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Self-cleaning performance of superhydrophobic hybrid nanocomposite coatings on Al with excellent corrosion resistance

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ABSTRACT

Protective ceramic-PANI, ceramic-poly(Ani-co-oPD) and ceramic-poly(Ani-co-oPD)-zinc stearate nanocomposite coatings were formed on Al surface by the processes involving anodization, electropolymerisation and electrodeposition under optimum conditions. The prepared nanocomposite coatings were evaluated by ATR-IR and XRD studies. SEM studies performed on nanocomposite coatings reveal that ceramic-poly(Ani-co-oPD)-zinc stearate nanocomposite coating shows a cauliflower-like cluster with crack-free morphology compared to ceramic-PANI and ceramic-poly(Ani-co-oPD) nanocomposite coatings. The mechanical properties of different nanocomposite coatings were measured using Vicker microhardness tester and Taber Abrasion tester. The ceramic-poly(Ani-co-oPD)-zinc stearate nanocomposite has higher mechanical stability. The corrosion resistance of the coatings measured by Tafel polarization and electrochemical impedance spectroscopy, shows that ceramic-poly(Ani-co-oPD)-zinc stearate nanocomposite coated aluminum has higher corrosion resistance than other coatings and bare Al. Wettability studies prove that superhydrophobic nature of ceramic-poly(Ani-co-oPD)-zinc stearate nanocomposite coating with contact angle of 155.8° is responsible for good self-cleaning property and excellent corrosion resistance of aluminum.

1. Introduction

Aluminum represents an important category of material because of its high technological value and wide range of industrial applications, especially in aerospace and household industries [1]. However, the application and development of aluminum alloys are limited due to their poor corrosion resistance. Aluminum alloy easily corroded by Cl^- in neutral aqueous solutions [2]. So far, many different methods have been developed to improve the corrosion resistance of aluminum (Al), one of most talented strategies is by applying anticorrosive coatings on Al surface [3,4].

Ceramic coating is a capable to combine advantages of the metal substrate and the ceramic materials, which can simultaneously meet mechanical properties and environmental service demands. So, many researchers have tried to improve the performance of the Al alloys by producing nanoceramic coatings on the aluminum surface such as SiO_2, TiO_2 and ZrO_2 [5,6]. Potassium titanium oxalate (PTO) are used is to prepare Al_2O_3–TiO_2 coatings which can retain the beneficial features of both TiO_2 and Al_2O_3. The addition of titania improves the toughness of alumina. During the process more amount of titanium ions incorporated into alumina coating leads to the formation of ceramic Al_2O_3–TiO_2 coating and hence the dense compact ceramic coating is formed [7].

Recently, conducting polymers such as polyaniline, polypyrrole and o-phenylenediamine (oPD) have been explored as novel protective coating materials [8,9]. Polyaniline (PANI) represents one of the most promising candidates owing to the ease of preparation and environmental stability [10,11]. Kamaraj et al. [12,13] have shown that the PANI films alone do not satisfactorily protect the surface against corrosion. Among the derivatives of PANI, poly (o-phenylenediamine), a highly aromatic polymer containing 2,3-diamino phenazine or quinoraline repeating unit has received significant attention [14,15]. The copolymers have properties such as enhanced thermal stability, chemical stability and good barrier properties etc. [16]. Zinc and zinc dust coatings have also been applied for the protection of metals against corrosion [17,18].

Nowadays the formation of self-assembled monolayers of water-repelling molecules is an alternative for corrosion prevention. It can serve as an effective barrier to keep water, atmospheric moisture, and oxygen from reaching the metal surface. Long-chain aliphatic acid linked to metal and metal oxide/hydroxide surfaces have been exploited as corrosion-resistant coatings [19–21]. This surface modification exhibited a composite surface-air-water contacting interface with excellent water repulsion behavior [22–24]. Because of the natural wettability and hydrophilic nature

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of Al surface, fabricating stable superhydrophobic film on Al alloy surface will improve corrosion resistance. For obtaining superhydrophobic property, the surface must be rough in nature [25–27]. The wet smooth surface is modified into rough surface by coating materials with low surface free energy.

Accordingly the corrosion behavior of Al modified with PANI nanocomposite, poly(Ani-co-oPD) nanocomposite, poly(Ani-co-oPD)-zinc stearate superhydrophobic coatings have been comparatively evaluated in this study. The superhydrophobic nature of poly(Ani-co-oPD)-zinc stearate nanocomposite primarily inhibits the corrosion of Aluminum. Our work may shed light on the eco-friendly and cost-effective method for fabrication of super hydrophobic surface which is not only applicable for aluminum but can also be extended to other metals.

2. Experimental

2.1. Materials

Commercially available Al foil (99% pure), Aniline, nitric acid, o-phenylene diamine, sodium hydroxide, sulphuric acid, phosphoric acid, potassium titanium oxalate (PTO), Stearic acid, zinc nitrate were purchased from Aldrich chemicals (Aldrich, India). All the chemicals were of analytical grade and used as such without further purification. All the electrolytes and reagents were prepared using double distilled water and used without further purification. During the formation of PANI coating on Al, the concentrations of sulphuric acid (0.5 M) and PTO (0.01 M) were maintained as constant. But the concentration of aniline monomer was varied between 0.1 M and 0.3 M. The simultaneous anodisation and electropolymerisation was carried out at Room Temperature (29 ± 1 °C) for 30 min at 21 V.

2.2. Fabrication of poly(Ani-co-oPD)-alumina ceramic coating

The pretreatment of Al foil was carried out as reported earlier [6]. The pretreated Al specimen was subjected to simultaneous anodization/polymerization process. Copolymerization was carried out in the bath containing 0.5 M H_2SO_4 and 0.01 M PTO with 0.2 M aniline and various concentration of oPD with and without addition of oPD (0.05–1.5 M) was used for electrosynthesis of PANI and poly(Ani-co-oPD) incorporated alumina-titania ceramic coating. Anodisation/Polymerization was carried out at 28 °C, 21 V for 30 min using a two-electrode configuration connected to a DC power supply with Al foil as anode having the working area of about 1 cm^2 and graphite sheet as cathode in a thermostatically controlled set up [7]. After polymerization, the specimen was washed with distilled water and dried.

2.3. Fabrication of zinc stearate superhydrophobic coating

The optimized poly(Ani-co-oPD) coated Al was used as cathode and lead as an anode in an electrolytic cell and DC voltage was applied to the two electrodes separated a distance of 2.0 cm. The electrodeposition of zinc stearate was carried out for 30 min at room temperature through applying of 15–20 V in a mixture of 0.1 zinc nitrate and 0.2 M Stearic acid dissolved in ethanol. After deposition, plate was rinsed with distilled water and dried at ambient temperature for the subsequent characterization.

2.4. Characterization

Nanocomposite polymeric coatings consists of PANI, poly(Ani-co-oPD) and poly(Ani-co-oPD)-zinc stearate coatings prepared over Al surface were characterized by Fourier transform infrared – attenuated total reflectance spectroscopy (Bruker – Tensor 27), over the wavelength range from 4000 to 400 cm^{-1}.

The degree of crystallinity of different coating on Al were examined using a Philips X-Pert X-ray Diffractometer (XRD) with CuK radiation of wavelength $\lambda = 1.54$ Å. The surface morphology of the as formed coatings was examined by Scanning Electron Microscope (SEM, FEI – QUANTA–FEG 250, Japan). All the samples were sputtered with thin gold film before SEM analysis to prevent surface charging effects.

Thickness of the all the prepared coating was evaluated using Dermitron thickness tester. Triplicate measurements were done to ensure the accuracy. Growth rate of the various coatings were determined by ratio of thickness to time period for which anodisation is carried out (in min).

Microhardness was measured by Vickers microhardness method using automatic microhardness tester HV 1000B (Acme Engineers, Pune) at 25 g load and 10 s dwell time. For assessing the adhesion of the coating on Al substrate, a standard test method (SCOTCH Tape method, ASTM D 3359-02) was used. The abrasion resistance of the coatings was measured as per ASTM D 4060 method tested at 1 kg load using SiC wheels at 100 cycles by using Rotary Abrasion tester (Caltech engineering services, Mumbai). The adhesion strength were studied by pull-out test according to the ASTM F1044, with at least five measurements for each specimen. The coated Al specimens (25 mm in diameter) were bonded to counter Al surface using quick set epoxy adhesive. After curing in an oven at 100 °C during 60 min the fixtures were subjected to pull-out test at a crosshead speed of 1 mm/min, using a universal testing machine (Model 5569, Instron).

Surface wettability of the coatings was tested using a video-based contact angle meter (OCA 15EC, Data Physics Instruments, Germany). An equal volume of distilled water was placed on every sample by using micropipette, forming a drop or spreading on the surface. Photographs were taken to record the shape of the drops and the contact angle was measured. Five measurements were taken at different locations of solid specimen and an average contact angle was calculated. The roughness of the resulting samples was measured employing a surface roughness measuring instrument (HOMMEL-ETAMIC W10, Germany).

The corrosion resistance of various coating was evaluated by electrochemical impedance spectroscopy and Tafel polarization studies. The corrosion studies were carried out in 3.5% NaCl at 30 °C using electrochemical workstation (CHI instruments, 760 model). A three electrode cell with various coated aluminum as working electrode, Ag/AgCl/saturated KCl as reference electrode and a platinum wire as counter electrode was used. The potentiodynamic polarization studies were carried out at a potential range from −0.250 to +0.250 V with respect to OCP at a sweep rate of 1 mV s^{-1}. EIS studies were carried out at open circuit potential using an electrochemical system for various coatings on Al samples. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the 0 MHz to 500 kHz frequency range using a 5 mV amplitude perturbation. All the measurements were recorded using internally available software and each electrochemical experiment was repeated at least three times to ensure the reproducibility. All the experiments were conducted in aerated and non-stirred conditions. In order to obtain accurate results, the experiments were repeated in triplicate.

3. Results and discussion

3.1. Influence of aniline concentration on PANI coatings

PANI incorporated alumina-titania coating with maximum thickness (32.7 μm) and growth rate (0.75 μm/min) was obtained