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Fabrication and characterization of self-assembled graphene oxide/silane coatings for corrosion resistance

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ABSTRACT

Flexible barrier films preventing corrosion are important for many industries ranging from engineering to medical to electronic materials. In order to improve the corrosion resistance ability of GO-based composite films, the Bis[3-(triethoxysilyl)propyl]tetrasulfide (BTESPT)/GO multi-layered films were layer by layer self-assembled on the surface of 2024 aluminum alloy (AA 2024). The results showed that the designed composite films obviously improved the corrosion resistance ability of AA2024 substrate. The composite films, especially for the middle GO layer, effectively hinders the corrosion reaction by reducing the rate of both the cathodic and the anodic reactions. Furthermore, the formation of Si–O–C covalent bonds based on the XPS analysis implies the improved binding force between silane film and the fabricated middle GO layer. After 40 days immersion in 3.5% NaCl solution, the composite films still had better corrosion resistance ability, which implied the fabricated composite films had better resistance to penetration ability for corrosive ions, and the corrosion mechanism was also analyzed for the long-term immersion process based on the EIS results.

1. Introduction

The surface modification of bulk materials plays central roles in modern chemical, biological and material science, and in applied science, engineering and technology [1,2]. Aluminum and its alloys have been widely used in many industries, due to the excellent physical and mechanical properties and a fair corrosion resistance, nevertheless it is susceptible to corrosion. AA2024 is one of Al alloys with excellent combination of low density, high specific strength, good formability, hence it is widely used in automobile and transportation industries, aerospace and marine applications. Such mechanical properties are achieved by the strengthening of the alloy matrix with a number of second-phase particles. Some particles, however, are not desirable from a corrosion prevention perspective. Therefore, it's important to develop a surface modification method to improve corrosion resistance of aluminum and its alloys. The traditional technology with good performance and low cost has been restricted due to the toxicity and carcinogenic nature of Cr^{6+}. As a result, to develop an environmentally friendly pre-treatment method for corrosion protection on stainless steel is urgent. A number of surface pretreatment techniques have been developed, among which silane-based pre-treatment is a promising and effective method [3–6]. Silanes as coupling agent have attracted much attention because of paint adhesion property, good corrosion inhibition and environmental friendly property. However, there are micro-pores and micro-cracks in the silane films, which decrease the corrosion resistance ability. The addition of dopants would be of great significance to remedy the surface defects of silane films. Different dopants have been added to improve the performance of single silane films, such as rare-earth cations [7–9], silica nanoparticles [10,11] and TiO_2 nanoparticles [12,13]. However, the present dopes few focuses on the long-term corrosion resistance ability, and it is difficult to hinder the penetration of Cl^- because of the presence of pores, especially for the long-time immersion experiments.

Recently, graphene has attracted much attention in many applications [14] due to its excellent properties, such as bigger specific surface area and higher chemical stability [15]. Many researchers have demonstrated that graphene coatings can protect metals from corrosion [16–21] because of the bigger physical barrier effect of graphene. Graphene has unique properties principally attributed to its 2D hexagonal lattice structure. This material possesses many distinctive properties including impermeability to gases, chemical (acid/base/salt) resistance, antibacterial potential, thermal stability, eco-friendliness, and most importantly-

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high specific surface area. The flexible surface chemistry of graphene with the abovementioned useful properties, provides a fertile research ground to achieve advanced performance in protective surface-coatings. The most recent studies suggest that graphene could be used as corrosion inhibition due to the unique impermeable 2D structure which simultaneously exhibits an exceptional barrier to reactive gases, liquids, salts and acids. The energy barrier for a single layer coating of graphene is high enough to block the diffusion of oxygen to the underlying metal interface, suggesting that the graphene is the thinnest corrosion barrier material ever known. Chen et al. [18] have reported that graphene films improve the oxidation resistance of Cu and Cu/Ni alloy in air by chemical vapor deposition (CVD). Sahu et al. [19] has developed a composite film containing graphene and polymer by an electrochemical technique on copper substrate. The graphene coating remained intact and showed robust resistance to corrosion with an inhibition efficiency above 94.3%. Kang et al. [20] coated Fe and Cu foils with reduced graphene oxide (rGO) sheets to improve oxidation resistance. The rGO-coated Fe and Cu foils were prepared by transferring rGO multilayers from a SiO_2 substrate onto them. Raman et al. [21] coated copper (Cu) with graphene to increase the resistance to electrochemical degradation.

Based on the above discussions and the larger specific surface area of GO, the GO doped polymer coating should have better corrosion resistance ability due to the good penetration resistance ability. However, some researchers found the corrosion resistance ability of the mixed coating of GO and polymer [19,20] only slightly increase, and almost no attention was paid to the mixed mechanism and the corrosion mechanism for the GO composite coatings. Moreover, it is also difficult to provide long-time corrosion resistance for metal with a single GO layer [22–24], which mainly comes from the formed defects and/or pores in the GO composite films, and the films is not sufficiently dense and easily change into the initiation sites of corrosion.

In this paper, the different composite films were prepared by the pulse electrodeposition method in order to improve mechanical properties and weak bonding intensity [25–29]. The graphene oxide was used as middle layer (Fig. 1) to avoid the disadvantages as a single film and contribute to strengthening the compactness of composite films. The corrosion properties of composite films were evaluated using the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements immersed in 3.5 wt.% NaCl solutions. The durability of the composite films was also investigated.

2. Materials and methods

2.1. Samples and solution preparation

The AA 2024 substrate was cut into coupon with dimensions of 12.5 mm × 12.5 mm × 2 mm. Samples were mechanically ground successively with SiC papers starting from 400 to 2000 grit size followed by final polishing using diamond paste, and cleaned ultrasonically in alkaline rinsing with NaOH solution. The 2 vol.% BTESPT solutions were prepared by adding the silane to a mixture of DI water and ethanol. The ratio of BTSPS/DI water/ethanol was 2/3/95 (v/v/v). The BTESPT solution was stirred for 30 min, the pH of the solutions was adjusted to 4.5 using acetic acid. The obtained solutions were pre-hydrolyzed at 25 °C for 48 h. And the graphene oxide was prepared by the Hummers' method [30].

2.2. Electrodeposition

Pulse electrodeposition was performed using a regular three electrode configuration in which the aluminum substrate served as the cathode and a platinum electrode acted as the anode and saturated calomel electrode was used as the reference electrode. In order to determine the deposition potential of different films, cyclic voltammetry tests were carried out on AA2024 aluminum alloy within different solutions. The BTESPT film was deposited at −0.9 and GO film was 0.4 V/SCE. The mixture BTESPT and GO film was deposited at −0.8 V/SCE. Within the mixture of the BTESPT and GO solution, the ratio of BTESPT/GO was 4/1(v/v), and the mixture was prepared by adding the GO solution into the BTESPT solution dropwise. For the layer by layer film, the deposition time of each layer was 150 s. And all the deposition procession were prepared at room temperature. The deposition was controlled using an electrochemical system (Autolab Pgstat 302N,

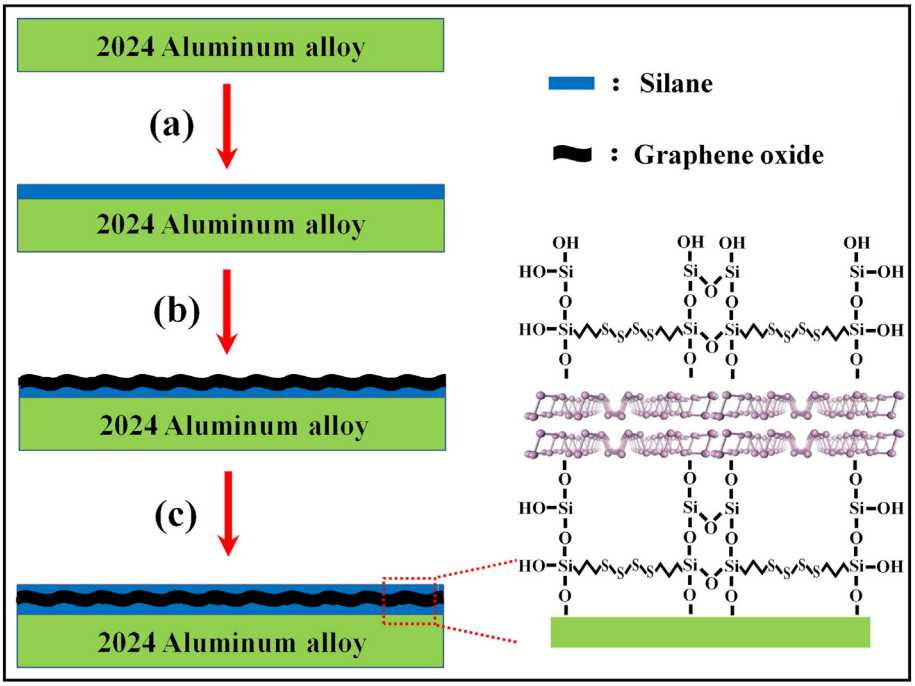

Fig. 1. Schematic diagrams for the preparation process and geometry of BTESPT/GO/BTESPT composite films.