Effect of heat treatment duration on tribological behavior of electroless Ni-(high)P coatings

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Abstract. Electroless nickel coating occurs through an autocatalytic chemical reaction and without the aid of electricity. From tribological perspective, it is recommended due to its high hardness, wear resistance, lubricity and corrosion resistance properties. In this paper electroless Ni-P coatings with high phosphorous weight percentages are developed on mild steel (AISI 1040) substrates. The coatings are subjected to heat treatment at 300°C and 500°C for time durations up to 4 hours. The effect of heat treatment duration on the hardness as well as tribological properties is discussed in detail. Hardness is measured in a micro hardness tester while the tribological tests are carried out on a pin-on-disc tribotester. Wear is reported in the form of wear rates of the sample subjected to the test. As expected, heat treatment of electroless Ni-P coating results in enhancement in its hardness which in turn increases its wear resistance. The present study also finds that duration of heat treatment has quite an effect on the properties of the coating. Increase in heat treatment time in general results in increase in the hardness of the coating. Coefficient of friction is also found to be lesser for the samples heat treated for longer durations (4 hour). However, in case of wear, similar trend is not observed. Instead samples heat treated for 2 to 3 hour display better wear resistance compared to the same heat treated for 4 hour duration. The microstructure of the coating is also carried out to ensure about its proper development. From scanning electron microscopy (SEM), the coating is found to possess the conventional nodular structure while energy dispersive X-ray analysis (EDX) shows that the phosphorous content in the coating to be greater than 9%. This means that the current coating belongs to the high phosphorous category. From X-ray diffraction analysis (XRD), it is found that coating is amorphous in as-deposited condition but transforms into a crystalline structure with heat treatment.

Keywords. Electroless coatings, Heat treatment, Hardness, Phase transformation, Friction, Wear

1. Introduction

Electroless Ni-P (EN) coating is prepared by an autocatalytic deposition of a Ni-P alloy from an aqueous solution onto a substrate without utilization of electric current [1]. The electroless bath typically includes an aqueous solution of metal ions, complexing agents, reducing agents and stabilizers, operating in a specific metal ion concentration, temperature and pH ranges. EN coating has got the ability to deposit uniformly on uneven surfaces or geometries. It provides a deposit that follows all the contours of the substrate without building up at the edges and corners. EN coatings
have got wide range of industrial applications because of their excellent mechanical, electrical, physical, corrosion, hardness, friction and wear resistance properties [2].

Heat-treatment plays an important role in improving the performance of EN coating by affecting the thickness, hardness, structure and morphology of deposit. With heat treatment, the amorphous and microcrystalline structure transforms into a crystalline structure containing mainly Ni and its phosphides. However, with higher heat treatment temperatures, Ni$_3$P becomes the dominant phosphide phase as it is more stable. The transformation into crystalline structure is mainly observed when the coating is heated at temperatures above 300°C. In some studies, the transformation to Ni$_3$P phase is direct while some have reported to detect intermediate phases of Ni$_5$P$_2$ and Ni$_{12}$P$_5$ [3, 4, 5]. Hardness of EN deposits normally increases with decreasing phosphorus content in as-deposited condition. The peak hardness of EN samples can be achieved after heat-treating at 400-450°C, by the formation of inter metallic Ni$_3$P stable phase [6, 7].

High hardness and natural lubricity enable the electroless nickel coatings to have good wear resistance [7]. Nava D. et al. [6] have achieved a hardness value of 990 HV by heating the coating at 500°C. However, they found that hardness of the Ni-P alloy coating decreased drastically upon increasing the annealing temperature above 500 °C. Comparing [8] on the basis of tribological properties under dry non-lubricated conditions for all heat treated, as deposited and un plated samples, it is observed that wear resistance is greatly increased with heat treatment (i.e. 260°C and 400°C for 25 h and 1 h). However, the treatment performed at 400°C is found to be more effective and has no influence on the frictional coefficient. At higher temperatures, the coating begins to soften because the nickel phosphate particles conglomerate, reducing the number of hardening sites. A record high hardness value of 910 HV$_{0.1}$ in as-deposited Ni-P coating (7.97 atomic % phosphorus) is obtained and high wear resistance is accordingly achieved [9]. M.H. Staia et al. [10] have prepared electroless Ni-P coating on acid based bath and heat-treated them at 260°C and 400°C for 25 h and 1 h. They found that the abrasive wear resistances of the coatings suffer after heat treatment. C. Yanhai et.al. [11] found that the micro hardness of as-deposited Ni-P increases with heat treatment temperature by either precipitation strengthening or solid solution strengthening mechanism depending on phosphorus content of the coating. Specimen heat treated at 400°C exhibits better friction and wear behavior compared to the as-deposited coating. In case of heat treatment at 200°C, specimen shows adhesive wear mechanism for high P coatings. It is investigated by A. Ramalho et al. [12] that wear performance were significantly improved for Ni-P and Ni-P + PTFE on high speed steel AISI 52100 substrate. Though Ni-P film (as-deposited) has the worst performance compared to others due to weak adherence with the substrate. But heat treatment improved the higher hardness and as well as wear characteristic. Going through the literatures, the absence of a systematic study involving the effect of both the heat treatment and its duration on tribological behavior of Ni-P coating is felt. Hence, in the current study, high P electroless nickel coatings are developed which are subjected to different heat treatment temperatures (300°C and 500°C) and durations (1- 4h). After heat treatment the hardness, friction and wear behavior of the coating is studied in detail. Further, the microstructural tests of the coating are performed to understand the reason behind the physical behavior of the coating.

2. Experiment

2.1. Electroless Ni-P coating development

Mild steel (AISI 1040) substrates of both square (15 mm X 15 mm X 2 mm) and pin shaped (Ø6 mm X 30 mm) samples are prepared for the deposition of electroless Ni-P coating. The samples are subjected to a ground finish. The samples are freed from foreign matter and organic products by pickling in acidic solution (37% hydrochloric acid) for one minute. Consequently, they are washed in distilled water followed by methanol cleaning prior to coating. The bath composition and operating conditions for Ni-P coating are selected after several experiments and the same is presented in Table 1.
The cleaned samples are activated in palladium chloride solution at 55°C temperature and placed in the bath for a deposition period of 2 hours. Deposition time is kept constant for each and every specimen so that the coating thickness remains approximately constant.

The average coating thickness is found to be around 12μm / h. The electroless set up used for the coating deposition is illustrated in Figure 1. After the deposition is completed, the samples are taken out of the bath and washed by distilled water.

| Bath Composition (g/l) | Operating Conditions |
|------------------------|----------------------|
| Nickel Sulphate & Nickel Chloride | 40 | pH | 4.5 |
| Sodium Hypophosphite | 24 | Deposition Temp. (°C) | 82 |
| Sodium Succinate | 12 | Bath vol. (ml) | 200 |

**Table 1.** Bath composition and operating conditions

2.2. **Heat treatment of electroless Ni-P coating.**
Heat treatment temperature and duration have great influence on the phase transformation and micro structural behavior of electroless Ni-P coatings. However, the present study is directed towards investigating mainly the effect of heat treatment duration on the coating performance. Hence, some samples are heat treated at 300°C and 500 °C for a duration range of 1- 4 hour. The heat treatment is
carried out in a muffle furnace (Make SUNBIM, India and Temp. Range 0°-1050°C). After heat treatment, the samples are cooled naturally under ambient conditions.

2.3. Hardness test of electroless Ni-P coating
The micro hardness test is performed by using Vickers hardness principle which is mostly used for small parts, thin sections or low thickness work. The Vickers method is based on a combination of mechanical and optical system (VMHT MOT, Technische Mikroskopie). A square base pyramid shaped diamond is employed for producing the indentation. Typically loads are very light, ranging from a few grams to one or several kilograms. The size of the indentation (length of the diagonals) is measured with the help of an optical microscope which is then converted to a hardness value using appropriate formula. Hence, the experiment is conducted with lower value of load (100 g-f) so that indentation depth is considerably lesser than the coating thickness.

2.4. Microstructure study of electroless Ni-P coating
Surface morphology study of the EN coatings is done by scanning electron microscopy (SEM) (JEOL, JSM-6360) in order to analyse the microstructure of the deposited coatings. EDX (Energy Dispersive X-ray Analysis) analysis is done in conjunction with SEM in an EDX analyser (Inca, Oxford) to study the composition of the EN coating. XRD (X-Ray Diffraction) analyser (Rigaku, Ultima) is used for identification of different phases in the Ni-P coatings both before and after heat treatment of coated samples.

2.5. Tribological study of electroless Ni-P coating
After the samples are prepared, the tribological tests are performed on a pin-on-disc type tribometer (TR-20LE-CHM-400, Ducom, India). These tests are done at constant track diameter of 60 mm, constant normal load (20 N) and constant speed (50 RPM) at ambient condition. Here EN-coated specimen (Ø6 mm × 30 mm) is kept fixed (stationary) by holder and the disc (165 mm × 8 mm in thickness) rotates. A 1:1 ratio loading lever is used to apply normal load on specimen with the help of loading pan. Normal load, frictional force and wear characteristic of electroless Ni-P coated samples are tested under dry condition, at ambient temperature (28°C) and relative humidity of about 40%. Each test is carried out for 600 seconds based on the low thickness of the coating [13]. The friction coefficient is recorded automatically during the tests. The wear rates (K) of all the Ni-P deposits are calculated by using the relation

\[ K = \frac{V}{(S \times F)} \]

where, \( V \) is the wear volume in ‘mm³’, \( S \) is the sliding distance in ‘m’ and \( F \) is the normal load in ‘N’ [11].

3. Result and Discussion

3.1. Morphological and Compositional study
It has been investigated that the chemical resistance of an electroless Ni-P deposit, to a large extent, is determined by its structure while the surface morphology is strongly dependent on the characteristics of electroless nickel plating [14]. Electroless Ni-P in general exhibits a nodular structure that resembles the surface of a cauliflower.

The grain size is of the order of 10µm (Figure 2a). Though some pores are visible, but they are very tiny in size and hence they may not be proceed up to the substrate surface. Similar observations are stated in the literature where the coatings obtained by different electroless baths results in microscopically heterogeneous coatings even though the phosphorus content of all the baths are same [2].

The surface morphology of the electroless nickel deposit is examined with SEM and the same is illustrated in Figure 2a. EDX results (Figure 2b) helped in determining the nickel and phosphorous content of the coating in terms of weight percentages. It is experimented that the as-deposited coatings contain around 15 wt. % of phosphorus and the rest is nickel. Hence, the coating is confirmed to be in the group of high phosphorous coating (P content above 9-10%).
3.2. Phase Structure analysis

In order to have an idea about the phase transformation behaviour of electroless Ni-P coating, XRD analysis of the coating is carried out for both as-deposited as well as heat treated samples. XRD analysis of Ni-P coatings is also conducted at different heat treated temperatures.

![Figure 2](image)

**Figure 2.** (a) Surface morphology and (b) EDX spectra of the as-deposited electroless Ni-P coating

It is found that the coatings are amorphous in as-deposited condition and also when heat treated up to a temperature of about 300°C. Beyond 300°C, the coating turns crystalline and sharp peaks of nickel and phosphide (Ni₃P) phases are observed [15]. After heating to 400°C, diffraction peaks corresponding to Ni viz. (111), (200) and (220); and Ni₃P (301), (321), (330), (420) and (312) etc. are observed in the XRD profile. The occurrence of Ni (111) plane in the XRD plot has also been observed by other researchers [16].

![Figure 3](image)

**Figure 3.** XRD profile of (a) As-deposited and (b) Heat treated sample (300°C and 500°C)

The XRD profile in Figure 3a shows that electroless Ni-P coating is amorphous in as-deposited phase. This is in coherence to the results of electroless nickel high P coatings as obtained by others [5]. The Fe (iron) peaks detected are from the steel substrate as the thickness of the coating may be insufficient to absorb all the X-rays. The nickel (111) peak is relatively narrower and much more intense than the other nickel peaks, revealing a very strong preferred orientation in that direction. The XRD profile of the deposit heated to 600°C shows sharper and distinct diffraction peaks of Ni and Ni₃P than that of 400°C profile (Figure 3b). The intensity of nickel (111) peak is found to be increased...
from 400°C profile indicating that the preferred orientation of nickel matrix is increased. Similarly strong orientation is observed for some planes of Ni₃P phase. XRD plot of 600°C also detects the diffraction peaks corresponding to NiO (021) (202) and (024) as observed in the XRD profile.

Figure 3b shows the XRD profile of samples heat treated at 300°C and 500°C for 1 hour. The diffraction peaks corresponding to nickel [(111) (200) (220)], wuestite [(200) (222) and iron (211) etc. are also found in XRD profile of 300°C heat treated sample. From XRD profile of 500°C heat treated sample, the similar crystal orientation are also observed [17] along with corresponding different nickel phosphide phases such as Ni₃P [(121) (222) (321)], Ni₁₂P₅ {(330) (242) (224)}, etc.

3.3. Hardness behavior
By using Vicker’s technique, micro hardness is measured for both as-deposited as well as heat treated samples which are presented in Figure 4, which represents the variation of micro-hardness of as-deposited samples which are heat treated at 300°C and 500°C for 1-4 hour respectively.

![Figure 4. Effect of heat treatment on coating hardness](image)

In general, it is observed that hardness increases with increase of heat treatment temperature with the precipitation of nickel phosphide phases [11]. As-deposited sample exhibit hardness at the range of 580-600 HV₀.₁. By the heat treatment hardness can be increased two fold, as observed for the sample heat treated at 500°C for 3 hours duration (1342 HV₀.₁).

As observed from XRD results of the sample heat treated at 500°C, nickel phosphide specially Ni₃P is detected more compared to sample treated at 300°C (Figure 3b). Ni₃P is harder and more stable than other nickel phosphide phases. Hence, the precipitation of Ni₃P phase may be attributing to the increased hardness of the coating. From the experimental result it can be found, that the duration of heat treatment has a significant effect on hardness of the coating. For 300°C, the sample exhibits an increasing hardness trend with heat treatment duration. However, the same trend is not observed in case of 500°C heat treated sample. For 500°C, the hardness falls for 2 hour heat treated sample and then rises for 3 hour sample and finally falls again for 4 hour sample (Figure 4). Maximum hardness is achieved for 3 hour heat treated sample.

As for 300°C heat treated sample, the micro-hardness increases sharply with the increase of heat treatment duration and the hardness varies from approximately 800 HV₀.₁ to 1150 HV₀.₁. This result implies that the higher micro hardness of as-deposited Ni-P specimen can be obtained by heat treatment and it significantly depends on heat treatment duration. This is because of the formation of
crystalline phases. Moreover, the precipitated phases are quite harder which may be obstructing the movement of dislocations in crystal lattice thereby contributing to the high hardness of the coating [17].

Now, the micro-hardness of Ni-P as-deposited coating mainly depends on the crystal structure and both heat treatment temperature and heat treatment duration. Furthermore, the crystallization for Ni-P deposit is vary from each other and basically depends on the phosphorus percentage and both the heat treatment temperature. As the grain size increases, the barrier to the motion of the dislocations during the plastic deformation decreases due to decrease in the grain boundary area, which ultimately leads to decrease in the hardness and strength of the coating. In the present study, the duration of heat treatment may be directly affecting the crystal structure of the coating resulting in grain refinement or coarsening of the coating microstructure. However, further investigation is in progress to determine the actual reason.

3.4. Tribological behavior
Heat treatment has profound effect on the friction performance of the coating. As-deposited coating Ni-P coating displays a higher friction coefficient than heat treated sample. Figure 5a shows that friction coefficient decreases almost eight times after heat treatment compared to as-deposited coatings. The decrease in friction coefficient may be attributed to the increase in hardness of the coating after heat treatment.

![Figure 5](image)

**Figure 5.** Effect of tribological behavior on (a) C.O.F. and (b) Wear rate vs. heat treatment duration

For harder surface, the chances of plastic deformation at the points of contact between the coating and the counterface are less [18] leading to lesser weld formations. However, there are other factors influencing the friction performance of the coating viz. coating microstructure, grain size, initial roughness of the substrate surface, etc. By comparing samples heat treated at 300°C with that at 500°C (Figure 5a), it is found that the latter exhibits lower friction coefficient.

Hence, it can also be concluded that heat friction coefficient has decreasing trend with respect to treatment temperature. Moreover, from the present study it is observed that friction coefficient in general decreases with increase in heat treatment duration at a particular temperature. However, in case of sample heat treated at 300°C, friction coefficient peaks when heat treated for 3 hours. As expected, wear performance of electroless Ni-P coating improves after heat treatment which is evident
from Figure 5b. The wear rate of as-deposited coating is found to be around 6.7 mm$^3$/N-m, which reduces by about ten times (0.65 mm$^3$/N-m) when heat treated at 500°C for 3 hours.

The improvement in wear resistance is normally associated with increase in hardness of the coating. Hence, good co-relation is observed between the hardness and the wear results in the current study. The wear resistance of samples heat treated at 300°C and 500°C exhibit a dip for 2 hour and 3 hour duration respectively. This high wear resistance may be as a resultant of the combination of hardness, microstructure as well as the surface layer formed on the coating. However, further exploration is required in this perspective.

4. Conclusion
The tribological behavior of electroless Ni-(high) P coating is investigated in the present study for samples heat treated at different heat treatment temperature and at various durations. It is found that hardness increases with increase in heat treatment temperature as well as duration. The maximum hardness is found to be around 1342 HV$_{0.1}$. Wear resistance is also found to be co-relative with the hardness results. The maximum wear resistance is found to be exhibited in case of samples heat treated at 300°C and 500°C for 2 hours and 3 hours respectively. Moreover, wear resistance of as-deposited Ni-P coating is found to increases by about ten times by suitable heat treatment. Friction coefficient of the coating is found to decrease with increase in heat treatment temperature as well as duration. The coating exhibits a nodular microstructure when observed under SEM. Hard phases of nickel phosphides is found to precipitate upon heat treatment which is believed to be the primary contributor towards increase in hardness of the coating.

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