



Electroless Ni-P/nano GO coatings for enhanced corrosion protection applications

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ABSTRACT:

Thenano composite coatings of Ni-P-GO was obtained on the pre-cleaned aluminum alloy substrate by electroless plating method. Nano graphene oxide (GO) finds extensive applications due to its unique properties. The microstructure and morphology of as plated composite coatings were investigated by EDX, scanning electron microscope and XRD studies. The corrosion behavior of the coatings with and without nano GO was determined in acidic and alkaline medium by potentiodynamic polarization, electrochemical impedance spectroscopy, neutral salt spray and atomic absorption spectroscopy. The composite coatings showed increased corrosion resistance due to the incorporation of nano GO. The microhardness of the coatings was measured by Vicker's hardness method and coating thickness was measured by non-destructive method using 3D optical profilometer.

Key words: Nano graphene oxide, SEM, XRD, polarization, EIS, neutral salt spray.

1. Introduction

Electroless nickel-based coatings finds extensive applications in industries due to its enhanced corrosion resistance, good abrasion resistance, non-magnetism, even thickness and improved microhardness^{1,2}. Electroless nickel deposits can be obtained uniformly on complex shaped objects. Electroless Ni plating on aluminum alloys is an effective method to modify wear resistance, hardness and corrosion properties^{3,4}. The performance of nickel-based coatings in terms of its tribological properties has been studied by many researchers^{2,5}. The mechanical and chemical properties Ni-P plating depends on phosphorus content⁶, degree of crystallinity, crystal size⁷ and plating bath conditions⁸. Ternary nickel coatings which provide better mechanical properties and improves corrosion resistance of the base metal has been reported in literature. These ternary coatings can be obtained by adding a third element into electroless plating bath and maintaining optimum conditions⁹⁻¹⁴.

Incorporation of nano particle into the electroless nickel coating, found to improve the thermal and mechanical properties at high temperature. However, controlling the phosphorus content and composition of third element in coating is a challenge¹⁵. Among the aluminum alloys, Al6061 is the most commonly used alloy for functional applications in space and automobile industries due to

its high strength to weight ratio and good formability^{16,17}. Even though aluminum and its alloys act as an excellent performer in anticorrosion conditions, there are few disadvantages of using aluminum in corrosive and abrasive environment. Hence, it requires proper surface treatment and plating technique to modify the surface characteristics of aluminum and its alloys.

Among the allotropes of carbon, graphite and its derivative graphene oxide nano particles finds extensive applications as electrode materials¹⁸, sensors^{19, 20}, energy storage devices^{21,22} due to its chemical, electrical and thermal properties. Graphene oxide is a material which contains carbon and oxygen. where carbon is having honeycomb lattice with crystal structure with two-dimensional sp²-bonded carbon material. Graphene oxide is having unique properties with good chemical, mechanical stability with high surface area, high thermal and electrical conductivity²³⁻²⁶.

Owing to higher stiffness, hardness and wear resistance of nano GO, in this research article the studies carried out on the development and characterization of nano GO reinforced electroless Ni-P composite coatings (Ni-P/nano GO) in a hypophosphite reduced bath solution on 6061-Al substrate in acidic medium is described. The effect of incorporation of nano GO on the microstructure and anticorrosion behavior of the composite coatings is reported.

2. Materials and methods

2.1. Materials

All the solutions were prepared by using analytical reagent (AR) grade chemicals and double distilled water. Aluminum alloy, Al6061 substrate procured from Pratham traders, Mumbai, India was used for electroless plating.

2.2. Measurement techniques

Elemental analysis of the samples was carried out with Link Ge Energy Dispersive Spectrometer (EDX) combined with a Noran Scientific analyzer, Model TN5500, USA, provides the spatial resolution for compositional analysis.

Surface morphology and microstructure of the samples was evaluated by Scanning Electron Microscope, TESCAN-VEGA3 LMU.

X-ray diffractometer, Philips, PW 1140/90, USA was used to obtain XRD patterns of the composite coatings and nano GO.

Potentiodynamic polarization studies were carried out in an aerated acidic and alkaline corrosive medium by using CH instruments 6086D with a platinum foil as the counter electrode and saturated calomel electrode (SCE) is used as a reference electrode in a three-compartment Pyrex glass cell. Tafel curves were obtained by dipping 1 cm² samples in different corrosive medium. Potential-current curves were recorded by polarizing the specimen to ± 200 mV anodically with respect to OCP at scan rate of 0.01 V/s.

Electrochemical Impedance studies were carried out for the coatings using an Autolab PGSTAT 30 (USA) with pilot integration controlled by GPES 4.9 software. 0.5 N NaOH and 0.5 N HCl solution at pH 5.0 was used as the test electrolyte. A time interval of 5-10 minutes was given for the system to attain a steady state open circuit potential (OCP). Then over the steady-state potential AC potential of 10mV was superimposed. The AC frequency was varied from 10 kHz to 100 mHz. The real part (Z^I) and imaginary part (Z^{II}) of the cell impedance were measured in ohms for various frequencies. All impedance data were fit to appropriate equivalent circuits using a complex non-linear squares fitting routine using both the real and imaginary components of the data.

The corrosion resistance of the coatings was also determined by neutral salt spray test as per ASTM B117 standard in a salt spray chamber. The samples were exposed to 5% sodium chloride solution for 96 hours in a salt spray chamber maintained at 38°C.

The protection efficiency of the coatings was measured by atomic absorption spectrometer (AAS) model G8908 Australia in 0.5N NaOH and 0.5N HCl medium with 3 hours of contact time.

3. Results and discussion

3.1 Development of electroless Ni-P/nano GO coatings

Graphene oxide was synthesized by modified hummer's method, by using graphite powder, sodium nitrate, potassium permanganate, Sulphuric acid, distilled water, hydrochloric acid at room temperature with continuous stirring for 15 hours.

Electroless Ni-P/nano GO composite coatings were developed on 6061-Al alloy substrate with composition Al 97.9%, Si 1.0%, Mg 0.2%, Cr 0.25% & Cu 0.25%. The plating was carried out on specimens with 20mm×20mm×2mm dimensions, using the following sequence of operations

1. Degreasing: oil and grease present on the aluminum substrate was removed by using trichloroethylene in an ultrasonicator for 10-15 minutes at room temperature.
2. Alkali cleaning: Alkali cleaning was carried out in an alkaline solution containing Na₂CO₃ 23 g/L, Na₂SiO₃ 10 g/L and Na₃PO₄ 8 g/L, at 65 ± 2°C for 2-3 minutes.
3. Pickling: Acid scales and the impurities on the surface was removed by dipping the samples in an acidic solution containing H₂SO₄, HNO₃ and HF for 1-2 minutes at room temperature.
4. Chemical polishing: Aluminum alloy were chemically polished by treating with 75 % H₃PO₄ and 5.0 % HNO₃ solution at 90±2 °C, for 30 seconds
5. Zincating: This process was carried out as per ASTM B253-87, by immersion of the substrate in a solution containing ZnO, NaOH and FeCl₃ at room temperature with continuous stirring for 15-20 seconds.

6. Loosely held Zinc layer was removed by stripping in a solution containing 1:1 HNO₃ at 25°C for 25 seconds.
7. Re-zincating was done for 50-60 seconds to get uniform and even zinc coating. The samples were washed with distilled water and air dried.

3.2 Co-deposition process

Electroless Ni-P/ nano GO plating was carried out in the solution as mentioned in table 1. After the deposition process, the samples were washed by distilled water and air dried. The plated samples were evaluated for further morphology, microstructural changes and corrosion behavior.

Table 1: Bath composition for electroless Ni-P/ nano GO coatings.

Bath constituent's(g/L)	Optimum conditions
NiSO ₄ .7H ₂ O: 25	Ultrasonication:6 hours pH: 4.5 Temperature- 95± 2 °C Time duration- 1 hour With continuous stirring
NaH ₂ PO ₂ : 15	
C ₂ H ₃ NaO ₂ : 20	
Glycine: 5	
Nano Graphene Oxide: 7.5	

3.3. Microstructure and morphology

EDX analysis

Figure 1a represents the elemental analysis of nano graphene oxide which confirms the presence of carbon and oxygen. Figure 1b depicts the EDX spectra of electroless Ni-P/nano GO coatings which shows the presence of nickel, phosphorous, carbon and oxygen.

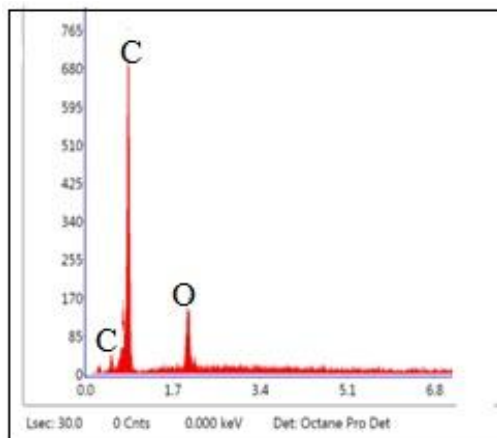


Figure 1a: EDX pattern for nano GO

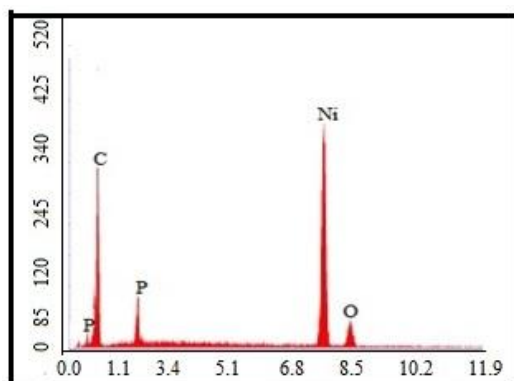


Figure 1b: EDX pattern of the composite coating

SEM analysis

Figure 2a and 2b represents the SEM images of nano GO and electroless Ni-P/nano GO coatings at different magnifications. Nano GO exhibits wrinkled nano buds paper like structure. The coating exhibit nodular globules which are uniformly distributed throughout the surface of the substrate. The black spots found in the micrograph represent GO particles embedded in Ni-P coatings. Scanning electron micrographs confirms that the nano GO particles are evenly distributed with spherical globules over the surface of the substrate.

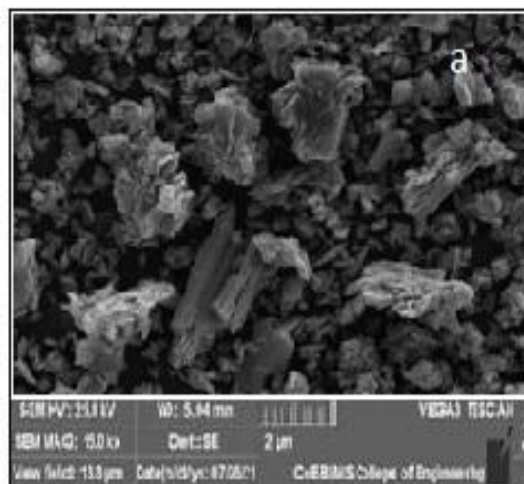


Figure 2a: SEM image of nano graphene oxide

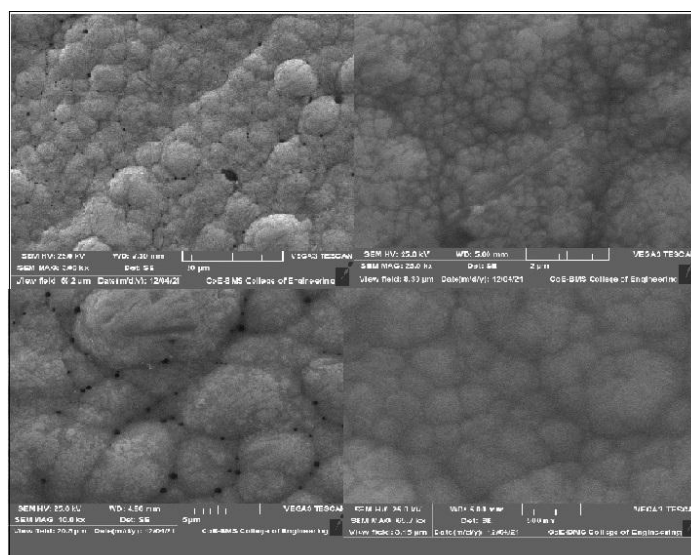


Figure 2b: Microstructure of a) Ni-P/nano GO with different magnifications

XRD analysis

Figure 3a and 3b represents the XRD pattern of nano GO and electroless nickel and Ni-P/nano GO composite coating. Figure 3a shows a sharp peak corresponding to the (001) atomic plane of GO where d-spacing increases due to the oxidation of Graphite. (111) phase is more predominant in electroless nickel coatings. Appearance of new phases was observed in the diffraction pattern of the composite coatings due to the presence of nickel- phosphorus and nano GO. X-ray diffraction analysis confirms graphitic structure of the composites.

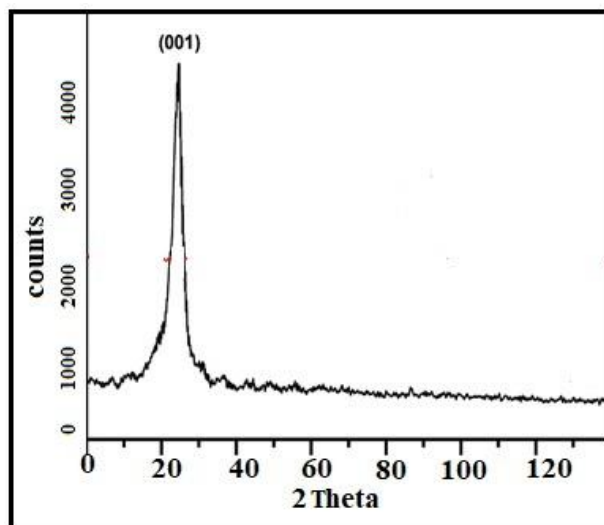


Figure3a: XRD pattern of nano GO powder

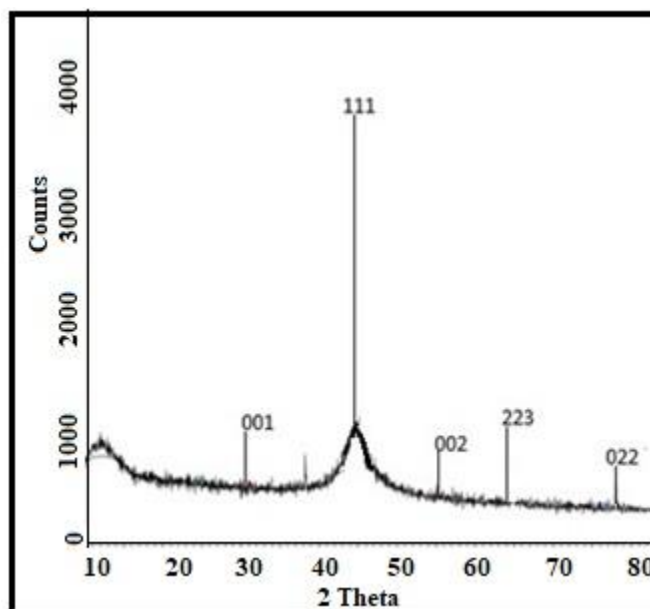


Figure 3b: XRD pattern of electroless Ni-P/nano GO

3.4 Corrosion studies

Potential dynamic polarization studies

The corrosion behavior of electroless Ni-P/ nano GO composite coatings was measured by using the potential dynamic polarization method in 0.5N NaOH and 0.5N HCL solutions. From figures 4 a & 4 b, it is clear that both cathodic and anodic curves follow the tafel behavior throughout the potential range. It is observed that the corrosion current density decreased with the incorporation of nano graphene oxide in electroless Ni-P coatings irrespective of the corrosive medium. The

corrosion current density of the composited coatings decreased significantly compare to electroless nickel-phosphorous coatings and bare aluminum as observed in figures. Following is the order of decrease in current densities of composite coating compare to electroless Ni-P and bare aluminum.

Electroless Ni-P/nano GO < electroless Ni-P < Bare Al

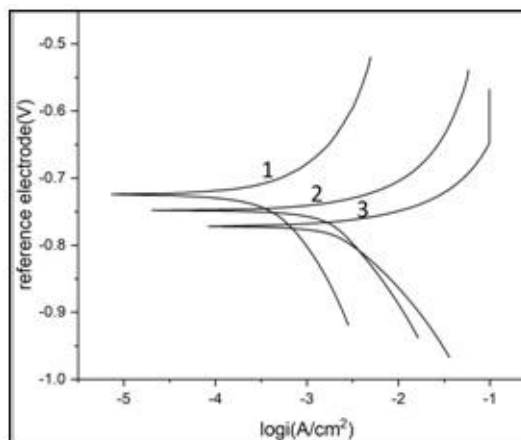


Figure 4a: Tafel plots in 0.5N HCl 1) Ni-P/nano GO 2) Electroless Ni-P 3) Bare Al-6061

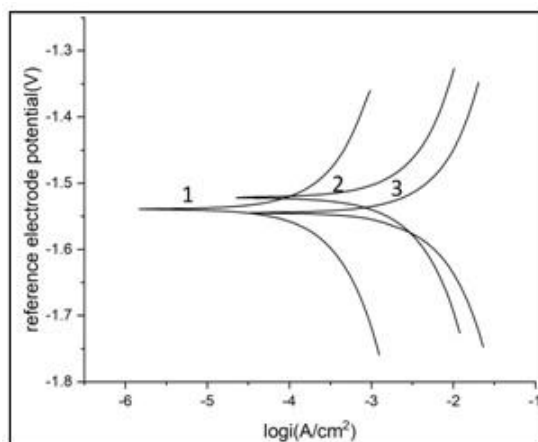


Figure 4b: Tafel plots in 0.5N NaOH 1) Ni-P/nano GO 2) Ni-P 3) Bare Al-6061

The low hydrogen overvoltage of electroless Ni-P/nano GO coatings is the main reason for decreasing the cathodic tafel slope. Anodic Tafel slope might be attributed to the slow kinetics in the presence of nano GO particles. Nano GO particles are having high electrochemical resistance compared with electroless Ni-P matrix.

Impedance results

The corrosion resistance of the electroless Ni-P and electroless Ni-P/ nano GO composite coating was studied by electrochemical impedance experiments. Figure 6a and 6b depicts the Nyquist plots of bare 6061-Al, electroless Ni-P and Ni-P/nano GO coatings in 0.5N NaOH and 0.5N HCl solutions respectively. The semicircle diameter for the nano GO reinforced coatings found to be greater compared to that of electroless Ni-P and bare aluminum, indicating polarization resistance of bare aluminum and binary Ni-P coatings is lower than Ni-P/nano GO coatings which is in agreement with the potentiodynamic polarization studies. The improved corrosion resistance of the composite coating is due to the incorporation of nano GO in the coating. The corrosion resistance of the bare aluminum, Ni-P and the composite coating is as given below:

Bare Al < Ni-P < Ni-P-nano GO

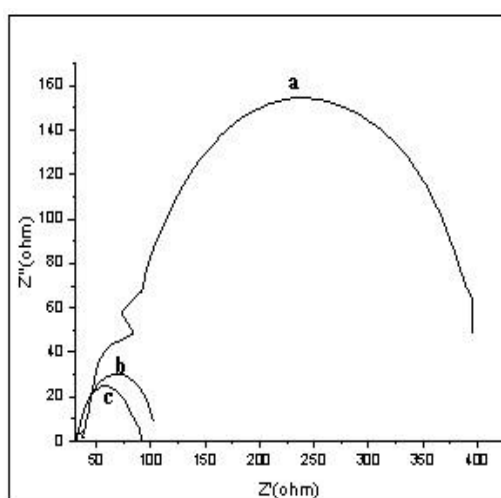


Figure 5a: Nyquist plots in 0.5N HCl a) Ni-P/nano GO b) Ni-P c) Bare Al-6061

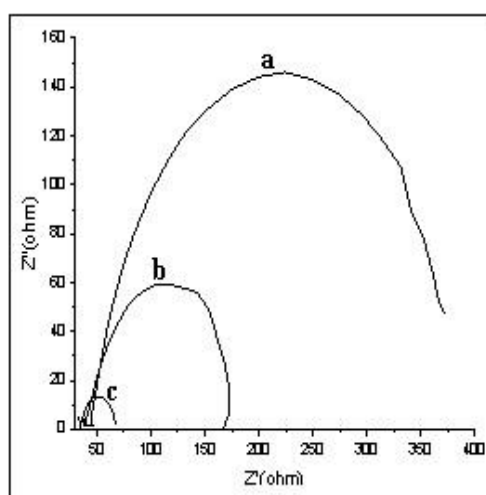


Figure 5b: Nyquist plots in 0.5N NaOH a) Ni-P/nano GO b) Ni-P c) Bare Al-6061

Figure 6a and 6b, depicts the bode magnitude and bode phase angle plots of bare 6061-Al, electroless Ni-P and nano GO reinforced composite coatings in 0.5N NaOH and 0.5N HCl solutions respectively. The observed higher phase angles and Z values of the composite coatings indicate enhanced protection ability in acidic as well as alkaline medium compared to Ni-P coatings.

The microscopically small pores and voids in the binary Ni-P coatings is filled by the nano particles resulting in the improved impedance and corrosion resistance in the composite coatings. It can also be observed from the figures that the protection efficiency of the coatings is higher in alkaline medium compared to acidic medium. The obtained values of solution resistance R_s , charge transfer resistance R_{ct} and double layer capacitance C_{dl} are fitted and the simple Randle equivalent circuit is presented in Figure 7.

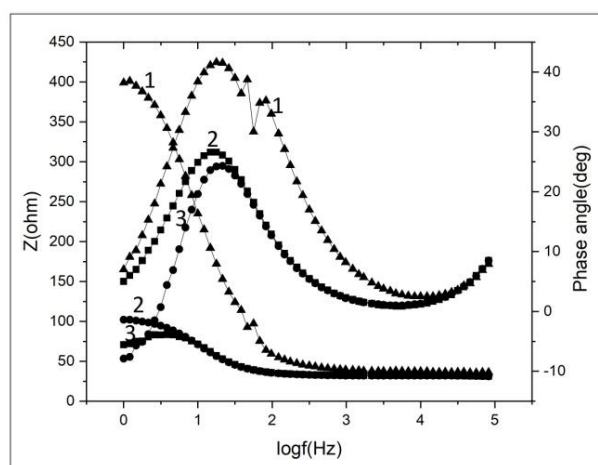


Figure 6a: Bode phase angle and Bode amplitude plots of 1) Ni-P/nano GO 2) Ni-P 3) Bare Al-6061 measured in 0.5N HCl medium

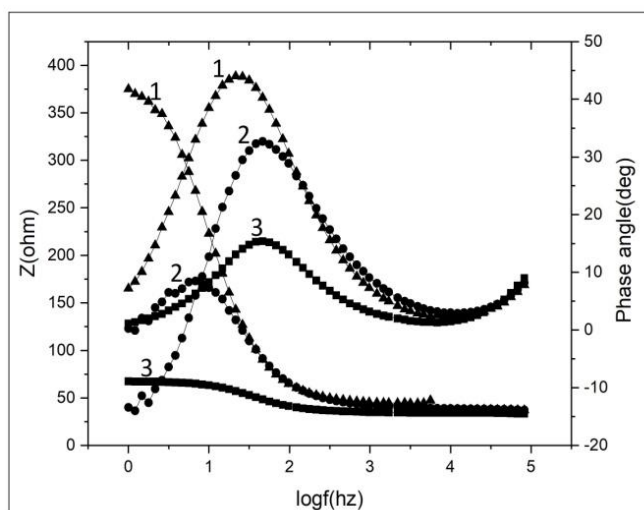


Figure 6b: Bode phase angle and Bode amplitude plots of 1) Ni-P/nano GO 2) Ni-P 3) Bare Al-6061 measured in 0.5N NaOH medium.

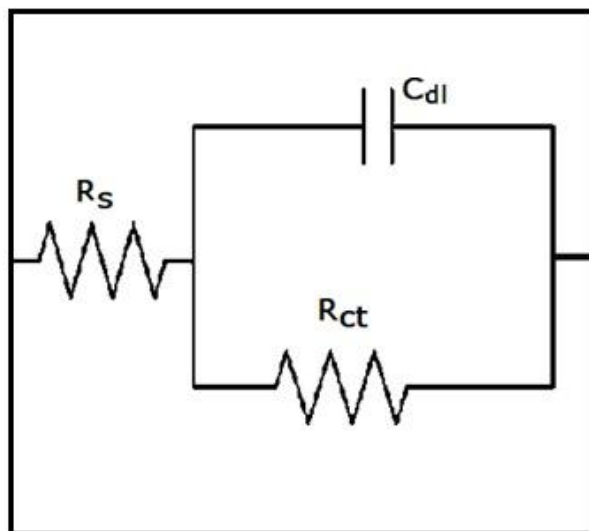


Figure 7: Equivalent circuit for EIS fitting

Neutral salt spray test

In order to evaluate the corrosion behaviour of the coatings in marine environment, the specimens were subjected to neutral salt spray test as per ASTM B117 standard. The specimens were exposed to the fog of 5% sodium chloride for 96 hours at pH 5. The test samples were removed after every 2 hours and evaluated for any degradation in the coating over the entire 96 hours of exposure time. The specimens were taken out of the chamber after 96 hours, washed with distilled water and air dried. Electroless Ni-P coating was stable for 78 hours, later degradation in terms of black spots was observed. Electroless Ni-P/nano GO samples were stable up to 86 hours without any degradation, later tarnishing of the coating associated with grey patches and pits were noticed when observed through 4X magnification lens.

Atomic Absorption spectroscopy analysis

Protection efficiency, surface coverage, and the amount of metal dissolved in acidic and alkaline medium is studied by atomic absorption spectroscopy. Table 2 depicts the corresponding values. From the table, it is observed that the amount of metal dissolved in the case of nano GO-reinforced ternary coatings is less than binary Ni-P deposits. This is due to the higher surface coverage and protection efficiency of Ni-P/nano GO coatings than Ni-P coatings in both alkaline and acidic media.

Table 2: Atomic Absorption spectroscopy results

system	Bare Al 6061		Electroless Ni-P		Electroless Ni-P/nano GO	
	NaOH	HCl	NaOH	HCl	NaOH	HCl
Amount of Al ³⁺ dissolved in 0.1 M solutions (g)	0.085	0.023	0.043	0.010	0.003	0.001
Surface coverage (Θ)	-	-	0.494	0.571	0.964	0.956
Protection efficiency (%)	-	-	49.411±0.0256	56.521±0.0345	96.470 ± 0.0135	95.652±0.0378

3.5 Thickness measurement

Thickness of the composite coating was measured by Optical Profilometer by Coherence correlation interferometry (CCI). CCI is a flexible 3dimensional technique used for surface analysis and topographical characterization of the thin films. The techniques provide 2D and 3D images of the surface. The high resolution with 0.01nm Z resolution over a full scan range plus 0.4 μm lateral resolution, over one million data points gives a true topographical image of the surface. One half of the substrate was masked with transparent tape and the composite coating was deposited on the other part of the substrate. After the plating, the mask tape was removed the substrate was washed with distilled water and air dried. Figure 8 shows 2D and 3D images of the coatings. The average thickness was found to be 10μm.

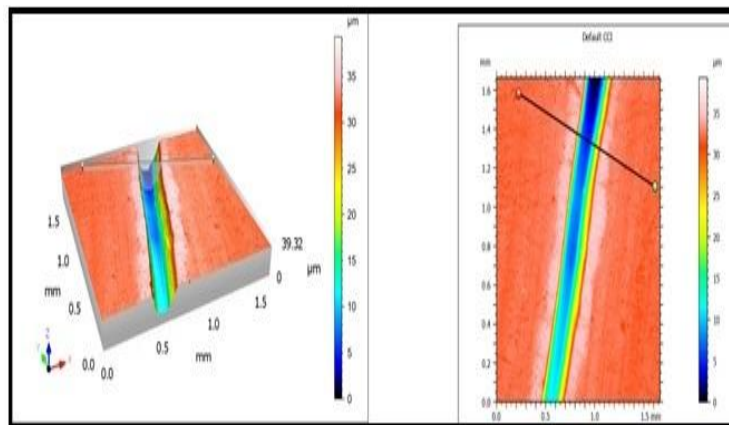


Figure8: Surface profilometry images in 2-dimension and 3-D respectively.

3.6 Micro hardness

Microhardness of the electroless Ni-P plated specimens with and without nano GO at different plating time intervals was measured by Vickers hardness method with 50g load. The indentation was done into the composite coating without affecting the base metal. Figure 9 depicts the effect of c-BN on the microhardness by varying plating time. The microhardness of the plating was found to increase with the addition of hard nano GO in the Ni-P matrix irrespective of plating time. There is a dispersive strengthening by hard nano GO and grain filling which increases the hardness of the composite coating. For Ni-P/nano GO plating, the values increased with increase in the plating time from 30 minutes to one hour, later it remained almost constant. Microhardness of the Ni-P and the composite coating obtained for 1 hour plating time was measured after subjecting the sample to heat treatment for 2 hours in a hot air oven at 250°C. The obtained results indicate that there is a remarkable increase in the microhardness of both the coatings after heat treatment owing to precipitation of the intermetallic Ni₃P in the coatings at high temperatures. The higher hardness of heat-treated Ni-P/nano GO may be due to incorporation of hard GO and transformation of Ni-P to Ni₃P phase^{27,28}.

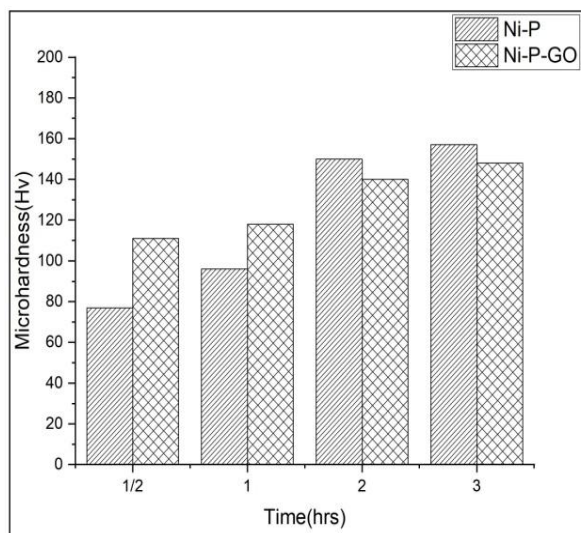


Figure 9: Effect of plating time interval on the microhardness of electroless Ni-P & Ni-P/nano GO coatings.

4. Conclusions

The Ni-P/GO nano composites were effectively deposited using an electroless technique on the previously cleaned Al alloy, Al 6061. The graphene oxide is distributed uniformly across the coatings, which have a spherical shape with blackspots. The EDX analysis confirmed the existence of GO in the coatings due to the detection of carbon and oxygen. X-ray diffraction analyses reveal the coatings have a graphitic structure and a partially crystalline morphology. Comparatively, the interfacial adhesion and microhardness of electroless Ni-P/nano GO composite coatings are superior to those of electroless Ni-P coatings. The corrosion resistance of the composite coating was greater than that of electroless Ni-P and bare aluminum as indicated by potentiodynamic polarization and impedance studies.

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