Wear behavior of electroless Ni-P-W coating under lubricated condition – a Taguchi based approach

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Abstract. The present study aims to investigate the tribological behavior of electroless Ni-P-W coating under engine oil lubricated condition to ascertain its suitability in automotive applications. Coating is deposited onto mild steel specimens by the electroless method. The experiments are carried out on a pin – on – disc type tribo tester under lubrication. Three tribo-testing parameters namely the applied normal load, sliding speed and sliding duration are varied at their three levels and their effects on the wear depth of the deposits are studied. The experiments are carried out based on the combinations available in Taguchi’s L27 orthogonal array (OA). Optimization of the tribo-testing parameters is carried out using Taguchi’s S/N ratio method to minimize the wear depth. Analysis of variance carried out at a confidence level of 99% indicates that the sliding speed is the most significant parameter in controlling the wear behavior of the deposits. Coating characterization is done using scanning electron microscope, energy dispersive X-ray analysis and X-ray diffraction techniques. It is seen that the wear mechanism under lubricated condition is abrasive in nature.

1. Introduction
Reduction of friction and wear is a major concern for every manufacturing industry. Hence, researchers have given wide attention to improve the tribological behavior of mating surfaces. Applying hard surface coatings which are also self lubricating in nature for the enhancement of tribological behavior has proved to be an efficient means for enhancing the working life of components undergoing rubbing action. Amongst several surface coating techniques, deposition by the electroless method has evolved over the past few decades to become a mature subject of research. They possess enhanced physical, mechanical, electrical and tribological properties compared to the electro-deposited coatings [1]. The electroless method is an autocatalytic process where a catalytically active substrate get coated when immersed into a bath containing an aqueous solution of the metal to be deposited, reducing agent, complexing agent, stabilizer, buffer, etc. A wide variety of substrates can be coated by this method since it does not involve the use of electricity. Most importantly the coating deposition is uniform throughout i.e. a sharp edge and a blunt hole receives the same amount of deposition. Several metals can be deposited by this method; though electroless nickel (EN) coatings are the most famous variants of this process [2]. Sodium hypophosphite reduced binary electroless Ni-P alloy coatings have high hardness, wear resistance, corrosion resistance and low coefficient of friction. Proper heat treatment and incorporation of hard particles or dry lubricants to form composite
EN coating improves the properties of the deposits further [3 – 5]. Ni-P alloy and composite coatings find wide usage in automobile, aerospace, chemical, electrical, machinery, mining and food processing industries [6, 7].

The addition of a transition metal like W to the binary Ni-P alloy coating results in higher hardness, wear and corrosion resistance, improved thermal stability and enhanced friction performance [8]. With the increase in tungsten content, the hardness as well as wear resistance of Ni-P-W coating increases. On proper heat treatment, the wear resistance increases further due to the precipitation of nickel and its phosphides which act as barriers for dislocation movement. The highest hardness and wear resistance is obtained when the coatings are heat treated at 500°C for 1h and tested under an applied normal load of 40 N [9]. Laser annealing is seen to improve the wear resistance further compared to annealing in a furnace [10, 11]. The use of design of experiments along with multi-criteria optimization techniques has been reported in several works to minimize wear, friction and improve corrosion resistance of electroless Ni-P-W coating [8, 12].

A thorough literature survey reveals that there are few literatures available where the friction and wear behavior of EN coatings have been investigated under lubricated condition. Ni-P, Ni-P-Cu, Ni-P-PTFE and Ni-B coatings are seen to offer good resistance to wear under bio-oil, water and engine oil lubricated condition [13 – 16]. Most of the research work concerning the friction and wear behavior of Ni-P-W coating is carried out under dry condition [8, 9]. The present study thus attempts to investigate the wear behavior of Ni-P-W coating under the influence of engine oil since EN coatings finds its use in automotive industries. To determine the optimum parametric combination for minimizing the wear depth of Ni-P-W coatings under lubricated condition, Taguchi method is used. Surface morphology, composition and phase transformation is analyzed using scanning electron microscope (SEM), energy dispersive X-ray analyzer (EDX) and X-ray diffraction (XRD) technique. A worn specimen is observed under SEM to determine the wear mechanism.

2. Experimental Details

2.1. Deposition of electroless Ni-P-W coating

AISI 1040 steel specimen (Ø6 × 30 mm) is used as the substrate material. The specimens are prepared with precision and of the aforesaid dimension to fit into an attachment which holds the pin vertically against a rotating counterface material. The samples are thoroughly rinsed in de-ionized water, degreased and acid pickling is done (50% HCl) to remove any surface oxide layer and corrosion products. The specimens are activated in palladium chloride solution at 55°C prior to their immersion into the electroless bath. This step is incorporated to kick-start the deposition as soon as the specimens are immersed into the bath. The electroless bath is prepared by mixing the chemicals in appropriate sequence as enlisted in Table 1. The operating conditions are also given in Table 1. After a deposition time of 3 hrs, the coated specimen is removed from the bath and rinsed in de-ionized water. The specimens are further subjected to heat treatment in a box furnace at 400°C for 1hr followed by slow cooling in the furnace. Heat treated Ni-P-W coatings are seen to offer high resistance to wear [9]. Finally, the heat treated Ni-P-W coated specimens are subjected to wear tests.

| Bath constituents         | Values | Operating condition | Values |
|---------------------------|--------|---------------------|--------|
| Nickel Sulphate           | 20 g/l | pH                  | 7-8    |
| Sodium Hypophosphite      | 20 g/l | Bath temperature    | 90±2°C |
| Sodium Citrate            | 35 g/l | Duration of coating | 3 h    |
| Ammonium Sulphate         | 30 g/l | Bath volume         | 200 ml |
| Lactic Acid               | 5 g/l  | Annealing temperature (for 400°C) |        |
| Sodium Tungstate          | 25 g/l | 1h in a box furnace |        |
2.2. Lubricated sliding wear tests and experimental design

The heat treated Ni-P-W coated specimens are subjected to wear tests on a pin–on–disc configuration tribological test setup (TR-20-LE-CHM-400, Ducom, India). The lubricant used is Servo PRIDE-40, which is a commercially available engine oil manufactured by Indian Oil. The coated pin presses against a rotating counterface disc (Ø165 × 8 mm) of EN 31 specification having a hardness of 62 HRc. Track diameter is set at 80 mm. The tribological testing parameters and their levels are shown in Table 2. The test parameters are applied normal load, sliding speed and sliding duration. They are varied at three levels as shown in Table 2. The response variable is wear depth. It is measured in terms of displacement (μm) caused due to the wear of the coating. A linear variable differential transformer (LVDT) is used to acquire the wear depth. The wear data is collected and displayed by a computer interfaced data acquisition system attached to the test setup. The experimental design considered for the present investigation is Taguchi’s L27 OA to analyze both the individual as well as interaction effect of the process parameters on the response variable. It can be noted here that for three control factors along with their three levels each can be analyzed using L9 OA. But in the present work, an attempt has been made to analyze the statistical significance of the process parameters as well as their interactions on the responses. Due to this, the degree of freedom of the experiment comes out to be 18. Hence, L27 OA having 26 degrees of freedom has been chosen. An initial test run is carried out by considering mid-level combination of the test parameters.

Table 2. Process parameters and their levels.

| Design factors | Unit | Levels  |
|----------------|------|---------|
| Load (L)       | N    | 10 20* 30 |
| Speed (S)      | rpm  | 60 80* 100 |
| Time (T)       | min  | 5 10* 15 |

*initial test conditions

2.3. Coating characterization

The surface morphology, composition and microstructure of EN coatings affect the tribological properties to a large extent [1]. Hence coating characterization is necessary to understand the wear behavior of Ni-P-W coating as well as to ensure deposit uniformity. To observe the surface morphology of electroless Ni-P-W coating in its as-deposited and heat treated condition, scanning electron microscope (SEM) (JEOL, JSM – 6360) is used. A cross cut section of a coated specimen is also observed under SEM to determine the coating thickness. After the tribological tests, a worn out specimen is viewed using SEM to determine the predominant wear mechanism. Composition analysis in terms of weight percentage of nickel, phosphorus and tungsten is done using energy dispersive X-ray (EDX) analysis (FEG, Quanta 250). The phase transformation of the coatings is studied using X-ray diffraction (XRD) (Rigaku, Miniflex) to analyze the effect of heat treatment.

3. Results and Discussion

3.1. Optimization using Taguchi’s S/N ratio analysis

The present investigation aims to find out the best parametric combination for minimizing wear depth of electroless Ni-P-W coating under lubricated condition using Taguchi’s method which tries to achieve high quality with low cost [17]. The use of a loss function called signal to noise (S/N) ratio is recommended based on quality characteristics such as higher – the – better, lower – the – better and nominal – the – best. Signal represents the mean whereas noise represents the standard deviation. A higher value of S/N ratio resembles that the experiment is less susceptible to the random noise factors affecting the system performance. In the present study, the analysis of S/N ratio is carried out...
considering wear depth as the response. Since wear is to be minimized, lower – the – better quality characteristics is used to calculate the S/N ratio (in decibels) which is given as follows:

\[ S/N = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}y_i^2\right) \]  (1)

where \( n \) is the number of observations and \( y \) is the observed data. The combinations of the parameters for all the experiments and their corresponding wear depths and S/N ratios are given in Table 3.

| Exp. No. | Parameter combinations | Wear depth (µm) | S/N ratio (dB) |
|----------|------------------------|----------------|---------------|
| 1        | L1 S1 T1              | 4.398          | -12.865       |
| 2        | L1 S1 T2              | 5.114          | -14.175       |
| 3        | L1 S1 T3              | 5.559          | -14.900       |
| 4        | L1 S2 T1              | 4.265          | -12.598       |
| 5        | L1 S2 T2              | 6.37           | -16.083       |
| 6        | L1 S2 T3              | 9.552          | -19.602       |
| 7        | L1 S3 T1              | 7.803          | -17.845       |
| 8        | L1 S3 T2              | 9.859          | -19.877       |
| 9        | L1 S3 T3              | 11.204         | -20.987       |
| 10       | L2 S1 T1              | 7.982          | -18.042       |
| 11       | L2 S1 T2              | 8.795          | -18.885       |
| 12       | L2 S1 T3              | 9.439          | -19.499       |
| 13       | L2 S2 T1              | 9.723          | -19.756       |
| 14       | L2 S2 T2              | 11.414         | -21.149       |
| 15       | L2 S2 T3              | 11.674         | -21.344       |
| 16       | L2 S3 T1              | 8.89           | -18.978       |
| 17       | L2 S3 T2              | 12.646         | -22.039       |
| 18       | L2 S3 T3              | 13.921         | -22.873       |
| 19       | L3 S1 T1              | 6.534          | -16.304       |
| 20       | L3 S1 T2              | 9.012          | -19.096       |
| 21       | L3 S1 T3              | 10.084         | -20.073       |
| 22       | L3 S2 T1              | 8.837          | -18.926       |
| 23       | L3 S2 T2              | 11.299         | -21.061       |
| 24       | L3 S2 T3              | 12.783         | -22.133       |
| 25       | L3 S3 T1              | 11.814         | -21.448       |
| 26       | L3 S3 T2              | 14.476         | -23.213       |
| 27       | L3 S3 T3              | 15.52          | -23.818       |

Since the experimental design considered is orthogonal, the average effect of each design parameter on the response can be estimated at different levels. The average S/N ratios at each level of load, speed and time for wear depth is enlisted in Table 4. It is also known as response table. The response table (Table 4) consists of delta values which assigns a rank to each parameter. The lowest value in a column is subtracted from the highest in the same column to ascertain the delta values. From Table 4, it can be seen that rank 1 is assigned to speed (S), indicating the highest influence on the wear depth. The main effects plot is shown in Figure 1. The optimum combination of the
parameters is obtained from the main effects plot for S/N ratio which is L1S1T1 i.e. lowest levels of load (10 N), speed (60 rpm) and time (5 min). The slope of the main effects plot also reveals to a certain extent the effect of a parameter on the response variable. It seems that all the three parameters are highly significant in the present investigation from Figure 1. Interaction effect of process parameters can be analyzed through the interaction plot of S/N ratio. The interaction effect of the process parameters such as load (L), speed (s) and time (T) on the wear depth of electroless Ni-P-W coating under lubricated condition is shown in Figure 2. In an interaction plot, non-parallelism and intersection of lines signify strong interaction between the parameters. In the present work, it can be clearly seen from Figure 2 that there is no significant interaction between the process parameters. Though, the actual contribution of the parameters and their interactions in controlling the tribological response as well as their statistical significance can be well understood from analysis of variance.

The result obtained from the optimization study reflects that lower wear depth is encountered at the combination of lowest level of the tribological test parameters. Hence, apparently it may seem that the results can be interpreted easily from mathematical relation given by Archard. But it is an established fact by now that the wear behavior exhibited by a surface coating is governed by several complex phenomena such as surface morphology, tribochemical reaction occurring at the interface of the mating surfaces, formation of thick oxide films at the tip of the asperities, etc. Therefore it is not always apparent that lowest combination of parametric values will yield optimum wear. The result obtained in the present study is an indication that such complex phenomenon does not govern the wear behavior of electroless Ni-P-W coating under lubricated condition.

| Level | L    | S    | T    |
|-------|------|------|------|
| 1     | -16.55 | -17.09 | -17.42 |
| 2     | -20.29 | -19.18 | -19.51 |
| 3     | -20.67 | -21.23 | -20.58 |
| Delta | 4.13  | 4.14  | 3.16  |
| Rank  | 2     | 1     | 3     |

Total mean S/N ratio = -19.169 dB

3.1.1. Analysis of variance (ANOVA)
To determine the statistical significance of the individual parameters and their interactions on the process response, analysis of variance (ANOVA) is carried out. It separates the total variability of the response into contributions of each of the factors and errors. ANOVA results are based on F-ratio.4. It is the ratio between the regression mean square and mean square error. The results of ANOVA for wear depth are given in Table 5 and the analysis is carried out at a confidence level of 99%. It can be seen that the highest contribution is from the sliding speed followed by applied normal load and sliding duration. The interaction terms do not cast a significant effect in controlling the response variable considered in the present work i.e. wear depth.

3.1.2. Confirmation test
The final step for a design optimization using Taguchi’s method is a verification test which is carried out at the optimal setting of the process parameters. It is carried out to validate the results obtained experimentally and the predicted response as well as find out the resulting improvement in the response variable compared to the initial test run. The predicted S/N ratio is calculated as follows:

$$\hat{\eta} = \eta_m + \sum_{i=1}^{O} \left( \bar{\eta}_i - \eta_{m} \right)$$

(2)
where $\hat{\eta}$ is the predicted S/N ratio, $\eta_m$ is the mean S/N ratio, $\eta_i$ is the mean S/N ratio at the optimal level and 'o' is the number of process parameters which is 3 in the present study. The results of the confirmation test are enlisted in Table 6. From the results it can be inferred that there has been an improvement of 39.17% in the S/N ratio of wear depth at the optimum combination of the test parameters compared to the initial test run. The predicted and experimental S/N ratios are seen to be in close agreement. Hence, Taguchi’s method is successfully applied to get an improvement in the wear performance of electroless Ni-P-W coating under lubricated condition.

**Figure 1.** Main effects plot of S/N ratio for wear depth.

**Figure 2.** Interaction plots for mean of S/N ratio (a) L vs. S (b) L vs. T and (c) S vs. T.
Table 5. Results of ANOVA for wear depth.

| Source | DF | Seq SS  | Adj MS  | F-ratio | %Contribution |
|--------|----|---------|---------|---------|--------------|
| L      | 2  | 84.045  | 42.023  | 67.12*  | 35.8         |
| S      | 2  | 85.466  | 42.733  | 68.26*  | 36.4         |
| T      | 2  | 49.496  | 24.748  | 39.53*  | 21.1         |
| L*S    | 4  | 5.83    | 1.457   | 2.33    | 2.5          |
| L*T    | 4  | 1.27    | 0.318   | 0.51    | 0.5          |
| S*T    | 4  | 3.82    | 0.955   | 1.53    | 1.6          |
| Error  | 8  | 5.008   | 0.626   | 2.1     | 2.1          |
| Total  | 26 | 234.936 |         |         | 100          |

*significant at 99% confidence level

Table 6. Confirmation test results for wear depth.

| Initial parameter | Predicted Parameter | Optimal Parameter |
|-------------------|---------------------|-------------------|
| Level             | L2S2T2              | L1S1T1            | L1S1T1 |
| Wear depth (±m)   | 11.414              |                   | 4.398  |
| S/N ratio (dB)    | -21.149             | -12.722           | -12.865|

Improvement of S/N ratio = 8.284 dB (39.17%).

3.2. Surface morphology, wear, composition and phase transformation analysis

The surface morphology of an as-deposited specimen is observed under SEM and shown in Figure 3(a). Nodulated structures are visible. There is no possible surface damage and the coating appears to be dense with no porosity. The effect of heat treatment on the surface morphology of the coatings is analyzed by observing a heat treated (400°C for 1h) specimen under SEM (Figure 3(b)). It can be seen that on heat treatment, the size of the nodules decreases and some amount of volume contraction takes place. The nodulated surface morphology leads to the low wear and friction of EN coatings [18]. A cross cut section of Ni-P-W coated specimen is illustrated in Figure 3(c). The thickness of the deposits is seen to be around 30 μm and quite uniform. The highest value of wear encountered by a specimen is seen to be 15.52 μm. Thus, only wear of the coatings has taken place. The SEM micrograph of a worn out specimen is shown in Figure 3(d). Surface smoothening effect can be observed and it can be deduced that abrasive wear is the predominant wear mechanism. The lubricant film prevents adhesion of the coating with the counterface material. Heat treatment also leads to the crystallization of the coatings resulting in precipitation of nickel and its phosphides. These phosphides have low mutual solubility with iron. Hence, abrasive wear of the coating is established. The synergistic effect of surface smoothening and the use of lubricant leads to low wear of electroless Ni-P-W coating under lubricated condition.

Composition analysis of the as-deposited Ni-P-W coating is done using EDX and the spectrum is shown in Figure 4. The peaks of nickel, phosphorus and tungsten are quite specific. As-deposited coating comprises mainly of 85% nickel, 11% phosphorus and 4% tungsten by weight. A high value of tungsten in the deposits leads to a high hardness of Ni-P-W (~48 HRc) resulting in improved wear resistance. Since the hardness of the coating is lower than the counterface material, the obtained wear depth can be considered to be only of the specimen and the disc suffers no wear.

Phase transformation analysis of the coating is done using XRD. For the as-plated Ni-P-W coating, the XRD plot is presented in Figure 5(a) while the heat treated plot is shown in Figure 5(b). The broad peak observed in the XRD plot for as-deposited Ni-P-W coating is the indication of amorphous nature.
On heat treatment, the coating becomes crystalline. This happens due to the precipitation of nickel and its phosphides as can be observed in Figure 5(b). Peaks of Ni and Ni$_3$P are visible. Due to the precipitation of phosphides (precipitation hardening) and solid solution strengthening by Ni(W) on heat treatment, enhanced hardness and wear resistance is obtained [19]. Thus, Ni-P-W coating is seen to offer high wear resistance under engine oil lubricated condition and has high potential of use in the automotive segment for reduction of wear of engine parts and bearings working under lubrication.

Figure 3. SEM micrographs of Ni-P-W coating (a) as-deposited (b) heat treated (c) cross-cut section and (d) worn surface.

Figure 4. EDX spectrum of as-deposited electroless Ni-P-W coating.
Figure 5. Plots of XRD analysis for Ni-P-W coating (a) as-plated and (b) heat treated.

4. Conclusion
In the present work, electroless Ni-P-W coating is deposited onto AISI 1040 steel specimens. The wear behavior of the heat treated deposits is investigated by varying applied normal load, sliding speed and sliding time on a pin – on – disc configuration tribological test setup. The experiments are carried out under engine oil lubricated condition. Taguchi’s design of experiment and optimization technique is gainfully applied to extract optimum wear resistance of the coating. The optimal parametric combination for minimum wear depth is realized from an applied normal load of 10 N, 60 rpm sliding speed and 5 min sliding duration. A significant improvement is obtained in the wear depth compared to the initial test condition. The predicted optimum S/N ratio and experimentally obtained one corroborate well with each other. Based on ANOVA results, sliding speed is seen to have the highest contribution to wear of the deposits under lubrication followed by normal load and sliding duration. The interaction effects are not seen to be significant. The surface morphology of the as-deposited as well as heat treated Ni-P-W coating reveals nodulated structures. The prevalent wear mechanism is observed to be abrasive in nature. The presence of nickel, phosphorus and tungsten is evident from the EDX analysis. As-deposited Ni-P-W coating is amorphous in nature. Heat treatment results in microcrystalline phases due to the precipitation of Ni$_3$P and Ni. Due to precipitation hardening and solid solution strengthening, high hardness and wear resistance of the coatings is observed under lubricated sliding conditions. Thus, Ni-P-W coating deposited by electroless method is found to be suitable for use under oil lubricated condition. This widens the scope of Ni-P-W coating for wear reduction in the automotive segment.

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