Progress in Organic Coatings 72 (2011) 748–754

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Copper/polypyrrole multilayer coating for 7075 aluminum alloy protection

Başak Doğru Mert[a,*], Ramazan Solmaz[b], Gülfeza Kardaş[a], Birgül Yazıcı[a]

[a] Çukurova University, Science and Letters Faculty, Chemistry Department, Balcali, 01330, Adana, Turkey
[b] Bingöl University, Science and Letters Faculty, Chemistry Department, 12000, Bingöl, Turkey

ARTICLE INFO

Article history:
Received 25 October 2010
Received in revised form 22 June 2011
Accepted 9 August 2011

Keywords:
Polypyrrole
FT-IR
TGA
SEM

ABSTRACT

The corrosion behavior of 7075 aluminum (Al), copper modified Al (Al/Cu), polypyrrole modified Al (Al/PPy) and copper (under layer)/polypyrrole (top layer) modified Al (Al/Cu/PPy) samples were investigated in 3.5% NaCl solution. The copper plating on aluminum was carried out from acidic copper sulphate solution by electroless method. Polypyrrole (PPy) was electrochemically synthesized on Al and Al/Cu electrodes from 0.1 M pyrrole containing 0.4 M oxalic acid solution using cyclic voltammetry technique. The films synthesized were characterized by Fourier transform infrared spectroscopy (FT-IR). The thermal stability of PPy films was investigated by thermogravimetric analysis (TGA). The surface morphologies were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The corrosion behavior of samples was investigated by electrochemical impedance spectroscopy (EIS) and anodic polarization curves. The data obtained showed that the synthesis of PPy on top of the Cu layer significantly enhances the corrosion resistance of Al by exhibiting a barrier effect against the attack of corrosive environment.

1. Introduction

Recently, aluminum and its alloys have taken a prominent place in many industrial applications. In particular, copper containing aluminum alloys (2024, 7075, etc.) are preferred in aerospace industry due to their superior mechanical properties such as light weight, low cost and corrosion resistance [1–5]. The corrosion of aluminum is reduced by the formation of a protective oxide layer. However, this layer corrodes readily in a variety of environments. Particularly, it is very susceptible in the presence of chloride ions. In order to improve the corrosion resistive properties of aluminum and its alloys, various applications have been adopted. A number of reports on the use of organic coatings for reducing the corrosion rate of Al have appeared in the literature, especially, pyrrole and aniline derivatives have been widely studied [6–20], Twite and Bierwagen [21] showed that, PPy and polyaniline (PANI) films exhibit a high protection ability for the corrosion of aluminum alloys. Kamaraj et al. [22] studied the electrochemical synthesis of PANI coating on aluminum 7075 alloy and investigated the corrosion behavior of coating in 1% NaCl solution. According to their experimental results, the PANI film could not protect the aluminum alloy due to galvanic interaction of PANI and aluminum surface exposed through pinholes and cracks. However, they found that the corrosion resistance property of PANI film could be substantially increased by post-treatment in cerium salt solution. It should be noted that, the synthesis of PANI and its derivatives is more difficult than PPy synthesis. PPy is one of the most commonly investigated conducting polymers due to its high stability and the low monomer oxidation potential. PPy film keeps its conductivity in a wide pH range. Furthermore, its thermal stability is very high and its mechanical properties are very good [13]. The adhesion of PPy and PANI coatings on aluminum is very poor and their electrochemical synthesis brings some difficulties due to aluminum oxide layer (Al_2O_3) [1,6–8].

The electrochemical polymerization of conducting polymers on oxidizable metals is preceded by the dissolution of base metals at a potential which is lower than the oxidation potential of monomer. Thus, the oxidation of metals appears as a simultaneous and competitive oxidation process at the potentials adequate for the formation of polymer. Hence, a successful electrochemical polymerization of conducting polymer on oxidizable metals demands a careful choice of solvent and/or supporting electrolyte and establishment of electrochemical parameters, which will strongly passivate the metal without impeding the electrochemical polymerization process [23]. Some papers [24,25] have reported significant results in the synthesis of polypyrrole on the reactive metals such as aluminum, the convenient medium is aqueous solutions such as oxalic acid. Additionally, some pre-treatments can be used before polymerization. These treatments are often used to improve the corrosion resistance of substrate or for purely aesthetic needs such as copper coating. Copper is more conductive than aluminum. Because of that, the polymerization of organic molecules can be easily accomplished on the copper substrate. However, copper is nobler than aluminum and aluminum–copper

---

* Corresponding author. Tel.: +90 322 338 6968; fax: +90 322 338 6070.
E-mail address: bdogru@cu.edu.tr (B.D. Mert).

0300-9440/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2011.08.006

interaction may cause micro-galvanic corrosion. As a result the corrosion products of aluminum (Al_2O_3, $Al(OH)_3$, etc.) may plug the pores of copper coating, which may increase the corrosion resistance of modified aluminum and shift mixed potential to nobler values [20].

The aim of this study was the electrochemical synthesis of an adherent PPy film on Al and copper modified Al/Cu electrodes. The corrosion behavior of the samples (Al, Al/Cu, Al/PPy, Al/Cu/PPy) was investigated by EIS and polarization techniques in 3.5% NaCl solution.

2. Experimental

All the chemicals were purchased from Merck. Pyrrole was freshly distilled before use and stored in the dark. The solutions were prepared with distilled water. The electrochemical measurements were carried out using a CHI 604 electrochemical analyzer under computer control. A conventional three-electrode set up, open to the atmosphere was used. The counter electrode was a platinum sheet (with 2 cm^2 surface area) and an Ag/AgCl was used as the reference electrode. All the potential values given in this paper were referred to this reference electrode. Al was a cylindrical rod with 0.25 cm radius. The surface area of working electrode exposed to test solution was 0.196 cm^2 while the rest of an electrode was isolated with thick polyester block and electrical conductivity was provided by a copper wire. The exposed surface of working electrode was polished using emery paper up to 1200 grade prior to experiments.

The copper plating was carried out chemically using a bath solution whose chemical composition was (wt%) 2.85% $CuSO_4{\cdot}5H_2O$ and 11.10% H_2SO_4. The Al samples were exposed to copper deposition bath over 12 h at room temperature. The thickness of layers was determined using a thickness meter (Exacto FN, 180-0202).

The electrochemical synthesis of PPy on Al and Al/Cu electrodes were achieved by cyclic voltammetry technique from a 0.1 M monomer containing 0.4 M oxalic acid solution. After synthesis, the polymer coated electrodes (Al/PPy; Al/Cu/PPy) were rinsed with distilled water to remove any attached monomer and/or oligomers and dried at 40 °C. The surface of electrodes was examined by SEM and AFM. The SEM images were taken using a Carl Ziess Evo 40 SEM instrument. The AFM images were taken using with Park SYSTEMS instrument. The chemical structure of polymer was analyzed by FT-IR spectrophotometer (PerkinElmer RX 1 FT-IR system, serial number 55148). For this aim, the polymer films were peeled off the electrodes' surfaces mechanically and their pellets were prepared with a bulk KBr. The PPy films were peeled off the electrodes' (Al/PPy and Al/Cu/PPy) surfaces mechanically then, thermal characterization was achieved by TGA. Thermal analyses data were obtained under nitrogen atmosphere using Pyriss Diamond TG/DTA Perkin-Elmer thermal analysis and Pyriss 7.0 data-processing system at a heating rate of 10 °C/min over a temperature range of 20–900 °C. The corrosion behavior of the electrodes was examined in 3.5% NaCl solution by EIS and anodic polarization curves. EIS measurements were recorded at open circuit potential after various exposure times. The frequency ranged from 10^5 Hz to 10^{-3} Hz and the amplitude was 0.007 V. The polarization curves were obtained potentiodynamically starting from open circuit potential (E_{ocp}) to 1.80 V (Ag/AgCl) with the scan rate of 0.004 V s^{-1}.

3. Results and discussion

3.1. Electrochemical synthesis

Fig. 1 shows the cyclic voltammograms of Al electrode recorded in 0.4 M oxalic acid solution in the absence and presence of 0.1 M pyrrole. As it can be seen from Fig. 1a, in the first forward scan, anodic current density increases up to 1.2 V (Ag/AgCl). The current density decreases with increasing cycle numbers as a result of aluminum hydroxides/oxides formation. In the presence of pyrrole (Fig. 1b), the monomer oxidation starts at nearly 0.7 V (Ag/AgCl). The broadened reduction peak observed at the reverse scan was related to the reduction of freshly produced PPy film. The oxidation and reduction current densities became greater after further cycles (Fig. 1b). The average thickness of PPy on aluminum is 18.31 μm, which was determined by the thickness meter.

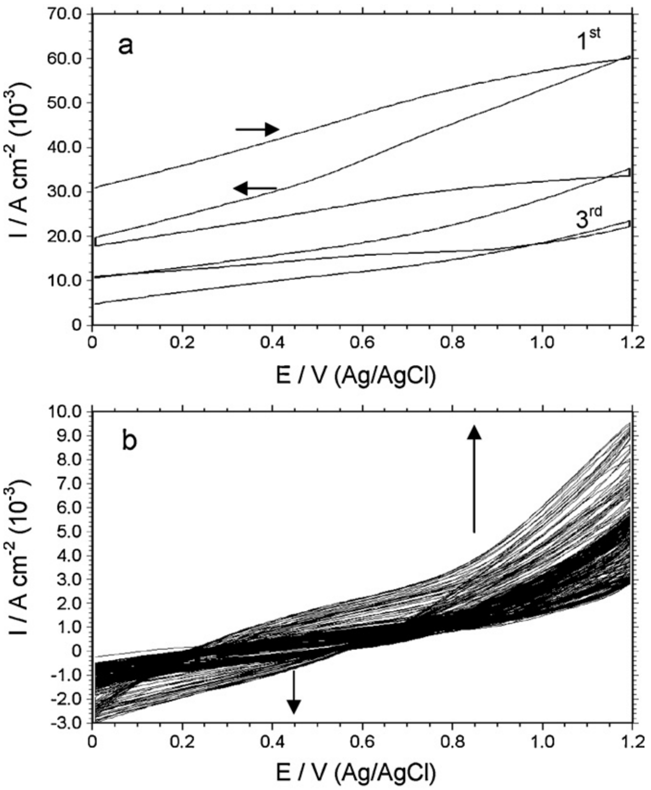

Fig. 1. The cyclic voltammograms recorded for Al electrode in 0.4 M oxalic acid (a) and 0.4 M oxalic acid + 0.1 M pyrrole (b) solutions; scan rate was 50 mV s^{-1}.

The PPy film was also prepared on the copper modified Al sample. The electroless deposition of copper on aluminum substrate was performed in acidic copper sulphate solution. In this condition, Al dissolves to Al^{3+} and Cu^{2+} ions reduced on Al surface according to following reaction:

$$2Al + 3Cu^{2+} \leftrightarrow 2Al^{3+} + 3Cu \qquad (1)$$

The average thickness of copper layer is 26.1 μm.

The cyclic voltammograms recorded for Al/Cu electrode in 0.4 M oxalic acid (a) and 0.4 M oxalic acid + 0.1 M pyrrole (b) solutions are shown in Fig. 2. As it is seen from Fig. 2a, during the first forward scan, the current density starts to increase around 0.1 V (Ag/AgCl) due to Cu dissolution in a monomer free solution [26,27]. This process continues in a wide potential range and the surface is passivated. The passive layer consists of insoluble copper (I, II) oxides [13]. At the reverse scan, the cathodic reduction peak around 0.2 V (Ag/AgCl) corresponds to the reduction of copper (I, II) species (Fig. 2a). In the monomer containing solution (Fig. 2b), the copper dissolution peak appears at the first forward scan, whereas the monomer oxidation peak is seen at 0.7 V (Ag/AgCl). On the other hand, the oxidation current densities increase at the earlier potential with increasing cycle numbers. This result could be associated with the formation of a thin PPy layer that is synthesized in the first