PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 1, 02NFC07(4pp) (2012)

Electropolymerized Coatings of Poly (o-anisidine) and Poly (o-anisidine)-TiO$_2$ Nanocompsite on Aluminum Alloy 3004 by using the Galvanostatic Method and Their Corrosion Protection Performance

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(Received 13 May; published online17 August 2012)

Poly (o-anisidine) (POA) and also poly (o-anisidine)-TiO$_2$ (POA-TiO$_2$) nanocomposite coatings on aluminum alloy 3004 (AA3004) have been investigated by using the galvanostatic method. The electrosynthesized coatings were characterized by FT-IR, SEM- EDX, SEM and AFM. The corrosion protection performances of POA and also POA-TiO$_2$ nanocomposite coatings were investigated in 3.5% NaCl solution by using the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The corrosion rate of nanocomposite coatings was found ~900 times lower than bare AA3004. The results of this study clearly ascertain that the POA-TiO$_2$ nanocomposite has outstanding potential to protect the AA3004 against corrosion.

Keywords: Aluminum, Nanocomposite, Polymer coatings, EIS, Polarization.

PACS numbers: 81.15.Pq, 81.05.Qk

1. INTRODUCTION

Over the years, various protection methods have been developed to prevent the degradation processes of Al and its alloys. Aluminum, a very reactive metal, forms a thin solid protecting film of oxide which prevents the further corrosion of the material [1].

Much research works done on the corrosion inhibition properties of conducting polyaniline coatings have focused on the protection of steel but only a few studies have been devoted to the protection of Al alloy by poly (o-anisidine). O-anisidine is a substituted derivative of aniline with a methoxy (-OCH$_3$) group substituted at the ortho-position. A review presented the use of poly (o-anisidine) for corrosion control, paying to structural alloys for the aerospace industry, such as Al 2024 [2], mild steel [3], platinum [4] and copper [5].

The incorporation of inorganic fillers into conducting polymer matrices by electrochemical polymerization processes have also been studied [6]. Zhu and Iroh [7] electrosynthesized polyaniline in the presence of TiO$_2$, ZrO$_2$ and SiO$_2$ nanoparticles on 2024 Al alloy. The potentiodynamic polarization behavior suggested a beneficial effect of the fillers on the corrosion resistance provided by polyaniline coatings, although no mechanistic information was provided. Lenz et al, electrosynthesized polypyrrole on mild steel in the presence of TiO$_2$ particles [8]. The polypyrrole/TiO$_2$ composite films show improved performance compared to the polypyrrole films that were attributed to the reduced porosity of the polymer through filling by TiO$_2$ particles.

The aqueous electrochemical process is an environmental friendly and efficient technique used to process conducting polymer coatings. It is widely preferred because of its simplicity and it also can be used as a one-step method to form coatings on metal substrates. It allows efficient control of the chemical and physical properties of the coatings, and it can also be easily adapted to large-scale production [9]. In this work, we have electrochemically synthesized strongly adherent POA and POA-TiO$_2$ nanocomposite coatings on Al alloy 3004 by using the direct electrochemical galvanostatic method. Then the coatings were characterized by FT-IR, SEM-EDX, SEM and AFM. The corrosion resistant properties of POA and POA-TiO$_2$ nanocomposite coated samples were then evaluated by polarization and EIS techniques in 3.5% NaCl.

2. MATERIALS AND METHODS

2.1 Materials

Aluminum alloy 3004 was used as the substrate. The metal sheet was cut into rectangular samples of 1 cm^2 area and 0.6 mm thickness soldered with Al-wire for an electrical connection. The metal sheet then mounted onto the epoxy resin to offer only one active flat surface exposed to the corrosive environment.

Navard Aluminum Manufacturing Group (Iran) supplied the AA3004 sheet. P-25 TiO$_2$ nanoparticles purchased from Degussa AG (Germany) that size range of the TiO$_2$ nanoparticles was 25-50 nm, other chemicals were purchased from Merck. O-anisidine was freshly distilled and stored in the dark. Electrochemical experiments and corrosion tests were carried out using an AUTOLAB PGSTAT 30 (Eco Chemie, Utrechtthe Netherlands) potentiostat/ galvanostat connected to a Pentium IV personal computer through a USB electrochemical interface. Pre-treated AA3004 was used as working electrode in the conventional three-electrode cell.

2.1.1 Pretreatment of AA3004

Before each experiment, the working electrode was abraded with a sequence of emery papers of different grades (280, 320, 400, 800, 1000, 1200 and 2000) and substrates were degreased with acetone and then dipped in 5%NaOH solution for 2 min to activate the

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surface. After this stage, the electrodes were cleaned with detergent powder to remove the black colored smudge formed over the surface and were washed thoroughly with running water and dipped in a concentrated HNO_3 solution for 30 s. The electrodes were then washed with distilled water and used for electropolymerization. Before each experiment, the working electrode was abraded with a sequence of emery papers of different grades (280, 320, 400, 800, 1000, 1200 and 2000) and substrates were degreased with acetone and then dipped in 5%NaOH solution for 2 min to activate the surface. After this stage, the electrodes were cleaned with detergent powder to remove the black colored smudge formed over the surface and were washed thoroughly with running water and dipped in a concentrated HNO_3 solution for 30 s. The electrodes were then washed with distilled water and used for electropolymerization.

2.2 Methods

2.2.1 Electropolymerization of POA and POA-TiO_2 Coatings on AA3004

Electropolymerization of POA was carried out by galvanostatic method from 15 mL solution that, are include of the 0.5 M oxalic acid and 0.2 M o-anisidine composition. As a typical procedure for the preparation of POA-TiO_2 nanocomposite coatings with 1 wt% of TiO_2 nanoparticles, a mixture of 0.5 M oxalic acid and 0.2 M o-anisidine monomer, with 1 wt% of dispersed TiO_2 nanoparticles prepared. Subsequently, the obtained solution was ultrasonic for 30 min in order to increase its uniformity.

Electropolymerization of POA and POA-TiO_2 nanocomposite over AA3004 surface were also carried out by keeping a fixed current for certain duration of time. In this regard, three current densities 5, 10 and 15 mA cm^{-2} were attempted and the corresponding potential transients were recorded for a period of 1800 s. Pretreated AA3004 was used as the working electrode in the conventional three-electrode assembly, having a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.2.2 Corrosion tests

The AA3004 samples with electropolymerized POA and POA-TiO_2 nanocomposite coatings were evaluated for their corrosion resistance properties in 3.5% NaCl by Tafel polarization and electrochemical impedance spectroscopy. The working electrode was first immersed in the test solution for 3600 s to establish a steady state open circuit potential (OCP).

3. RESULTS AND DISCUSSION

3.1 Galvanostatic Synthesis

The E-t transient curves were obtained during the formation of POA-TiO_2 nanocomposite coatings on aluminum for three different applied constant current densities 5, 10 and 15 mA cm^{-2} deposition time of 1800 s (Fig. 1). As can be seen in Fig. 1, the polymerization potential value was about 16.5 V versus SCE for all applied current densities. On the other hand, coatings of homogeneous appearance were obtained at various applied current densities. At higher applied current densities, the induction times were shorter. Thus, when the applied current density is higher, the substrate can be covered by the passive layer in a shorter time. This passive layer inhibits the further dissolution of Al^{3+} without affecting the other electrochemical processes. In other words, the electrode surface behaves like an inert metal [10].

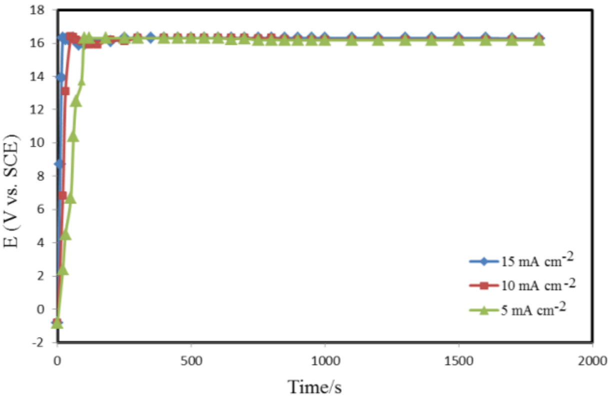

Fig. 1 – E-t curves under galvanostatic polymerization conditions in 0.5 M oxalic acid solution containing 0.2 M o-anisidine and 1 wt% dispersed TiO_2 nanoparticles for AA3004 electrode at various current densities (mA cm^{-2}).

The galvanostatic procedure gave rise to the deposition of green coatings, characteristic of POA in the emeraldine oxidation state, on the surface of AA3004 which was washed with water and ethanol and coating with adhesive remained on the surface.

3.2 Spectroscopic characterization

The typical FT-IR absorption spectra for TiO_2, POA and POA-TiO_2 nanocomposite containing 1 wt% TiO_2 nanoparticles are shown in Fig. 2.

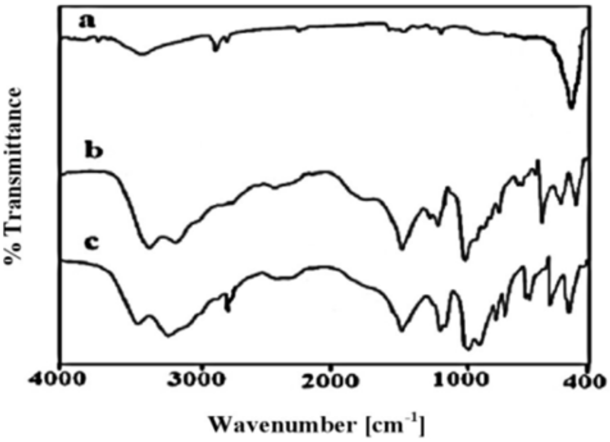

Fig. 2 – FT-IR spectra (a) TiO_2 nanoparticles, (b) POA and (c) the POA-TiO_2 nanocomposite.

The characteristic for POA peaks were observed at 3300, 3100, 1600, 1210, 1130 and 800 cm^{-1}, in agreement with the literature reported [2]. The bands at approximately 1490 and 1570 cm^{-1} are due to the benzenoid and quinoid ring units, respectively. It was found that the POA film formed by galvanostatic conditions contained both benzenoid and quinoid moieties. There are other characteristic peaks at 1210 and 1150 cm^{-1}, due to 1, 2, 4-trisubstituted benzene rings. The broad intense band below 1200 cm^{-1} is due to Ti-O-Ti vibration [11-13], all of which confirm the presence of TiO_2 nanoparticles in the POA-TiO_2 nanocomposite.

3.3 Scanning Electron Microscopy (SEM) and EDX Analysis

SEM micrographs of the surface of uncoated AA3004 and POA-TiO_2 nanocomposite-coated samples at current densities of 15 mA cm^{-2} are shown in Fig. 3. Images show that nanoparticles are uniform, global and slightly agglomerated. Further observation indicates that the morphology of samples is very dense and uniform and may be beneficial to enhancing the corrosion protection due.

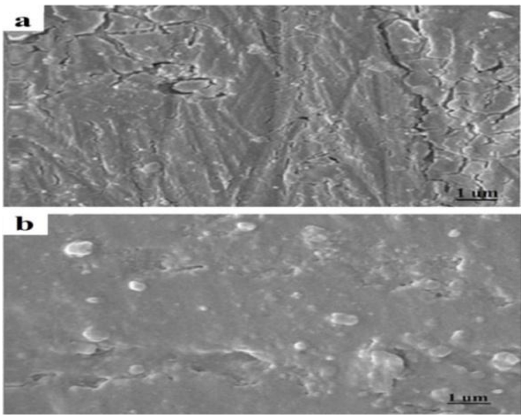

Fig. 3 – SEM images of the (a) abraded AA3004 and (b) electrosynthesized POA-TiO_2 nanocomposite coated AA3004 for 15 mA cm^{-2}.

The EDX data of POA-TiO_2 nanocomposite containing 1 wt% TiO_2 sample is shown in Fig. 4. Nano-TiO_2 shows a peak around 4.7keV and are intense peak appears at 1.5, 1.8keV is related to Ti-O. Aluminum exist in the surface shows a peak toward 2.5keV [14]. These results confirm that Ti-O exists in the nanocomposite structure on aluminum alloy surface.

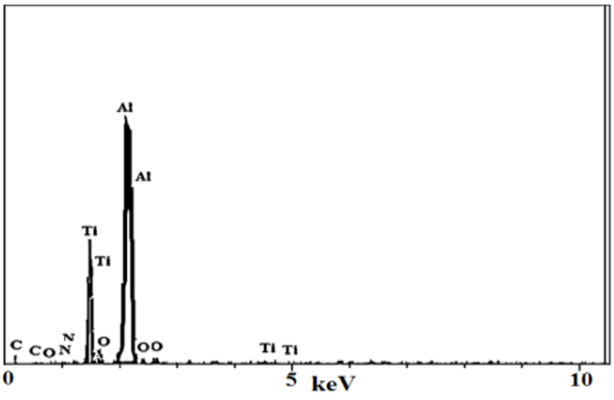

Fig. 4 – EDX pattern of the electrosynthesized POA-TiO_2 nanocomposite coated AA3004 for 15 mA cm^{-2}.

3.4 Corrosion Protection Evaluation of the Coatings

The corrosion protection performance of POA-TiO_2 nanocomposite and POA coatings synthesized under galvanostatic conditions were examined in an aqueous 3.5 wt% NaCl solution using potentiodynamic polarization and EIS studies.

The typical potentiodynamic polarization curves for uncoated AA3004, POA-TiO_2 nanocomposite coated AA3004 in an aqueous 3.5% NaCl, are shown in Fig. 5. As shown in the curves, the corrosion potential for POA-TiO_2 nanocomposite coated AA3004 has shifted to more positive potentials, about 138 mV vs. SCE higher than the uncoated AA3004 (anodic protection). The electrochemical protection is caused by the increase of the corrosion potential and the formation of a protective passive layer on Al surface due to redox catalytic properties.

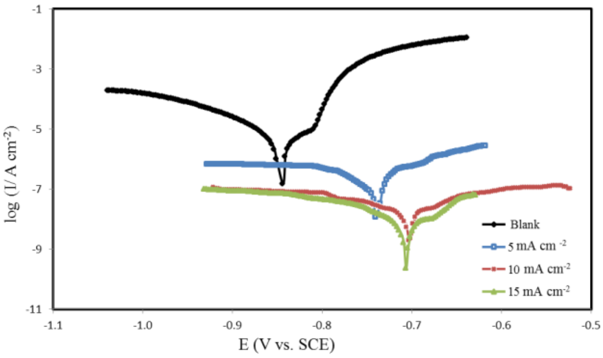

Fig. 5 – Polarization behavior of electropolymerzied POA-TiO2nanocomposite- coated on AA3004 at various current densities (mA cm^{-2}) in 3.5% NaCl.

From the results it can be found that the corrosion rate of Al is significantly reduced as a result of the reduction in corrosion current. The corrosion rate of the POA-TiO_2 nanocomposite coated AA3004 is found to be 9.3×10^{-5} mm year^{-1} and for pure POA is 4.7×10^{-4} mm year^{-1}, which is~ 900 and ~ 180 times lower than those observed for uncoated AA3004, respectively.

It can be seen that the corrosion current of POA-TiO_2 nanocomposite-coated was lower than and protection efficiency is upper than for POA coated AA3004. Therefore, it was found that the incorporation of TiO_2 nanoparticles in the POA matrix promotes the anticorrosive efficiency of the POA-TiO_2 nanocomposite coating on AA3004. However enhanced corrosion protection by the POA-TiO_2 nanocomposite over the protection by POA might result from the nanolayers of TiO_2 dispersed in the POA matrix as filler that increase of the diffusion pathway corrosive agents such as oxygen gas, hydrogen and chloride ions [11, 15].

In this study, electrochemical impedance spectroscopy was also used to evaluate the corrosion activity variation for AA3004 coated with the POA and POA-TiO_2 nanocomposite.

The Nyquist impedance plots of uncoated AA3004, POA-TiO_2 nanocomposite and POA coated AA3004 recorded in an aqueous 3.5% NaCl solution are shown in Fig. 6.

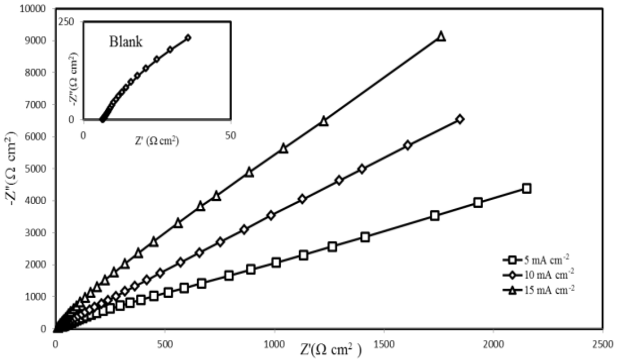

Fig. 6 – Nyquist impedance plots for uncoated AA3004 and POA-TiO_2 nanocomposite coated AA3004 in aqueous solution of 3.5% NaCl.

The charge transfer resistance (R_{ct}) values are approximately 41.1 and 71.2 kΩ cm² for POA and POA-TiO_2 nanocomposite coated AA3004 which are about 12.4 and 21.5 times higher than uncoated AA3004 respectively. The higher value of R_{ct} is attributed to the effective barrier behavior of the POA-TiO_2 nanocomposite coating. It can be found that the incorporation of TiO_2 nanoparticles into the POA matrix exhibited better charge transfer resistances than for POA coated AA3004 electrodes.

3.5 AFM Characterization

AFM is a powerful technique to investigative the surface morphology at nano- to micro-scale and has become a new choice to study the influence of coatings on the generation and the progress of the corrosion at the metal/solution interface. The typical AFM images of abraded AA3004 (image a), pre-treated AA3004 after corrosion (image b),POA coatings after corrosion (image c) and POA-TiO_2 nanocomposite coatings grown by an applied current density of 15 mA cm^{-2} after corrosion (image d) are shown in Fig. 7. A comparison of image d shows that the POA-TiO_2 nanocomposite coating protects the AA3004, which does not change dramatically.

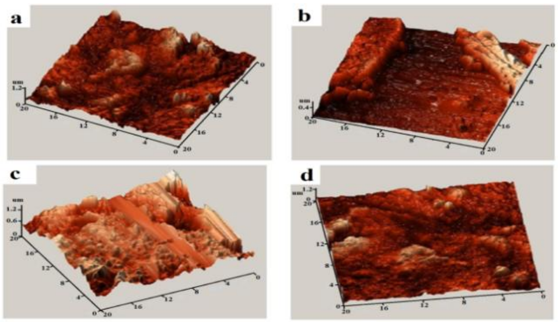

Fig. 7 – AFM of abraded AA3004 (image a) pre-treated AA3004 after corrosion (image b), POA coating after corrosion (image c) and POA-TiO_2 nanocomposite coatings grown by an applied current density of 15 mA cm^{-2} after corrosion (image d).

4. CONCLUSIONS

The direct electrochemical synthesis of POA and POA-TiO_2 nanocomposite coating in an aqueous solution containing oxalic acid and o-anisidine monomers with dispersed TiO_2 nanoparticles for nanocomposite on AA3004 have been demonstrated. Uniform electrodeposition, compact and strongly adherent coatings can be obtained under galvanostatic condition. This study reveals that the POA-TiO_2 nanocomposite coating has excellent corrosion protection properties and can be considered a potential coating material to protect AA3004 against corrosion in aqueous 3.5% NaCl. The enhanced corrosion protection effect of the POA-TiO_2 nanocomposite relative to POA in the form of coating on metallic surface was attributed to the combination of the redox catalytic property of POA and the barrier effect of the TiO_2 nanoparticles dispersing in the composite.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of the work by the University of Kashan Research Council.

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