

Study of Solid Particle Erosion & Electrochemical Behaviors of Graphene Enriched Ni-P Coatings

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ABSTRACT

Surface erosion and erosion-corrosion are among major degradations in the hydrocarbon industries and are driven by the attributes of process streams and materials of construction for process equipment(s)/ piping. Despite significant corrosion and wear resistance, the performance of Ni-P coatings is inhibited due to fracture and cracking by the impact of erosive particles in the process streams. This study involves the preparation of graphene incorporated Ni-P coatings by adding various concentrations of graphene in Ni-P plating bath under stirring conditions. The solid particle erosion behavior of Ni-P coatings was studied under two different erodent velocities of 35 ms⁻¹ and 52 ms⁻¹ and three different incident angles as 45°, 60°, and 90°. Indent size and morphologies were characterized using the microscopic examination. The electrochemical behavior of ternary Ni-P coatings was studied using Potentiodynamic Polarization testing against 3.5 wt.% NaCl solution. Graphene addition improved the electrochemical and wear behavior by the reduction of porosities and improved hardness, respectively.

Key words: Ni-P coatings, graphene, solid particle erosion, corrosion behavior

INTRODUCTION

Pipelines, process equipment for hydrocarbon production and refining industries are prone to numerous degradation mechanisms arising from service conditions namely temperature, pressure, corrosivity, flow velocity etc. Among numerous damage mechanisms, erosion damage from high velocity fluids and abrasive particles is quite prevalent. Various types of erosion damage(s) reported so far are liquid droplet erosion, vapor bubble erosion, cavitation, abrasive particle erosion, and erosion-corrosion etc. ¹ The extent of erosion is influenced by many attributes of erodent such as shape (i.e., asperity), hardness, density, impingement angle etc. Moreover, the process conditions and substrate properties (hardness,

toughness, surface smoothness) also determine susceptibility to erosion damages. Certain applications in the refining industry require the fluidization of powdered catalysts via steam or air pressure which renders the material of process equipment (reactor, regenerator etc.) susceptible to erosion. Furthermore, the turbulent zones in piping systems (e.g., bends, reducers etc.) have high propensity of erosion damage. Erosion damage from steam impingement in boiler's piping system leads to a more complex and irreparable corrosion namely boiler water condensate corrosion.² The corrosion products in the form of debris and chips can sometimes act as erodent thereby aggravating the material loss from erosion-corrosion damage. In addition, higher velocities of the process streams may damage the protective films, thereby accelerating the metal loss rate.

Industry specifications have recommended certain velocity limits to establish IOW (integrity operating windows) for minimizing the erosion risk(s).³⁻⁴ For instance, gas velocities should be $< 70 \text{ ms}^{-1}$ to avoid the erosion damage in gas condensate system(s).³ Nature of service also governs both upper and lower velocity limits of materials. For example, there are recommended velocities for managing the risk of amine corrosion in carbon steel. It should be $1\text{-}2 \text{ ms}^{-1}$ and 6 ms^{-1} for rich amine and lean amine, respectively. Despite erosion damage from the impact of high velocity fluids, risk of fouling (likely at lower velocities) touts for increasing the velocities of the fluid streams especially in the heat exchanger applications. Liquid velocities below 1 ms^{-1} result in fouling and sedimentation in fresh and brackish water applications.²

Coatings are among the economical measures to extend the life span of materials via improvement of surface attributes. The limitation of coatings is the degradation from erosion, cracking, corrosion, radiations etc. Graphene is a sp^2 hybridized allotrope of carbon which is known for high hardness, very high surface area to weight ratio, high strength along with remarkable optical and electrical properties. The application of graphene and graphene-derivatives (Graphene oxide, reduced graphene oxide etc.) is trending in protective coatings due to impermeability, barrier properties and high charge carrier mobility of graphene that allows the alternate path to seeping electrolyte and flowing electrons, thereby improving the corrosion resistance of coating matrix and underlying substrate.⁵⁻⁸ A previous study by Dailin et. al. has investigated the impact of CNT (Carbon nanotubes) on the erosion and corrosion behavior of Zinc rich epoxy coatings.⁹ Ni-P coatings are known for their excellent corrosion resistance for many decades but their widespread usage in the hydrocarbon application is mainly challenged by their lower toughness that leads to cracking and subsequent wear under various static and dynamic loads. The ternary coating's synthesis using graphene and Ni-P have not been extensively studied. Previous studies by Rana et. al. and Tamilarasan et. al. investigated the pure erosion and erosion-corrosion behavior of Ni-P-Graphene coatings in slurry pot conditions.^{7,10} Another study by Rana et. al. has shown the sliding wear and tribological behaviors of Ni-P-Graphene coatings.¹¹ Solid particle erosion behavior (i.e., under dry conditions) of this coating system has not been fully explored. Solid particle erosion (SPE) is meant to understand the erosion behavior of coatings in the presence of dry, stand-alone particles. This research study investigated the solid particle erosion behavior of as plated Ni-P coating and graphene added Ni-P coatings. Ni-P and graphene added Ni-P coatings were prepared on AISI 1018 steel substrate in electroless plating bath. SPE was conducted using two different impingement velocities (i.e. 35 ms^{-1} and 52 ms^{-1}) and three different impingement angles as 45° , 60° and 90° , respectively. The craters were analyzed via microscope to understand the failure modes.

EXPERIMENTAL WORKS

Single layer graphene suspension (1 wt.%) was purchased followed by Raman spectroscopic checks to confirm the presence of graphene as well as number of layers within graphene sample. 1.0 liter of electroless plating solution was prepared using industrial grade Ni-P chemical and de-ionized water. Graphene suspension was added in plating baths in the concentrations of 3 ml/L, 6 ml/L and 10 ml/L to achieve graphene concentrations of 30mg/L, 60mg/L and 100 mg/L, respectively in the electroless plating bath. Another plating bath of Ni-P solution was prepared without graphene suspension. Temperature of each plating bath was kept at 90°C whereas pH of solution was maintained between 4.6 and 4.8. Polished coupons ($1 \mu\text{m}$ finish) of AISI 1018 steel were immersed in an alkaline solution for degreasing and cleaning followed by etching with 15 wt.% sulfuric acid for a duration of 10 seconds. The

etched specimens were submerged in the Ni-P plating bath for pre-coating for a duration of 30 minutes. After pre-coating, the samples were removed from Ni-P plating bath and immersed in the graphene added Ni-P plating baths for a duration of 3 hrs. under a stirring speed of 100 rpm. Coating samples were designated as Ni-P-30mg G, Ni-P-60mg G and Ni-P-100mg G w.r.t corresponding concentration of graphene in plating bath which were 30mg/ L, 60 mg/ L and 100 mg/L, respectively. After coating, the samples were removed from plating baths followed by rinsing, drying, and storage in desiccator. The cross-sections of coated specimens were prepared by high precision cutting employing CBN blade, followed by mounting in resin and polishing.

2.1 Characterization works

SEM & EDS (energy dispersive spectroscopy) were conducted on cross-section using Hitachi S-4700 to account for coating thickness and concentration (in wt. %) for constituent elements (Ni, P, and graphene) in the coating matrix, respectively. Line-scan analyses were also conducted via EDS to visualize the presence of graphene alongside the entire thickness of coating. Vickers hardness checks were conducted on coating cross-sections via diamond indenter (under 100 g load). Diagonal size of indent i.e. d (in μm) was measured from microscopic examination followed by calculations of Vickers hardness (H_v) as: ¹²

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

Whereas d = average of diagonal length for pyramid-shaped indent
 P = applied load in Newtons (0.98 N)

SPE (solid particle erosion) tests were conducted on polished coating surfaces (finish 1 μm) using erodent balls (diameter: 1 mm) made from WC. Schematic arrangement for solid particle erosion testing apparatus is shown in Figure 1. Referring Figure 1, the erodent particle was placed in the particle housing where it was fed with pressurized air under two different pressures (30 psi and 60 psi). Prior to SPE checks on the candidate samples, particle velocities under two air pressures were measured by using two equi-spaced (30 mm) photo-interrupters placed at the end of barrel. The photo interrupters were aimed to measure the time particle took to travel pre-determined distance (i.e. 0.03 m) between two photo interrupters. The particle velocity (in ms^{-1}) was calculated using Eq. (2) as: ¹³

$$\text{Velocity} = \frac{0.03}{\text{time}} \quad (2)$$

The velocity measurements were repeated multiple times followed by averaging. The average velocities were found as 35 ms^{-1} and 52 ms^{-1} under air pressures of 30 psi and 60 psi, respectively. Sample with polished surface were mounted on the vice adjusted at an angle of 45°. The WC erodent ball particle was placed in the particle housing and was supplied with air under a pressure of 30 psi through adjusting the pressure regulator and opening of solenoid valve. Same steps were repeated for each candidate sample under both pressures of 30 psi & 60 psi and by altering the impact angles to 60° and 90° by adjusting the vice position. The craters produced over the surface of each sample under two different velocities and three different impact angles were examined via optical microscope.

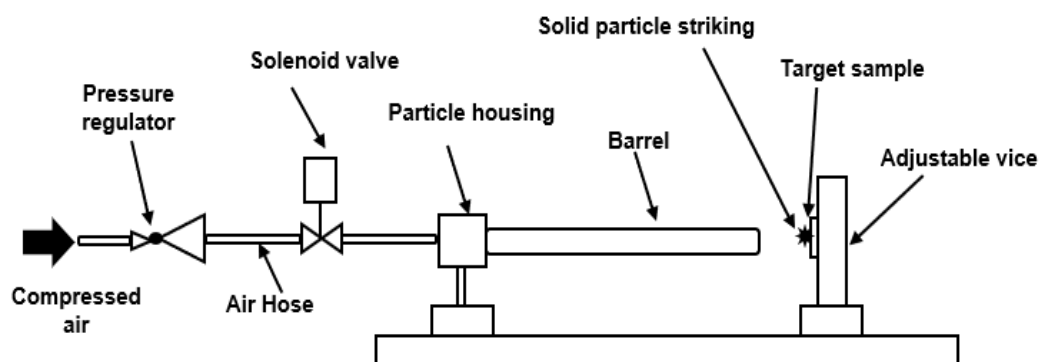


Figure 1: Schematic arrangement for solid particle erosion test setup

2.2 Potentiodynamic polarization test

Coatings were characterized for their electrochemical behavior using potentiodynamic polarization test employing potentiostat as per guidelines of governing standard.¹⁴ Surface of candidate samples were polished followed by cleaning with acetone and deionized water to remove any surface containments. Each sample (as working electrode) was placed in a corrosion cell installed with SCE (saturated calomel electrode) as reference and Pt as counter electrode. Testing was carried out using electrolyte (3.5 wt.% NaCl solution) and below tabulated parameters.

Table 1: Parameters for static corrosion test

Test temperature	Room temperature
OCP duration	90 minutes
Scan rate	0.167 mV/sec
Cathodic polarization volts	- 0.25 V (below OCP)
Anodic polarization volts	+ 0.25 V (above OCP)

Densities of composite coating matrix (ρ) were calculated using fractional wt. % and density of each constituent element. Whereas equivalent weights (EW) were calculated using below equation:¹⁵

$$EW = \frac{1}{\left\{\frac{f_1 \times e_1}{Z_1}\right\} + \left\{\frac{f_2 \times e_2}{Z_2}\right\} + \left\{\frac{f_3 \times e_3}{Z_3}\right\}} \quad (3)$$

Where f = Weight fraction of constituent element (wt. % from EDS results)

e = Ion exchanging capacity of constituent element (e.g. 2 for Ni, 5 for P)

Z = Atomic weight of constituent element

Corrosion current i.e., I_{corr} was calculated from the slope of Tafel plots, while corrosion current density i_{corr} (i.e., current density of opposing reactions at reversible potential) was calculated using following equation:¹⁵

$$i_{corr} = \frac{I_{corr}}{Area} \quad (4)$$

CR (corrosion rate) was calculated according to below equation:¹⁵

$$CR = \frac{0.00327 \times i_{corr} \times EW}{\rho} \quad (5)$$

$$\% \text{ increase in corrosion resistance} = \frac{CR \text{ of NiP} - CR \text{ of graphene added NiP}}{CR \text{ of NiP}} \quad (6)$$

RESULTS & DISCUSSION

3.1 Graphene characterization

Raman spectrum of graphene sample is shown in Figure 2. Raman spectrum indicates three different peaks namely D, G & 2D peaks that reveal defects in graphene, presence of graphene and number of layers, respectively from the shape, intensity and wave number.¹⁶ The wave number of D-peak is 1348 cm^{-1} , whereas intensity of D-peak is 10,769 a.u. On the other hand, wave numbers for G-peak and 2D peaks were found as 1595 cm^{-1} and 2681.46 cm^{-1} respectively. Here wave number of D-peak is closer to that reported by the supplier i.e. 1352.7 cm^{-1} .¹⁷ D-peak intensity is quite dominant which indicates that sample contains graphene (rather graphite) with some defects.^{16,18-19} Defects in the graphene are inherent from synthesis method whereas defect-free graphene is generally synthesized via CVD (chemical vapor deposition). Wavenumber for G-peak is 1595 cm^{-1} which approximates to the reported wavenumber for GO (graphene oxide) i.e. 1590 cm^{-1} as well as wavenumber reported by manufacturer.¹⁷ Furthermore, the overall shape of spectrum is consistent to the spectrum reported for RGO (reduced graphene oxide).²⁰ Therefore, it can be deduced that this graphene sample under study was produced by the reduction of GO. Finally, wave number of 2D peak i.e. 2681 cm^{-1} is in proximity to that for single layered graphene i.e. 2680 cm^{-1} .²⁰⁻²¹

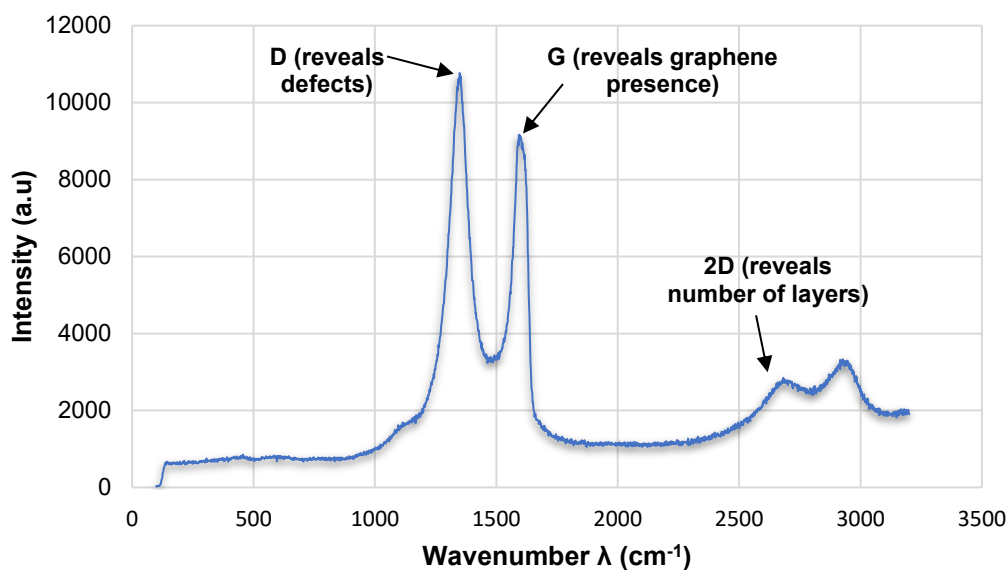


Figure 2: Raman spectrum for graphene specimen

The presence of graphene had negligible influence on the deposition kinetics as the deposition rates for all coatings (i.e. with and without graphene addition) were found as $18\text{--}20 \mu\text{m/hr}$ which is consistent with previous study.²² Figure 3 (a) and Figure 3 (b) show the micrographs revealing cross-sections of Ni-P-30mg G coating. Line scan EDS of Ni-P-30mg G coating in Figure 3 (b) reveals the through-thickness incorporation of graphene (as blue line). Whereas Figure 3 (d) shows EDS map of Figure 3 (c). It is