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Development and Characterization of Reduced Graphene Oxide-Based Nanocomposite Coatings

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Abstract

Nanoparticles synthesised by various chemical methods are extensively used in textiles, medicine, agriculture and industrial applications. Due to its physicochemical properties, reduced graphene-oxide (r-GO) is a nanoparticle used in multiple fields. Reduced nano-graphene oxide powder was synthesised by using graphite powder. Ni-P coatings with nano r-GO were developed on the pretreated aluminium alloy Al-6061 using sodium acetate as a complexing agent by electroless plating technique. UV-visible spectrophotometric studies carried out the screening of complexing agents. The surface characteristics and microstructure of the plated samples were investigated by EDAX, SEM and XRD. EDX confirmed the presence of GO in the coatings. The coatings were found to have Spherical globules with black spots. XRD studies indicate the graphitic structure of the coatings. The coatings were also examined by adhesion and microhardness tests.

Keywords: *Composite Coating, Microhardness, Reduced Graphene Oxide, UV-Visible Spectrophotometer*

1.0 Introduction

Aluminum and its alloys are used extensively in industrial applications especially under corrosive environments due to its inherent properties[1]. Al-6061 finds extensive application in aerospace and automotive industries owing to its low density, high strength and good formability.[2] However, Environmental conditions containing carbon dioxide with saline composition and polluted air result in the development of a thin porous oxide film on the aluminium surface and cause corrosion reactions[3,4]. Hence, a correct surface preparation method and deposition technique are to be adopted to improve the properties of aluminium and its alloys[5].

Microhardness, corrosion and wear resistance of aluminium and its alloys can be modified by a simple electroless plating method[6,7]. Electroless nickel-phosphorous platings provide deposits with uniform thickness, better adherence, superior corrosion resistance, and improved wear and abrasion resistance[8-10]. It is also reported in literature that ternary electroless deposits developed by adding a third element into the plating bath, provide improved mechanical properties and resistance to corrosion compared to binary alloy coatings[11-16]. Ni-P-based nanocomposite coatings provide crack-free coatings with higher corrosion resistance. Ni-P coatings with Graphene oxide nanoparticles have been used in the electronic industry as electrode materials[17], sensors[18,19], and energy storage devices[20-22] owing to their excellent thermal and electrical properties.

This research work presents the synthesis of reduced graphene oxide nanoparticles and co-deposition of the same with nickel by electroless method using complexing agents. The microstructure, morphology and microhardness of the coatings have been investigated.

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2.0 Materials and Measurement Techniques

Aluminium alloy, Al-6061 substrate with composition Al- 97.9, Mg-1.0, Si- 0.6, Cu- 0.25, Cr- 0.25%, with dimensions 20 x 20 x 1 mm was used for the deposition of nanocomposite coatings. LR-grade chemicals and distilled water were used for the pretreatment and or the development of the coatings.

PC-based double beam UV-Visible Spectrophotometer, 2202, Systronics, was used for screening of different complexing agents.

Elemental analysis and the morphology of the nanocomposite coatings were obtained by EDX and SEM studies.

X-ray diffractometer was used to get the XRD patterns of the composite coatings.

The microhardness of the composites was evaluated by the Vickers hardness method using a diamond indenter.

2.1 Synthesis of Reduced Graphene Oxide

Reduced Graphene Oxide (r-GO) was prepared by using a chemical vapour deposition process. Graphite powder was mixed with sodium nitrate and concentrated sulphuric acid was added with continuous agitation. The homogeneous mixture obtained was stirred for 60 minutes maintaining room temperature using a magnetic stirrer. To the same solution, potassium permanganate was added and stirred for around 10 hours at room temperature. To this solution, 500 ml of distilled water was added followed by 30% Sulphuric acid. This solution is washed with Hydrochloric acid and deionized water to obtain Graphene Oxide.

2.2 Co-deposition Process

Aluminium 6061 alloy substrate with 2 mm diameter and 2mm thickness dimensions was used for electroless plating. The Al-6061 substrates were polished with sandpaper and precleared with isopropyl alcohol using an ultrasonic bath. Later the samples were subjected to alkali and acid treatment. Before coating the substrates with Ni-P/nanographene oxide, it was subjected to a zincing process as this provides better adherence for electroless deposits[23].

3.0 Results and Discussion

3.1 Screening of Complexing Agents

The screening of complexing agents was carried out by using a double-beam UV-visible spectrophotometer. Complexing agents play an important role in providing fine-quality deposits. Different complexing agents were screened for Ni^{2+} ions. Figure 1 depicts the UV-visible absorption spectrum of complexing agents individually and in combination. Sodium acetate was found to form weak complexes with Ni^{2+}ions.

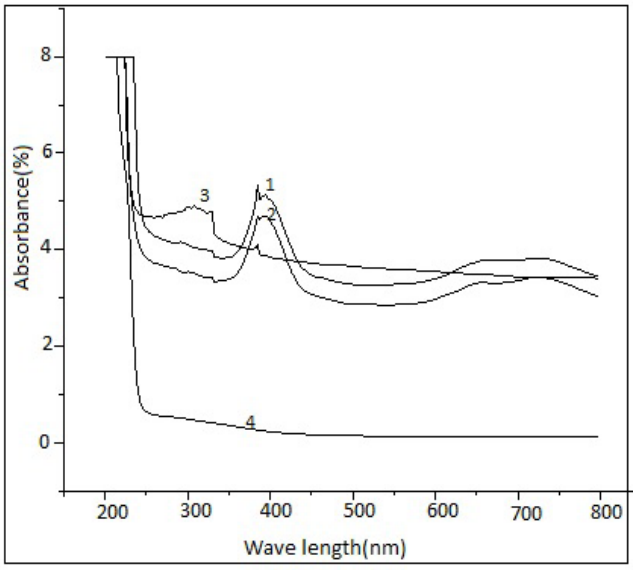


Figure 1. UV-Visible spectra **1)** Ni^{2+}+Sod.acetate + r-GO **2)** Ni^{2+} + r-GO **3)** nano r-GO **4)** Sodium acetate.

Electroless Ni-P/nano r-GO coating was developed on pre-cleaned Al-6061 samples in an electrolyte solution comprising nickel sulphate, sodium hypophosphite, sodium acetate and nano graphene oxide. The composite coatings were obtained by continuously stirring the solution at 300 rpm, at 90°C for 60 minutes.

3.2 Microstructure and Morphology

EDX studied the specimen's elements composition. It confirmed the presence of elements viz., Ni, P, O and C in the composite coatings.

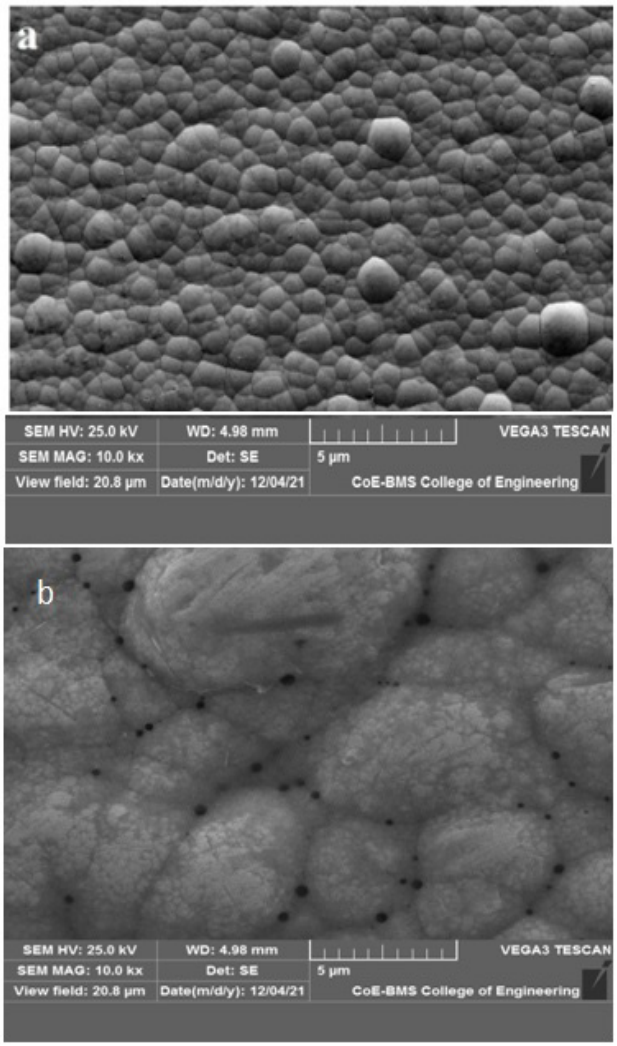


Figure 2. SEM images for **a)** Electroless Ni-P coatings **b)** electroless Ni-P/nano r-GO coatings.

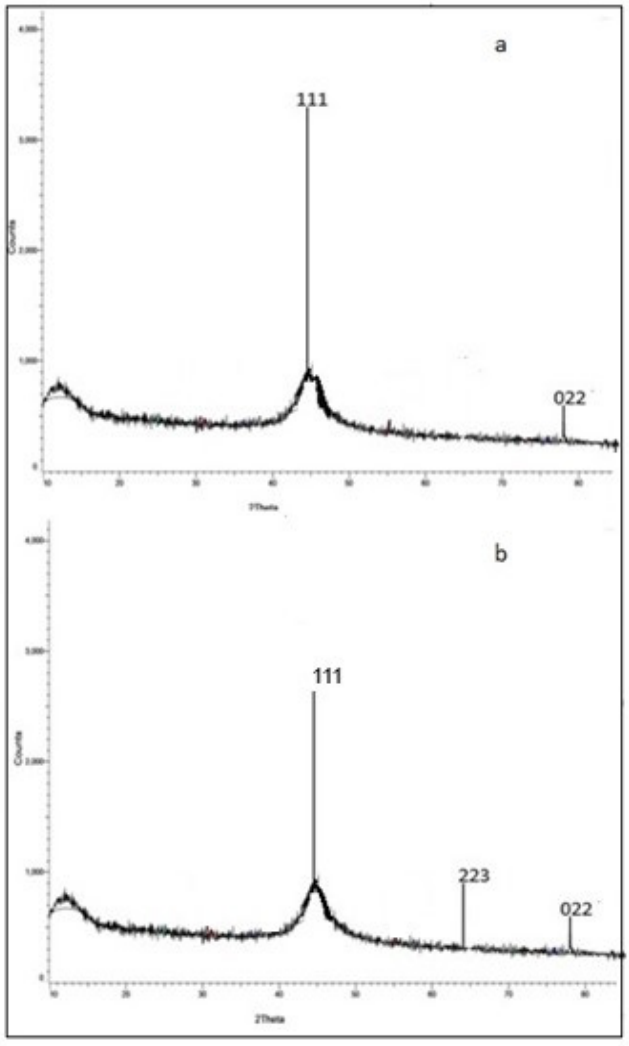


Figure 3. XRD pattern of a) Ni-P b) Ni-P/nano r-GO coatings.

Figure 2 represents the scanning electron micrograph of electroless nickel and composite coatings. Electroless nickel coatings exhibit spherical structures with a uniform distribution of particles throughout the surface of the substrate. The presence of r-GO particles as black spots in the coatings was confirmed in Figure 2b. SEM images show spherical globules of nanographene oxide particles along with nickel phosphorous deposits.

To investigate the effect of the presence of the nano r-GO on the crystalline morphology of Ni–P coatings XRD analysis was carried out. Figure 3 represents the XRD pattern of the binary and ternary composite coating. Phase (111) is more eminent in binary nickel coatings. The diffraction pattern of the nanocomposite coating with nano r-GO consisted of phases (223) and (022) in addition to the (111) phase, confirming the graphitic structure.

3.3 Evaluation of the Coatings

3.3.1 Adhesion

The adherence of the nanocoatings to Al-6061 was examined using the Scotch tape peel-off method[24]. In this test, 100 squares of 4 mm were scribed through the coatings. A one-inch pressure-sensitive tape was applied tightly over the coating by rolling a roller covered with rubber over the tape twice. The pressure-sensitive tape

was then taken off quickly at 90° to the coating and later it was inspected for any detachment or irregularities under a 4X magnification lens. The coating was found to adhere to the surface firmly.

3.3.2 Microhardness

The Microhardness of the binary nickel-phosphorous coatings and ternary nickel-phosphorous/nano r-Go coatings was determined by the Vickers hardness method. The microhardness of electroless Ni-P and the composite coatings was found to be 100 and 130 VHN respectively. Improvement in the microhardness of the coatings is due to the incorporation of r-GO and its uniform distribution in the coatings.

4.0 Conclusions

Ni-P/nano r-GO composite coatings were successfully deposited on the precleaned Al alloy Al 6061 by a simple electroless method. The composite coatings comprise of spherical structure with black spots indicating the even distribution of reduced graphene oxide in the deposit. EDX results showed the presence of carbon and oxygen which confirms the presence of nano r-GO in the coatings. XRD studies indicate the graphitic structure with partially crystalline morphology of the coatings. Ni-P/nano r-GO coatings exhibit relatively better interfacial adhesion and microhardness in comparison with binary Ni-P coatings.

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