Progress in Organic Coatings 115 (2018) 94–99

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Preparation and corrosion resistance of hydrophobic zeolitic imidazolate framework (ZIF-90) film @Zn-Al alloy in NaCl solution

Xuejun Zhang[a,b,*], Yang Zhang[a], Yanling Wang[a], Di Gao[a], Huanxin Zhao[a,*]

[a] College of Environment and Safety Engineering, Shenyang University of Chemical Technology, Shenyang 110142, People's Republic of China
[b] The Key Laboratory of the Inorganic Molecule-based Chemistry of Liaoning Province, Shenyang 110142, People's Republic of China

ARTICLE INFO

Keywords:
ZIF-90 film
Protective coatings
Corrosion resistance
Hydrophobic
Electrochemical impedance spectroscopy

ABSTRACT

A zeolite imidazolate framework-90 (ZIF-90) film with corrosion resistance was prepared on the surface of Zn-Al alloy by solvent thermal synthesis method employing a thinking of "twin zinc source". The crystal structure and morphology of the ZIF-90 film was confirmed by X-ray diffraction (XRD) and secondary electron microscopy (SEM), respectively. The properties of the film, adhesion and the hydrophobicity were tested by the method of cross-cut test and water contact angle measurement. The potentiodynamic polarization curves indicates that the existence of the film decreases the corrosion current density of the Zn-Al alloy, and the plots and appropriate equivalent circuit models calculated from the electrochemical impedance microscope (EIS) measurements reveals that the hydrophobic ZIF-90 surface considerably improves the corrosion resistant performance of Zn-Al alloy.

1. Introduction

Considering the benefits of excellent heat resistance, no hydrogen embrittlement, well paint adhesion ability, and the simple preparation technology, Zn-Al alloy is widely used in aerospace, transportation, automotive parts, etc. However, their applications are also hindered due to intergranular corrosion, easy to crack in a damp environment, resulting in lower corrosion resistant. The conventional chromium conversion coating is a powerful method to improve the corrosion resistance of a metal or/and alloy. Unfortunately, chromium conversion coating contains carcinogenic and toxic hexavalent chromium (Cr^{6+}), it is being inhibited by many countries [1]. Thus, environmentally friendly green protective coatings are expected. Nowadays, a substantial number of approaches have been developed to prolong the life of metal materials, such as electroless plating [2], thermal oxidation [3], non-metallic protective coating [4], electroplating [5] and chemical conversion [6].

In the past ten years, metal-organic frameworks (MOFs), composed of metal centers linked by organic ligands, have sprung up as a unique class of porous materials due to their potential in many applications such as gas adsorption and storage, membrane separation, chemical sensors, and drug delivery [7–14]. In particular, zeolitic imidazolate frameworks (ZIFs) based on transition metals and imidazolate linkers, a subclass of MOFs [15,16] have emerged as a novel type of porous materials for the fabrication of thin films. Compared with conventional molecular sieving membranes, ZIFs replace bridging oxides with organic imidazolates, which result in zeolite-like properties such as permanent porosity system, uniform pore size, supernormal thermal and chemical stability [17–24]. More importantly than these distinctive properties, from both simulation [25] and experimental investigation [26], ZIFs materials are accompanied with an inherently hydrophobic framework, exhibiting an ideal hydrophobic property. ZIFs comprised of metal ions and organic imidazole-based ligands can form a complete 2-Dimensional and 3-Dimensional structure, and the topology is rich in π bonds.

Recently, a SOD topology ZIF-90 through a solvothermal reaction of zinc (II) and imidazolate-2-carboxyaldehyde was proposed by Yaghi and co-workers [27], exhibiting similar microporous morphological and topology structure to ZIF-8 [28]. The water contact angle of the ZIF-90 surface is 93.9° in despite of the existence of small hydrophilic aldehyde group [29]. Furthermore, ZIFs have been evaluated for their applicability in the aqueous environment and used to adsorb pollutants [30], showing highly stable in aqueous phase.

However, ZIF-90 materials used as membranes have been fabricated on metal oxides substrate, for example, ZIF-90 films @Al_2O_3 [31]. Considering these features, such as the hydrophobic, stable in aqueous condition, easily prepared on the surface of metal or/and alloy, ZIFs can be feasible to be used as a protective coating of a metal or/and alloy in aqueous phase. Herein, in this study, we proposed to *in situ* synthesize ZIF-90 on the surface of a Zn-Al alloy by means of "twin zinc source"

* Corresponding authors at: College of Environment and Safety Engineering, Shenyang University of Chemical Technology, Shenyang 110142, People's Republic of China.
E-mail addresses: xjzhang_syict@163.com (X. Zhang), zhaohuanxin@syuct.edu.cn (H. Zhao).

https://doi.org/10.1016/j.porgcoat.2017.11.013
Received 6 January 2017; Received in revised form 5 October 2017; Accepted 18 November 2017

Table 1
The composition of the Zn-Al alloy.

Element	Zn	Al	Cd	Fe	Cu	Pb	Si
Content (wt.%)	Bal.	0.3–0.6	0.05–0.12	0.005	0.005	0.006	0.125

technique with the aim to investigate the corrosion resistance capability in a 3.5 wt.% NaCl solution.

2. Experimental

2.1. Preparation of ZIF-90 film on Zn-Al alloy sheet

The composition of Zn-Al alloy is shown in Table 1, denoted as Zn-Al in the following context. Prior to the synthesis, the Zn-Al used as substrate were cut into rectangular sheets with a size of 15 × 12 × 0.25 mm, grinded with 400 and 800 grade emery paper in turn, and then cleaned with acetone and ethanol for 5 min in an ultrasonic bath, respectively.

A "twin metal source" method was employed in the synthesis of ZIF-90 film, with which the metal ions come from the surface of the metal supports may provide homogeneous nucleation sites for the continuous film growth, and participate in the coordination reaction with the organic lagands together with the metal ions in the synthesis solution. Usually, the film manufactured by dual metal source method is more compact, has higher mechanical strength and shows better combination with the supports compared with usual *in situ* synthesis methods [32]. Here, conditions for the growth of ZIF-90 films are mainly according to previous work [23] despite of minor adjustments. The synthesis solution, which contains 1.6 mmol imidazole-2-carboxaldehyde ($C_4H_4N_2O$, Sinopharm Chemical Reagent Co., Ltd., > 99%) as ligand and 0.4 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Sinopharm Chemical Reagent Co., Ltd., > 99%) as zinc source in 8 mL dimethyl formamide, was stirred for about an hour until clear. To get a uniformly coating, the pretreated Zn-Al sheet was vertically hung in the Teflon-lined stainless steel autoclave which was filled with synthesis solution. After 6 h of solvothermal reaction at 60 °C in air-circulating oven, the reactor was cooled down to room temperature in cool water. The preliminary obtained ZIF-90 membrane was washed with ethanol several times, and then dried at 60 °C overnight. Consequently, a white to yellowish layer was formed on the surface of the Zn-Al sheet.

2.2. Characterization and test

In order to characterize the morphology and phase compositions of the film, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were utilized, respectively. SEM micrographs of the bare Zn-Al alloy and as-prepared ZIF-90 films were taken on a JSM-6360LV electron microscope. All samples were sprayed with gold before SEM measurements. XRD patterns of the prepared ZIF-90 films were recorded at room temperature under ambient conditions with Bruker D8 CEVANCE X-ray diffractometer with Cu*Kα* radiation (λ = 1.54059 Å) at 40 kV and 40 mA, with a step of 0.02° in 2θ, scanning from 5° to 50°.

The adhesion between the thin film and the substrate was investigated employing the cross-cut test, and the test was performed using BYK5123 cross-cut tester and Leica M165 stereoscopic microscope.

The hydrophobicity of the as-prepared ZIF-90 film was evaluated by measurement of the water contact angle (CA) using a DSA100.

2.3. Electrochemical measurements

To evaluate the anti-corrosion property of ZIF-90 film, the bare Zn-Al and the ZIF-90 coated sheet were both immersed in 3.5 wt.% NaCl corrosive medium without agitation at room temperature for 30 min. The electrochemical measurements were performed using a Paratat 2273 of America. The potentiodynamic polarization measurements and EIS measurements were implemented using a conventional three electrodes system. The specimens under investigation (bare Zn-Al sheet or ZIF-90 coated Zn-Al sheet) served as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a platinum electrode acted as the counter electrode. The polarization curves were obtained at a scanning rate of 0.1660 mV/s and the potential value ranged from −0.25 V up to 0.35 V. The EIS measurements were performed with frequency decreasing from 100 kHz to 0.001 Hz, and a 10 mV amplitude was applied. All electrochemical measurements were carried out three times to ensure good reproducibility. The results of potentiodynamic polarization and EIS measurement were analyzed by fitting data with CorrView and ZView software.

3. Results and discussion

3.1. Characterization of ZIF-90 film

Through solvothermal reaction, the Zn-Al sheet was completely coated with a white to yellowish ZIF-90 layer. The phase composition of the as-prepared ZIF-90 membranes was identified by XRD. As can be seen in Fig. 1, all characteristic peaks of the as-prepared layer match well with those of the simulated ZIF-90 reported previously [23], besides the Zn-Al signals from the substrate. Moreover, the relative intensities of the diffraction peaks of them are similar, confirming that a pure-phase ZIF-90 layer with high crystallinity is formed on the surface of Zn-Al alloy.

The surface morphologies of bare Zn-Al surface and the ZIF-90 layer are shown in Fig. 2. There are still some scratches on surface of the bare polished substrate (Fig. 2a).While, after the reaction, a continuous, dense and uniform film which is completely coated on the surface of Zn-Al sheet can be observed on the 500 times magnification picture (shown in Fig. 2b). Moreover the morphology of the membrane was observed more in detail at a higher 2000 times magnification, and proven to be defect-free and well intergrown polyhedron crystals.

The adhesion between the thin film and the substrate significantly influences the durability of the thin film. Test of adhesion between the ZIF-90 film and the Zn-Al alloy substrate was performed under dry condition, and the appearance of the crosscut area is shown in Fig. 3. The adhesion of the ZIF-90 film is rated at level 0, for that the edges of the cuts are completely smooth and none of the squares of the lattice is detached, according to the classification of the adhesion given in ISO 2409:2013.

As shown in Fig. 4, the surface of the as-prepared ZIF-90 film shows

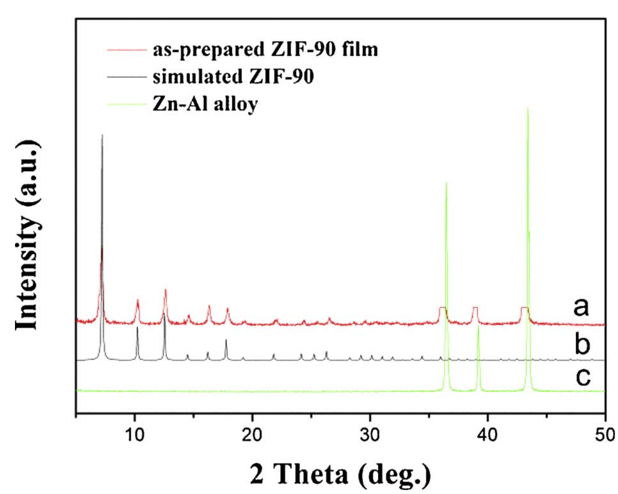

Fig. 1. XRD patterns of (a)simulated ZIF-90 and (b) the prepared ZIF-90 film supported on Zn-Al sheet.