Progress in Organic Coatings 125 (2018) 358–364

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Corrosion protection behaviour of r-GO/TiO_2 hybrid composite coating on Magnesium substrate in 3.5 wt.% NaCl

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ARTICLE INFO

Keywords:
Synthesis
r-GO
TiO_2
Coating characterization
Corrosion behaviour

ABSTRACT

The current behavioral study investigated the effect of incorporation of two nanomaterials namely reduced graphene oxide(r-GO) and Titanium di oxide (TiO_2) (synthesized by chemical reduction method) upon improving the corrosion resistance of pure Magnesium (Mg). Crystalline nature of synthesized TiO_2 was analyzed through x-ray diffraction; UV vis spectroscopy showed its UV absorbance peak near 300 nm. TiO_2, r-GO and r-GO/TiO_2 coating over Mg is done by the way of electrode position technique for different time intervals. Analysis over electrochemical corrosion behaviour reveals that Mg coated with r-GO/TiO_2 showcased better corrosion resistance when compared to bare Mg. Energy-dispersive X-ray spectroscopy and element mapping results exposed for the elementary confirmation as well as uniform dispersion of nano materials. Reduction in corrosion rate is notified for samples coated at 3 min time interval. Improvement in corrosion resistance of r-GO/TiO_2 coatings is mainly due to the high impermeability of r- GO to resist Mg^{2+} ions dissolution in chloride media.

1. Introduction

Magnesium (Mg) and its alloys have potential application in aerospace and transport industries due to its attractive mechanical properties such as low density, excellent machinability and better damping resistance. But however Mg and its alloys have high chemical reactivity, poor wear and corrosion resistance [1–4]. Besides, Mg undergoes severe galvanic and pitting corrosion and majorly these facts limit their wider range of application [5]. To minimize the corrosion of Mg and its alloys, several protective methods are followed in recent years such as composite fabrication, electrochemical plating, anodizing, conversion coatings and organic coatings [6,7]. Under composite fabrication, for the sake of improving the essential properties of matrix material, either expensive hard abrasive particles like SiC, Al_2O_3, B_4C, BN, AlN or the low cost and easily available fly ash, rock dust, E-waste were put as reinforcement and have accomplish something good in their research by getting hold of enhanced properties [8–12].

On the other hand, being eventual that yet material research is made of important binaries and as because material coating deposition have got expertise in the recent past besides being economically viable, organic coating technique has also proven to be an effective method. Also, the availability of vast array of different materials that can easily be overturned into a high quality coating material appropriate for surface treatments, have eased to put in use many newer Mg based composite materials exhibiting enhanced surface properties and add them to affirmative product portfolio. Even then it has certain drawbacks like that of porosity and non-uniformity over the surface of coated components and hence there is a need of newer coating methodology in order to obtain uniform coating that too with minimal surface defects [13]. In due course because of additions by modern technology it is often demanded for a coating with multi functional properties wherein for such cases carbon-based materials are preferred.

Now a days graphene based coating has been projected as a better alternative anti-corrosive coating for most of the metals and was also proved to be more advantageous than the earlier Ni, Cr type of materials. At this juncture it is essential to haul out a more economical and feasible method for depositing graphene over metal surface [14] and so electrodeposition technique used for depositing ceramic, polymer and metal particles over metal to fabricate composite coatings with attractive properties such as higher hardness, better wear and corrosion resistance has been widely studied. There are several reports focusing on the use of inorganic oxides such as SiO_2, ZrO_2 and TiO_2 on metal substrates for improving the corrosion resistance of coated material [15,16].

Among them,TiO_2 serves as an excellent anti corrosion material due to its fascinating properties such as chemical stability, self-lubricating

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https://doi.org/10.1016/j.porgcoat.2018.02.022
Received 5 September 2017; Received in revised form 9 February 2018; Accepted 21 February 2018
0300-9440/

and heat resistance. There are a few outstanding researches in which graphene and TiO_2 are used as coating material to enhance corrosion resistances of base substrate. Hu et al. developed TiO_2 coating over AZ31 Mg alloy using liquid phase deposition route, followed by an annealing treatment with varying temperature (250°, 300°, 380°) and timing(1.5 h, 2 h, 3 h). They studied the influence of annealing temperature on corrosion resistance of coated substrate by Tafel polarization method. Researchers established that corrosion resistance of the developed coating increases at annealing temperature (250 °C) [17]. TiO_2 nanotube based protective coating was fabricated by Li et al. over AZ91D magnesium alloy using pulsed DC magnetron sputtering method. They investigated the corrosion behaviour of developed coating under simulated body condition using Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic polarization method. Results demonstrate that addition of TiO_2 improves the corrosion resistance of substrate material and further anodization on deposition of Ti by magnetron-sputtering methodology (supposed to be a promising method) have helped to decrease the fast degradation rate of Mg alloys [18]. Polymer (Polyaniline) based TiO_2 coating over ZM Mg alloy was developed by Sathiyanarayanan et al. using oxidative polymerization method besides adopting salt spray method to investigate the corrosion resistance of fabricated coating. Their results revealed that combination of TiO_2 and Polyaniline have shown better efficiency to protect Mg alloy [19].

Ni-TiO_2 based multi-layer coating was developed by Shiyan Zhang et al. using electroless plating for Ni and electro -deposition method for TiO_2 and investigated the corrosion behaviour of composite coating by EIS and Potentiodynamic polarization method under 3.5% NaCl electrolyte solution. Results show that corrosion resistance of Ni-TiO_2 coated AZ91D Mg composite improved five times higher than that of the AZ91D Mg alloy [20]. Electrophoretic deposition technique was adopted by Quezada et al. to develop reduced graphene oxide(r-GO) coating over carbon steel. Herein EIS and polarization method were utilized to investigate the corrosion behaviour of fabricated anticorrosive-coated base material. The result shows that addition of r-GO decreases three times the corrosion rate of carbon steel [28]. Selvam et al. synthesized graphene by electrochemical exfoliation method and deposited over Mg alloy (AZ91) through electrodeposition method. Corrosion behaviour of this coating was investigated taking on Tafel polarization and EIS analysis under three different corrosive electrolytes such as NaCl, KCl, and Na_2SO_4. They observed that graphene coating exhibits better corrosion resistance especially in KCl electrolyte [5].

Electrodeposition method was adapted by Kavimani et al. for developing r-GO/SiC coating over Mg and have further examined the corrosion behaviour of developed coating using Tafel polarization method under 0.1 M NaCl and Na_2SO_4 solution. Results established were such that combination of r-GO and SiC have better delamination strength and inhibition efficiency [21]. Zhao et al., developed Graphene Oxide (GO) coating over AZ31 Mg alloy using plasma electrolytic oxidation method with varying percentage of GO (1 g/L, 2 g/L, 3 g/L). They to investigate the corrosion behaviour of the so developed coating adopted EIS method and corresponding results attained illustrates that 2 g/L GO coating show signs of better corrosion resistance [22].

Most of the studies reported that incorporation of graphene and TiO_2 in coated substrate helps in improvising the corrosion resistance. What so ever, by visualizing the available literatures, until now, corrosion related studies based on the usage of reduced graphene oxide(r-GO) and TiO_2 as a coating material for Mg and allied composites was not yet reported elsewhere. Hence, headed by the formulations of the aforesaid novelty, this research deals in core for the development of hybrid coating(r-GO/TiO_2) over Mg for different interval of time (2 min, 3 min & 5 min) and explore the corrosion behaviour of the newer hybrid composite coating in 3.5% NaCl.

2. Experimental procedure

2.1. Synthesis of TiO_2 nanoparticles

The detailed procedure for r-GO synthesis is already reported in our previous work [21]. For TiO_2 synthesis analytical grade of chemical was utilized without any purification. *n*-Heptane and Titanium Tetra Isopropoxide (TTIP) purchased from Sigma-Aldrich was used as the source for TiO_2. Chemical reduction method was used for TiO_2 synthesis. In a typical procedure, 28.7 ml of TTIP was mixed with 100 ml of *n*-Heptane and the mixture is kept stirring for 2 h duration. Following the procedure of continuous stirring, 7.8 ml of distilled water was added drop wise. After successful addition of distilled water, the resultant mixture was kept at room temperature for about 76 h and then the same was filtered and calcinated at 70 °C for 24 h and further at 200 °C for 2 h.

2.2. Sample preparation for corrosion studies

For electrodeposition practicals, pure Mg strip is mirror polished with different grade of SiC abrasive sheets. During every polish, the strips were cleaned with distilled water and acetone in order to remove the metal debris attached to it. r-GO,TiO_2 and r-GO/TiO_2 nanocomposite coatings were done by adopting linear electrodeposition method wherein as procedure 5 mg of $MgCl_2$ was dissolved in 50 ml of ethanol and appropriate amount of TiO_2 was dispersed and further sonicated for 1 h duration. Two well-polished Mg strips were immersed into the solution mixture and then 12 V potential was applied at different time intervals (2 min, 3 min & 5 min) just for comparing the coating deposition; and after this successful completion, coated strips are dried overnight at 85°C. The same procedure was followed in line for all other nanocomposite coatings viz. r-GO, r-GO/TiO_2 designed in order to accomplish the research hypothesis.

2.3. Material characterization

The phase and crystalline nature of the prepared samples were analyzed by powder X-ray diffractometer (PXRD) (BRUKER D8 ADVANCE). The samples were scanned over the 2-theta range of 10°–80° at room temperature (298 K). The observed peak positions and the relative intensities of the powder pattern were identified in comparison to the reference diffraction data. The surface morphology of coated samples are examined under scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDAX) (JEOL JSM-6610LV, Japan) being operated at 20 kV. UV–vis visible absorption spectroscopic experiments were as usual carried in 700–200 nm wavelength range using Perkin Elmer (Lambda 35) UV–vis Spectrometer.

2.4. Electrochemical corrosion studies

Corrosion behaviour of the coated samples were investigated in detail as per the requirements of the research by using CHI604C electro chemical work station. This USA make work station utilizes three electrode setup, adopting platinum wire as counter electrode, saturated calomel electrode as reference electrode and coated strip as working electrode. Corrosion behaviour of all of the coated samples was studied in 3.5 wt% NaCl electrolyte. Tafel polarization is carried out between −0.2 V to −2 V at the scan rate of 0.01 V/s and all the experiments were repeated thrice so as to confirm the accuracy of the attained results.

3. Result and discussion

3.1. XRD confirmation for TiO_2

Obtained XRD pattern for synthesized TiO_2 is showcased in Fig. 1. The obtained peaks well coincides with the anatase phase of TiO_2 in