

Effect of Graphene Incorporation on Erosion-Corrosion Performance of Electroless Ni-P Coatings

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ABSTRACT

Erosion-corrosion is a dominant degradation in plant assets and influenced by various attributes of erodent such as velocity, corrosivity, shape, size, density, angle of attack and hardness, etc. Although Ni-P electroless coatings are famous for anti-corrosion and anti-wear properties; there is still room to improve these attributes that will pave its way towards various industrial applications. In this research work, various compositions of ternary Ni-P-graphene coatings were produced via the addition of different concentrations of graphene (30 mg/L, 60 mg/L, and 100 mg/L) into the electroless plating bath. Microstructural characterizations of coatings were conducted along with surface topography. Erosion-corrosion behaviors of the produced coatings were characterized using slurry pot erosion-corrosion testing employing AFS 50-70 Silica sand and 3.5 wt.% NaCl solution. The dominant wear mechanisms were identified using the SEM examination of surfaces after the erosion-corrosion test. High hardness, impermeability, and electrical properties of graphene concurrently improved the pure erosion, and erosion-corrosion attributes.

Key words: Ni-P coatings, graphene, erosion-corrosion, synergistic effects

INTRODUCTION

Erosion and erosion-corrosion are among the numerous degradations for piping and equipment in the hydrocarbon processing facilities.¹⁻² Erosion-corrosion is also known for versatility of failure modes (pitting, micro-cutting, under-deposit corrosion, gouging etc.).^{1,3} During erosion-corrosion, material loss rate is significantly higher than the sum of material loss rate due to pure erosion and pure corrosion acting separately. In certain instances, the shape and morphology of damaged surface and scale debris reveal tell-tale of damage mechanisms.⁴ Some applications of carbon steel in the

petroleum industry (e.g. alkaline sour water systems) require certain flow rate (10 fps – 20 fps) to manage cooling water corrosion as well as fouling deposits in case of heat exchangers. ¹ Whereas higher velocities beyond 20 fps can jeopardize the integrity of carbon steel due to erosion and/ or erosion-corrosion damages.

Process equipment for oil sands processing (centrifuges, vessels etc.) and transportation (pumps, pipelines, valves etc.) are highly prone to erosion-corrosion and erosion damages. Erosion-corrosion and pure erosion are driven by number of factors that include (but not limited to) particle attributes (velocity, angle of attack, size, shape, weight/ density, hardness), material attributes (hardness, ductility, corrosion resistance, geometry) as well as service conditions (chemistry, corrosivity, temperature etc.). In the recent years, there have been considerable efforts to combat this degradation with detailed focus on each mitigation facet e.g., use of higher Mo containing alloys to resist organic acid corrosion or keeping higher corrosion allowances by allowing more wall thickness in design phase. Material up-gradations and surface modifications through re-designing are other possible solution to ensure the integrity of process equipment which in turn are accompanied by significantly higher capital costs. Coatings are among effective measures that can protect the material's surfaces by preventing the exposure to the environment and service conditions. Electroless Ni-P coatings are known for their better adhesion properties, and the absence of grain boundary (from amorphousness) is the reason for excellent corrosion resistance of Ni-P coatings. Moreover, the absence of solvents in electroless Ni-P coatings is another advantageous aspect that eliminates workmanship efforts in terms of drying and curing, etc. The downside of Ni-P coating is the potential wear under erosive environments which undoubtedly needs further attention of researchers.

This research work addresses the abovesaid imitation by adding graphene to synthesize ternary Ni-P coating followed by the investigation of erosion, erosion-corrosion rates and governing mechanisms. Graphene, which is one atom thick allotrope of carbon, was used as a candidate for ternary coatings due to its attributes namely higher hardness, lower density, higher impermeability as well as hydrophobic nature. ⁵⁻⁷ Also, there have been numerous composite coatings reported so far that are developed by enrichment of graphene and its derivatives with improved corrosion and wear/ erosion behaviors. ⁸⁻¹² Tamilarasan and Rana have recently reported significant improvement in EC and tribological behaviors, respectively due to enrichment of graphene in the Ni-P coating matrix. ¹³⁻¹⁴ In this research study, four different coatings were synthesized in electroless plating bath by addition of three different concentrations of graphene (i.e., 30mg/L, 60 mg/L, and 100 mg/L). SPEC (slurry pot erosion corrosion) tests were conducted on polished surface (600 Grit) of AISI 1018 steel, as plated Ni-P coatings, and graphene enhanced Ni-P coatings. SPEC tests were conducted for 6 hr using erodent solution comprising AFS 50-70 silica sand and 3.5 wt.% NaCl solutions, under a velocity of 2-3 ms⁻¹. All samples were subjected to pure erosion, erosion-corrosion, pure corrosion as well as erosion enhanced corrosion to characterize the failure modes and understand the synergistic effects. The governing wear mechanisms and failure modes were identified via microscopic examination of surfaces after SPEC tests.

EXPERIMENTAL WORKS

2.1 Coating samples preparation

Mono-layered graphene suspension (1 wt. %) was purchased from US Research Nano-Materials Inc. Raman testing was conducted to cross-verify number of layers as well as to confirm the presence of graphene or graphite. Low carbon steel (AISI 1018) was used as substrate that was cut to a rectangular shape (18 mm x 10 mm x 6mm) followed by machining to smoothen the sharp corners.

The surface of the specimen was grinded using SiC paper followed by polishing to 1 μm finish using mon-crystal diamond solution.

In the meanwhile, Ni-P plating solutions were prepared in two separate baths (1.0 L each) by mixing Industrial grade Ni-P plating solutions (Make: Nichem[†]) in the deionized water. Ni-P plating solution comprised nickel sulfate as a salt and sodium hypophosphite as a reducing agent. 3 ml of graphene suspension was added to one plating bath to achieve a graphene concentration of 30 mg/L. Both plating baths were maintained at a temperature of 85 - 90 °C under continuous stirring. The polished substrates were submerged in an alkaline bath for 5 minutes to remove off any grease or debris from the surface followed by rinsing with de-ionized water. The cleaned samples were then etched with 15 wt. % H_2SO_4 for 10 seconds to remove any passive scale. The specimens were immediately rinsed with de-ionized water followed by immersion in the Ni-P plating bath. After 30 minutes of pre-coating, samples were taken out of Ni-P plating bath and submerged in the other plating bath that was added with graphene. Coating was carried out in graphene added plating bath for 3 hours, that yielded graphene added Ni-P coating namely Ni-P-30mg G. Same steps were repeated by preparing graphene added plating baths by adding 6 ml and 10 ml of suspension to formulate Ni-P-60mg G and Ni-P-100mg G coatings, respectively. The pH of plating baths was maintained in the optimum range of 4.6 – 4.8 via frequent dripping of ammonium hydroxide in the plating bath.^{5,14} Arrangement of electroless plating bath is shown in Figure 1. Coatings cross-section were prepared by cutting using CBN blades followed by mounting in epoxy resin and polishing.

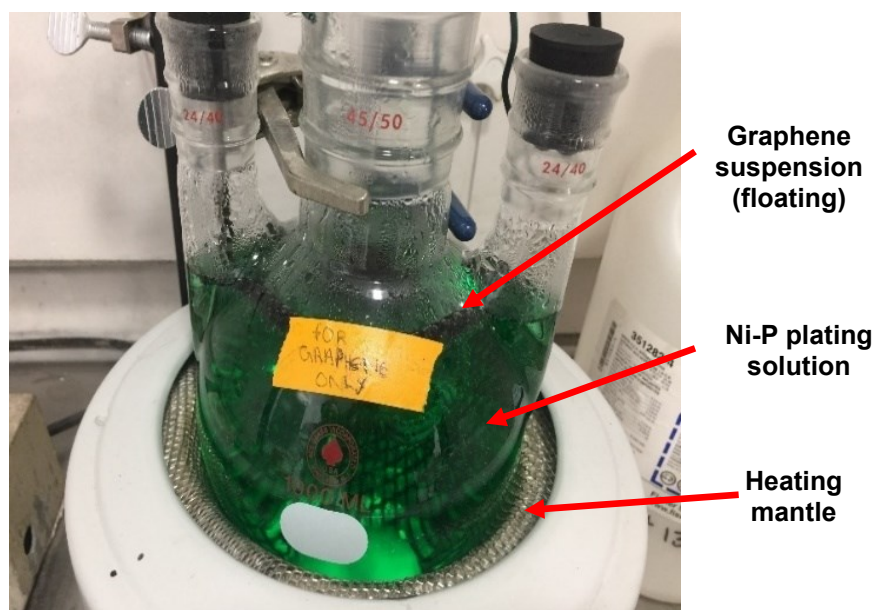


Figure 1: Electroless plating bath arrangement

2.2 Surface and microstructural characterization of coatings

SEM/EDS examinations were conducted at cross-sections of coatings to visualize the distribution of graphene platelets as well as to quantify constituent elements in the coating matrix. Topographic analyses were conducted on the surface of as-coated samples using a high precision laser confocal microscope. Images were captured under magnification of 200x followed by stitching, 3D topographic imaging and surface roughness measurements. Whereas micro-hardness checks were conducted on cross sections by Vickers hardness tester using diamond pyramid indenter (under 100 g load) as per guidelines of applicable standard.¹⁵ Indent sizes (i.e., diagonal lengths) were measured using microscope followed by the calculation of Vickers hardness using below equation (1):

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$$H_v = 1.8544 \times \frac{P}{d^2} \quad (1)$$

Whereas d = average diagonal for indent (μm)

P = applied load (i.e., 0.98 N)

2.3 Slurry pot erosion-corrosion testing

Prior to slurry pot erosion-corrosion (SPEC) testing, edges of all samples were ground smooth perpendicular to each other to remove any chamfers from the corners. An electrical contact was attached to each sample for electrochemical assessment and control. All faces of samples (except the test surface) were covered with epoxy. The samples were mounted in SPEC tester as per schematic arrangement shown in Figure 2. The slurry pot erosion-corrosion unit consists of 4-litre glass vessel to hold the slurry, a neoprene-lined impeller that is rotated to impel the slurry against the test surfaces, a heating/cooling system (chiller) and a three-electrode cell with a Gamry PC4/750 potentiostat to allow for electrochemical assessment as well as cathodic protection control. Electrochemical tests were conducted in-situ (working electrode) vs. SCE (saturated calomel electrode) and Pt as counter electrode. Slurry pot erosion-corrosion test parameters are summarized in Table 1.

Table 1: Slurry pot erosion-corrosion (SPEC) test parameters

Slurry composition	AFS 50-70 silica sand (35 wt.%) + NaCl (3.5 wt. %)
Impeller speed	900 rpm
Slurry temperature	45 °C
Test duration	6 hr
Erodent impact velocity at 900 rpm	0.26 - 2.21 ms^{-1}

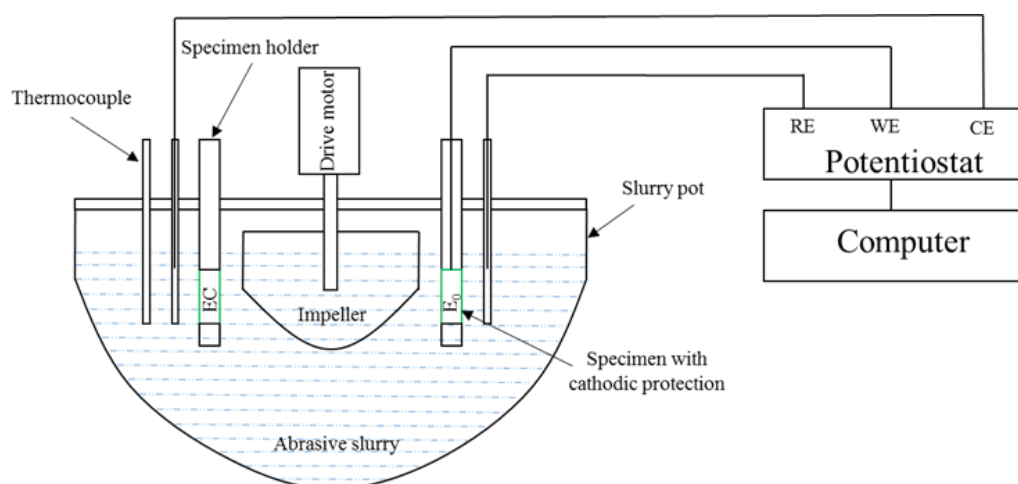


Figure 2: Schematic arrangement for slurry pot erosion-corrosion tester

Size of AFS 50-70 silica sand particles as measured from SEM was 212-300 μm . The erodent particle-target impact velocities (tabulated above) were determined by briefly exposing polished soft

metal (pure Cu, annealed at 450°C) specimens in SPEC test to dilute slurry of spherical particles (60-70 glass bead). The normal particle impact velocity was then calculated from the depth of the resulting craters.¹⁶⁻¹⁷ Experimentally derived normal impact velocity during SPEC test is 0.26-2.21 ms⁻¹.¹⁸ Erosion-corrosion test was conducted by exposing the sample to the slurry as per above tabulated parameters. Pure erosion test was conducted using similar arrangement, but samples were cathodically protected to resist the corrosion. On the other hand, pure corrosion tests under flowing condition were conducted using 3.5 wt.% NaCl solution (without the abrasive particles), while AFS 50-70 silica was subsequently added to the electrolyte to account for the effect of erosion-enhanced corrosion. The material loss rates were measured by weighing samples on a high precision micro-balance (having accuracy of 0.01 mg) before and after SPEC test. Material loss rates were calculated and reported in cm³/h/cm² using following equation:

$$\text{Material loss rate (K)} = \frac{\text{Mass loss}}{\text{Density} \times \text{Surface area} \times \text{Test duration}} \quad (2)$$

The erosion-corrosion synergy values were determined according to the criteria of applicable ASTM standard, where the total material loss under erosion-corrosion conditions (K_{ec}), is related to the synergistic component (K_s) as:¹⁹

$$K_{ec} = K_{eo} + K_{co} + K_s \quad (3)$$

Where, K_{ec} = total material loss rate due to erosion-corrosion

K_{eo} = material loss due to pure erosion

K_{co} = material loss rate only due to pure corrosion

and K_s = synergistic contribution

Furthermore, total material loss rate (K_{ec}) can also be divided into the following components:

$$K_{ec} = (K_{eo} + \Delta K_e) + (K_{co} + \Delta K_c) = K_e + K_c \quad (4)$$

Whereas K_e = total erosion rate, K_c = total corrosion rate, ΔK_e = corrosion-enhanced erosion and ΔK_c = erosion-enhanced corrosion. Equation (4) provides more detailed information on key contributors to E-C loss. Synergistic contribution (K_s) and its various components can be calculated/expressed by combining equation (3) and (4) as:

$$K_s = \Delta K_e + \Delta K_c = K_{ec} - (K_{eo} + K_{co}) \quad (5)$$

$$\Delta K_c = K_c - K_{co} \quad (6)$$

$$\Delta K_e = K_s - \Delta K_c \quad (7)$$

RESULTS & DISCUSSION

Figure 3 (a) shows typical cross section of coating revealing a uniform deposition on the substrate. Line scan EDS analysis on Ni-P-30mg G coating's cross-section in Figure 3 (b) reveals graphene presence throughout the thickness of coating. SEM micrograph and area EDS scan for the coating are shown in Figure 3 (c) and 3 (d), respectively. Evidently, graphene nano-platelets achieved uniform distribution throughout the coating matrix without any noticeable agglomeration or clustering. Whereas all coating compositions achieved similar deposition rates of 16-20 µm/hr.