



Chemical modification of hydrotalcite coating for enhanced corrosion resistance



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ABSTRACT

This work provided a facile strategy to enhance the corrosion resistance of hydrotalcite coating by the chemical modification of the coating with 8-hydroxyquinolate anions. It shows that the chemical modification treatment induces the phase conversion of hydrotalcite coating by the intercalation of corrosion inhibitor into the coating. The hydrotalcite coating with unique layer micro/nanostructure not only serves as an effective template for the chemical modification of the coating, but also acts as a reservoir for the enhanced corrosion protection performance by releasing the accommodated corrosion inhibitor, when it suffers from local corrosion attack in aggressive environments.

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1. Introduction

The widespread adoption of light metals and their alloys is required to meet the demand of the sustainable development of the society due to the enhanced energy saving and environmental protection together with further reduced cost of equipment. However, light metals and their alloys are prone to suffer from severe corrosion attack in aggressive environments, which hinders their wide applications in various fields. Many efforts have been made to enhance the corrosion resistance of light metals and alloys. Up to now, various coating methods were adopted to protect metallic materials, including anodic oxidation [1–4], electroplating [5], organic coating [6,7], chemical conversion coating [8–14] and so on. Among these coatings, a new kind coating called self-healing coating has provided potential solutions to this problem. It can provide active corrosion protection which utilizes the corrosion process as a trigger to induce corrosion inhibition [15]. Self-healing coatings have aroused wide interest of researchers and become a research hotspot due to their unique protection function. Therefore, various strategies have been introduced to impart self-healing function to coatings. Andreeva et al. [16–18] initially deposited polyelectrolyte multilayers to protect metal substrate through blocking the corrosion processes according to their pH-buffering ability. Balkus et al. [19] introduced self-healing poly-TiCl₄ multilayers through the site-specific delivery of metal oxide nanoparticles by smart reactive composite fibers. Subsequently, Yabuki and Okumura [20] designed a three-layer coating consisting of a super-

absorbent polymer as the middle layer and vinyl-ester polymer as the base and top layer. When the scratched specimen was monitored in a corrosive solution, the released SAP particles would swell as much as 40 times to fill in the scratched space. Meanwhile, Schaefer and Miszczyk [21] have provided a different strategy to realize self healing ability of the coating by using the cathodic protection function of introduced metal nanoparticles.

Besides, it should be noted that encapsulation and release of corrosion inhibitors is also another effective way to confer the smart self-healing protection function on coatings [22,23]. Inhibitors have been directly incorporated into organic coatings to improve corrosion resistance [24,25]. However, chemical reactions between inhibitors and coating matrix can easily induce the inactivation of inhibitors and decline of coating barrier properties. Therefore, a key point in achievement of self-healing coatings is to develop proper containers or reservoirs for the storage and release of inhibitors [26]. Such reservoirs could be effectively used to not only encapsulate the desired inhibitors in the inner cavity for a long period, but also protect the encapsulated inhibitors from interaction with the coating matrix, preventing their deactivation and oxidation [27]. Consequently, various hollow porous materials have been extensively used as containers for the encapsulation of corrosion inhibitors such as metal oxide [28–33], CaCO₃ [34], cerium molybdate [35,36], hydroxyapatite [37], mesoporous silica [15,38], halloysite nanotubes [39,40], 3D cross-linked network [41–43], micro-pits [44] and organic microcapsules [45]. In addition, layered double hydroxides (LDH) named as hydrotalcite like compounds (HT) or anionic clays are also used as versatile containers for the storage of corrosion inhibitors. Generally, LDH can be expressed by the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]A^{n-}_{x/n}m\text{H}_2\text{O}$,

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where the cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer and the anion A^{n-} is located in the hydrated interlayer galleries [46]. At present, it has been proved that chemical modification of hydrotalcite compounds is an effective strategy to enhance their corrosion protection performance. Mahajanam et al. have shown that the introduction of vanadate or Ce^{4+} into hydrotalcite confers both barrier protection and active protection on the coating [47,48]. Zheludkevich et al. demonstrated that the mechanism by which the inhibiting anions can be released from the LDHs underlines the versatility of these environmentally friendly structures [49–54]. Recently, an environmentally friendly corrosion inhibitor phytic acid was also successfully added to modify the hydrotalcite (HT) film by adsorption and ion exchange approaches. The modified film showed superior stability and lasting protective efficiency, and also provided self-healing corrosion protection property [55]. Besides, Yan et al. extended the concept of self-healing via dissolution/recrystallization of LDH to improve the corrosion resistance of aluminum alloy [56]. Therefore, it is obvious that layered double hydroxides have already displayed apparent advantages over traditional corrosion protection materials, which make LDHs possess versatile potentials in the fabrication of “smart” coating for corrosion protection of metals.

In this work, a facile strategy for direct chemical modification of hydrotalcite is demonstrated to enhance the corrosion protection performance of the coating on Al substrate. The effects of chemical conversion treatment on the structure of LDH were investigated together with its corrosion protection mechanism in 3.5 wt.% NaCl aqueous solution.

2. Experimental

2.1. Preparation of LDH coating

Al sheets (Al: 99.75%, Fe: 0.25%) with dimension of $5 \times 1.5 \times 0.03 \text{ cm}^3$ served as the substrates. The Al sheets were ground by emery paper #600, #800, #1000 successively. The ground Al sheets were cleaned by ultrasonication in acetone for 15 min, and then rinsed with deionized water and finally dried at room temperature. Subsequently, a mixed solution (100 mL) containing 2.56 g $Mg(NO_3)_2 \cdot 6H_2O$ and 4.8 g NH_4NO_3 was prepared, and a diluted ammonia solution (1%) was then slowly added until the pH reached 9 [46]. Then the stable solution was stirred and put into an autoclave (100 ml). The substrates were vertically immersed in the above water solution for hydrothermal reaction at 100 °C for 36 h. Then, the substrates with LDH coating were removed, rinsed with deionized water, and air dried at room temperature.

2.2. Modification of LDH coating

An aqueous solution (100 mL) containing 0.29 g 8-hydroxyquinoline (8HQ) was prepared, and a diluted NaOH aqueous solution was then slowly added until the pH reached 11. Subsequently, the Al substrates with LDH coating were vertically immersed in the sodium 8-hydroxyquinolate (NaHQ) solution for 6 h at room temperature. Then, the substrates were removed, rinsed with deionized water, and air dried at room temperature. Finally, the converted coatings were thermally annealed at the temperature of 100 °C, 200 °C, 300 °C, 400 °C or 500 °C.

2.3. Characterization of sample coating

The microstructures of synthesized sample coatings were characterized by scanning electron microscopy (SEM) using JSM-6360LV (JEOL, Japan) microscope at the voltage of 20 kV. Energy

dispersive X-ray (EDX) microanalysis of the samples was performed using NOVA NanoSEM 450 (FEI, American) during SEM measurements. The crystal structure of the samples was characterized by X-ray diffraction (XRD) on a Rigaku-DMax 2400 diffractometer equipped with the graphite monochromatized Cu $K\alpha$ radiation flux at a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range 5–80°. Then, the coatings were scratched off the substrate and the thermal stability of the scratched powders was estimated by thermogravimetric analysis (TGA) using a Perkin Elmer (Pyris Diamand S II, Perkin Elmer Life and Analytical Sciences Inc., Waltham, MA) analyzer at a heating rate of $10^\circ \text{ C min}^{-1}$ in air. The scratched samples were also characterized by FT-IR spectroscopy, which was performed with an EQUINOX 55 spectrophotometer (Bruker, Germany) over the wavelength range 400–4000 cm^{-1} .

2.4. Electrochemical tests

Electrochemical tests were employed to evaluate the corrosion protection performance of the coating. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were performed on the prepared hydrotalcite coating and that chemically modified with 8-hydroxyquinolate during the period of 12 days immersion in 3.5 wt.% NaCl aqueous solution. All the electrochemical tests were conducted after the open circuit potential being steady at ambient temperature ($25 \pm 2^\circ \text{ C}$) without stirring in a three-electrode system which consists of the tested sample as working electrode, a Pt foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The sample was encapsulated with epoxy resin, leaving an area of 1 cm^2 exposed to 3.5 wt.% NaCl aqueous solution. Potentiodynamic polarization curves were measured at a scanning rate of 1 mV/s in the potential range from -1.1 V to 0.2 V (vs. SCE). EIS measurements were conducted at open circuit potential (the real OCP) on an electrochemical workstation CHI660D (Shanghai Chenhua Device Company, China) in the frequency range of 10^5 – 10^{-2} Hz and the sinusoidal potential perturbation was 5 mV.

3. Results

3.1. Characterization of sample coating

Fig. 1 shows the micrographs and macrographs of the prepared samples. It can be seen that after the chemical modification of hydrotalcite with NaHQ, the color of the modified coating appears to uniformly changes from white to yellow, as shown in Fig. 1a and c. The amplified SEM images in Fig. 1b and d show that the hydrothermally synthesized hydrotalcite coating displays the layer micro/nano structures consisting of vertically cross-linked nanosheets, which is in accordance with Guo's work [57]. After the chemical modification, the modified coating still displays the similar cross-linking layer structure with a high specific area and no apparent change in morphology can be observed as compared to that without chemical modification. Besides, the coating was also characterized by EDX, as shown in Table 1. It can be seen that O, Mg and Al elements were detected in the hydrotalcite and modified coatings, while C and N elements were also detected in the modified coating.

Fig. 2 shows TGA and DTG curves of various samples. It can be seen in Fig. 2a that the weight loss of 8HQ begins at 75 °C and a maximum weight loss peak can be observed at 125 °C. This peak is assigned to the thermal evaporation of 8HQ. As to hydrotalcite coating, there are four weight loss stages appearing at 130, 316, 392 and 480 °C in the DTG curve of the sample. The first weight loss stage below 130 °C is attributed to the release of surface interlayer water. The other weight loss stages in the temperature

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