International Journal of Scientific Research in Modern Science and Technology
ISSN: 2583 -7605 (Online)
© IJSRMST | Vol. 4 | Issue 3 | March 2025
Available online at: https://ijsrmst.com/
DOI: https://doi.org/10.59828/ijsrmst.v4i3.302

Structure Characterization and Parametric Evaluation of Low Phosphorus-Nickel Alloy Electroless Deposits

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ABSTRACT

Nanocrystalline nickel-phosphorus (Ni-P) deposits were synthesized by electroless deposition on mild steel. The samples were degreased and pre-treated before starting the deposition process. The Ni-P was deposited on the samples by placing the mild steel substrate in the neutral plating bath at 85-90^{0}C for 90 minutes. The surface morphology of the coating was analyzed using Scanning Electron Microscopy. Energy Dispersive X-ray Spectroscopy was used to estimate nickel and phosphorus in the foil. Analysis of thickness and hardness was performed manually using a formula and by Vickers microhardness tester, respectively. Differential Scanning Calorimetry (DSC) was used to determine the temperature for phase transformation. A wear test was done to determine the effect of coating on the Coefficient of Friction (COF) of the substrate. The thickness of the Ni-P deposits was in the range of 31.71 µm to 34.88 µm when plating was carried out for 90 minutes. It was found that the synthesized samples had a nanocrystalline structure because of low phosphorus content and the hardness of the sample was increased by 22.21% with heat treatment. During phase transformation, the nanocrystalline structures were converted into crystalline form. The COF was decreased for the electroless Ni-P-coated mild steel in comparison to the uncoated mild steel substrate. However, the heat treatment improved the wear property (20 to 10 microns) and the COF (0.19 to 0.12) in the coated substrate.

Keywords: *Electroless Nickel-Phosphorus (Ni-P) Coatings, Surface Morphology, Chemical Characterization, Coating Thickness, Wear Resistance*

INTRODUCTION

Plating is the coating of a thin layer of metal on a conductive or non-conductive base metal surface. This process is very important in modern industrial applications. The electroplating method metal can do it is coated on another metal by electrolysis using a power source such as a battery or rectifier, to improve the metal's corrosion resistance, appearance, special surface properties, and mechanical properties. On the other hand, electroless plating uses a chemical deposition process - instead of an external electrical current - to achieve the desired result of metal deposition. Generally, acidic and alkaline baths have been used for depositing alloys. Electroless bath solution comprises of various components and each of these performs an essential role in the coating process**.** In electroless nickel (EN) deposition, the reducing agent (Hypophosphite ions ($H_2PO_2^-$)) and the nickel source (nickel ions (Ni^{2+})) are dissolved into a plating bath. The reduction reaction occurs in an active surface where hypophosphite oxidizes into orthophosphate reducing the Ni^{2+} into atomic nickel. During the reaction, some reducer agent is also reduced. If the reducer is hypophosphite the plated nickel film contains some phosphorus [1, 2].

Nowadays, the electroless-Ni (EN) method is no longer a single type of coating but an entire family of coatings [3]. Some of the important characteristics of these coatings are superior corrosion and wear resistance, excellent uniformity, a wide range of thicknesses, mechanical and physical properties, good solderability, and surface lubricity [4]. In addition, EN coatings can be applied on different substrates (conductive and nonconductive) since no external current is applied to the component [5-7]. The diversity of the EN method has resulted in a wide range of its applications in various industries.

In the electroless plating method, metallic ions are catalytically reduced by a reducing agent present in an aqueous solution, and the metal is subsequently deposed without the use of electrical energy. The reaction is autocatalytic, and as it starts, the presence of catalyst metal keeps the reaction going. The range of thickness of the electroless deposited metal coating will be from a few microns to 100 microns. Various metals can be plated using the electroless plating method, but EN deposits exhibit excellent corrosion and wear resistance. In Ni-P electroless process, the reducing agent in the bath is oxidized and reduced Ni^{2+} ions are deposited on the substrate surface. The use of hydrated sodium hypophosphite during the electroless process is for ease and better process control. It helps to reduce metal ions to a metal state on the activated surface and produces uniform deposits over all surfaces. The phosphorus content of EN deposits controls their microstructure and properties [8,9]. The phosphorus content results in the self-lubrication of the EN deposits. The low phosphorus content increases deposited hardness but reduces corrosion resistance. EN coating deposition initiated on the substrate proceeds in three dimensions during the plating process. The three-dimensional growth of the deposit depends on the rate of plating on each part of the substrate surface.

Several characteristics of EN plating have resulted in the increasing popularity of this technique. Unlike the electroplating technique, it can be carried out without any excessive build-up on edges and projections on a variety of substrates (metallic and non-metallic) to which the solution has access. Its unique property is to coat flat as well as blind surfaces evenly, i.e., through this technique the intricate part geometries can be plated uniformly.

Here, it is important to state that the deposition rate in the horizontal direction is faster than vertical direction, and this makes the coating pore-free. Its less porous property makes it better corrosion-resistant than electroplates. It requires a very simple arrangement of apparatus (oil bath, beakers, Potential of Hydrogen (pH) meter and thermometer along with mechanical stirrer) as compared to electroplating (i.e., power supplies, electrical contacts, and other apparatuses). By this technique, non-conducting substances such as glass, plastic, etc., can be coated easily. Several combinations of electroless deposits have extraordinary or even unique magnetic properties. Besides, electroless Ni-P coatings have wide industrial applications owing to their excellent mechanical, physical, and electrical properties [10].

Nanostructured materials are valuable in various technological sectors, including electronics, aerospace, catalysis, ceramics, magnetic data storage, and biomedicine. For example, nanostructured titanium oxide can be fashioned into nanotubes/nanowires and thin films at near-ambient conditions, potentially broadening the scope of titania applications [11]. This includes uses in nanoelectronics, chemical sensing, solar cells, large-area windows and displays, and invisible security circuits, as well as the incorporation of biomolecules and temperature-sensitive moieties.

Hence, the present study aimed to synthesize low phosphorus nanocrystalline nickel alloy deposits on mild steel (0.16-0.29% carbon by weight) / stainless steel (SS) (minimum of 10.5% chromium content by mass and a maximum of 1.2% carbon by mass) using EN plating method, conduct morphological characterization and evaluate the effect of heat treatment on the Phase transformation of the Ni-P alloy deposits in addition to using appropriate methods for measuring parameters of wear loss and COF of electroless Ni-P coated mild steel substrate.

MATERIALS AND METHODS

A. Synthesis of Electroless Ni-P alloy Deposits

The synthesis of low phosphorus nickel deposits was conducted as per the procedure mentioned by Wolfgang [12]:

I. **Preparation of Plating (Neutral Hypophosphite) Bath:**

Preparation of 250 ml of plating bath solution was done by taking 187.5 ml of water, 12.5 ml of Autotech Eleven Low Phosphorus 350A solution, and 50 ml of Autotech Eleven Low Phosphorus 350B solution in a clean beaker of 400 ml using measuring cylinder. pH meter was used to set the pH of the plating bath solution to 7.3 by adding 50% Ammonia (a Base) to increase the pH of the solution.

II. **Pretreatment of the substrate**:

A mild steel specimen was used as the substrate. The specimen was cleaned using Tri-Chloro-Ethylene (TCE) to remove the grease layer which is usually applied on it for corrosion resistance. In the case of a corroded specimen, buffing is done to remove the rust and to smoothen or polish the surface. The specimen was cleaned or ultrasonicated using Acetone to remove the minute grease particles from the surface of the specimen. The specimen was subjected to a cathodic current strike to remove impurities from the surface of the substrate. For the cathodic strike, the mild steel substrate was connected to the cathode, and another SS plate was connected to the anode of the Direct Current (DC) power supply. Both the specimens were dipped in 10% Sodium Hydroxide (NaOH) solution and the current was set to 1.2 A and was passed for a minute. It was then rinsed with tap and distilled water. The specimen was dipped in 50% Sulfuric Acid (H_2SO_4) for 30 seconds. It was rinsed with tap and distilled water.

III. **Plating on the substrate:**

The plating bath prepared was heated in the water bath to attain a temperature in the range 85-90^{0}C. After the temperature was attained, the pretreated specimen was dipped in the plating bath for 90 minutes. The thickness of the coating depends on the time for plating. For an hour, the deposition is usually around 10 to 25 micrometers. The specimen was taken out from the plating bath and dried using SalonDry Compact 1000W Drier.

B. Studies on surface morphological characteristics of the Ni-P deposits using Scanning Electron Microscope (SEM)

I. **Principle**: SEM is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The interaction between electrons and atoms in the sample produces various signals that contain information about the composition of the sample and the surface topography.

II. **Metallographic examination of deposits without heat treatment:** The sample with Ni-P deposit was subjected to metallographic sectioning in which a small part of the sample was cut using a cutting machine.

After sectioning, the cut sample was ultrasonicated in Acetone for 10 minutes. After ultrasonicating, the sample was placed in SEM and the microstructure of the sample was observed using SmartSEM software.

C. Chemical characterization of Ni-P coatings using Energy-dispersive X-ray spectroscopy (EDX analysis)

I. **Principle:** EDX analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. It depends on the interaction of the X-ray excitation source and a sample. Its characterization capabilities are largely due to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum.

II. **EDX analysis of the Ni-P deposit without heat treatment:** The sample with Ni-P deposit was subjected to metallographic sectioning in which a small part of the sample was cut using a cutting machine. After sectioning, the cut sample was ultrasonicated in Acetone for 10 minutes. After ultrasonicating, the sample was placed in SEM and the EDX analysis was conducted using SmartSEM software to get the composition percentage of nickel and phosphorus content in the coatings.

D. Evaluation of thickness and hardness of the electroless Ni-P coatings

I. **Calculations of the thickness of Ni-P Coating without heat treatment using formula:**

(a) **Principle:** The formula for calculating thickness is:

$$Thickness, t = \frac{(w_2 - w_1) \times 10^4}{\rho_{Ni} \times A} \ in\ \mu m$$

Where,

w_1 is the initial weight of the specimen in g

w_2 is the final weight of the specimen in g

ρ_{Ni} is the density of nickel in g/cm^3 which is equal to 7.9 g/cm^3

A is the Surface Area of the specimen or the total area to be coated in cm^2

(b) **Procedure:** Before plating, a mild steel specimen was cut in the required shape to get the required surface area. The surface area and initial weight of the specimen was noted down as an observation. The final weight of the plated specimen was noted down to find the thickness of the coating using the formula.

II. **Calculations of the hardness of Electroless Ni-P deposit as plated and after heat treatment, using Vickers microhardness tester:**

(a) **Principle:** The basic principle of the Vickers microhardness tester is that it can be used for all metals and has one of the widest scales among hardness tests. The Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH) is the unit of hardness given by the test. The hardness number is estimated by the load over the surface area of indentation and not the area normal to the force which is therefore not the pressure. Vickers hardness test is used because the indenter used is small in size, which reduces the risk of possible damage to the test material. The indenter can be used for any kind of material, irrespective of its hardness. The resulting calculations are independent of the size of the indenter. It has a very wide scale, compared to other hardness tests a single test force is applied. The Vickers hardness number (VHN) is calculated using the following formulas:

$$A = \frac{d^2}{2\sin(136°/2)}$$

where *A* is the surface area of the resulting indentation in square millimeters and *d* is the average length of the diagonal left by the indenter in millimeters.

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2}\ [kgf/mm^2]$$

where F is the load in kgf, d is in millimeters and HV is the VHN in kgf/mm^2.

(b) Procedure for heat treatment: A paste of Zinc Oxide (ZnO) and Boric Acid (BH_3O_3) was made by taking 1 g of ZnO and 0.25 g of BH_3O_3 and mixing with a mixture with a small amount of water (ZnO and BH_3O_3 because of their high thermal resistance). The paste was applied on the Ni-P plated specimen and dried using a SalonDry Compact 1000W Drier. The specimen was then wrapped around with nickel foil and was kept in a crucible. The crucible was then kept in the furnace and the temperature of the furnace was adjusted from room temperature to 400^0C. The sample was heated in the furnace for 1 hour after the temperature inside the furnace attained 400^0C. The furnace was then switched off and the sample remained in the furnace until the temperature of the furnace attained room temperature. The sample was taken out of the furnace and washed with tap and distilled water. The sample was cleaned with acetone using cotton to remove the past of ZnO and BH_3O_3. The sample was ultrasonicated using acetone for 10 minutes to remove the paste completely.

(c) Preparation of resin mold:

(i) Preparation of copper coating: Before making a resin mold, the electroless-deposited specimen was first coated using copper or nickel which serve as protective cladding or mounting means in that they minimize any rounding-off of the edge of the electroless deposit in the subsequent polishing stages, such protective layer should be around 20 µm. Ni-P plated samples (with and without heat treatment) were subjected to ultrasonication for 10 minutes. The ultrasonicated samples were given a cathodic current for some time to remove the oil. The samples were then dipped in 50% H_2SO_4 for some time and then placed in a copper sulphate solution that contains two copper plates that are connected to the positive terminal and the samples to the negative terminal of the DC power supply for 30 minutes for the current set to 0.5 or 0.7 A. Both the samples (with and without heat treatment) were taken out from the solution and the copper coatings were deposited on them.

(ii) Preparation of resin mold: After the samples were copper plated, the samples were subjected to sectioning using a cutting machine in which a part of both the samples were cut. The Struers CitoPress-15 molding machine was switched on. The upper anvil was removed, and the lower anvil of the machine was raised by pressing the up button. The Anti-stick powder was applied on both the upper and lower anvil to remove the mold easily after completion. The samples were placed in the center of the lower anvil. The lower anvil of the molding machine was lowered by pressing the down button. 15 ml of Condufast powder was slowly applied using a funnel in the molding machine. The quantity of the powder depends on the height of the sample placed. Clarofast or copper powder can also be used to get a transparent or reddish-brown resin mold. The upper anvil of the molding machine was closed, and the machine was started by pressing the start button. After 5 minutes, the upper anvil was removed, and the lower anvil was raised by pressing the up button to get the resin mold containing the cross sections of both heat treated and plated sample.

(iii) Polishing of the resin mold: Polishing of the resin mold is done to obtain a smooth and shiny surface by rubbing it or using a chemical action, leaving a surface with a significant specular reflection. The face of the mold which provides the cross-section of the two samples was polished by placing it on the grit/polish papers that were placed on the grinding/polishing machine for a time depending on the

E.

speed of rotation. The polish papers were placed in the polishing machine in increasing order of their grit numbers: 100P, 180P, 400P, 800P, 1000P, 1200P, 2400P, 4000P. After polishing the mold with 4000P polish paper, the face of the mold was placed on the paste made by mixing 1-micron Alumina powder with a small amount of water applied on the velvet cloth which was placed on the grinding machine. The mold was placed until the smooth and shiny image of the cross-section of the two samples was obtained (Figures 1 and 2). The polished face of the mold was placed on the anvil of the Vickers microhardness tester. The Ni-P coatings of both the samples were located and were subjected to indentations by the Vickers Diamond indenter of the Vickers microhardness tester by adjusting the load to 0.05 kgf or 50 gf and the dwell time to 10 seconds. Using the software, the VHN for Ni-P coatings of both the samples was noted down for 5 readings. The average of the 5 readings was taken to get the VHN for both samples.

Figure 1: The polished resin mold

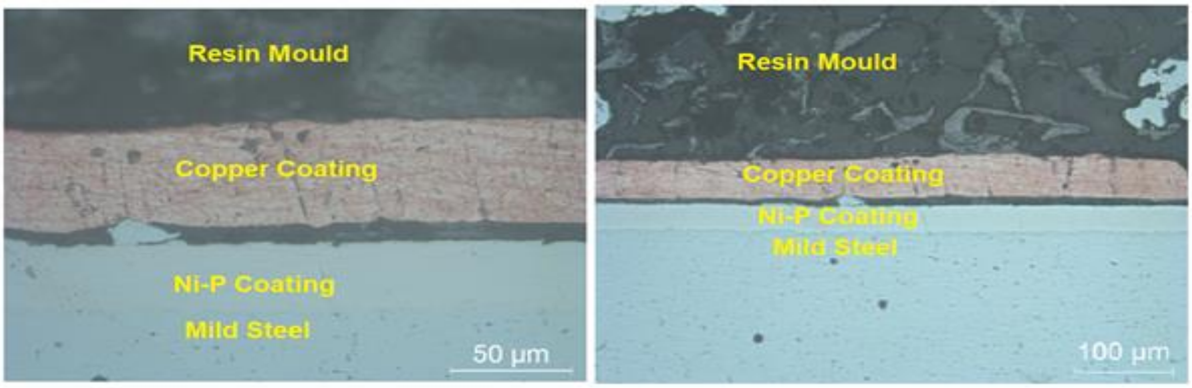

Figure 2: Layers of resin mold in polished sample as observed under LEICA DM IRM (Inverted Research Metallurgical Microscope at 50 µm and 100 µm)

(d) **Measuring hardness and thickness using Vickers microhardness tester:** The polished face of the mold was placed on the anvil of the Vickers microhardness tester. The Ni-P coatings of both the samples were located and were subjected to indentations by the Vickers Diamond indenter of the Vickers microhardness tester by adjusting the load to 0.05 kg or 50 gf and the dwell time to 10 seconds. Using the software, the VHN for Ni-P coatings of both the samples was noted down for 5 readings. The average of the 5 readings was taken to get the VHN for both samples.

E. Characterization of the phase transformation changes in Ni-P alloy deposits due to heat treatment as a function of temperature using DSC

I. **Principle**: DSC independently measures the rate of heat flow to a sample and a standard that are at the same temperature. Differential thermal analysis is the measurement of the difference in temperature between a sample and a reference as heat is applied to the system. This method is sensitive to endothermic and exothermic processes including phase transitions, dehydration, decomposition, redox, or solid-state reactions. DSC is a very useful method to study the physical and thermal properties of heat-dependent reactions such as precipitation processes.

II. **Preparation of Ni-P foil:**

(a) **Preparation of Plating (Neutral Hypophosphite) Bath:** Preparation of 2 liters of plating bath solution was done by taking 1500 ml of water, 100 ml of Autotech Eleven Low Phosphorus 350A solution and 400 ml of Autotech Eleven Low Phosphorus 350B solution in a clean beaker using measuring cylinder. Using pH meter, set the pH of the plating bath solution to 7.3 by adding 50% Ammonia (a Base) to increase the pH of the solution.

(b) **Pretreatment of the substrate**: A SS specimen with lacquer on one surface was used as the substrate. The specimen was cleaned using acetone by wiping with cloth. The specimen was washed using detergent and rinsed with distilled water. The specimen was subjected to cathodic cleaning to remove impurities from the surface of the substrate. For cathodic cleaning, the SS substrate was connected to the cathode, and another SS plate was connected to the anode of the DC power supply. Both the specimens were dipped in 10% NaOH solution and the current was set to 2.4 A and was continued for a minute. It was then rinsed with tap and distilled water, respectively. The specimen was dipped in 50% H_2SO_4 for 30 seconds. It was rinsed with tap and distilled water. The specimen was dipped in the plating bath solution and was again connected to the cathode and a pure nickel specimen to the anode of the DC power supply to give a nickel current strike. The current was set to 0.5 A and the process continued for 2 minutes to get a thin layer of Ni-P deposited on the specimen.

(c) **Plating on the substrate:** The plating bath prepared was heated in the water bath to attain a temperature in the range of 85-90^{0}C. After the temperature was attained, the pretreated specimen was dipped in the plating bath for 2 hours. The specimen was taken out from the plating bath and dried using a SalonDry Compact 1000W Drier. The Ni-P layer was removed from the surface opposite to the surface coated with lacquer using a blade to obtain Ni-P foil.

III. **Phase transformation study:** To study the effect of heat treatment on the phase transformation of Ni-P foil, a DSC study was conducted. The DSC scans were initiated at 49 °C and completed at 573 °C. The output was in milliwatts (mW). The net heat flow to the reference pan (i.e., relative to the sample) was obtained by subtracting the baseline data from the heat flow data of the test samples and recorded as a function of temperature. The baseline data were obtained by scanning an empty reference pan through the same temperature range as the test samples. The temperature of transformation from amorphous (nanocrystalline) to crystalline phases was analyzed. At least two samples of each material were scanned to ensure reproducibility. The results obtained were found to be reproducible.

F. Measurement of wear loss and COF of electroless Ni-P coated mild steel substrate and study the effect of heat treatment

I. **Principle:** A wear test is performed to evaluate the wear property of a material to determine whether the material is adequate for a specific wear application. The damaging, gradual removal or deformation of material at solid surfaces is known as wear. There are two causes of wear: mechanical (e.g., erosion) or chemical (e.g., corrosion) [13]. The value that shows the relationship between the force of friction between two objects and the normal reaction between the objects that are involved is known as the COF. The COF can be determined using the following formula:

$$\mu = \frac{F_f}{F_n}$$

where F_f is the frictional force, μ is the COF, and F_n is the normal force.

II. Procedure for the Reciprocating Wear test:

A buffed (uncorroded) mild steel specimen was marked 60 mm x 20 mm using a Vernier height gauge with a V-block as a support. The 60 mm x 20 mm mild steel specimen was cut using Bharat Machinery and Spares Shearing Machine into three specimens of size 20 mm x 20 mm. Ni-P plating was done on two specimens in the same method as in Part A of the experimental procedures. After plating the two samples, one of the two samples was heat treated by applying a paste of ZnO and BH_3O_3, which was made by taking 1 g of ZnO and 0.25 g of BH_3O_3 and mixing it with a small amount of water because ZnO and BH_3O_3 have high thermal resistance. The paste was applied on the Ni-P plated specimen and dried using a SalonDry Compact 1000W Drier. The specimen was then wrapped around with nickel foil and was kept in a crucible. The crucible was then kept in the furnace and the temperature of the furnace was adjusted from room temperature to 400^0C. The sample was heated in the furnace for 1 hour after the temperature inside the furnace attained 400^0C. The furnace was then switched off and the sample remained in the furnace until the temperature of the furnace attained room temperature. The sample was taken out of the furnace and washed with tap and distilled water. The sample was cleaned with acetone using cotton to remove the past of ZnO and BH_3O_3. The sample was ultrasonicated using acetone for 10 minutes in order to remove the paste completely. Then all three samples: uncoated, coated, and heat-treated samples were tested one by one using Tribo corrosion Tester (Reciprocating type: CM-9084). Alumina Ball was used as the indenter, and it was fixed in the machine. A load of 5 N (two 2 N and one 1 N) was placed on the machine. Using Winducom software, the stroke length was set to 10 mm, Speed to 100 rpm, Frequency to 2.35 Hz, and Test Duration to 20 minutes.

III. The total sliding distance covered in the reciprocating wear test is calculated as follows:

Stroke Length = 10 mm

Distance covered in one rotation of crank = 2 x 10 = 20mm

Speed of crank = 100 rpm

∴ Distance covered in one minute = 20 x 100 = 2000 mm

∴Distance covered in 20 minutes = 20 x 2000 = 40000 mm = 40 m

Hence, the total sliding distance is 40 m.

After clicking on Start, the Reciprocating Wear Test started on the sample which continued for 20 minutes (Figure 3).

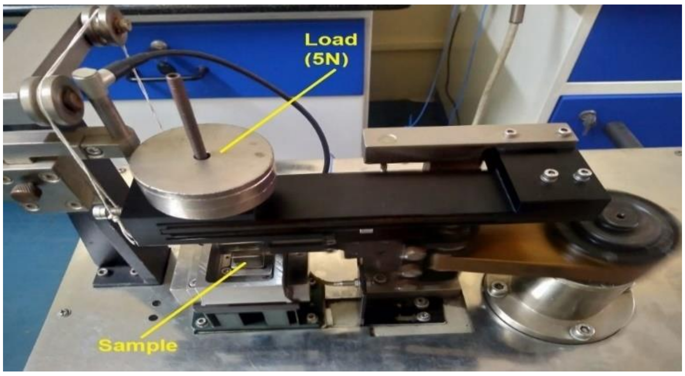

Figure 3: Reciprocating Wear Test on the Sample

After 20 minutes, the test stopped automatically and the mean readings of the COF and wear loss in microns were noted down and the graph of wear loss versus Time and COF versus Time was extracted using the software.

RESULTS AND DISCUSSIONS

A. Synthesis of Electroless Ni-P alloy Deposits

As-plated low phosphorus EN alloy deposited specimen along with mild steel specimen are shown in the figure 4. To find out the coating thickness, the specimen was weighed before and after the electroless Ni-P deposition, and the obtained results are given in Table 1.

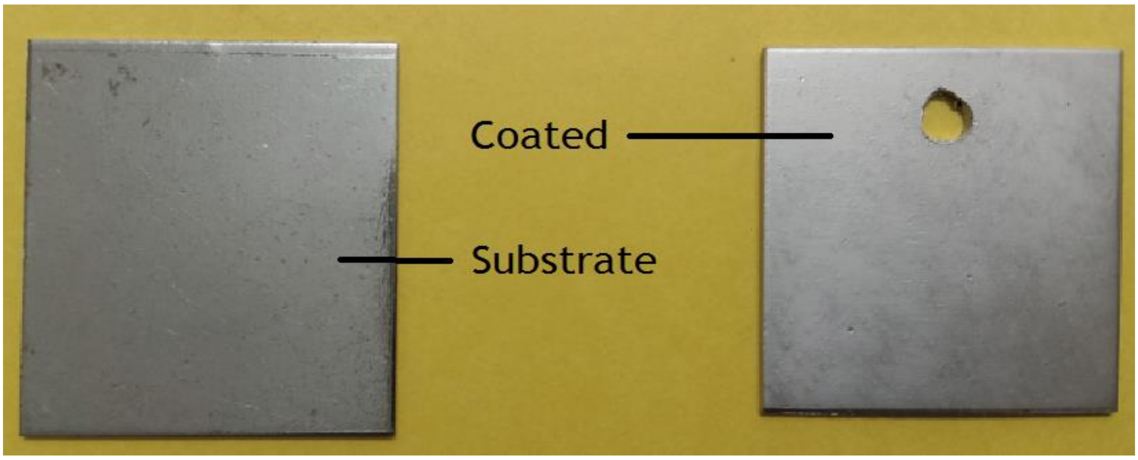

Figure 4: Ni-P Coated and uncoated Ni-P mild steel specimen

Table 1: Increased weight of the samples after deposition

Observation	Initial weight of specimen, W1 (g)	Plating bath volume (ml)	Time for the reaction (minutes)	Final weight of the specimen, W2 (g)
Sample 1	3.23	400	90	3.51
Sample 2	2.88	400	90	3.14
Sample 3	2.96	400	90	3.21
Sample 4	4.03	400	90	4.38
Sample 5	3.60	400	90	3.95

The deposition of the Ni-P layer on mild steel substrate by the electroless process as obtained in this study showed that the bath conditions and composition were important for the process, and this is a well-established method that has been proposed by many researchers. The SEM photos showed the presence of cauliflower-like microstructures which could be crystalline (β) because of the low content of phosphorus (1-5%) in EN coating as revealed by EDX analysis.

B. Studies on characterization of surface morphological profile of the Ni-P deposits using SEM

The surface morphologies of electroless deposited Ni–P coatings were investigated using SEM (Figures 5 and 6). From the surface image (Figure 6) it is evident that these coatings exhibited nodular morphology.

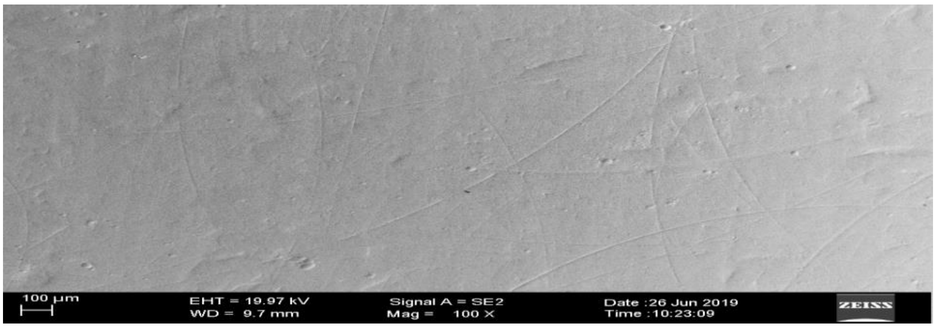

Figure 5: Surface SEM photos of low phosphorus electroless deposited nickel alloy (100 x magnification)

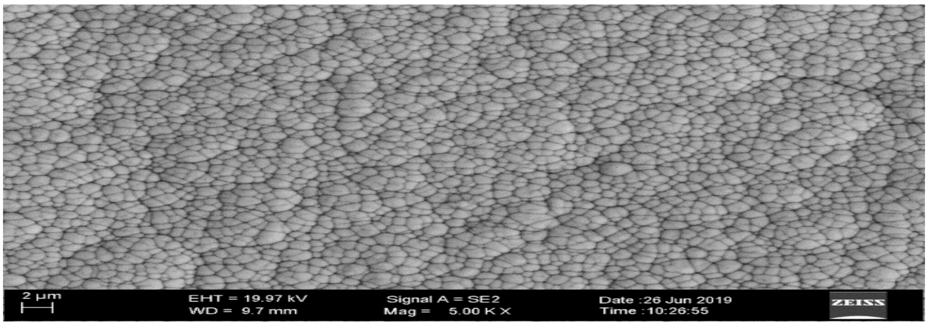

Figure 6: Surface SEM photos of low phosphorus electroless deposited nickel alloy (500 x magnification)

In the as-deposited state, all the coatings exhibited nanocrystalline structure [12]. The microstructure of the electroless Ni–P deposits changes from having a mixture of nanocrystalline and amorphous phases to a fully amorphous phase when the phosphorus content increases. This reveals that the phosphorus content of the Ni-P deposits play a vital role in the phase transformation and controls their microstructures.

C. Chemical characterization of Ni-P coatings using EDX analysis

The elemental composition of the coatings was determined by EDX Analysis and is given in Table 2 (K refers to K-shell of an atom, which is the innermost electron shell, where X-ray emissions occur when electrons are ejected or displaced during an EDX analysis). From Table 2 the amount of phosphorus co-deposited during electroless plating is about 5 wt.% indicating low phosphorus deposit [12].

Table 2: Elemental composition of Electroless Ni-P deposit as revealed by EDX Analysis

Element	**Weight%**	**Atomic%**
P K	5.23	9.48
Ni K	94.77	90.52
Totals	100.00	

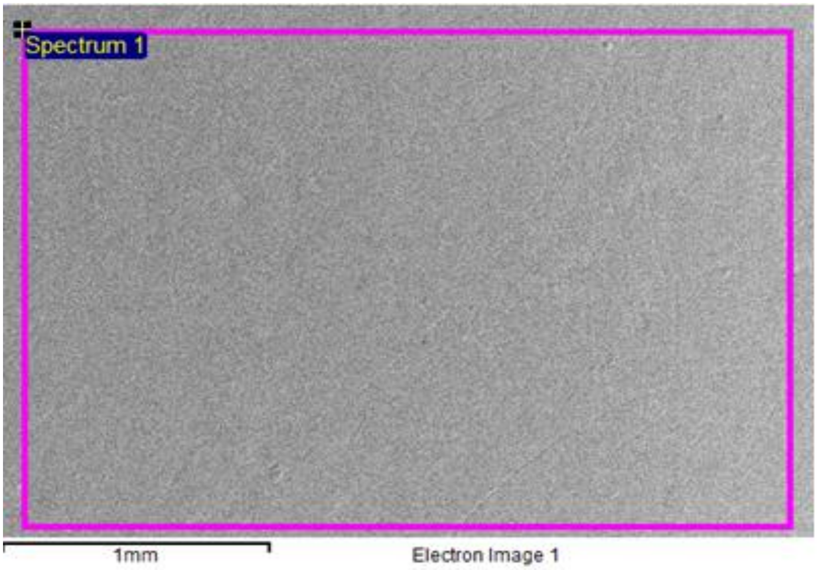

Figure 7: Area of EDX Analysis

The results obtained in Table 2 were measured from this area (Figure 7) using SmartSEM software.

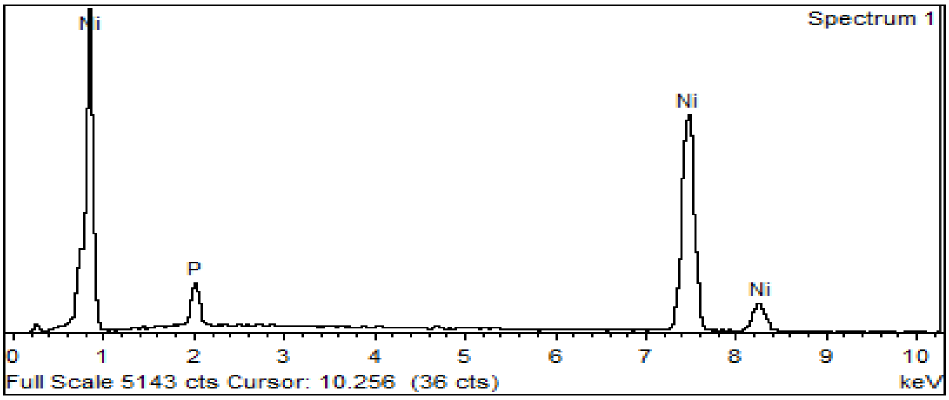

Figure 8: EDX spectrum of electroless Ni-P (Counts/sec vs Energy Graph)

The Counts vs Energy Graph or EDX Spectrum (Figure 8) from EDX Analysis gives us the chemical composition of the Ni-P coating. The presence of phosphorus along with nickel peaks shown in the EDX spectrum confirmed the electroless Ni-P alloy.

D. Evaluation of coating thickness and microhardness of Ni-P coatings

I. **Evaluation of coating thickness of Ni-P deposits:** As shown in Table 3, our results showed that when plating was carried for 90 minutes, the thickness of 5 samples of electroless Ni-P deposits showed that the values ranged from 31.71 to 34.88 µm when calculated manually using the formula.

Table 3: Thickness values as observed in five samples of electroless Ni-P alloy deposits calculated using formula

Observation	Initial weight of specimen W1 (g)	Plating bath volume (ml)	Time for the reaction (minutes)	Final weight of the specimen, W2 (g)	Surface area (initial) cm^2	Thickness (t) (W2-W1)x10^4 7.9 x Surface area (µm / 90 min)
Sample 1	3.23	400	90	3.51	2x2.15x2.4=10.6	34.32
Sample 2	2.88	400	90	3.14	2x2.15x2.4=10.32	31.83
Sample 3	2.96	400	90	3.21	2x2.2x2,2=9.68	32.42
Sample 4	4.03	400	90	4.38	2x2.8x2.55=14.28	31.71

Sample 5	3.60	400	90	3.95	2x2.5x2.55=12.75	34.88

The thickness values when calculated manually using the formula showed variation due to errors in measuring weight, surface area, pH of the plating bath, bath temperature, nickel and reducing agent concentration, presence of metallic impurities, etc. it is well-established that the thickness of coating increases with increase in time plating and decrease in deposition rate.

II. **Effect of heat treatment on the hardness of Ni-P deposit as observed using Vickers microhardness tester:** Results of the present study (Table 4) showed that heat treatment increased hardness (803.2 VHN or 803.2 HV with a 0.05 kg load) of the Ni-P alloy deposits (Sample 1) in comparison to as plated sample (Sample 3) (657.2 VHN or 657.2 HV with a 0.05 kg load).

Table 4: Effect of heat treatment on the hardness of electroless Ni-P alloy deposits using Vickers microhardness Tester (50 gf)

Parameters	**Readings of Sample (3) as plated**					**Average**
Hardness (VHN)	615	644	644	675	708	657.2
	Readings of the sample (1) after heat treatment					
Hardness (VHN)	782	846	782	824	782	803.2

Imprint of indentations made on as-plated and heat treated Ni-P coating cross-sectional specimens is shown in Figures 9 & 10, respectively. It is evident that the indentation size is smaller in heat treated deposit compared to as-plated indicating the higher hardness exhibited by the heat treated specimen. It is well-known that the as-plated Ni-P coatings are either nanocrystalline or amorphous (metastable) depending on the phosphorus content co-deposited in Ni-P matrix. Upon heat treatment at 400ºC/1 hour of the as-plated specimens results in crystalline structure consisting of crystalline nickel and nickel phosphide (Ni_3P). Hence, the presence hard Ni_3P exhibits the higher hardness compared to as-plated coatings.

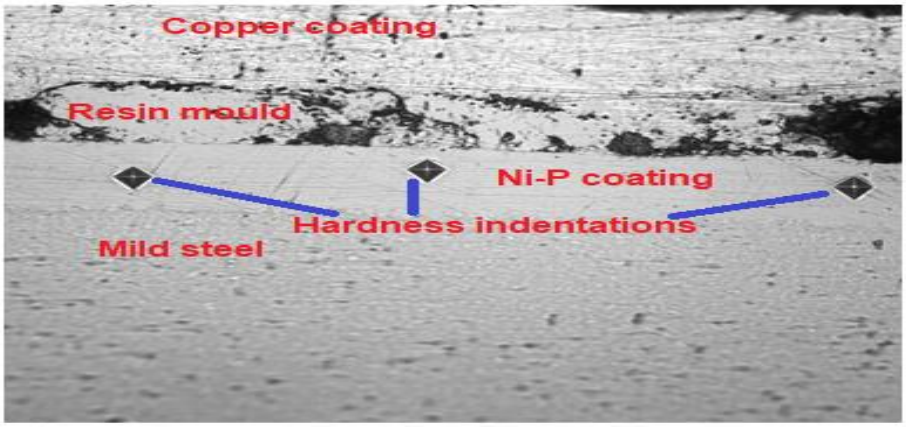

Figure 9 : Electroless Ni-P coating as deposited after hardness testing

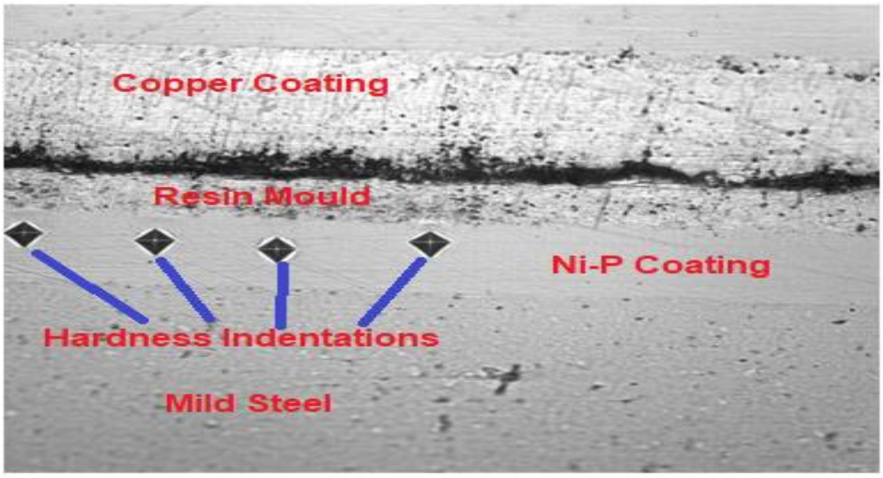

Figure 10: Heat treated (400^oC for 1 hour) Electroless Ni-P coating after hardness testing

The changes observed in hardness during heat treatment at 400^oC might be due to the precipitation of various Ni$_3$P particles [14]. which may produce changes at the microstructural level. However, the formation of lattice defects and the coarsening of Ni$_3$P particles may be responsible for the observed decrease in hardness beyond 400°C [1]. On the other hand, the precipitation of fine nickel crystallites and hard intermetallic Ni-P particles during the crystallization of the amorphous phase may increase hardness as observed in heat-treated samples [15 -18].

E. Phase transformation behavior of Ni-P deposits

The effect of heat treatment on phase transformation changes in the microstructure of EN coatings was studied using the DSC method. Figure 11 shows the DSC thermographs of as-plated EN coatings. The phase transformation from nano-crystalline-to-crystalline form was shown by two exothermic peaks, one at 340 ± 10^0C and the other peak at 400 ± 10^0C. A previous study has revealed the involvement of more than one intermediate phase in the conversion of amorphous Ni-P solution to crystalline form. Our observation that phase transformation occurs up to 404.67 is inconsistent with the results of a previous study [13]. which reported that the transformation temperature of EN coatings was independent of the phosphorus content. However, our observations are in agreement with the finding of a previous report [18] that transformation temperature peaks obtained during a DSC scan, depend on both chemical composition and phosphorus level of the EN solutions. We also observed two exothermic peaks, one at 346.03^0C corresponding to the crystalline of Face Centered Cubic (FCC) nickel and the other peak at 404.67^0C corresponding to the nucleation of Body Centered Tetragonal (BCT) Ni$_3$P [19].

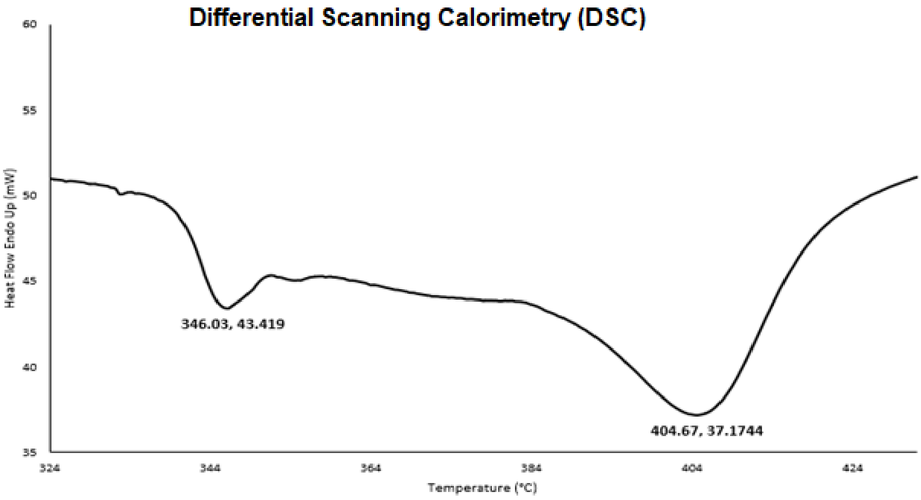

Figure 11: DSC thermograph of electroless Ni-P coating

F. Measurement of wear loss and COF of electroless Ni-P coated mild steel substrate and study the effect of heat treatment

As shown in Figures 12-14 and Table 5, it is evident that the wear loss and COF values were higher for mild steel substrate in comparison to Ni-P plated samples. Heat-treated Ni-P specimens exhibited reduced wear loss and COF compared to both as-plated Ni-P and mild steel specimens.

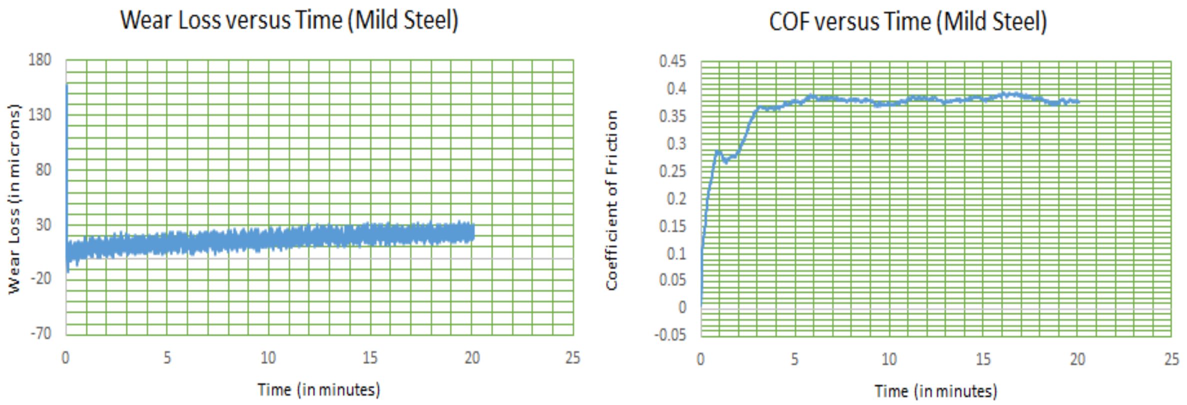

Figure 12: Wear loss and COF versus time for mild steel

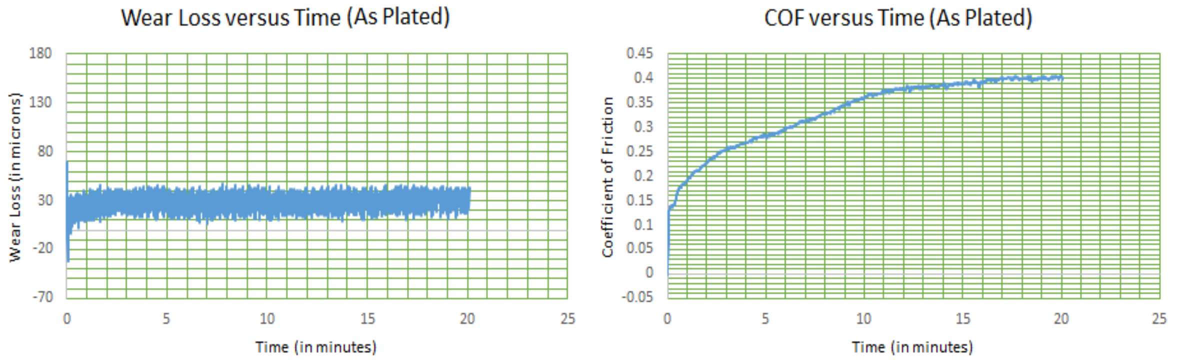

Figure 13 : Wear loss and COF versus time for Ni-P coated mild steel

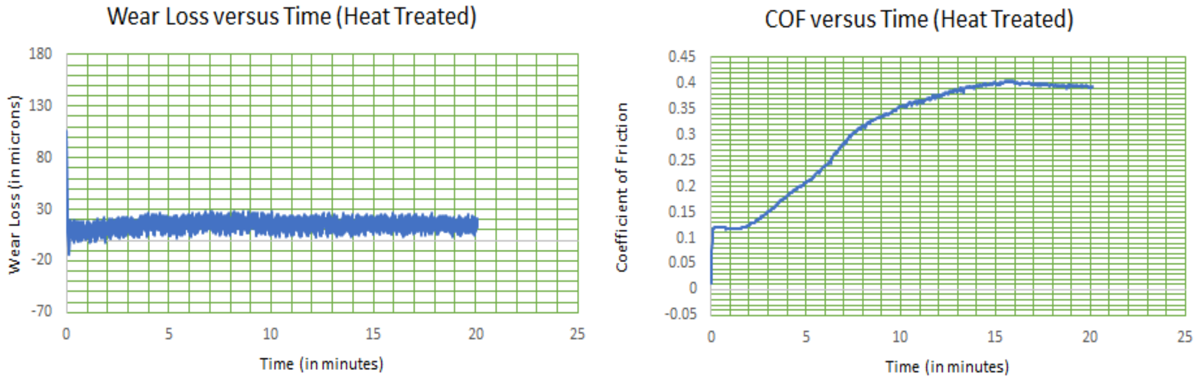

Figure 14: Wear loss and COF versus time for heat treated Ni-P coated mild steel

Table 5: Results of wear test of the samples for the load of 5 N

Sample	Mean Wear loss (microns)	Mean COF
Base sample	25	0.25
As-plated sample	20	0.19
Heat-treated (400°C for 1 hour) sample	10	0.12

The data in Table 5 showed that mean wear loss values obtained from Winducom 2008 software were 25 (±3) microns for mild steel substrate, 20 (±6) microns for electroless low phosphorus Ni-P plated Mild steel, and reduced to 10 (±4) microns for heat treated electroless low phosphorus Ni-P plated Mild steel. Mean values for COF were 0.25, 0.19, and 0.12 for mild steel, plated mild steel, and heat treated (400ºC for 1 hour) electroless low phosphorus Ni-P plated Mild steel respectively. Wear is damage to a solid surface and involves the progressive loss of material. The observed improvement in wear properties in terms of wear loss and mean COF of the substrate due to coating and heat treatment is by the previous report [20] and may prove useful in industrial applications.

CONCLUSION

From the results of the present project work, we conclude that by controlling proper bath conditions, temperature, pH, as well as bath compositions, the synthesis of nanocrystalline Ni-P deposits having low phosphorus content, was possible by electroless process. The nanocrystalline cauliflower-like microstructure of electroless Ni-P deposits as observed in SEM analysis could be due to the low phosphorus status of the coatings as evidenced by elemental evaluation through EDX analysis. Thickness values of the Ni-P deposits ranged from 31.71 to 38.88 µm/90 minutes. Heat treatment of the electroless Ni-P deposit up to 400°C for one hour enhanced the hardness of the deposit by 22.21%. Two exothermic peaks were revealed by DSC analysis at 346.03°C and 404.67°C corresponding to the phase transformation temperature from nanocrystalline to a crystalline form of Ni-P respectively. Wear test when applied to electroless Ni-P coated mild steel substrate showed that the wear resistance of the mild steel substrate increased in electroless low phosphorus Ni-P coating and increased furthermore after heat treating the coated substrate. The COF also reduced from 0.19 to 0.12 in heat treated sample.

ACKNOWLEDGEMENT

The authors sincerely acknowledge the Surface Engineering Division, Council of Scientific and Industrial Research (CSIR) – National Aerospace Laboratories (NAL), Bangalore, Karnataka, India, for providing the opportunity and necessary resources to conduct this research. Special thanks to Dr. J. N. Balaraju for his guidance and support throughout the study.

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Cite this Article

Parankush Koul and J. N. Balaraju, **"Structure Characterization and Parametric Evaluation of Low Phosphorus-Nickel Alloy Electroless Deposits"**, ***International Journal of Scientific Research in Modern Science and Technology*** *(IJSRMST), ISSN: 2583-7605 (Online), Volume 4, Issue3, pp. 01-17, March 2025.*

Journal URL: *https://ijsrmst.com/*

DOI: *https://doi.org/10.59828/ijsrmst.v4i3.302*.