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Halloysites and mesoporous silica as inhibitor nanocontainers for feedback active powder coatings

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ABSTRACT

We carried out comparative study of the effect of inhibitor-loaded nanocontainers on corrosion protection performance of polyepoxy powder coatings employing neutral salt-spray test (5% NaCl, 35 °C, different time). We demonstrated that halloysites and mesoporous silica particles loaded with corrosion inhibitor 8-hydroxyquinoline can be homogeneously distributed in powder coating effectively reducing corrosion of the metal substrate over 1000 h of salt-spray test. Addition of only 2 wt.% of inhibitor encapsulated in both nanocontainers to the powder coating is sufficient to decrease the delamination effect by 2–3 times and suppress the formation of the pitting corrosion.

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1. Introduction

Self-healing activity of the materials is based on their feedback action. Causes-effect relations between material constituents form a loop where the output responding to the environment input (like local pH-changes during corrosion process) [1]. The input can be also an external signal applied to the material (light or mechanical force). The output is the restoring functionality of the initial material, in our case corrosion protection ability of the coatings. First simple approach for providing feedback healing to the organic coatings is to directly introduce corrosion inhibitors in the pretreatment, primer or topcoat layers of the coatings [2]. The idea behind is the response to the coating damage by diffusive or stimuli-induced release of the inhibitor from the coating matrix. Contrary to the expectations, direct introduction of the inhibitor into coating matrix results, in most cases, in the significant reduction of its corrosion protection performance [3]. Very low solubility of inhibitor leads to its deficit in the damaged area. In the opposite case of too high solubility, metal substrate can be protected for only a relatively short time due to rapid leaching of inhibitor from the coating. Inhibitor freely dispersed inside the active matrix is often subjected to spontaneous leakage [4]. Another drawback, which can appear due to high solubility, is the osmotic pressure initiating blistering and, finally, delamination of the coating [5,6].

Very successful approach to impart feedback functionality to a coating is incorporation into coating matrix the encapsulated inhibitor [5,7]. Capsules or nanocontainers can isolate encapsulated corrosion inhibitor from coating matrix, terminate spontaneous leakage of inhibitor and, at the same time, provide controlled release of the inhibitor directly into the corroded area on demand. In general, containers in the size range of 20 nm to 50 µm require shell which has to be stable, permeable to release/upload inhibitors and possesses other desired functionalities (magnetic, catalytic, conductive, targeting, etc.). There are several approaches demonstrated so far for nanocontainer systems: (i) polymer containers [8], (ii) halloysites [9], (iii) nanocontainers with polyelectrolyte shell [10], (iv) layered double hydroxides [11], (v) ion-exchange organic resins [12], (vi) conductive polymer matrixes [13] and, finally, (vii) mesoporous inorganic materials [14].

The current level of the development of nanocontainer-based self-healing coatings has large number of the highly-efficient examples on the laboratory scale [15,16]. So, this research can be checked for feasibility of commercial application. However, there are two main difficulties to make this transition: the costs of the nanocontainers and the availability of the valid results of the industrial corrosion protection tests (mostly salt-spray tests). The first problem requires the search of the cheap nanocontainer hosts which can be available in large-scale quantities. Halloysites and mesoporous silica particles can be perfect candidates. They are much cheaper comparing to the other types of nanocontainers and commercially available in large quantities [17]. Moreover, the interest in using inorganic nanocontainers is that their mechanical and

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thermal stability allow their utilisation in different coating layers (pre-treatment, primer, topcoat) subjected to high mechanical loads or significant thermal stresses.

Halloysites are defined as two-layered natural aluminosilicates, chemically similar to kaolin, which have a predominantly hollow tubular structure in the submicrometer range [18]. Self-healing properties of the benzotriazole and 8-hydroxyquinoline loaded halloysite nanotubes were studied in zirconia–silica sol–gel coatings deposited on the surface of aluminium alloy A2024 by periodic measurements of SVET (Scanning Vibrating Electrode technique) current density profiles [9]. The maximal anodic current reduced down to the noise level within 4.5 h for benzotriazole-loaded halloysites while the maximal current density did not remain constant at the noise level for 8-hydroxyquinoline-loaded halloysites. To prevent undesirable leakage of the loaded inhibitor from the halloysite interior at neutral pH, the outer surface of the inhibitor-loaded halloysite nanotubes was modified by deposition of alternating polyelectrolyte multilayers (poly(allylamine hydrochloride)/poly(styrene sulfonate)) [19]. Loading benzotriazole, mercaptobenzimidazole and mercaptobenzothiazole into halloysites made them active for protection of copper [20,21]. The release rate of inhibitor was controlled by the formation of metal–benzotriazole stoppers at tube endings. Formation of the pH-controlled metal–inhibitor complex was studied for Cu(II), Fe(II), Fe(III) and Co(II) ions. The best release control was achieved for Cu–complex. Some corrosion was evident within the first fifteen days, but then it was suppressed with the release of inhibitors in the coating defects. Efficiency of the halloysite lumen loading ascended in the order of benzotriazole < mercaptobenzothiazole < mercaptobenzimidazole corrosion inhibitors.

Another type of the nanocontainers with inorganic scaffold is mesoporous particles. The material of these particles has to be inert to the corrosion inhibitors. Therefore, only titania and silica particles can be applied for most inhibitors, and the silica ones have beneficial properties—high specific surface area and inertness to the ultraviolet irradiation, which is important for outdoor coatings. Due to these characteristics, mesoporous silica particles were quickly developed as delivery tool for biomedical applications [22,23]. The incorporation of mesoporous nanocontainers ($\approx 1000 \text{ m}^2/\text{g}$ specific surface area) into inorganic sol–gel coatings improved significantly the coating corrosion resistance [24]. On one hand, the coating barrier properties were enhanced by reinforcement of the coating matrix due to introduction of mechanically stable, robust silica nanoparticles. On the other hand, the large amount of encapsulated inhibitor (up to 80 wt.%) and its controlled release upon corrosion attack provided superior corrosion inhibition. Additional advantage of the silica nanocontainers is the possibility to tailor hydrophobic surface functionality to disperse them in solvent-born coatings. Mesoporous SiO_2 functionalised with octyl groups and loaded with benzotriazole showed ten-fold greater corrosion protection performance in polyester-based

commercial coatings than that coating without nanocontainers [25]. Silica nanocontainers with 80 nm size demonstrated high barrier (Electrochemical Impedance Spectroscopy, EIS) and self-healing (SVET) properties of the coatings while the increase of the nanocontainer size to 700 nm reduced the coating corrosion resistance by the factor of two remaining coating physical properties (thickness and adhesion) comparable to 80 nm nanocontainers [26]. Similar to the halloysite nanotubes, the release of the encapsulated inhibitor can be controlled by metal complexes formed in the pore openings on the silica surface. Cu–benzotriazole complex formed at the openings of silica mesopores can release the encapsulated inhibitor and biocide (benzalkonium chloride) either at pH lower than 5 or in presence of sulphide ions (about 0.6 ppm) providing corrosion protection and antifouling action at the same time [27]. Immobilisation of photoresponsive azobenzene molecular switches into the npores instead of metal ions makes mesoporous silica nanocontainers sensitive to UV light reversibly releasing/up-taking benzotriazole under UV–vis irradiation and thus showing continuous self-healing ability under external stimuli [28].

Despite large number of the papers devoted to the nanocontainer-based self-healing coatings, most of them use lab-scale analytical methods for characterisation of their self-healing performance: EIS, polarisation, SVET and various adapted electrochemical techniques. Only a few papers [29] analysed the efficiency of the nanocontainer-based coatings using industrial methods. Here, we attempt to reduce this “transfer gap” and present comparative analysis, done by industrial neutral salt-spray test (ISO 9227), of the corrosion protection performance of halloysites and mesoporous silica particles as nanocontainers loaded with corrosion inhibitor 8-hydroxyquinoline (8-HQ) and impregnated into polyester powder coating. Coatings with and without nanocontainers were tested on bare low carbon steel substrates.

2. Experimental procedure

2.1. Materials

Corrosion inhibitor 8-hydroxyquinoline, ethanol, acetone, HCl, NaOH and NaCl were purchased from Sigma–Aldrich and used without further purification. Halloysites were provided by Atlas Mining Company (Dragon mine deposit, Utah, USA) and mesoporous silica particles were purchased from Grace, USA (SYLOID® C803 silica). Halloysites are naturally occurring layered kaolin aluminosilicates with hollow tubular structure. The aluminum hydroxide and the silicon oxide layers are bond covalently with each other. The bilayer rolls up to a tube, i.e. a hollow cylinder with alumina layer inside and silica layer outside [30].

Halloysite nanotubes from Dragon Mine deposit have elongated form with average length around $1 \mu\text{m}$ with outer diameter around 50 nm and inner lumen of 15–20 nm diameter (Fig. 1A).

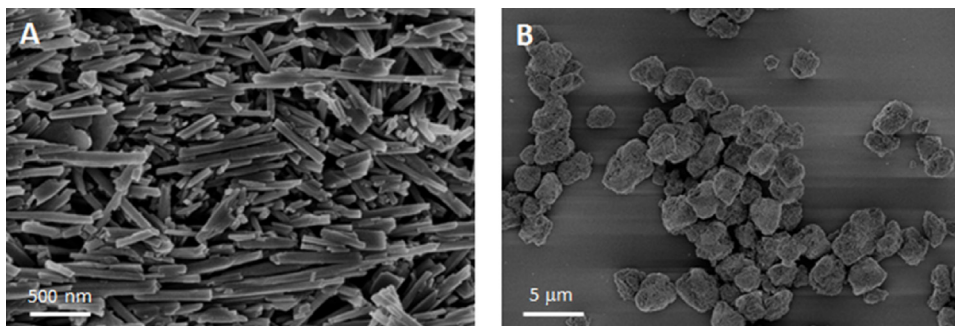


Fig. 1. SEM images of halloysite nanotubes and mesoporous SiO_2 particles used as nanocontainers.

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