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Accelerated self-healing performance of magnetic gradient coating

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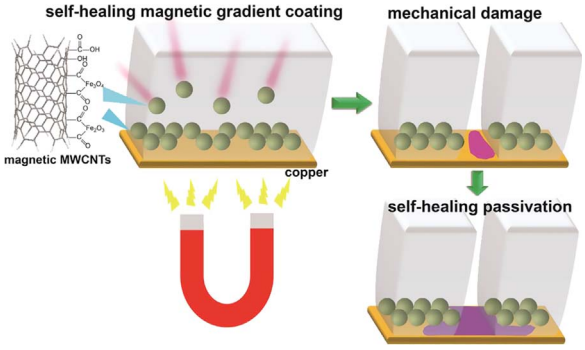
GRAPHICAL ABSTRACT

Self-healing acceleration of scratched self-healing magnetic gradient coating with synthetic magnetic carbon nanotube microcapsules as functional additives.



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ABSTRACT

In this study, we present the novel self-healing magnetic microcapsule preparation of poly(urea-formaldehyde) embedded with benzotriazole (BTA) and magnetic multi-wall carbon nanotubes (MWCNTs) to accelerate the self-healing efficiency of the coating significantly. The BTA played a role of the corrosion inhibitor, while the magnetic MWCNTs served as a target for the formation process of self-healing magnetic gradient (SMG) coating. The magnetic microcapsules could be easily as well as rapidly migrated in the coating solution via an external magnetic field. The SMG coating not only shortened the migration route of the released BTA, but also accelerated quickly the formation of a passivation film, and the corrosion of the copper was hindered, after the coating was damaged mechanically. It was further demonstrated that initial self-healing efficiency of SMG coating was approximately 6.4 times more than that of self-healing coating without magnetism. The present work successfully demonstrated the accelerated self-healing activity of magnetic MWCNTs microcapsules in protecting copper surfaces. The outcomes might help to magnetize the material and guide future design of self-healing coating.

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1. Introduction

Organic coatings were widely used in marine industrial and marine structures for the anti-corrosion applications of the metals including steel, copper, magnesium alloys, and aluminum alloys. The life of organic coatings could be prolonged by modifying the molecular structures of the coating to achieve the self-compacting ability [1–4], and adding some fillers to own their self-protective ability [5–7]. While self-healing materials have recently attracted great attention due to their autonomous recovery ability after unwanted external damage [8–10]. When the coating was broken by mechanical shock, scratch, or impact force, the damaged area of the coating accelerated the metal corrosion. Coating materials were functionalized by self-healing approaches to reform a passive barrier blocking the passage of oxygen and water after mechanical damage. Self-healing coatings in service had the advantages of automatic curing ability and environmental suitability in comparison with a route coating without or with nanoparticles [11,12]. Thus, smart coating needed urgently to prolong the life of the damaged coating.

Classical self-healing coatings, which usually relied on resin hardened involving self-healing functional additives like self-healing microcapsules [13–15], fibers [16], spatially dispersed in the coatings, were a general approach to delay metal corrosion and coating failure. Gap-filling approach and inhibitor passivation approach were mainly two kinds of achievable self-healing applications by functional additives.

Self-healing efficiency of encapsulated gap-filling approach to protect metallic substrates against corrosion relied on the migration of self-healing materials and dynamics process of polymerization reaction. Healing materials coupled with corrosive agents could be trapped under the healed coating film, when a self-healing procedure occurred by filling a gap in a corrosive environment. The trapped agents served as potential corrosion inducers and possibly generated severe pitting corrosion. The development of pitting corrosion produced the lack of good adhesion and led to promoted under-film corrosion, when water reached the metal.

A kind of self-healing approach with encapsulated corrosion inhibitors [17,18] was reported to settle the issue of the under-film corrosion. The encapsulated corrosion inhibitors reacted with metallic surface and formed a passivation layer on the damaged metallic surface, which was not only to hinder the further oxidation of metal, but also to inhibit the corrosion of metal substrate. However, self-healing inhibitors randomly dispersed in this approach. Sometimes, there were not enough self-healing inhibitors to form a deactivation film to inhibit metal corrosion along the micro cracks, when mechanical damage on the self-healing coating occurred. In contrast, an increase quantity of inhibitor microcapsules was a feasible method to improve the self-healing effect.

However, an increase concentration of the microcapsules inevitably caused more micro defects in the coating, which added directly penetration routes of the water. Moreover, self-healing additives were not near enough to the metal substrate, which were easily carried away by the flowing solution.

Inspired by the functionality of the targeted drug delivery [19–21], magnetic materials were proposed to incorporate into self-healing microcapsules, which could be aggregated on the surface of the metal with the help of an external magnetic field. Magnetic targeted delivery of magnetic iron oxide composites was an achievable strategy for magnetic functionalization of the microcapsules. Several types of iron oxides such as magnetite and maghemite [22] were very promising candidates and carried out in the field of magnetic materials including Fe_3O_4 magnetite, α-Fe_2O_3 (hematite, weakly ferromagnetic or antiferromagnetic), γ-Fe_2O_3 (maghemite, ferrimagnetic), FeO (antiferromagnetic), ε-Fe_2O_3 and β-Fe_2O_3. Hence, multi-wall carbon nanotubes (MWCNTs) modified with iron oxides were synthesized to separate and remove inorganic and organic pollutants [23–25].

We report herein for the first time the preparation of magnetic benzotriazole (MBTA) microcapsules and self-healing magnetic gradient (SMG) coating. The self-healing microcapsules of the coating could be assembled on the surface of the metal substrate targeted by ferromagnet. The transmission route of released BTA from MBTA microcapsules was obviously shorter than that of non-magnetic microcapsules, and the released BTA quickly formed a passivation film on the damaged cracks. We also demonstrated that self-healing efficiency of SMG coating was nearly 6.4 times more than that of self-healing coating without magnetism. The synthesis approach was a very facile and versatile procedure for making magnetic self-healing microcapsules and was considered to be low cost and suitable for marine engineering.

2. Experiment procedure

2.1. Materials

Purified MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. Sodium hydroxide, hydrochloric acid, and ethanol were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd, and $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, and castor oil were obtained from Aladdin Co., Ltd. China. Sodium dodecyl benzene sulfonate, urea, 37 wt% formaldehyde solution, benzotriazole (BTA), ammonium chloride, resorcinol, and 1-octanol were obtained from Sigma Aldrich. All chemicals were used as received. Copper was purchased from Shanghai BaoSteel. Epoxy resin and polyamide resin were purchased from Zhenjiang Banbao Resin Co., Ltd (Zhenjiang, China). The water used in all the experiments was produced by a Millipore Milli-Q Plus 185 purification system and had a resistivity level higher than 18.2 MΩ cm.

2.2. Synthesis of magnetic MWCNTs

Fig. 1 showed the flow diagram of the synthetic magnetic MWCNTs and magnetic microencapsulation procedure via in situ polymerization in an O/W emulsion with a self-healing agent (BTA) as a core and the magnetic MWCNTs as a magnetic target.

Oxidized MWCNTs were prepared by oxidization with 3 M HNO_3 [23,26]. Briefly, 2 g of MWCNTs was added into 250 mL 3 M HNO_3, and the mixture was ultrasonically stirred for 24 h, filtrated, rinsed with water until the pH reached about 6, dried in the oven at 80 °C for 8 h, and then calcined at 450 °C for 4 h (step 1).

The magnetic MWCNTs were prepared from a suspension of 1.0 g oxidized MWCNTs in a 150 mL solution of 3.0 g $FeCl_3{\cdot}6H_2O$ and 1.5 g $FeSO_4{\cdot}7H_2O$ at 70 °C under N_2 gas condition. 20 mL 0.5 M NaOH solution was added dropwise to precipitate iron oxides (step 2). After that, the mixture was adjusted to pH 11 and stirred for 1 h. The mixture was kept at 70 °C for 4 h and was washed 3 times with water (step 3). The obtained magnetic MWCNTs were dried in an oven at 80 °C for 3 h.

2.3. Synthesis of MBTA microcapsules

MBTA microcapsules were synthesized via modified in situ polymerization. In brief, 15.00 g of urea, 1.40 g of resorcinol, and 2.00 g of ammonium chloride were successively dissolved in 200 mL of water under 1000 rpm agitation. 20 mL of a 3% (%wt) aqueous solution of sodium dodecylbenzenesulfonate was then added to the mixture at room temperature. Then, 5 g of BTA was dissolved in 20 mL of castor oil as solvent. The BTA solvent was slowly added into the mixture, forming an emulsion of oil and water. Magnetic MWCNTs were ground artificially in the agate mortar for 10 min. Then, they were added into the emulsion (step 4). The resulting emulsion was stirred to homogeneity for 40 min, after which it was slowly adjusted to pH 3.5 by drop-wise addition of 0.01 M hydrochloric acid (step 5). One to two drops of 1-octanol was added to eliminate any resulting surface bubbles, after which 32.00 g of a 37% (%wt) aqueous solution of formaldehyde was added. The mixture was submerged in an ice bath and ultrasonically treated for 30 min at a frequency of 15 kHz (step 6). The temperature