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ELECTROLESS Ni – P – W COATING: PREPARATION AND CHARACTERIZATION

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ABSTRACT
Electroless nickel (EN) plating is getting popularity as a hard coating for industrial applications due to its high hardness, uniform thickness, good wear resistance and excellent corrosion property. The ternary alloy Ni-P-M, where M is a transition metal such as W, Co, Mn has superior properties compared to binary Ni-P alloy. The Ni–P–W alloy deposit on the mild steel surface was obtained by the electroless process. Nickel sulphate and sodium tungstate were used as metal ion sources, respectively, and sodium hypophosphite used as reducing agent. The coating was characterized for its composition, structure, morphology, surface roughness and microhardness. The EDX analysis shows the presence of Ni, P and W in the deposit. The SEM observation showed the presence of dense and coarse nodules in the ternary coating. The surface roughness was measured by Talysurf profilometer and the microhardness was measured by UHL VMHT microhardness tester.

Keywords: Electroless Coating, Ni-W-P, Roughness, Hardness.

1. INTRODUCTION
Electroless nickel (EN) plating is an autocatalytic process where the substrate develops a potential when it is dipped in electroless solution called bath that contains a source of metallic ions, reducing agent, complexing agent, stabilizer and other components. Due to the developed potential both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process. The credit for the invention of electroless method goes to Brenner and Riddell [1]. Since then this process has found extensive use in mechanical, chemical and electronic industries due to their excellent mechanical, physical, electrical, corrosion and tribological properties, due to this type of features electroless coatings have found extensive use in different industrial applications such as the coatings in machinery construction, textile machinery, chemical and plastic industries, automobile industry, hydraulics, mining industry, offshore technology, oil and gas industries, electrical and electronic industries, aerospace and printing industry. Another advantage of EN coatings is that it can be applied to a variety of substrate materials and plated uniformly on intricate part geometries. EN coating is an autocatalytic deposition of a Ni alloy from an aqueous solution onto a substrate without the application of electric current. Thus the electroless deposition process is different from the conventional electroplating processes, which requires an external source of direct current in order to reduce nickel ions in the electrolyte to nickel metal on the substrate. The overall reaction of electroless metal deposition is [2]

$$M^{Z+} + Red_{solution} = M_{lattice} + Ox_{solution} \qquad (1)$$

According to the mixed-potential theory of electroless deposition, the overall reaction can be decomposed into one reduction reaction and one oxidation reaction, the anodic partial reaction is

$$Red_{solution} = Ox_{solution} + me \qquad (2)$$

and the cathodic partial reaction is

$$M^{Z+} + Ze = M_{lattice} \qquad (3)$$

The equilibrium (rest) potential of the reducing agent, $E_{eq,Red}$ must be more negative than that of the metal electrode, $E_{eq,M}$, so that the reducing agent Red can function as an electron donor and M^{z+} as an electron acceptor.

The electroless bath typically consists of an aqueous solution of metal ions, reducing agents, complexing agents and stabilizers, with specific operating conditions like metal ion concentration, temperature, and pH ranges. The deposition rate, the properties of coated compound and the structural behaviour of the deposits mainly depend upon the plating bath constituents and conditions such as the type and concentration of the reducing agent, stabilizer, pH and the bath temperature etc. Electroless coating can be broadly classified into three categories viz. alloy and poly-alloy coatings, composite coatings and pure metallic coatings. Among electroless nickel coating, Ni-P coating has already gained immense popularity. The basic electroless Ni – P coating has been used as a functional coating due to the advantage of surface roughness [3], friction [4], wear resistance [5] and corrosion properties. The properties and microstructures of EN coatings depend on the amount of phosphorous alloyed in the deposit [6]. For achieving a superior hard and wear resistant surface the Ni-B coating draws the attention of many researchers. The properties of Ni-B coatings are mainly controlled by their boron content. Heat treatment is also found to strongly influence both the physical properties like hardness as well as the electrochemical properties. The research for improved tribological properties has lead to the formation of duplex coatings of Ni-P and Ni-B and three component coatings of Ni-B-P. Composite coatings with improved wear resistance have been formed by incorporating several particles in Ni-B coatings, viz. diamond, alumina and silicon carbide [7]. Although electroless nickel alloy coatings can serve a lot of purpose, the requirement for improved properties such as higher hardness, low friction, lubricity, anti-sticking and anti-wear properties has led to the incorporation of many soft and hard particles in the matrix of the electroless nickel. A number of alloys can readily be deposited by combining metals that are independently deposited electrolessly from the similar baths at the same time there are certain metals that cannot be deposited by the autocatalytic mechanism can be induced to co-deposit with an electrolessly depositing metal. Choice of the particles depends on the required Choice of the particles depends on the specific property that is required. In the field of tribology, electroless nickel based alloy coatings can mainly be divided into two categories those are lubricating composite coatings and wear-resistant composite coatings, according to the types of the doped inorganic and/or organic particulates [8]. For the improvement of tribological performances many researches are developing and investigating newer variants of electroless nickel coatings like Ni-W-P, Ni-Cu-P, Ni-P-TiO_2, Ni-P-SiC etc. It is considered that the incorporation of a typically transition metal such as W, Co, Mn, Re and Mo in the binary Ni-P alloy could lead to superior properties than the binary Ni-P coating. So the research could be extended for the ternary Ni-P-M alloy where the M is the transition metal. Pearlstein and Weightman [9] first presented the Ni-W-P ternary alloy in 1963 and since then, many investigations on electroless Ni-P-W ternary alloy were reported. As tungsten, a refractory metal itself cannot be deposited from any aqueous solution. However, tungsten alloys with the iron group transition metals can be readily deposited from aqueous solutions containing tungsten ion [10]. A major factor contributing to increased resistance to mechanical abrasion of electroless coating is hardness. There are three major parameters affecting the hardness of these coatings, namely, tungsten content, time, and the temperature of the applied post heat treatment. The hardness of a EN deposit is especially important when superior wear resistance is required. The incorporation of tungsten in to the nickel matrix led to the solute hardening and enhanced the hardness. It also exhibits excellent properties such as mechanical properties, tribological properties and corrosion resistance. Even small amount of tungsten codeposition affects the chemical composition, morphology and roughness of binary Ni – P deposits. Surface roughness and hardness have a large impact on the mechanical properties such as fatigue behaviour, corrosion resistance, creep life, etc. It also affects other functional attributes of machine components such as friction, wear, light reflection, heat transmission, lubrication, electrical conductivity etc. Palaniappa et. al. [11] showed that with the increase of tungsten content within the nickel matrix results more wear resistance. The coefficient of friction increases with the increase of applied normal load and found to be higher in as-plated condition when compared to the heat-treated (300˚C) coatings and the maximum hardness achieved for Ni-W-P coatings, when it is heat treated at 500˚C for 1 h.

The present investigation focuses on the preparation of the ternary Ni – P – W deposits containing nickel sulphate as the nickel source, sodium hypophosphite as reducing agent and sodium tungstate as source of tungsten. The purpose of the present study is to investigate the surface roughness and microhardness of uncoated specimen and that of Ni – P – W coated specimen and then compare the results.

2. EXPERIMENTAL

2.1 Coating deposition

Mild steel (AISI 1040) specimen of size 20 mm × 20 mm × 8 mm is used as the substrate material for the deposition of the electroless Ni – P – W coating. Shaping, parting, milling processes are used accordingly for the preparation of the sample. The sample is then subjected to surface grinding process. The sample is mechanically cleaned from foreign matters and corrosion products. After that the MS sample is cleaned using distilled water. After that a pickling treatment is given to the specimen with dilute (50%) hydrochloric acid for one minute to remove any surface layer formed like rust followed by rinsed in distilled water and methanol cleaning. A large number of trial experiments are performed before deciding the bath composition.

Table 1 indicates the bath composition and the operating conditions for successful coating of electroless Ni-W-P. Nickel sulphate is used as the source of nickel while sodium hypophosphite is the reducing agent. Sodium citrate is used as the complexing agent with lactic acid playing the role of a stabilizer. The bath is prepared by adding the constituents in appropriate sequence. The pH of the solution is maintained around 7-8 by continuous monitoring with a pH meter. The cleaned samples are activated in palladium chloride solution at a temperature of 55°C. Activated samples are then submerged into the electroless bath which is maintained at a temperature between 88-92°C with the help of a hot plate cum stirrer attached with a temperature sensor also submerged in the solution. The deposition is carried out for a period of 3 hours. The range of coating thickness is found to lie around 20-25 microns. After deposition, the samples are taken out of the bath and cleaned using distilled water. The schematic diagram of the electroless setup is shown in Figure 1.

Table 1: Electroless bath composition and operating condition

Bath Constituents	Values
Nickel Sulphate (g/l)	20
Sodium Hypophosphite (g/l)	20
Sodium Citrate (g/l)	35
Ammonium Sulphate (g/l)	30
Lactic Acid (g/l)	5
Sodium Tungstate (g/l)	25
pH	7-8
Temperature	90±2˚C
Duration of coating	3 hrs
Bath volume (ml)	200

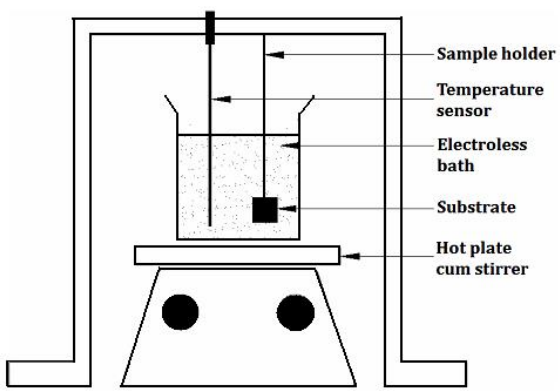

Fig 1. Sketch of electroless set up.

2.2 Surface morphology and composition study

Scanning electron microscopy (SEM) (JEOL, JSM-6360) is used to study the surface morphology of the EN Ni – W – P coating. Energy dispersive X-ray analysis (EDX) (EDAX Corporation) is done in conjunction with SEM for the study of the composition of the deposit in terms of the percentage of nickel, phosphorous and tungsten in the coating.

2.3 Roughness measurement

A stylus and skid type profilometer, Talysurf (Taylor Hobson, Surtronic 3+) is used to measure the roughness of the electroless Ni-W-P coatings. The cut-off length of the instrument is set to 0.8 mm with a Gaussian filter and evaluation length of 4mm, the traverse speed of the stylus is 1 mm/s. Roughness measurement on the electroless Ni-W-P coatings is repeated four times in different orientations and the average of the measurements is taken as the response for the actual experiment. The parameter evaluations are microprocessor based. The measured profile is digitized and processed through the dedicated advanced surface finish analysis software Talyprofile for evaluation of the required roughness parameters.

2.4 Microhardness measurement

The surface hardness is measured by the UHL VMHT microhardness tester with an indentation load of 0.5 kg and dwell time 15 seconds before and after the coating. Hardness measurement on the electroless Ni-W-P coatings is repeated for ten times at different locations and the average of the measurements is taken as the response for the actual experiment. The hardness of the sample which is measured in Vicker's hardness (HV) scale. However the HV value can be converted to Rockwell (HRc), Knoop (HK) as well as Brinell hardness scale.

3. RESULTS AND DISCUSSION

3.1 surface morphology and composition

Energy dispersed x-ray analysis (EDX) was performed to study the composition of the coating. The EDX analysis shows that the electroless coating contains 88.57% Ni, 7.62% P and 3.81% W. The EDX spectra of the coating surface are shown in Fig.2. The surface morphology of the Ni-W-P coating is observed by scanning electron microscopy (SEM). The SEM micrograph of the coated surface is shown in Fig. 3. Randomly distributed globular particles can be seen on the surface of the substrate. The morphology of the uncoated AISI 1040 substrate was also investigated, which showed a similar wavy profile caused by the mechanical polishing process. The coated surface is optically smooth and of low porosity. The small amount of porosity is due to the trapping of hydrogen gas bubbles formed during the plating process. The surface of the Ni – P – W coating is appeared to be dense.

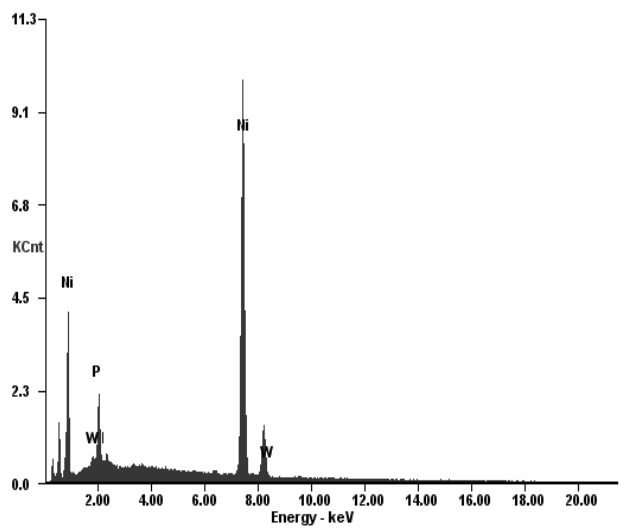

Fig 2. EDX spectra of Ni-P-W coating

3.2 Surface roughness

The surface roughness is the most influencing

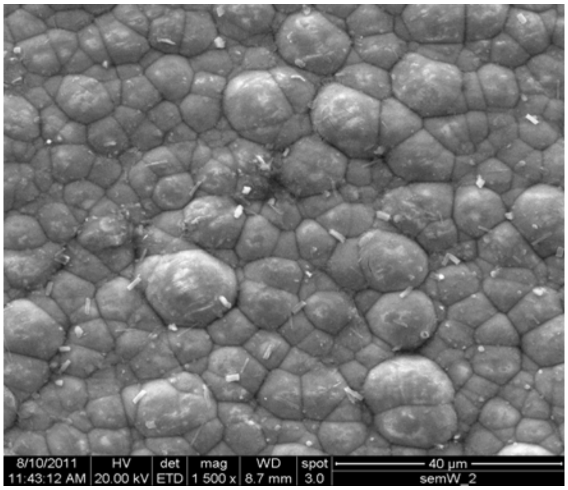

Fig 3. SEM micrograph of Ni-P-W coating

parameter for the mechanical properties of the material. The surface roughness of the sample before and after coating was measured. At least 10 measurements and calculations were performed under each scan area, with a minimum traverse length of 4mm of the stylus. Before coating the average surface roughness (R_a) of the mild steel sample was 0.40 µm and after coating the average surface roughness (R_a) reaches a value of 0.48 µm. Fig. 4 shows the variation of the surface roughness before and after coating. Here it can be seen that the surface roughness increases slightly after coating. This increase of surface roughness is due to the accumulation of the globular particles of the deposited material. Fig.5 shows the optical micrograph of the cross section of the coating. Here it can be seen that due to the variation of distribution of tungsten particle during coating process the surface roughness increased. It was observed that the sputtered Ni-W-P surface is relatively smooth than the conventional electroless coating [12]. Heat treatment process further increases the surface roughness as the deposit changes from amorphous to crystalline structure.

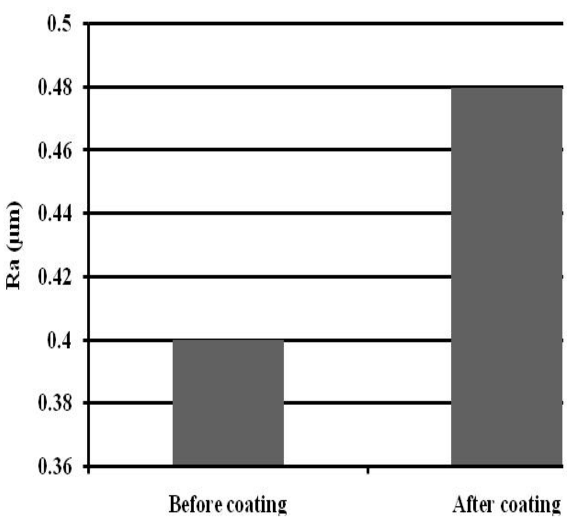

Fig 4. Variation of surface roughness due to coating

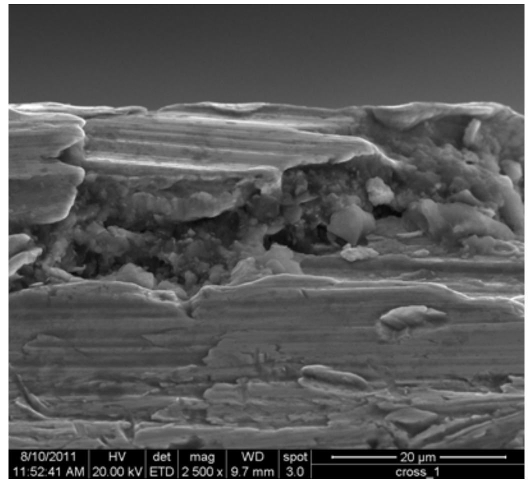

Fig 5. Optical micrograph of cross section

3.3 Microhardness

The hardness of the deposits could be increased by adding tungsten either in an amorphous or crystalline state. Fig. 6 shows the variation of microhardness of the specimen before and after coating using a diamond indenter microhardness tester. The indentation spot on the coated surface is shown in Fig.7. The comparison shows that the hardness increases a significant amount after coating. It is due to the presence of the hard particle tungsten. The deposits with tungsten content greater than 40wt. % possess hardness higher than that of substrate. M. Palaniappa et. al.[10] showed that the maximum hardness achieved for Ni-W-P coatings, when it is heat treated at 500˚C for 1 h. This increase in hardness is due to the dual effect of phosphide precipitation and solid solution strengthening. When heated at 600˚C, there is further decrease in the hardness values of both binary and ternary alloy deposit. The hardness of the crystallized Ni-W-P alloy is more than that of Ni-P alloy due to the formation of the Ni-W solid solution. Thus introduction of tungsten element in the Ni-P deposit not only improves the thermal stability but also enhances the microhardness of the electroless deposits.

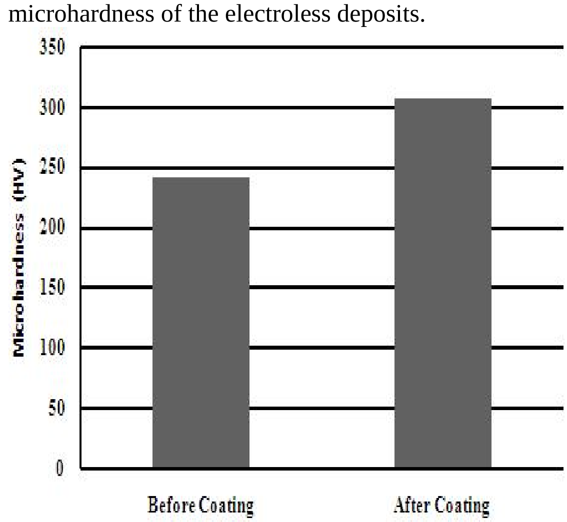

Fig 6. Variation of micro hardness due to coating

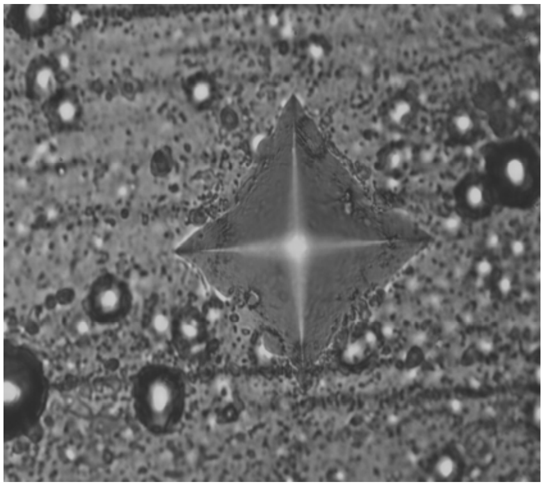

Fig 7. Indentation during micro-hardness measurement

CONCLUSION

From the results of roughness and microhardness it is revealed that the deposition of Nickel, Phosphorous and the hard particle Tungsten on the mild steel substrate not only increase the roughness but also increase the microhardness of the coated sample than the base metal. The hardness of the deposits could be increased by adding tungsten to the binary Ni-P coating either in an amorphous or crystalline state. This is because the EDX analysis shows that the coating film contains more than 3% Tungsten. By varying the percentage of the Tungsten present in the coating the hardness of the coating can be varied.

4. REFERENCES

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