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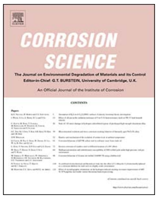

Synergetic active corrosion protection of AA2024-T3 by 2D- anionic and 3D-cationic nanocontainers loaded with Ce and mercaptobenzothiazole

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ABSTRACT

In the current paper the corrosion inhibition synergy between Ce^{3+} loaded NaY-zeolite (NaY-Ce) and 2-Mercaptobenzothiazole (MBT) loaded Zn-Al layered double hydroxide (LDH-MBT) containers is presented. Solutions and water-borne epoxy coatings containing different ratios of the two loaded carriers were prepared and their protection of AA2024-T3 and damaged coatings characterized using global and local electrochemical techniques and other complementary tools. The coatings containing container-combinations showed exceptional corrosion protection over a broad range of NaY-Ce:LDH-MBT weight ratios, with 90:10 being the optimal. The current work landmarks the need for synergetic inhibiting studies devoted to carrier-inhibitor systems in coatings.

1. Introduction

Passive protective coatings are one of the most widespread approaches for corrosion protection of metallic substrates. Their protection mechanism is based on restricting the ingress of water and corrosive species to the metal-coating interface [1]. However, upon damage they fail to fulfil their protective function. In protective coatings, self-healing properties aiming at restoration of their corrosion protective function upon damage can be extrinsically introduced by incorporating corrosion inhibitors into the coating formulation [2–6]. For years, chromate compounds have been the most effective inhibitors for different metallic substrates. Yet, due to their toxicity and environmental regulations, their short and mid-term replacement by more benign inhibitors is necessary.

The quest for environmentally friendly alternatives to Cr(VI) compounds has revealed the beneficial aspects of rare earth metals (REM) such as cerium (Ce) in supressing corrosion of Al alloys [7,8]. Nevertheless, so far no single-species replacement for chromates has been reported, from an equivalent performance perspective. The synergistic effects of inhibitor combinations can offer a promising route to outperform Cr(VI) species [9]. Rare earth organophosphates such as Ce dibutyl phosphate and Ce diphenyl phosphate with corrosion inhibition performances comparable to those of Cr(VI) compounds, are a new class of multifunctional corrosion inhibitors showing synergistic corrosion protection for AA2024-T3 [10–13]. Selective deposition of Ce on Cu-rich intermetallics and formation of an organic film by the organic part of the inhibitor covering the entire surface is proposed as the most feasible mechanism for synergy of these compounds [13].

Despite the advances in the development of multifunctional inhibitors with synergistic properties, their direct implementation into coatings formulation may be associated with inevitable drawbacks such as chemical interactions between inhibitor and matrix followed by coating degradation and loss of inhibitor activity [14]. Entrapment of corrosion inhibitors in inert host structures, referred hereafter as micro- and nano-containers, not only can isolate active agents from coating components but can also control the release of the inhibitors. Zeolite and clay particles have lately attracted considerable interest as host structures for corrosion inhibitors due to their high loading capacity and ion-exchange capability [15,16].

Zeolites are microporous aluminosilicate crystalline particles exhibiting a 3-dimensional (3D) framework which consists of sodalite cages connected through hexagonal prisms. Zeolites possess negative surface charge. This negative charge is compensated by cations loosely bonded to their framework [17,18]. Cationic active species such as Ce^{3+} and La^{3+} ions can be entrapped within the structural cages of zeolite particles via cation exchange process [19–21]. The release process of the entrapped inhibitors in such containers is stimulated by corrosion activities involving pH changes and presence of cationic

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species (M^{n+} and H^+). Selective leaching of the inhibitive ions to the damage site can reinforce the protective oxide layer, guaranteeing the long-term protection for the metallic substrate. Combination of Ce^{3+} and La^{3+} loaded zeolites in the corrosion protective coatings has led to an improved active protection as a result of synergy between the two employed inhibitors [22]. Successive loading of two different inhibitors (Ce^{3+} and diethyldithiocarbamate (DEDTC)) in a single zeolite carrier has also been reported with promising results based on a two steps/two triggers release concept [23]. The organic-inorganic hybrid coatings containing such carriers exhibited a noticeable improvement in active protection of AA2024 compared to the ones loaded with single inhibitor-loaded zeolites.

Layered double hydroxides (LDHs) are a class of anion-exchangeable clay particles consisting of stacks of positively charged 2-dimensional (2D) mixed-metal hydroxide layers. The positive charge of these frameworks is compensated by intercalation of anionic species between the hydroxide layers [24–26]. Inhibitor doped LDH particles can limit the release events to corrosion triggered phenomena such as pH changes or presence of anions released as a result of corrosion processes. Successful entrapment of anionic inhibitors in LDH has been reported in the literature [27–31]. Following the previous work with zeolites [23], both anionic and cationic inhibitors were recently loaded into single LDH showing slight improvements compared to LDHs loaded with either of inhibitors [32]. Although the synergistic effect of anionic inhibitors doped separately in LDH nano-containers has been addressed in a few publications [29], the potential synergy between the cationic inhibitor doped containers and the anionic inhibitors doped ones has not been reported yet.

In the present work, preparation and characterization of extrinsic healing corrosion protective coatings containing combination of cationic and anionic inhibitor doped containers is described. To this aim NaY zeolite and Zn-Al LDH were doped with Ce^{3+} and 2-Mercaptobenzothiazole as cationic and anionic inhibitors, respectively. Due to the different release mechanisms (pH range and anion/cation exchange) of the aforementioned inhibitors from their hosts (LDH or NaY-Zeolite) a synergetic effect can be expected. The morphology and composition of the micro-/nano-containers were studied using a combination of characterization techniques confirming successful loading of the employed inhibitors. Monitoring the inhibitor release profiles of the micro-/nano-containers as a function of NaCl concentration and solution pH provided valuable information on the possible synergistic corrosion protection mechanism. Furthermore, waterborne epoxy extrinsic healing coating containing individual inhibitor doped containers as well as their combination were prepared and evaluated using global and local electrochemical characterization techniques.

2. Experimental

2.1. Materials

Unclad AA2024-T3 was received from AkzoNobel and used as metallic substrate. A waterborne model epoxy-amine coating with fast drying at room temperature was kindly provided by Mankiewicz GmbH. Cerium(III) nitrate hexahydrate (99%, MW = 434.22 $g\ mol^{-1}$), 2-Mercaptobenzothiazole (97%, MW = 167.25 $g\ mol^{-1}$) referred hereafter as MBT were purchased from Sigma-Aldrich and used without further purification as corrosion inhibitors. NaY zeolite (CBV 100, SiO_2/Al_2O_3 molar ratio: 5.1, Na_2O Weight%: 13.0) was purchased from Zeolyst International.

2.2. Nanoparticles synthesis and loading

2.2.1. NaY zeolite inhibitor loading

The single inhibitor doped Y zeolite was prepared via exchange of the available Na^+ cations in the Y zeolite cages with Ce^{3+}. The ion exchange process was carried out in a $Ce(NO_3)_3$ solution containing over 300% excess of Ce^{3+} cations with respect to cation exchange capacity (CEC) of NaY zeolite ensuring maximum exchange of Na cations with Ce^{3+} inhibitors [23]. The exchange process was conducted by addition of NaY zeolite into a 0.3 M $Ce(NO_3)_3$ solution with volume/particle ratio of 20 $ml\ g^{-1}$ at 60 °C. The Ce^{3+} doped NaY zeolites referred hereafter as NaY-Ce, were washed and filtered followed by drying at 60 °C for 24 h, yielding NaY zeolite with 12 ± 0.5 wt.% of Ce^{3+} cations.

2.2.2. Zn-Al LDH inhibitor loading

Inhibitor doped Zn-Al LHDs were prepared by co-precipitation followed by ion-exchange according to procedures described in literature [28]. In the first step, 0.5 M Zn $(NO_3)_2 \times 6H_2O$ and 0.25 M Al $(NO_3)_3 \times 9H_2O$ solution (V = 50 mL) was slowly added to 1.5 M $NaNO_3$ (V = 100 mL, pH 10) under vigorous stirring at room temperature, keeping the pH constant (pH 10 ± 0.5) by addition of 2 M NaOH solution. The resulting material was subjected to hydrothermal treatment (65 °C for 24 h) and consequently centrifuged and washed several times with boiled distilled water. A small fraction of LDHs was dried at 50 °C for characterization, while the remaining portion was used in the ion-exchange reaction [28,29]. The nitrate-containing LDH precursor was dispersed in a solution of 0.1 M NaMBT (pH ≈ 10) under argon atmosphere, yielding LDH nano-containers with 30 ± 5 wt.% of MBT. The total amount of this solution (120 mL) was split into two portions of 60 mL to promote the exchange in two separate steps. Finally, the MBT-loaded LDHs were washed four times with boiled distilled water, frozen, and then dried by lyophilization at −78 °C [28,29].

2.3. Pigment characterization

2.3.1. Morphology

Scanning electron microscopy (SEM): Particle morphology of the employed micro- and nano-containers were characterized using a high resolution JEOL SEM (JSM-7500F) operating at 5 kV. Additionally, the composition of the inhibitor doped and un-doped containers were studied by energy-dispersive X-ray spectroscopy (EDS) using JSM-7500F operating at 15 kV.

Dynamic light scattering (DLS): The particle size distribution of the micro- and nano-containers and their zeta potentials were measured using a Malvern Zetasizer 4 instrument.

X-ray diffraction (XRD): The structure of the inhibitor doped and un-doped LDHs was studied by XRD. The measurements were performed using Philips X'Pert difractometer with Cu K_α radiation source.

2.3.2. Release kinetics

The release profiles of inorganic (Ce^{3+}) and organic (MBT) inhibitors from NaY and LDH containers were monitored by UV–vis spectroscopy using a PerkinElmer Lambda 35 medium performance spectrophotometer in the spectral region of 220–400 nm. Unlike Ce^{3+}, the absorption spectra of MBT show two pH-sensitive peaks within the studied spectral range [33]. Therefore, MBT calibration curves were obtained at two different pH values; the natural pH of the solution and at pH = 10. The calibration was performed at the defined values using absorption peaks of λ = 318 nm and λ = 252 nm for MBT and Ce^{3+}, respectively [33,34].

To study the release kinetics, the inhibitor doped containers were dispersed in an aqueous solution with volume/particle ratio of 400 $mL\ g^{-1}$ under constant stirring. The effect of potential release triggering parameters were studied by systematic variation of NaCl concentration and pH values (NaCl concentrations = 0, 0.05 and 0.5 M, pH values = 2, 4, 6.5 and 10). The suspensions were continuously stirred at 200 rpm. At definite time intervals, 2 mL samples were taken and filtered for analysis.