film surface with an exposure area of 4 cm^2. The brief description of samples used in this study is presented in Table 4.

2.2. Methods

2.2.1. Inductively coupled plasma (ICP) and UV–visible

The concentration of inorganic and organic inhibitors released from the zeolite particles in the sodium chloride solution was measured using ICP analysis (Varian Vista Pro ICP-OES) and UV–vis absorption spectra (6715 UV/vis spectrophotometer Jenway), respectively. The UV–vis absorption spectra of 1 mM MBI solution was used as a reference.

2.2.2. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX)

The morphology and elemental analysis of NaX zeolite particles were investigated using FESEM/EDX Model MIRA/TESCAN.

A HRSEM-EDX Model Camscan mv2300 was used to survey the surface of bare metals after 24 h of immersion in the test solutions and analyze the surface of intact and defected coatings. A cross-sectional view of intact coatings was also provided using the instrument.

2.2.3. X-ray photoelectron spectroscopy (XPS)

The surface of steel after 24 h exposure to 3.5% NaCl-Z(Mix) solution was further analyzed by XPS analysis using Specs EA 10 Plus model. This measurement was accomplished at the pressure of 10^{-9} MBIr and radiation source of Al Kα. The calibration of binding energy was carried out according to the reference peak of carbon at 285 eV.

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