Wear Characteristic of NiP/Bio Material Coating Using Electroless Method

[1] Jagatheeswaran. M. S, [2] Naveen. K , [3] Manipandi. A. S, [4] Suheal. A
[1,2,3,4] Department of Mechanical Engineering,
Panimalar Engineering College
Chennai, India

***Abstract*— The study on the use of hyroxyapatite particles as a reinforcement with electroless NiP matrix has been successfully implemented on the mild steel substrate.The morphological test is conducted using Scanning electron microscopy (SEM). Wear test is carried out using Pin-on-disc apparatus. The NiP/hyroxyapatite (1.0 g/l) composite coating presents a low friction force with minimum mass loss when compared to NiP coated and uncoated specimens. The higher weight percentage of Hyroxyapatite particles reinforcement has shown a decrease in the wear resistance, which is due to the bath instability.**

Key words: Hyroxyapatite, Electroless,Wear, Friction

I. INTRODUCTION

Tribology is the study of science and engineering of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear. The tribological interactions of a solid surface's exposed face with interfacing materials and environment may result in loss of material from the surface. The process leading to loss of material is known as "wear". Major types of wear include abrasion, friction (adhesion and cohesion), erosion, and corrosion. Wear can be minimized by modifying the surface properties of the solids by one or more "surface engineering" processes (also called surface finishing) or by use of lubricants (for frictional or adhesive wear). To date Electroless nickel plating is the flourishing technology in surface coating. Electroless nickel plating (EN) is an auto-catalytic chemical technique used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid work piece, such as metal or plastic. Unlike electroplating, it is not necessary to pass an electric current through the solution to form a deposit. This plating technique is to prevent corrosion and wear. EN techniques can also be used to manufacture composite coatings by suspending powder in the bath. Mild steel is the most common form of steel because its price is relatively low while it provides material properties that are acceptable for many applications. However, mild steel is limited in tribology applications due to its poor friction and wear properties. To overcome this, NiP coating is commercially followed on the mild steel for surface property improvement.So this project is focused on study the effect of hybrid reinforcement (Hyroxyapatite) on NiP coating under dry sliding conditions.

These different properties are brought about by varying the different alloying elements mixed with iron in the production of steel. Alloying elements even carbon act as hardening agents, preventing dislocations from occurring inside the iron crystals which allow the lattice layers to slide past each other. This is the reason why steel is harder than iron, and why mild steel which contains a lower amount of carbon than other steels is a more ductile variety of the material.

Aigui Tang et al. (2015) studied that using the electrophoretic–electrochemical deposition method can remarkably increase the particle content in the composite coatings. The results of friction and wear tests showed that the Ni–PTFE composite coating exhibited the lowest friction and the Ni–nano-Al_2O_3 composite coating possessed the best wear resistance.Cheng Yanhai1 et al. (2014) found that the electroless Ni-Cu-P-PTFE deposits with different PTFE contents were prepared on mild steel (1015) substrate surface by adjusting different process parameters and investigated, such as surface morphology, phase composition and micro hardness, as well as adhesion strength and friction properties. Haleh Jafari, et al. (2016) studied the effects of silver nanoparticles (AgNPs) at 1% wt. and different concentrations of hyroxyapatite nanofiber(CHNF) (1.5–6% wt.) on tensile properties, water vapor permeability (WVP), solubility, swelling, colorproperties and morphological characteristics of chitosan nanocomposite films were studied.Iman R. et al. (2011) investigated the effects of the addition of three types of surfactants (cationic, anionic, non-ionic) at different concentrations in the plating bath on the deposition rate, PTFE content and surface morphology of electroless NiP/PTFE composite coatings. The effects of the surfactant type and concentration on the corrosion properties of NiP/PTFE coatings were also studied. The corrosion resistance was increased by the incorporation of PTFE particles into the NiP matrix. The level of improvement depended largely on the type and concentration of the applied surfactants. Jagatheeshwaran M.S., et al. (2016). as a preliminary work, revealed the advantages of using sea shell particles (SSPs) as reinforcement on the tribological performance of the NiP coating on En8 steel substrate. Jagatheeshwaran M.S., et al. (2016) revealed the importance of calcinations of sea shell particles before their use to reinforce NiP composite coatings to achieve low friction and wear resistant property. NiP/calcinated sea shell particles (Cal.SSP) and NiP/non calcinated sea shell particles (SSP) composite coatings have been fabricated on En8 steel using electroless process with various dispersions of SSP and Cal.SSP. Rodriguez.V et al. (2016). PEEK from the tribological view point presents relatively high friction forces during un lubricated sliding but the wear rates are remarkably low.De Silva R.T. et al. (2016) studied that Chitosan nanocomposite thin films were fabricated by incorporating MgO nanoparticles to significantly improve its physical properties for potential packaging applications. Optimum mechanical properties of chitosan composites were yielded at 5%weight of MgO concentration, where tensile stress and elastic modulus significantly improved by 86 %

and 38 %, respectively, compared to those of pure chitosan films.Zalaznik M. et al.(2016). have found that all the particles, irrespective of their composition and size, reduce the friction(upto30%); however, the nanoscale particles require a higher concentration to form an effective low friction tribo film.. Co-deposition of hard particles and dry lubricants into the NiP coating has improved the friction and wear resistance properties of the coating.

A. *Chemical composition*

Mild steel has various levels of carbon, silicon, manganese, sulphur and phosphorus content in it. The following table 1 shows the chemical composition of mild steel.

TABLE I. CHEMICAL COMPOSITION OF MILD STEEL

Carbon	0.43-0.50%
Silicon	0.40% max
Manganese	0.70-0.90%
Sulphur	0.040% Max
Phosphorus	0.040% Max

II. METHODOLOGY

The foll C) figure1 shows the methodology of this project. It es procurement of materials, performing electroless n ating and conducting friction and wear test using pin on disc apparatus.

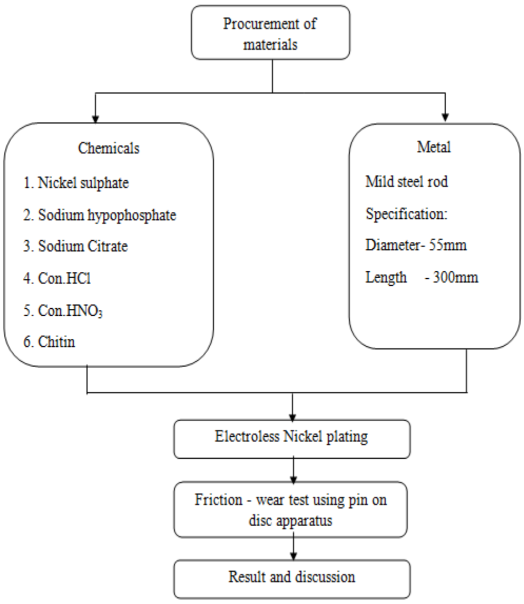

Figure 1. Methodology

A. *Construction*

When designing an electroless nickel plating facility, it is necessary to look first at the chemical and operational objectives. If planning for a specific job or part to be plated, then the following factors should be considered: (a) the type of chemistry required and the shape of the part; (b) production time required per unit; (c) possible/probable expansion; and (d) space availability for current installation. Chemical bath is prepared by adding the following chemicals in double distilled water. They are Nickel sulphate 18 g, Sodium hypophosphite 23g, Sodium citrate 13g, Lead acetate 0.001g, Hyroxyapatite 2.5g. Now using magnetic stirrer stir the mixture for two hours to get particles distributed uniformly all over the bath. After two hours add hyroxyapatite in the bath and supply heat to the bath. Duration of heat supply is one hour. Clean the mild steel sample with soap solution until all the impurities over the surface is removed. Now dip the sample in distilled water to remove any soap particles which present over the surface. After getting pure sample dip it in solution which has water and hydrochloric acid in 7:3 ratio respectively. Now the whole bath placed in the oil bath which was placed over the magnetic stirrer. Connect the one end of heater filament to the temperature controlling equipment and another end is placed in oil bath. Direct supply of heat to the chemical bath is to be avoided to prevent the bath destabilization. Temperature of whole system is maintained at 80 ºC.

Figure 2.

B. *Working*

The electroless metal plating with adding reduction agents to the electrolyte is based on the oxidation of the reducing agent with release of electrons which then in turn reduce the metal ions. To achieve a controlled deposition from such solutions the metal deposition has to happen through the catalytic influence of the substrate surface. The electrolytes contain besides the complex ion compounds of the metals to be deposited also stabilizers, buffer and accelerator chemicals, and a suitable reduction agent.These electrolytes are usually operating at elevated temperatures (50° – 90°C). The deposits contain besides the metals also process related foreign inclusions such as for example decomposition products of the reduction agents. Now the surface of the sample is fully activated. Immerse the sample into the chemical bath for about two hours.The partial anodic and cathodic reaction for electroless nickel deposition with hypophosphite are usually written as follows:

Anodic
Oxidation of H_2P0_2
$H_2PO_2 + H_2O \longrightarrow H_2PO_3 + 2H^+ + 2e;$
i_{Rcd} = hypophosphite oxidation current
Cathodic
$Ni^{+2} + 2e \longrightarrow Ni';$
i_{Ni} = nickel deposition current
$2H^+ + 2e \longrightarrow H_2;$
i_H = hydrogen evolution current
$H_2PO_2 + 2H^+ + e \longrightarrow P + 2H_2O;$
i_P = phosphorus deposition current

At steady state equilibrium potential (mixed potential), the rate of deposition is equal to the rate of oxidation of hypophosphite (anodic current, ked), and to the rate of the cathodic reactions (cathodic current, $i_N + i_H + ip$). That is:

$$i_{dcposition} = i_{Rcd} = i_{Ni} + i_M + ip$$

The hyroxyapatite particle which is impregnated in the chemical bath will get hitch up over the surface of mild steel. The above reaction which is stated will happen until the equilibrium of the system reached.

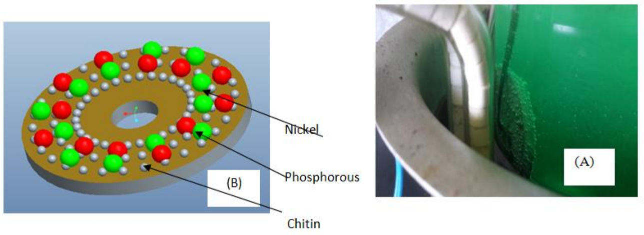

Figure 3. A) Coating of hyroxyapatite over mildsteel
B) Schematic representation of NiP Hyroxyapatite coated surface

III. RESULTS AND DISCUSSIONS

A. *Evaluation of Friction and Wear*

For an evaluation of friction and wear behaviour of uncoated specimen, NiP and NiP/Hyroxyapatite composite coatings, friction and wear test results were obtained using the pin-on-disc apparatus. The mass of the samples before and after the wear test were measured to precision using a 0.0001 g accuracy balancing machine.

Load specification
Applied mass = 0.5 kg
Speed of the disc = 350 rpm
Wear track radius = 35 mm

TABLE II. WEAR TABLE

Sample	Mass Of Sample Before Wear (g)	Mass Of Sample After Wear (g)
Uncoated	113.4768	113.4612
NiP coated	112.8926	112.8872
NiPC coated (0.5 g/l)	113.5764	113.5745
NiPC coated (1.0 g/l)	112.6942	112.6936
NiPC coated (1.5 g/l)	113.0072	113.0058
NiPC coated (2.0 g/l)	113.2468	113.2438

Sample	Mass Loss Of Sample
Uncoated	0.0156
NiP coated	0.0054
NiPC coated (0.5 g/l)	0.0019
NiPC coated (1.0 g/l)	0.0006
NiPC coated (1.5 g/l)	0.0014
NiPC coated (2.0 g/l)	0.003

B. *Mass loss table*

The mass of the tested specimens before and after the wear test is shown in Table 2. It is evidenced that the mass loss is decreased after the dispersion of Hyroxyapatite particles in the electroless bath. Among uncoated, NiP and NiP/Hyroxyapatite (0.5 g/l, 1.0 g/l, 1.5 g/l and 2.0 g/l) composite coating, NiP/hyroxyapatite (1.0 g/l) composite coating presents a minimum mass loss of 0.0006 g followed by 0.0014 g of NiP/hyroxyapatite (1.5 g/l) coating, 0.0019 g of NiP/hyroxyapatite (0.5 g/l) 0.003 g of NiP hyroxyapatite (2.0 g/l), 0.0054 g of NiP coating and 0.0156 g of uncoated specimens. The mass loss of NiP coated substrate is slightly higher than the NiP/hyroxyapatite (2.0g/l) composite coatings and hence the effect of reinforcing the Hyroxyapatite particles has a great impact on the reduction of material loss. The minimum mass loss of NiP/hyroxyapatite (1.0g/l) composite coating is due to better bonding property of the NiP matrix and the Hyroxyapatite particles. The distribution of Hyroxyapatite in the electroless bath has strengthened the NiP matrix providing enough lubricity and cohesion to withstand the stress and rupture developed during the sliding test.

C. *Friction Force Measurement*

The friction force of uncoated, NiP and NiP/hyroxyapatite composite coating measured using pin on disc apparatus.Among all the tested materials, NiP/hyroxyapatite composite coating exhibits a lower friction force followed by NiP and uncoated substrate. A recent study suggests that roughness of the surface plays a vital role on rate of wear and friction force, as the high rough surface wear more quickly with higher friction force than smooth surface. Hence, in order to evaluate the impact of the roughness value, all the specimens are measured using a TESA contact profilometer and the results are shown in table 4.1.3. It is clear that there is considerable change in the roughness value after the reinforcement of hyroxyapatite in the NiP matrix. Roughness has no role on the friction force as the NiP/hyroxyapatite (2.0 g/l) composite coating presented a low friction force with a high roughness value. Uncoated specimens present a high friction force compared to other tested specimen. During the sliding test, the contact of counter face and mild steel substrate results in heat generation at the asperities and these hard asperities of mild steel get displaced as wear debris on wear track, which is the primary reason for the high friction force of uncoated specimen. NiP coating presents a low friction force with a roughness value of 0.45 µm next to 0.33µm of uncoated specimen.

TABLE III. SURFACE ROUGHNESS

Sample	Roughness value(µm)
Uncoated sample	0.33
NiP coated sample	0.45
NiP hyroxyapatite coated sample	0.85

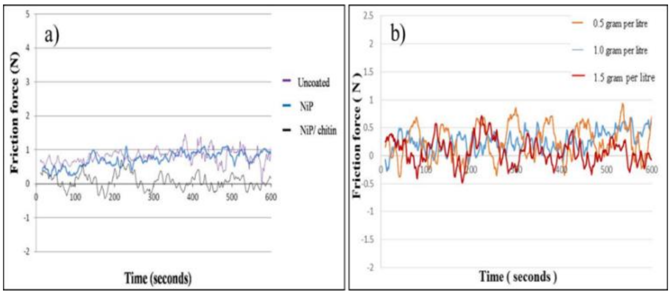

Figure 4. friction force curve of a) NiP/Hyroxyapatite (2.0 g/l) composite coating and, b) various weight dispersion (0.5 g/l, 1.0 g/l and 1.5 g/l) of NiP/Hyroxyapatite composite coating.

The heat generated during the wear test generally softens the NiP film which acts as a lubricant giving a low friction force of 0.06948 N. Different surface treatments of NiP coating and incorporation of various particles into the NiP matrix lead to a change of the microstructure of the coating thus resulting in modified friction and wear behaviour. For example reinforcement of hard ceramic particle in to the NiP matrix increases the friction force and incorporation of soft and lubricous particles like PTFE and graphite decreases the friction force. Hence the reinforced particle certainly has a huge impact on the friction and wear behaviour. NiP/hyroxyapatite composite coating presents a low friction force with a minimum mass loss which is similar to Morphology study of NiP and NiP/Hyroxyapatite composite coating

Microstructure of NiP-based coatings is composed of characteristic globular shaped grains.A typical cauliflower structure was pictured for NiP coatingwith close grains and without voids. There is no void and cracks on themorphology of theNiP coated surface,which evidences a homogenous distribution of theNiP on the substrate.The morphology of NiP/Hyroxyapatite (1.0 g/l) composite coatinglooks non homogeneous and hardened in contrast to the NiP coating. Thehardened NiP matrix allows the hyroxyapatite particles to stick firmly inthe matrix. This enables the coating to resist the wear when subjectedto sliding. In addition, the non homogeneous distribution of matrix andhyroxyapatite provides enough lubricity and cohesion to withstand the stress developed during the sliding test. Different surface treatments of NiP coating and incorporation of variousparticles into the NiP matrix lead to a change of the microstructure ofthe coating thus resulting in modified friction and wear behavior.For example reinforcement of hard ceramic particle in to the NiPmatrixincreases the friction coefficient and incorporation of soft and lubricous particles like PTFE and graphite decreases the friction coefficient.

D. *Wear track Analysis*

Normally, in polymers different wear mechanisms are simultaneously active, depending on the whole tribo system including the type of material and the surface characteristics. The most pronounced wear mechanism observed in Figs. 8 are adhesion and abrasion. The adhesion is related with shearandde formation of a hyroxyapatite polymer which is indirect contact with the counter surface. Generally adhesion is identified as the dominant wear mechanism in all polymer reinforced NiP composite coating. It is due to the entrapping of wear particles on the sliding contact, producing a transfer film on the wear track. This transfer film played a major role on the improvement of the friction and wear property. At some locations of NiP coating, removal of transfer film is also observed. As stated that transfer film coverage and bonding to the counter surface significantly affects the wear behavior of polymeric materials. The formation of film not only depends on the sliding speed but also on the loads. A larger presence of wear particles was observed with NiP sample, which is attributed to abrasive plastic deformation. SEM image studies have reported that the addition of Hyroxyapatite particle in hard matrix, decreases the ploughing effect as compared to NiP coated sample. It is also important that other factors such as composition and volume of there inforcement material in the polymeric matrix have an influence on the wear behaviour.

Particles of wear debris (NiP and steel) were found to be embedded into the Hyroxyapatite clusters (Fig. 2b). Mechanical mixing of components was observed. Main mechanism of coatings degradation is adhesive and oxidative wear off at the contact points where high flash temperature is generated. Wear debris are more oxidised than initial coating. Hyroxyapatite content in all locations of NiP/Hyroxyapatite containing coatings was sufficiently high indication that it is covering the whole surface. According to literature typically volume fraction of polymer reinforcementrangesfrom5to20% could affect the wear property. On favor of that, higher reinforcement of hyroxyapatite particles results into a deterioration of the wear behavior. The sliding behaviour of the steel surfaces is mainly governed by adhesion and abrasion as mentioned above. The soft nature of Hyroxyapatite which is poorly adhered to the counter surface and is rapidly removed as wear debris. This thick and discontinuous transfer film, which is designated as secondary layer in this paper, covers the steel counter surface and is read hered to the polymer. This secondary layer is formed when the generated wear particles are mechanically milled and further thus entrapped between the contacting surfaces. Some ploughed grooves along the sliding direction are observed in the counter surface, which are the characteristics of abrasive wear. Lackoftransfer film formation showed higher wear rate in the NiP coated sample, whereas, the transfer film formation of NiP/Hyroxyapatite composite coating provided a protective effect to damage giving thus a better wear resistance than the NiP coating and uncoated substrate.

IV. CONCLUSION

The study on the use of hyroxyapatite particles as a reinforcement with electroless NiP matrix has been successfully implemented on the mild steel substrate.Based on the experimental result and analyses, following conclusion has been obtained.The NiP/hyroxyapatite (1.0 g/l) composite coating presents a low friction force with minimum mass loss when compared to NiP coated and uncoated specimens. However fluctuation in the friction force was observed in the form of valleys and ridges. This is due to the hyroxyapatite debris which gets pile up in the wear track, which is also a reason for the negative wear depth of NiP/hyroxyapatite composite coating. Because of the reinforced hyroxyapatite particles, there is an enhancement in the lubrication of NiP matrix, which drastically reduced the friction and wear of the mild steel. The higher weight percentage of Hyroxyapatite particles reinforcement has shown a decrease in the wear resistance, which is due to the bath instability.

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