Materials and Design 186 (2020) 108299

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Design alternate epoxy-reduced graphene oxide/epoxy-zinc multilayer coatings for achieving long-term corrosion resistance for Cu☆

Tianhao Ge [a,b], Wenjie Zhao [a,*], Xuedong Wu [a], Yangmin Wu [a], Lu Shen [a], Xiaojing Ci [a,b], Yanlin He [b]

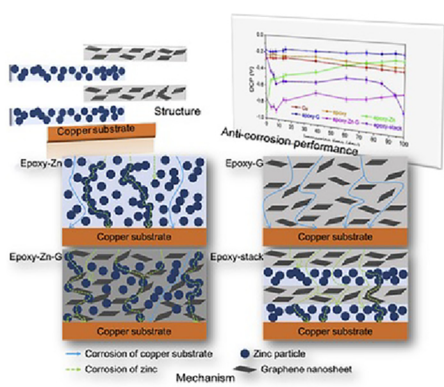
[a] *Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China*

[b] *School of Material Science and Engineering, Shanghai University, Shanghai, 200444, China*

HIGHLIGHTS

- An alternate epoxy-reduced graphene oxide/epoxy-Zinc multilayer coating is designed for enhancing anticorrosion.
- The alternate structure can achieve an analogous sustained release effect of zinc particles.
- The coating with alternate structure achieves longer protection than single structure in 3.5 wt% NaCl solution.
- The coating with alternate structure shows strong adhesion strength in acidic environment for 432 h.

GRAPHICAL ABSTRACT



alt-text: Image 1

ARTICLE INFO

Article history:
Received 25 July 2019
Received in revised form 20 October 2019
Accepted 22 October 2019
Available online 09 November 2019

Keywords:
Graphene
Zinc-rich coating
Alternate structure
Ionic liquid
EIS
Corrosion

ABSTRACT

To make good use of the barrier effect of graphene nanosheets and to reduce the uneven dispersion of zinc particles caused by its sedimentation, coating with alternate structure containing rGO was developed to provide Cu a long-term corrosion protection. Ionic liquid was used to obtain a better dispersion of rGO in solvent, which was proved by TEM, SPM images and sedimentation experiment. The enhanced long-term anti-corrosion protection of alternate coating was revealed by electrochemical tests. OCP and EIS results showed enhanced barrier performance of epoxy-G compared with epoxy and improved sacrificial anode protection of epoxy-Zn-G compared with epoxy-Zn. Tidal range-corrosion simulation test was also performed to show that the alternate coating can stick on copper substrate without peeling off even in harsh corrosive environment for 432 h. Furthermore, EIS, XRD, and XPS spectra together proved that the excellent anti-corrosion property of alternate coating was originated from the combination of sacrificial anode protection provided by zinc-rich-epoxy layer with barrier protection provided by rGO-doping-epoxy layer. This combination makes it reality to protect copper substrate from corrosion for longer time immersion in 3.5 wt% NaCl solution compared with epoxy-Zn-G.

☆ We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

* Corresponding author.
E-mail address: zhaowj@nimte.ac.cn (W. Zhao).

https://doi.org/10.1016/j.matdes.2019.108299

1. Introduction

Cu is one of the first-known and vital-utilized metals. Cu possesses excellent alloying ability, which enables it to form various kinds of copper-alloys with other elements, satisfying the strength, ductility, resistance to softening, and machinability requirements of modern engineering. The electric potential of Cu is more positive compared with reactive metals such as Al and Mg, which makes Cu not tend to erode. However, erosion will occur once under long-term exposure to briny environment. For example, chemical corrosion and galvanic corrosion will attack copper components in seawater environment. In face of such situation, protection measures should be taken seriously.

Painting anti-corrosion coating, as a cheap and effective method, has been taken for a long time to protect metal substrate from corrosion attack. Possessing good mechanical and chemical stability, epoxy resin is the most used matrix for protective coatings [1,2]. However, pure epoxy protective coating can only act as passive barriers against corrosive media with no feedback countermeasures [3,4]. Once exogenous factors infiltrate into the epoxy coating, epoxy coating's barrier capability will be attenuated greatly. Besides, inherent defects would be generated during the consolidation of epoxy resin, which leads to the formation of diffusion paths for corrosive media [5,6]. To make up for the scarcity of epoxy resin, zinc-rich epoxy coatings were put forward. As an effective anti-corrosion coating, zinc-rich epoxy coating has been widely utilized in a series of industrial fields to protect the metal substrate away from corrosive media [7,8]. In the zinc-rich epoxy coatings, zinc particles can provide a sacrificial anode protection after the intrusion of exogenous corrosion media. Moreover, the corrosion products of zinc can form a passivation layer to prevent further corrosion [9,10].

Later on, with increasing study of graphene, graphene-doping epoxy coatings were put forward. Considering the chemical inertness and impermeability of graphene, impregnation of graphene nanosheets as fillers into epoxy resin can extend the propagation path length of the corrosive media in the coating [11–15]. Liu et al. [16] used graphene as an inhibitor in waterborne epoxy coatings and found that comparing to the neat epoxy coating, the composite coatings displayed outstanding barrier properties against H_2O molecule. However, if graphene agglomerates in epoxy resin, it will lose its advantages as an ultrathin two-dimensional nano-filler, such as diameter-to-thickness ratio and labyrinth effect. To solve the dispersion problem, modifiers or dispersers were utilized to chemically equip graphene with specific functional groups to cope with the van der Waals force physically, and many works about graphene's derivatives began to show up. Wang et al. [17] filled reduced graphene oxides with various contents of oxygen-containing functional groups into epoxy matrix and demonstrated that excellent corrosion protection behaviors come from the synergism of modified rGO's barrier effect, impenetrability, and hydrophobicity. In the work of Luo et al. [18], reduced sulfonated graphene containing free amine groups was prepared and uniformly doped in the waterborne polyurethane coating to improve the anticorrosion performance of the coating. Yang et al. [2] functionalized graphene with 3, 4, 9, 10-perylene tetra carboxylic acid (PTCA-G) and reported that the significant improved corrosion resistance of PTCA-G/epoxy coating can be ascribed to the good dispersion and barrier performance of PTCA-G composite in the epoxy coating.

However, in regard to zinc-rich epoxy coating and graphene-doping epoxy coating, there are certain shortages separately. For zinc-rich epoxy coating, a high volume of 92 wt% zinc is required in the final coating to ensure a sufficient electrical contact between zinc and metal substrate to realize cathodic protection [9]. Superabundant of zinc can undermine the flexibility of the coating and reduce its adhesion capability [12,19]. When it comes to graphene-doping-epoxy coating, graphene is cathodic to most metals and can promote corrosion at graphene-metal interfaces, becoming the criminal to accelerate metal oxidation and thus weakening the mechanical properties of metal components [11,20]. To solve the problems existing in coatings mentioned above, doping graphene into zinc-rich-epoxy coating has been evaluated [21–23]. Teng et al. [7] introduced zinc-reduced graphene oxide into zinc-rich coating to promote the reduction of GO and the dispersion of rGO nanosheets, getting an enhanced anti-corrosive coating. Zhou et al. [24] embedded reduced graphene oxide/graphene oxide nanosheets in epoxy zinc rich coating to reinforce its corrosion resistance. Shen et al. [1] reported that modifying zinc-rich epoxy coatings with graphene can effectively cut down the dosage of zinc without deteriorating the performance of the anti-corrosion coating. However, with the existence of zinc particles, the distribution direction of graphene nanosheets is influenced, which means many graphene nanosheets would lay at angles to the base metal in epoxy resin, thus weakening its barrier effect.

Based on discussions above, an idea strikes us that if a new coating structure can be designed to take advantage of current epoxy-based coatings and eliminate their disadvantages at the same time. We put forward an alternate anti-corrosion coating, in which zinc-rich-epoxy layer and rGO-doping-epoxy layer overlay each other in turn. RGO owns higher electroconductivity than that of GO, and it is easier to be modified with ionic liquid than graphene. The copper substrate was firstly coated with a layer of zinc-rich-epoxy coating to make use of its sacrificial anode protection. According to Cheng et al. [9], zinc powder has higher sedimentation rate than rGO, it can sink into the lower part of the epoxy resin. To reduce the uneven dispersion of zinc particles, the zinc-rich-epoxy layer was designed to be separated by an rGO-doping-epoxy layer. On the top of the alternate coating laying an rGO-doping-epoxy layer to make the surface chemically inert. Firstly, This structure equips the whole coating with sacrificial anode protection and more uniform distribution of zinc particles than an entire zinc-rich-epoxy coating as explained above. Secondly, the whole coating owns good barrier capability and avoids the direct contact between rGO and copper compared with an rGO-doping-epoxy coating. Thirdly, the distribution directions of rGO nanosheets are not affected by zinc particles and rGO-doping-epoxy layers can work as excellent barriers to obtain an analogous sustained release effect in contrast to a zinc-rich-rGO-epoxy coating. To equip rGO with better dispersibility, ionic liquid (1-ethyl-3-methylimidazolium dicyanamide) was utilized [25,26]. To appraise the protection capability of the stratified anti-corrosion coating comprehensively, long-term electrochemical tests were performed in commonly-used 3.5 wt% NaCl solution, corrosion processes of the copper substrates protected were evaluated under tidal range-corrosion simulation in acidic 5 wt% NaCl solution, and surface morphologies for different corrosion stages were analysed in commonly-used 3.5 wt% NaCl solution. The electrochemical protection of the coatings for short and long periods as well as their adhesion capability under harsh corrosive environment were also concluded in this work. It is discovered that the coating with alternate structure possesses the longest electrochemical protection capability and excellent adhesion capability under harsh environment, shedding light on the application of coatings with new alternate layered structure in anti-corrosion field.

2. Experimental section

2.1. Materials

Epoxy resin (MU-618) and curing agent (CU-600) were provided by Runtan New Materials Technology of Shanghai Co., Ltd., China. Zinc powder was provided by Sigma-Aldrich LLC. RGO was provided by Morsh Co., Ltd., China. The ionic liquid (1-ethyl-3-methylimidazolium dicyanamide, named EMIM DCA) was purchased from Aladdin Industrial Corporation.

2.2. Preparation of copper substrate

The copper cubes with side length of 1 cm and copper plates with side length of 10 cm were ultrasonicated in ethanol for 30 min to