CORROSION PROTECTION ABILITY OF POLY-3-AMINO-1,2,4-TRIAZOLE /TIO_2 COMPOSITE ON ALUMINIUM IN 3.5% NACL MEDIUM

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Abstract

In this study, we report here the electrochemical synthesis of poly-3-amino-1,2,4-triazole/TiO_2 (p-ATA/TiO_2) composite on aluminum by cyclic voltammetry technique. The polymer composite was characterized by FT-IR and compared with bare TiO_2. Further, XRD studies suggested the crystalline behaviour of TiO_2 in the polymeric composite. Corrosion protection efficiency of bare and polymer composite coated aluminium electrode was studied by EIS and potentiodynamic polarization measurements. The surface morphology was examined by SEM images. The results of the study revealed the corrosion protection efficiency of polymer composite, which could be due to the synergism between organic polymer and inorganic oxides. Further the physical barrier property of the composite could be attributed to the TiO_2 particles dispersed in the polymer.

Keywords: *3-amino-1,2,4-triazole; coatings; TiO_2; copper; corrosion protection.*

Introduction

Aluminium and its alloys are commercially important and widely used in the fields of aerospace, automobile, electronic products and construction industry in view of their properties such as easy modeling, low density, high ductility and high mechanical intensity [1-3]. However, they are easily prone to corrosion under severe conditions. Research is focused on various ways to improve the corrosion protection property of Aluminium and its alloys.. Among the various methods, organic coatings applied to metal surfaces have gained much attention. Coatings offer corrosion protection by introducing a barrier to water and oxygen permeability, ionic transport and electrical conduction. Traditional surface conversion methods such as chromating are being replaced by eco-friendly coatings [4,5]. Now a days, attention has been focused on polymer coatings to provide excellent corrosion resistance properties. W. Qafsaoui et. al., has reported the electropolymerization of 3-amino-1,2,4-triazole on aluminum alloy and its inhibitive effect in sulphate solution containing chloride ions. Incorporation of inorganic fillers into conducting polymer matrices provide enhanced corrosion resistance properties. This could be due to the presence of inorganic fillers reduces the porosity of polymer [6]. The objective of the present work is to report the protective effect of poly-3-amino-1,2,4-triazole (p-ATA/TiO_2) composite on aluminium in 3.5% NaCl medium.

Experimental Details

Materials

Cylindrical (1 cm^2) aluminium rods embedded with an epoxy resin was used as working electrode. Before each experiment, the electrode surface was abraded with emery paper with various grades (#1 to #7) and then ultrasonically cleaned in 1:1 acetone, ethanol mixture. Cyclic voltammetry studies and electrochemical experiments were carried out with conventional three electrode cell-assembly. Platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. All potentials referred to this paper are with respect to SCE. Corrosion test solutions were prepared using deionized water.

Electrosynthesis of Composite Coating

Composite coating was electrochemically synthesized from the mixture containing 0.1 M 3-amino-1,2,4-triazole (ATA), 0.5 M NaOH and 0.001 M TiO_2 in suspension. The bath composition was sonicated in ultrasonic bath for 30 mts to disperse the TiO_2 in the electrolyte medium. Then it was continuously cycling the potential between – 0.7 to 1.7 V vs SCE at a scan rate of 50 mV/s. Fifteen cycles have been carried out on electrode surface and then the modified working electrode was taken out of the bath, dried and used for further studies.

Characterization of Polymer Composite

FT-IR spectrum was recorded for polymer composite and TiO_2 using KBr pellets with JASCO FT-IR 460 plus instrument. The XRD pattern was recorded with an analytical X-ray diffractometer (Model X'Pert, PRO) with monochromatic Cu, Kα radiation (30 kV and 20 mA). The surface morphology of the electrode was examined by SEM micrographs using VEGA3 TESCAN model.

Corrosion Test

The corrosion protection efficiency of polymer composite was evaluated by EIS and polarization measurements. Impedance measurements were recorded using CHI 760d electrochemical analyzer. The impedance spectra were obtained with the frequency range of 100 kHz–0.1 Hz, with a signal amplitude of 5 mV at open circuit potential (OCP). The bare and polymer composite coated aluminium electrode was immersed in test solution at the free corrosion potential to attain steady state. Potentiodynamic polarization curves were obtained in the potential range of ± 300 mV vs OCP at a scan rate of 5 mV/s.

Results and Discussion

Cyclic Voltammetry Studies

Cyclic voltammogram recorded for p-ATA/TiO_2 composite is shown in Fig. 1. During forward scan, the anodic current started to increase continuously around 0.2 V vs SCE. On increasing the number of cycles, the current density values decreased. This could be due to the formation of thicker films on aluminium surface.

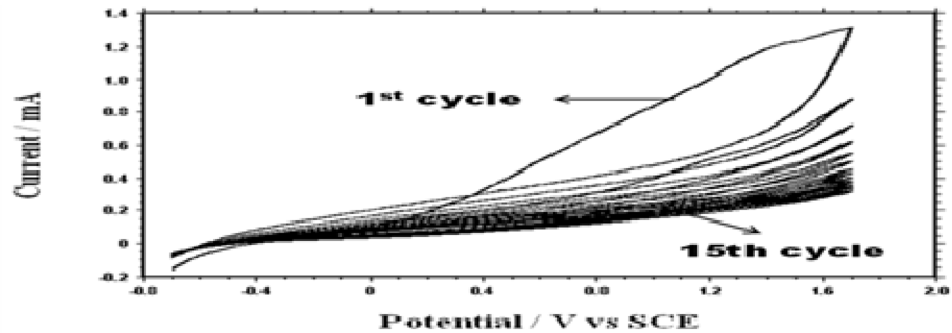


Fig.1 Cyclic voltammogram of p-ATA/TiO_2 composite on Al

FT-IR Analysis

Fig. 2 represents the FT-IR spectrum of bare TiO_2 and p-ATA/TiO_2 composite. In Fig. 2(a), the bands at 3424 and 1634 cm^{-1} were due to the presence of OH groups on the TiO_2 surface [7]. The Ti-O stretching frequency appeared at 670 cm^{-1} as a broad band. This band sharpened in the polymer composite due to the interaction of TiO_2 with polymer (Fig. 2(b)). In the polymer composite, N-H stretching frequency appeared at 3451 cm^{-1}. A band at 1634 And 1117 cm^{-1}

corresponds to NH_2 bending and C-N stretching vibrations respectively. Thus the results of IR not only revealed the polymerisation of ATA but also revealed the impregnation of TiO_2 in to the polymeric matrix.

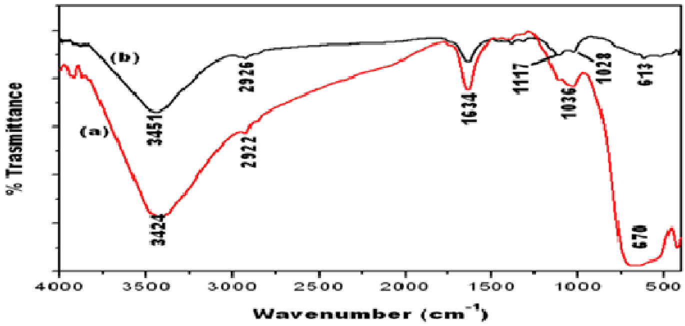


Fig.2 FT-IR spectrum of (a) TiO2; (b) p-ATA/TiO2 composite

XRD Studies

The XRD pattern of p-ATA/TiO_2 composite is shown in Fig. 3. The 2θ values at 39, 65 and 79° confirmed to the presence of titanium in the polymeric composite.

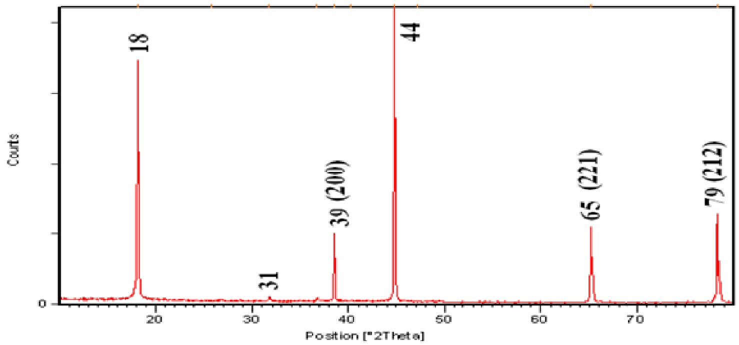


Fig.3 XRD pattern of p-ATA/TiO_2 composite

Electrochemical Impedance Spectroscopy

The Nyquist plots for bare and polymer composite coated Al electrode is shown in Fig.4. The calculated impedance and polarization values are shown in Table 1. From the Fig, it is clearly seen that the R_{ct} value of the polymer composite is higher than that of bare Al electrode. Since R_{ct} corresponds to corrosion resistance property, higher R_{ct} value suggested the good corrosion protection efficiency. The presence of well dispersed TiO_2 particles enhances the oxygen barrier properties [8].

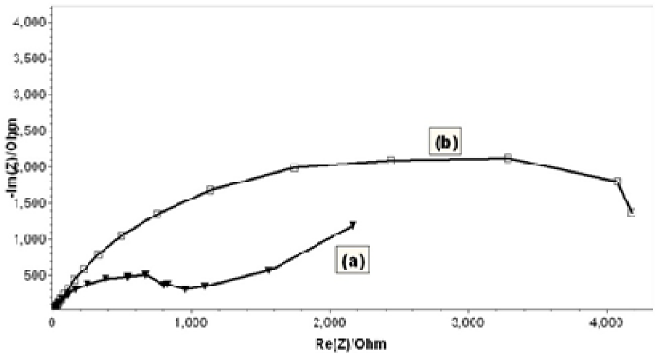


Fig. 4 Impedance diagram for (a) bare and (b) polymer composite coated Al

Potentiodynamic Polarization Measurements

Fig. 5 represents the potentiodynamic polarization curves for bare and polymer composite coated aluminium electrode in 3.5% NaCl medium. The i_{corr} value decreased to 5.5 μA/cm² for polymer composite coated Al electrode. It suggests the prevention of electron transfer from solution to electrode surface and thus protects the Al metal from corrosion. E_{corr} value also shifted to nobler side. From these results, we can confirm the corrosion protection efficiency of p-ATA/TiO_2 composite on Al electrode

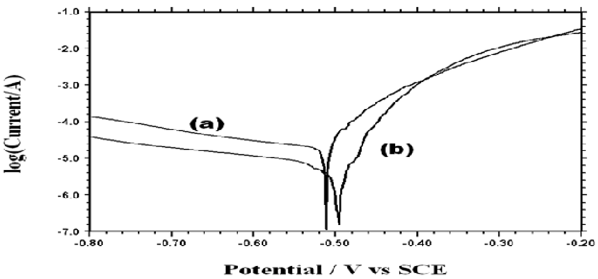
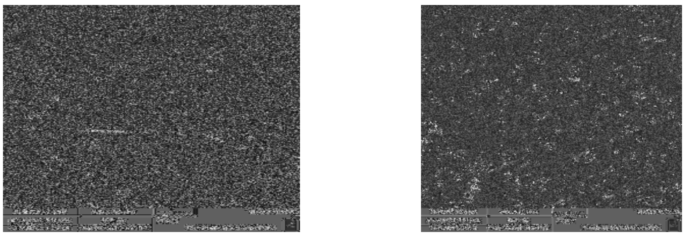


Fig.5 Polarization curves for (a) bare and (b) polymer composite Coated Al SEM images

SEM micrographs of bare and polymer composite coated aluminium electrode are shown in Fig. 6. Several cracks and pits are seen in Fig.6 (a). The distribution of TiO_2 particles in the polymer composite is evidenced from Fig.6 (b).



(a) **(b)**

Fig.6 SEM micrographs of (a) bare and (b) p-ATA/TiO_2 Composite on Al electrod

Table 1 Impedance and Polarization Values for Bare and Polymer Composite Coated Al Electrode in 3.5% NaCl

Electrode	R_s (Ω cm²)	R_{ct} (Ω cm²)	Q_{dl} (Ss^n/ cm²)	Q_n	– E_{corr} (mV vs SCE)	i_{corr} (μA/cm²)	IE (%)
Bare	2.8	1276	1.6 x10^{-4}	0.6	512	46.6	–
p-ATA/TiO_2 composite	5.2	5709	1.7x10^{-5}	0.8	495	5.5	87

Conclusions

The study reveals the corrosion protection efficiency of p-ATA/TiO_2 composite on aluminium electrode. Polymer composite was duly characterized by FT-IR and XRD studies. EIS and Tafel polarization measurements assess the corrosion protection efficiency of polymer composite. The results of study revealed the higher protection of p-ATA/TiO_2 composite. The reason could be due to the presence of TiO_2 in the polymeric matrix which enhances the oxygen barrier property and also due to the synergism between organic polymer and inorganic particles.

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