

## Structural and Functional Characterization of electrodeposited Ni/Graphene nanocomposite coatings

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### Abstract

Creative nano (Cnano), as a partner in the H2020 EU funded DIAGONAL project, has developed a series of nickel nanocomposite coatings utilizing graphene as the reinforcing agent. The house lab scale experiments encompass varying current conditions, both direct and pulse current methods, as well as different surfactants, anionic (SDS), cationic (CTAB), and non-ionic (PEG). Furthermore, the investigation delves into the influence of diverse graphene concentrations on the structure, morphology, and properties of the resultant Ni-graphene nanocomposite coatings. Through our work, it was ascertained that pulse plating, specifically with a 50% duty cycle, emerges as the optimal current condition for the successful integration of graphene nanosheets into the coating matrix. Additionally, preliminary findings suggest that SDS, anionic surfactant, yields coatings of superior quality characterized by higher carbon content. The properties of the coatings were comprehensively analyzed using SEM-EDS, XRD, contact angle measurements, Raman spectroscopy, optical microscopy, Taber abrasion testing, and Vickers microhardness assessments.

**KEYWORDS:** Nickel Electroplating, Nanocomposite coatings, Graphene reinforcement

### 1. INTRODUCTION

Metal and alloy electrodeposition is of wide industrial interest and finds application in various fields including surface finishing, electrowinning, and electrorefining. It is widely employed to enhance the aesthetic appeal, customize surface properties, and prevent corrosion of diverse items ranging from household components to advanced technological devices [1]. Hard Chromium (HC) electroplated coatings have dominated the surface treatment industry for almost 100 years; however, the manufacturing of HC coatings requires the use of hexavalent chromium (Cr<sup>6+</sup>) compounds which are classified as carcinogens and mutagens and are therefore restricted under REACH [2].

Cnano is currently investigating Ni-matrix nanocomposite coatings, reinforced with different 2D or ceramic nanoparticles, to replace HC in specific industrial applications. When nanoparticles are introduced into metal matrices through electrodeposition, it markedly alters the characteristics of the coatings [3]. Electrodeposition of nickel-based nanocomposites leads to remarkable improvements of the coatings' overall properties. Specifically, Ni-matrix nanocomposite coatings exhibit enhanced hardness, stability in diverse corrosive conditions, and strong adhesion to the substrate [4]. Therefore, they offer a safer and more sustainable alternative compared to HC. Recently, some investigations were done to produce graphene reinforced Ni-matrix composites to

improve the electrical, mechanical, and physical properties of the materials. Graphene displays exceptional characteristics, notably wear resistance, alongside its versatile physicochemical properties encompassing electrical, optical, and self-lubricating qualities. Notably, graphene serves as an outstanding reinforcement agent, for enhancing the corrosion resistance of metal matrix composites [5].

The main challenge during the electrodeposition of nanocomposite coatings is the agglomeration of submicron and nanosized particles dispersed in the electrolyte due to the high ionic strength of the electrolyte and the surface free energy of particles. This may lead to nanocomposite coatings with poor mechanical properties due to the non-uniform distribution of the reinforcing particles in the metal matrix. Therefore, several attempts have been made to achieve a high co-deposition content and a uniform distribution by monitoring the effect of the surfactant and the plating conditions on the agglomeration rate and the content of nanoparticles incorporated in the metal coating [6].

In this study, a series of Ni/Graphene (**Ni/Gr**) nanocomposite coatings were produced at lab scale using a standard Ni-Watts electrolytic bath containing commercially available graphene nanoplatelets. The effect of different surfactants co-added in the electrolyte to improve the dispersion of graphene was examined. Specifically, SDS (sodium dodecyl sulfate), CTAB (cetrimonium bromide) and two types of PEG (polyethylene glycol) were used. Additionally, the influence of various electroplating conditions was investigated, varying the current density and the current type. This comprehensive exploration aimed to analyze how these parameters collectively impact the electrolytic deposition process and the mechanical, morphological, structural, and physicochemical properties of the resulting Ni-Matrix/Graphene nanocomposite coatings.

## 2. METHODOLOGY

The electrodeposition of Ni-matrix nanocomposite coatings was achieved using a Watts-type bath. The Watts bath, with a volume of 1 L, contained the usual amounts of the Ni (II) salts, namely NiSO<sub>4</sub> and NiCl<sub>2</sub>, boric acid (H<sub>3</sub>BO<sub>3</sub>) as a pH buffering agent, and saccharin as an additive to improve the final properties of the coating (stress and brightness). A nickel plate was used as the anode and a brass round substrate was used as the cathode. The substrate was cleaned with acetone, ultrasonicated in water and etched via immersion in a 20% HCl solution prior to electrodeposition to clean the surface from impurities and oxides. The cathode was masked to selectively electroplate a surface area of approximately 14 cm<sup>2</sup>.

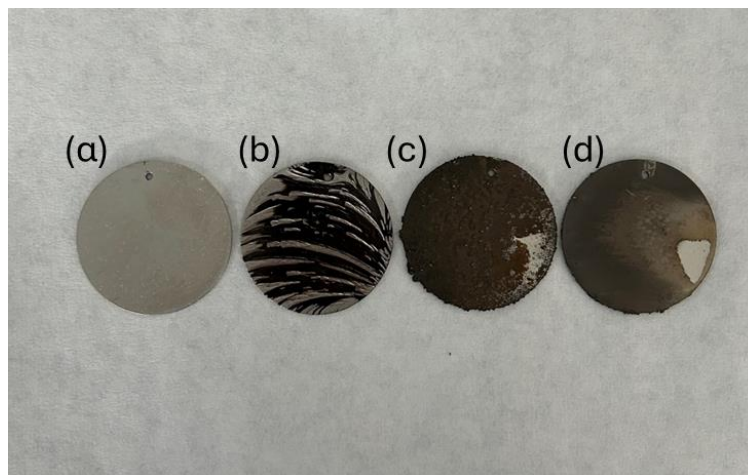
The investigation began by selecting the appropriate surfactant. Initial experiments were conducted using SDS, CTAB and PEG with a molecular weight of 400 (PEG400), or 6000 g/mol (PEG6000). To produce Ni/Gr nanocomposite coatings, a graphene dispersion in water was first prepared. Gr (0.2 g) was added under stirring in 300 mL of reverse osmosis water and ultrasonicated for 15 min using a Sonotrode. Afterwards, the surfactant (0.4 g) was added in the mixture and the ultrasonication treatment was continued for 45 min. The dispersion was transferred into 500 mL of a freshly prepared Watts-type electrolyte bath and the total volume was adjusted to 1L. The Ni/Gr electrolyte was ultrasonicated for 1 h before electrodeposition.

To ensure a uniform dispersion of the Gr nanoplatelets and homogeneous hydrodynamic conditions, magnetic stirring was employed. The temperature of the electrolytic bath was maintained at 50°C and the pH of the bath was adjusted to pH = 4, by adding dropwise an aqueous NH<sub>3</sub> solution. For the electrodeposition process, both direct and pulse current (10 Hz) conditions were employed, using a Metrohm Autolab PGSTAT12 Potentiostat/Galvanostat Electrochemical System. The electrodeposition time was adjusted to obtain a final coating thickness of approximately 30 μm. To optimize the electroplating conditions, current densities of J = 1, 2, and 5 A/dm<sup>2</sup> were examined under direct current conditions. Finally, pulse current conditions were employed with a duty cycle

20% and 50% and a current density of  $J = 1$  or  $2 \text{ A/dm}^2$ . The quality of the produced Ni/Gr nanocomposite coatings was evaluated in terms of physicochemical, mechanical, and morphological properties.

### 3. RESULTS AND DISCUSSION

The identity of the surfactant had a pronounced effect on the quality of the final coating. The use of a cationic surfactant such as CTAB led to coatings of very poor quality with large areas without any electrodeposit or with burnt surface. Similar results were obtained when non-ionic surfactants were used (PEG). By contrast, when SDS, an anionic surfactant was used, Ni/Gr coatings with very good mechanical properties were obtained. As a result, the subsequent experiments aimed at optimizing the electrodeposition parameters using SDS as the surfactant.

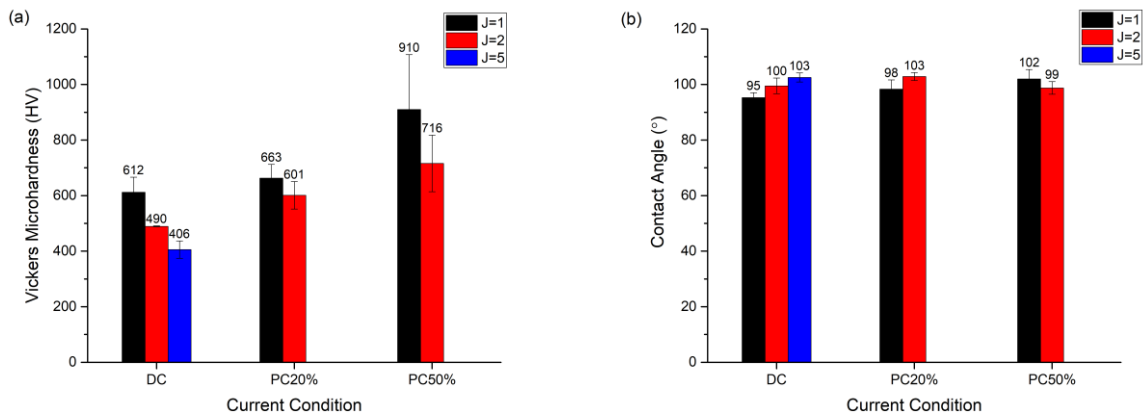


**Figure 1:** Produced Ni-Matrix/Gr nanocomposite coatings using (a) SDS, (b) CTAB, (c) PEG400, (d) PEG6000

#### 3.1 Microhardness and contact angle of the nanocomposite coatings.

The Vickers microhardness of the Ni/Gr nanocomposite coatings using SDS as the surfactant decreased with increasing current density under direct current conditions, as shown in Figure 1. A similar trend was observed when pulse current was applied with a 20% duty cycle. Regardless, the Vickers microhardness of  $>600 \text{ HV}$ , obtained with  $J = 1 \text{ A/dm}^2$  was significantly higher compared to pure Ni metal coatings ( $420 \pm 15 \text{ HV}$ ), produced under identical electroplating conditions. It's worth noting that when pulse current was applied microhardness was increased for both samples with  $J = 1, 2 \text{ A/dm}^2$ . Importantly, applying pulse current with a duty cycle of 50% resulted in the highest Vickers microhardness values of  $910 \pm 197 \text{ HV}$  ( $J = 1 \text{ A/dm}^2$ ) and  $716 \pm 61 \text{ HV}$  ( $J = 2 \text{ A/dm}^2$ ).

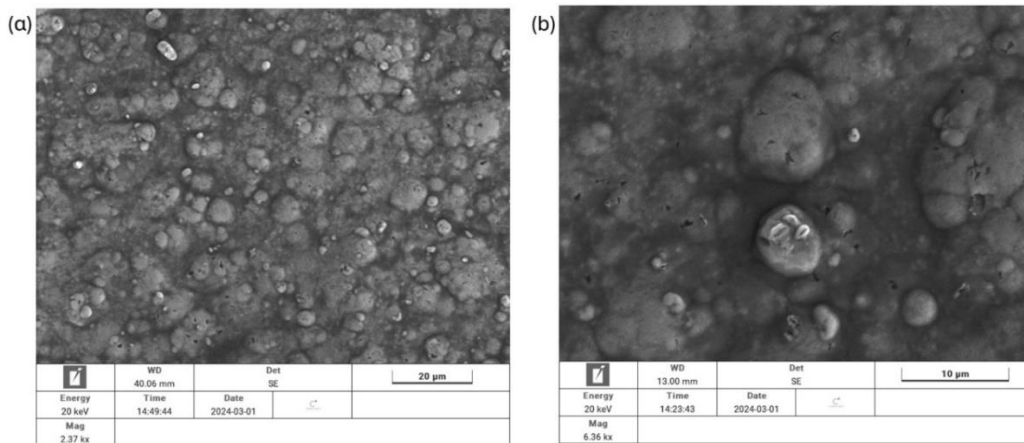
Concerning the contact angle measurements, the effect of current density and current type was less pronounced. For  $J = 1 \text{ A/dm}^2$ , the highest contact angle of  $102 \pm 3^\circ$  was obtained when pulse current with a duty cycle of 50% was applied. It should be reminded that the CA of a pure Ni metal coating, under identical electroplating conditions is  $95^\circ$  [7]. This in turn means, that the incorporation of Gr in the Ni matrix increased both the microhardness and the hydrophobicity of the coating. Likewise, for  $J = 2 \text{ A/dm}^2$ , the contact angle of the Ni/Gr coatings was around  $101 \pm 2^\circ$ . The coatings produced with a current density of  $J = 5 \text{ A/dm}^2$  were rejected due to relatively less sufficient quality and properties.



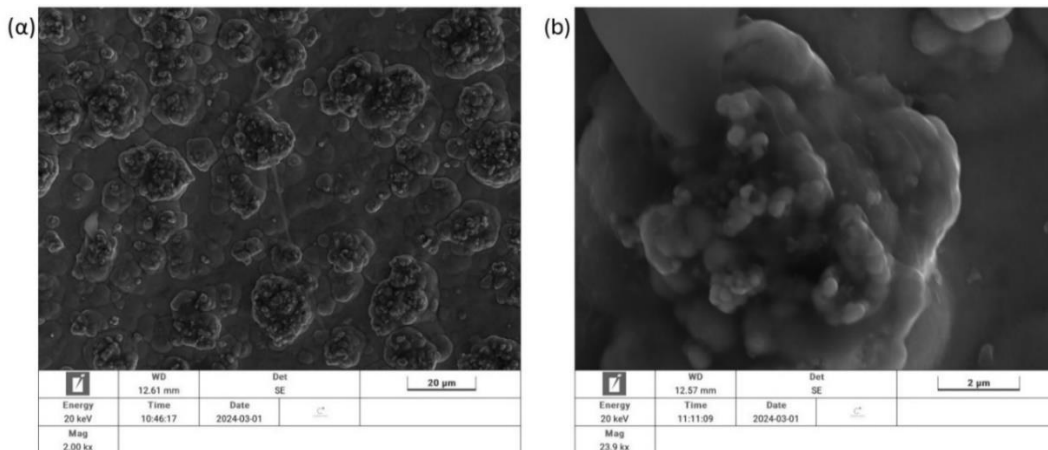
**Figure 2:** (a) Vickers Microhardness and (b) Contact Angle of Ni/Gr nanocomposite coatings: DC: Direct Current, PC: Pulse Current with  $\nu = 10\text{Hz}$  and duty cycles of 20% and 50%.

### 3.2 Surface morphology analysis

The microhardness and contact angle measurements suggested that applying pulse current with a current density of  $J = 1 \text{ A/dm}^2$  resulted in excellent microhardness and hydrophobicity. Figures 2 and 3 show the SEM images of the coatings produced with a duty cycle of 20% and 50% respectively.



**Figure 3:** SEM micrographs of Ni/Gr nanocomposite coatings on a scale of (a)  $20\mu\text{m}$  and (b)  $10\mu\text{m}$ , applying pulse current ( $\nu=10 \text{ Hz}$ ) with a duty cycle of 20%.



**Figure 4:** SEM micrographs of Ni/Gr nanocomposite coatings on a scale of (a)  $20\mu\text{m}$  and (b)  $10\mu\text{m}$ , applying pulse current ( $\nu=10 \text{ Hz}$ ) with a duty cycle of 50%.

Applying a higher duty cycle of 50% resulted in a more granular structure due to the longer  $t_{on}$  that allowed for the creation of more nucleation sites. As Figure 3 (b) shows, nickel crystals have been grown on the graphene nanoplatelets. Graphene has a negative surface charge, so it attracts nickel cations that serve as nucleation sites on the graphene surface.

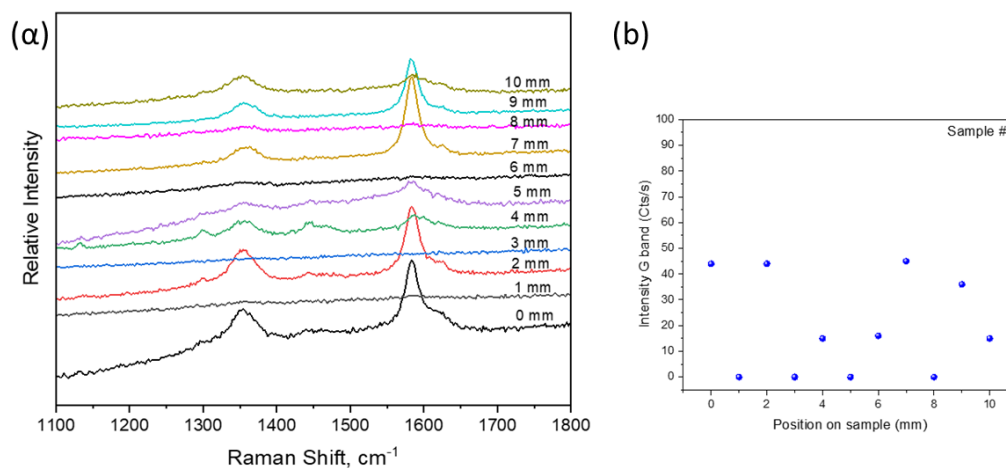
Through EDS and elemental mapping, the content of carbon in the two regions shown in Figure 2 and Figure 3 was measured.

**Table 1:** Carbon content measured by EDS.

Sample	Region 1	Region 2
J=1 A/dm <sup>2</sup> d.c.=50%	17.5%	24.1%
J= 1A/dm <sup>2</sup> d.c.=20%	23.2%	30.4%

### 3.3 Raman Spectroscopy

Figure 5 depicts the Raman spectrum of the sample with J = 1 A/dm<sup>2</sup>, d.c.=50%. It's notable that most of the measured spots exhibited the characteristic G-band associated with graphene nanoplatelets.



**Figure 5:** Raman spectrum of Ni-Matrix nanocomposite coatings using Graphene: : DC: Direct Current, PC: Pulse Current with  $\nu = 10\text{Hz}$  and duty cycles of 20% and 50%.

For the samples produced by direct current, the surface presents agglomerations and almost none of the measured spots present the G-band associated to graphene nano-platelets.

### Conclusions

For nickel nanocomposite coatings with graphene nanoplates, the presence of the anionic SDS surfactant in the electrolytic bath led to a more uniform distribution of Graphene in the Ni matrix, compared to cationic or non-ionic surfactants. Investigation into the parameters governing the applied current revealed that pulse current, particularly when employed with a duty cycle of 50%, produced coatings with high carbon content and excellent microhardness values.

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